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Reactions of ceric ammonium nitrate: I. with substituted cycloheptatrienes, II. with diazoalkanes, III. with sodium azide and olefins

Medford Dwight Robbins
Iowa State University

Reactions of ceric ammonium nitrate

I. With substituted cycloheptatrienes

II. With diazoalkanes

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by

Medford Dwight Robbins

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Signature was redacted for privacy.

Dean of Graduate College

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Of Science and Technology
Ames, Iowa

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INTRODUCTION

Cerium(IV) has been used as an oxidant of organic compounds for many years (1), but the scope and utility of this powerful oxidant has not been fully realized. This dissertation includes several studies on the reactions of ceric ammonium nitrate (CAN) in realms not considered before and illustrates its tremendous versatility.

The work in Part I was initiated by Trahanovsky, Young and Robbins (2) who found that 1,3,5-cycloheptatriene was oxidized by CAN to high yields of benzaldehyde and benzene and presented evidence strongly implicating the tropylium ion as an intermediate. This reaction has been extended to several substituted cycloheptatrienes. From the study of phenylcycloheptatrienes it has been possible to establish more clearly the steps leading to the tropylium ion.

In Part II are presented some novel reactions of CAN with diazoalkanes. Phenyldiazoalkanes in general lead to high yields of stilbenes with a predominance of the cis isomer while other diazoalkanes yield the parent carbonyl or alkyl nitrate. This reaction is of particular interest because it strikingly illuminates the role radical cations may play in diazoalkane chemistry.

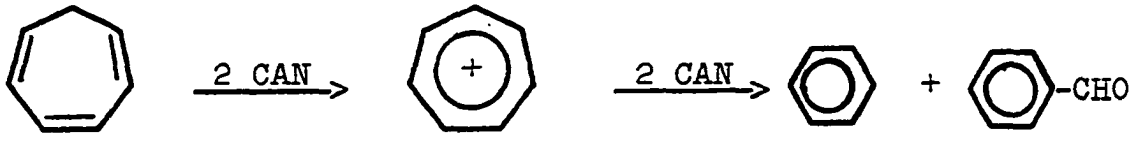
The reaction of sodium azide and CAN in the presence of olefins is reported in Part III. No nitrogen is produced

and α-azido-β-nitratoalkanes are isolated in high yields. This may be the first example in which the azido radical is trapped in the cerium(IV) oxidation of azide ion. Furthermore, the products may prove to have interesting physiological properties.

PART I. REACTIONS OF CERIC AMMONIUM NITRATE WITH SUBSTITUTED CYCLOHEPTATRIENES

INTRODUCTION

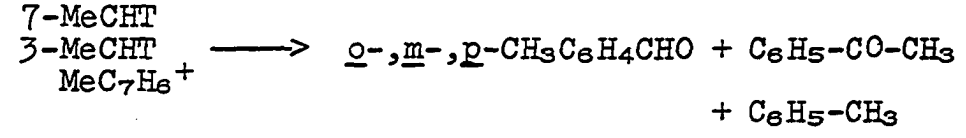
Among all possible metal ion oxidants, cerium(IV) is the least likely to find wide use as an oxidant for olefins (1). One-electron oxidants are often used as polymerization catalysts and rarely yield simple products. However, Trahanovsky, Young and Robbins (2) have reported the surprising results that 1,3,5-cycloheptatriene (CHT) may be oxidized to benzaldehyde and benzene in yields greater than 80 per cent by ceric ammonium nitrate.



($C_7H_7^+$)

Evidence for the tropylium ion intermediate was compelling.

This oxidation has been extended to methylcycloheptatrienes (MeCHT) and to phenylcycloheptatrienes (PhCHT). MeCHT appears to follow closely the oxidation of CHT and the products are those expected by analogy with CHT, o-, m-, and p-methylbenzaldehyde, toluene, and acetophenone. 7-MeCHT, 3-MeCHT, and the methyltropylium ion ($MeC_7H_8^+$) all give the same products in the same proportions:



PhCHT has little analogy with CHT. 7-PhCHT gives benzophenone and diphenylmethanol, the other PhCHT's give products similar to MeCHT, and the phenyltropylium ion ($PhC_7H_8^+$) yields a truncated set of products:

7-PhCHT $\xrightarrow{4\ CAN}$ Ph_2CHOH + $Ph_2C{=}O$

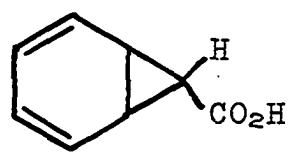
1-, 2-, or 3-PhCHT $\longrightarrow$ Ph_2CO + Ph-Ph + o-,m-, and p-PhC_6H_4CHO

$PhC_7H_8^+$ $\longrightarrow$ Ph_2CO + Ph-Ph + p-PhC_6H_4CHO + m-PhC_6H_4CHO

Several mechanistic approaches are suggested. It is concluded that the most rational explanation involves a combination of CHT-type reactions and of Wagner-Meerwein-like shifts of an intermediate prior to the tropylium ion.

HISTORICAL

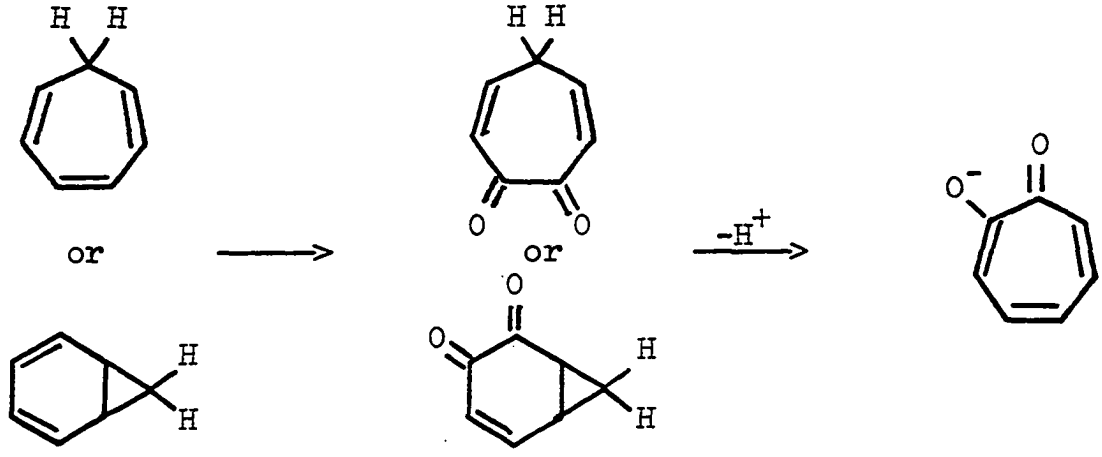
The first reported oxidation of a cycloheptatriene was that of Merling (3) in 1891 who used potassium dichromate in sulfuric acid as the oxidant and isolated benzaldehyde, benzoic acid, and small amounts of carbon monoxide. In 1896 Büchner (4) oxidized 1,3,5-cycloheptatriene-7-carboxylic acid (pseudophenylacetic acid) with alkaline potassium permanganate and characterized benzoic, terephthalic and trans-cyclopropanetricarboxylic acids as reaction products (The trans-cyclopropanetricarboxylic acid probably arose from the trimerization of ethyl diazoacetate used in the preparation of the starting material.). It is interesting to note that on the same page that he reported the formation of terephthalic acid, Büchner suggested a norcaradiene structure for his "pseudophenylacetic acid":



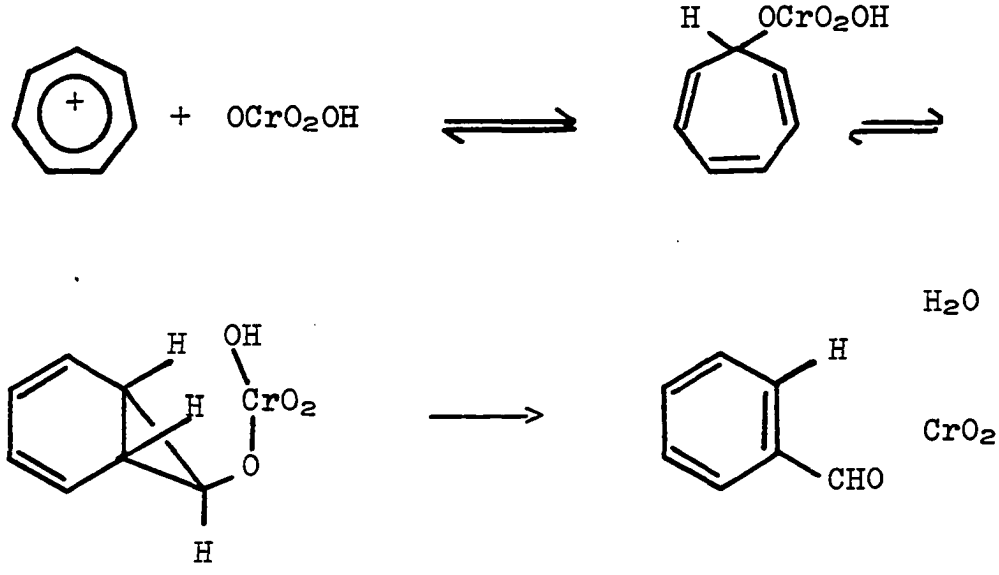
Although hindsight surely renders it more so, there can be little doubt the formation of terephthalic acid from such a structure would be exceedingly difficult.

The next reported oxidation of CHT was 55 years later when Doering and Knox (5) used potassium permanganate as the oxidant and isolated a 6.3 per cent yield of α-tropolone.

The reaction appeared to be simply the oxidation of an olefin in the normal manner followed by loss of a proton:



The actual structure of CHT (norcaradiene or cyclic triene) was not known at the time, so Doering illustrated a method by which the observed product could be derived from either structure. In 1957 Doering and Knox (6) reported several reactions of the tropylium ion, including the oxidation by chromic acid or silver ion to benzaldehyde. Doering suggested that Westheimer's mechanism (7) be applied for chromic acid oxidation and that ring closure be effected by use of a norcaradiene intermediate. No rationalization was made for use of the norcaradiene structure other than the statement that "Like other aromatizing rearrangements in the tropilidene and tropolone field, expression in terms of the norcaradiene valence tautomer, although never necessary, is simplest." His mechanism is as follows:



The silver ion oxidation was suggested to proceed through tropyl alcohol, although there was no evidence for such an intermediate.

In 1958 Dewar (8) reinvestigated Büchner's oxidation of cycloheptatriene-7-carboxylic acid with a variety of oxidants (see Table 1). The diversity of products suggested to them that at least two types of oxidations were taking place.

Table 1. Products of the oxidation of cycloheptatriene-7-carboxylic acid with a variety of oxidants[a]

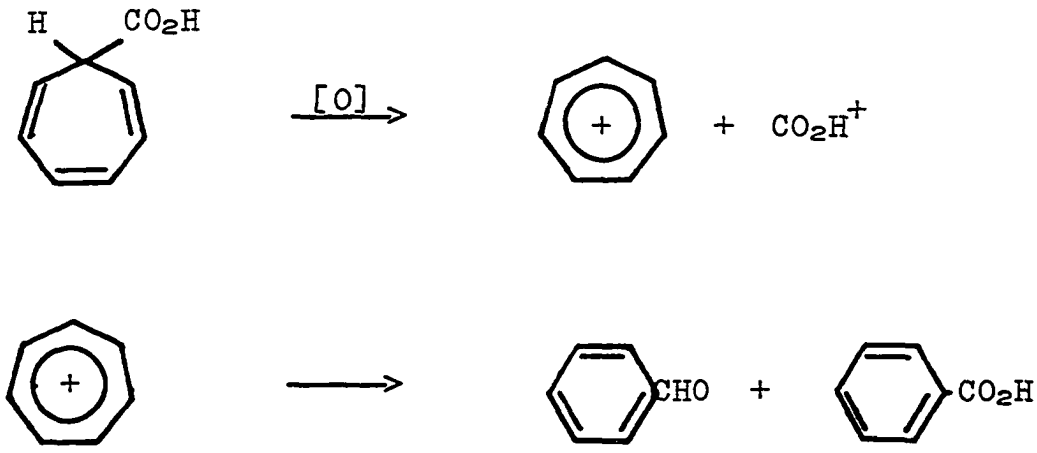
Oxidant	Products
Acidic MnO_4^-	Tropylium ion, benzaldehyde, benzoic acid
Neutral MnO_4^-	Benzaldehyde

[a]Reproduced from reference 8.

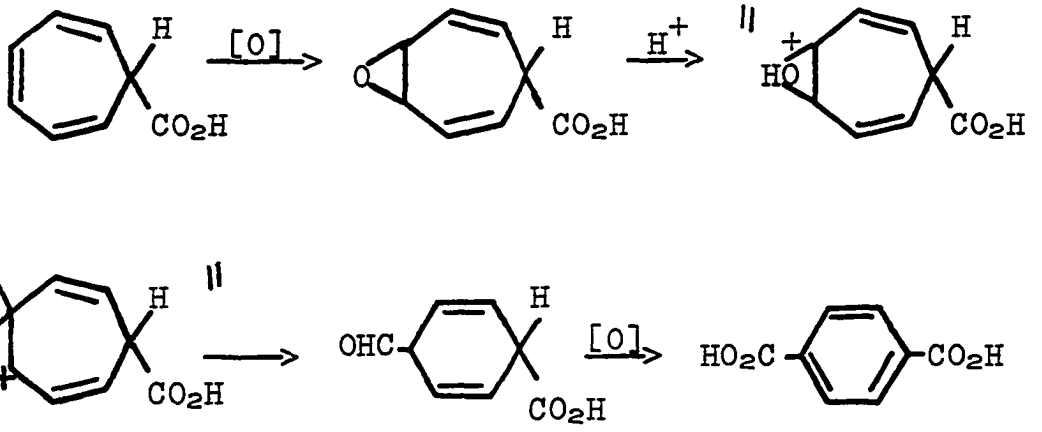
Table 1 (Continued)

Oxidant	Products
Alkaline MnO_4^-	Terephthalic acid
$Pb(OAc)_4$	Tropylium ion
$Na_2S_2O_8$	Tropylium ion, terephthalic acid
CAN	Tropylium ion
Alkaline H_2O_2	CHT-1-COOH
Acidic H_2O_2	No Reaction
HNO_3	Benzoic acid, terephthalic acid
HIO_4	Tropylium ion, benzoic acid, benzaldehyde, terephthalic acid
CrO_3	Terephthalic acid

The tropylium ion was formed by oxidative decarboxylation and benzaldehyde and benzoic acid arose from tropylium ion:

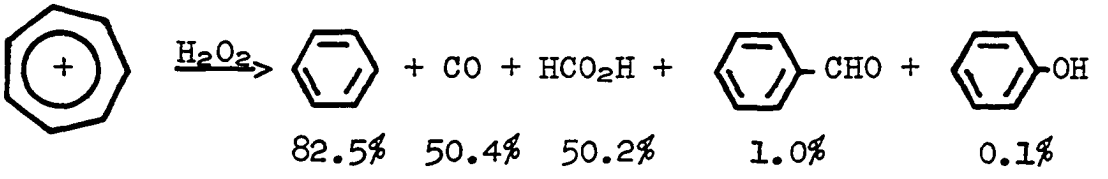


Terephthalic acid was produced by attack on a double bond, epoxidation, and Wagner-Meerwein rearrangement:



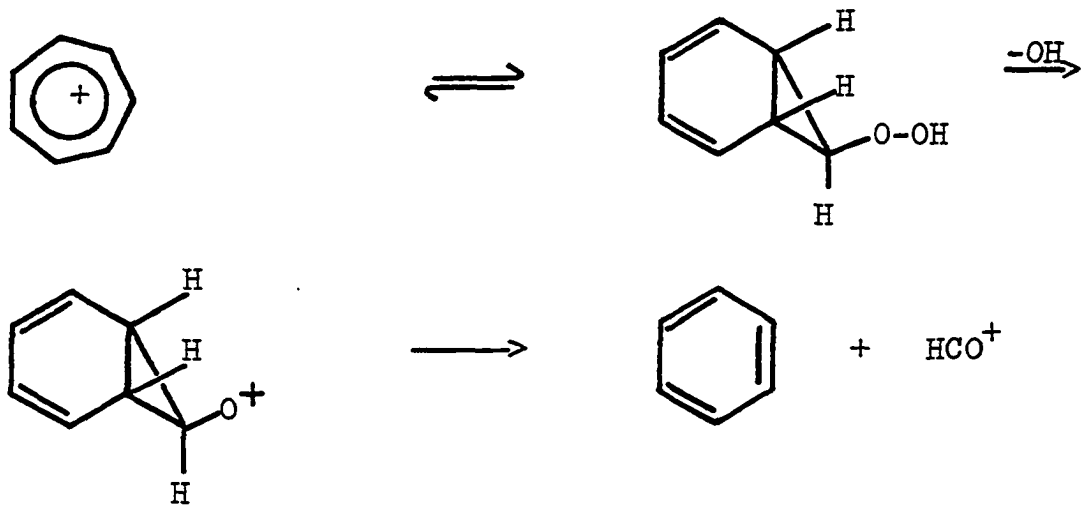
(The steps enclosed in parenthesis were supplied by this author.) Because the identity of the double bonds are retained, only phthalic and terephthalic acid are predicted. Indeed, no iso-phthalic acid has ever been reported for the oxidation of cycloheptatriene-7-carboxylic acid.

In 1959 Volpin (9, 10, 11) oxidized tropylium bromide to benzene with hydrogen peroxide:

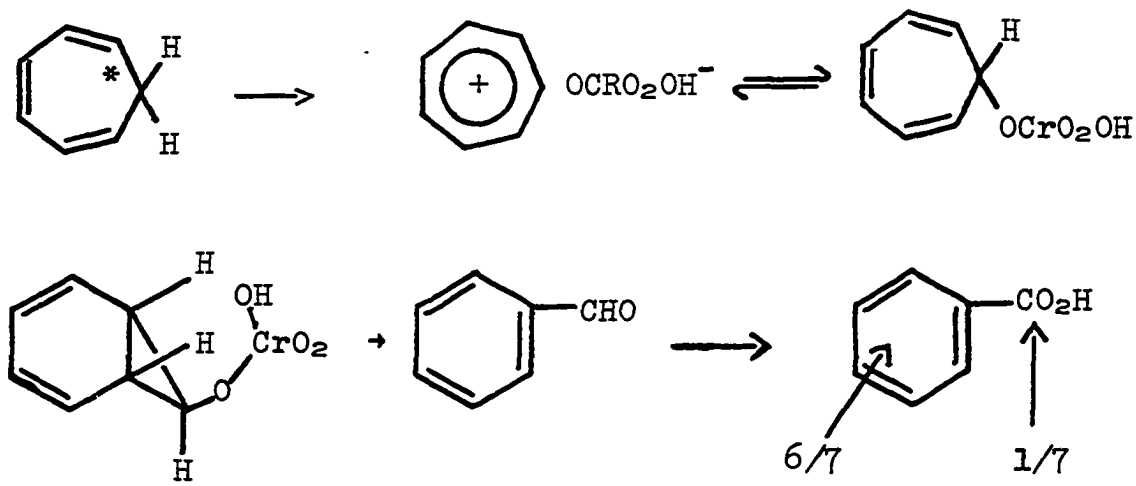


Evidence was presented that the reaction did not proceed via a free radical, benzaldehyde, or tropone. A mechanism

reminiscent of Doering's (6) was suggested:

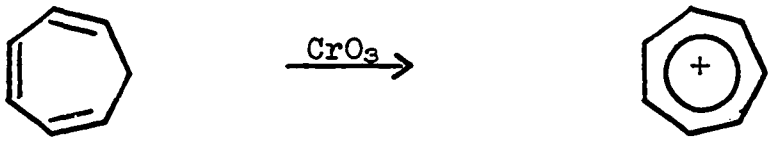


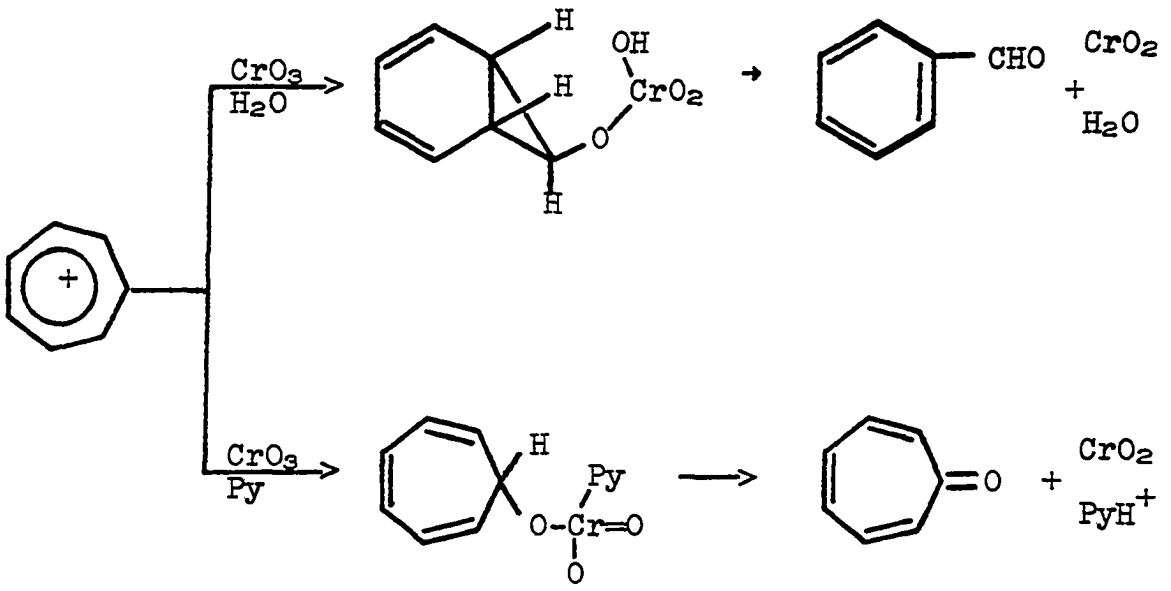
In 1959 Geske (12) electro-oxidized CHT to the tropylium ion. In 1961 Juppe and Wolfe (13) oxidized cycloheptatriene-C^{14} with chromic anhydride to benzoic acid. Approximately 6/7 of the C-14 label was in the benzene ring and 1/7 was in the carboxyl carbon. These results indicated an intermediate with C_7 symmetry and the following mechanism involving the tropylium ion (D_{7h}) was presented:



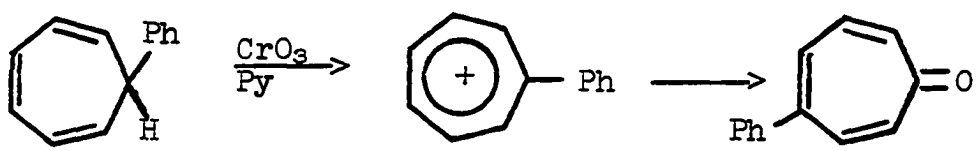
The last steps of the mechanism are those of Doering (6). The first steps are maddeningly incomplete. It is not obvious why Dewar's mechanism for CrO_3 oxidations (8) should not operate with CHT itself, which, if applied, would give all of the C-14 in the ring and none in the carboxyl carbon (the 7-carbon always remains in the ring). Although the evidence for Dewar's mechanism is exceedingly strong, it cannot account for Juppe's results. Unfortunately, Juppe did not repeat his work or place any limits on its accuracy. Furthermore, the CHT-7-C-14 was prepared by the photolytic decomposition of diazomethane-C-14 in benzene and it is possible the CHT thus formed may have isomerized.

Nozoe, Mukai, Tezuka and Osaka (14) have found that tropone can be obtained in 30 per cent yield by oxidizing CHT with chromic anhydride in pyridine. A 40 per cent yield of tropone can be obtained similarly from tropylium ion. This is the first incidence of tropone formation with chromic anhydride and Nozoe suggested the base which removes the proton at C-2 in the norcaradiene structure of Doering (6) is the significant factor:





Pyridine is not as strong a base as hydroxyl and is considerably larger. This may shift the oxidation toward tropone formation and loss of the α instead of β proton. An even more interesting result is the formation of low yields of 4-phenyltropone from 7-PhCHT. Lower yields were obtained if 3-PhCHT was used as the starting material. Nozoe implied the intermediate $PhC_7H_6^+$ was attacked only at the 4,4'-carbons:

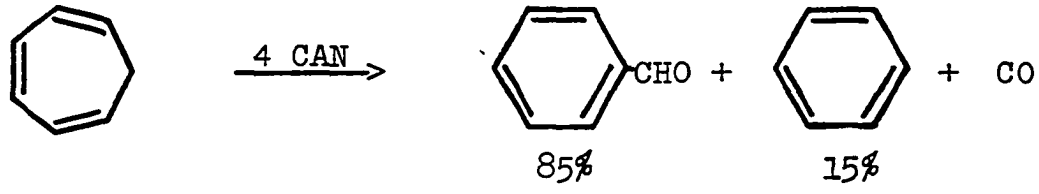


It might be noted that Ikemi, Nozoe, and Sugiyama (15) have found that 3- and 4-phenyltropone is formed when $PhC_7H_6^+$ is

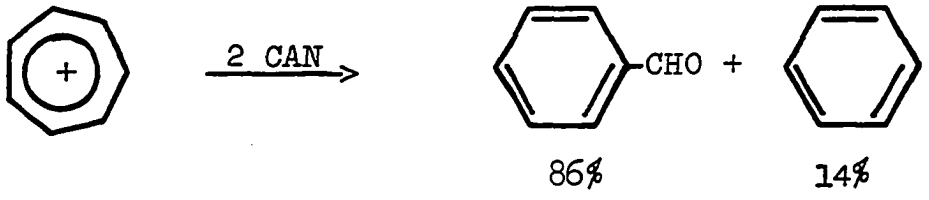
treated with sodium bicarbonate.

Radlick (16) obtained a 25 per cent yield of tropone when CHT was oxidized with selenium dioxide. In 1967 Harmon (17) oxidized CHT with mercuric iodide and iodine to tropylium salts.

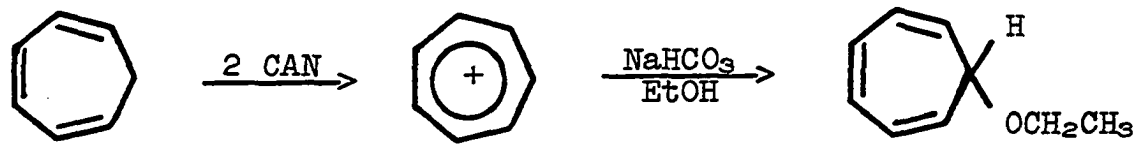
Finally, Trahanovsky (2) has oxidized CHT to benzaldehyde and benzene in yields approaching 90 per cent with ceric



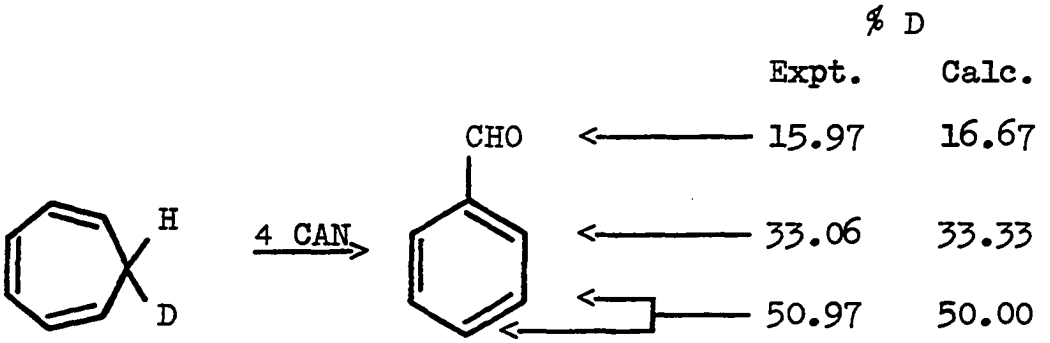
ammonium nitrate. A considerable amount of evidence was collected which indicated the tropylium ion is an intermediate. Tropylium fluoborate was oxidized to benzaldehyde and benzene in a ratio of 86/14, similar to the ratio found with CHT.



Furthermore, ethyl tropyl ether could be isolated from the reaction mixture of CHT and two equivalents of CAN. It is known that ethyl tropyl ether is obtained when solutions of tropylium ion in ethanol are neutralized with sodium bicar-



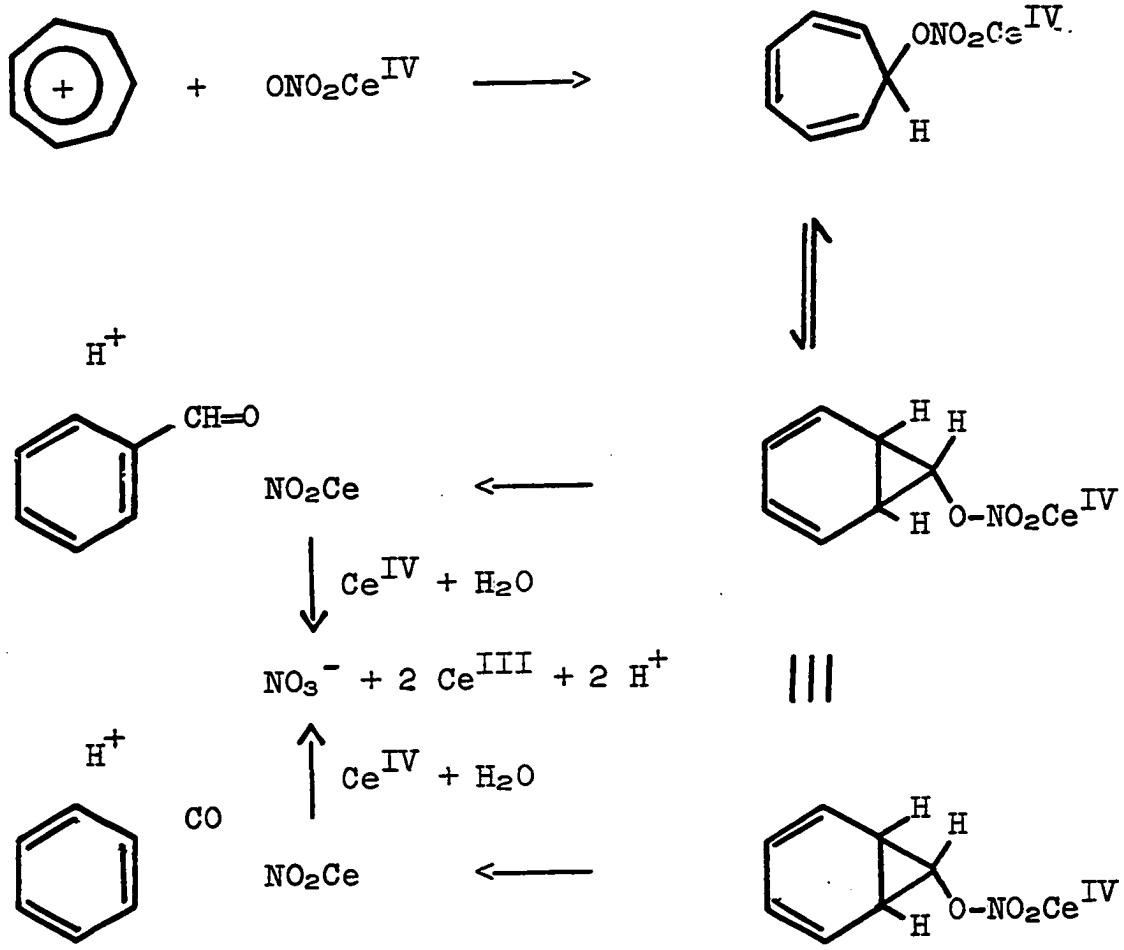
bonate (18). Finally, the oxidation of CHT-7-d_1 gives benzaldehyde in which the deuterium is randomly distributed:



	% D	
	Expt.	Calc.
CHO ←	15.97	16.67
←	33.06	33.33
←	50.97	50.00

The yields of benzaldehyde and benzene are unchanged in a wide variety of solvents, including anhydrous media. Thus, the source of the oxygen for benzaldehyde and the base that removes the proton (compare Doering's mechanism) must be constant in all the solvent systems. Obviously, the only constant course of oxygen is the nitrate ion. All of these results are incorporated into the mechanism presented in Scheme I.

Scheme I


+
ONO_2Ce^{IV}
ONO_2Ce^{IV}
H
H^+
CH=O
NO_2Ce
H H
H O-NO_2Ce^{IV}
$Ce^{IV} + H_2O$
$NO_3^- + 2\ Ce^{III} + 2\ H^+$
H^+
$Ce^{IV} + H_2O$
CO
NO_2Ce
H H
H O-NO_2Ce^{IV}

RESULTS

Methylcycloheptatrienes

The mixture of methylcycloheptatrienes was prepared very conveniently by vacuum pyrolysis at 400°. The ratio of 7-MeCHT to the other isomers was obtained by comparing the integral at δ 1.25 (C_7-H + C_7-Me for 7-MeCHT) to the integral at δ 2.2 (C_7-H_2 + methyl groups for other isomers). These figures are given in Table 2. The ratio of 7-MeCHT to the

Table 2. Ratio of isomers of methylcycloheptatrienes

	Area	Area/Proton	Per Cent
C_7-H + C_7-Me (7-MeCHT)	18	18/4 = 4.5	17.2
C_7-H_2 + Me (Isomers)	108	108/5 = 21.6	82.8

other isomers corresponds closely to that for the thermal equilibria of Conrow (18). Egger (19, 20) has pyrolyzed 7-MeCHT at 150-300° and found that at temperatures above 226°, 85 per cent of the starting material is converted to a mixture of 1-, 2-, and 3-MeCHT with the 3-Me isomer being in most cases the most abundant.

7-MeCHT, 1-, 2-, 3-, and 7-MeCHT, and $MeC_7H_8^+$ were oxidized rapidly and smoothly to toluene, acetophenone, and the methylbenzaldehydes by four equivalents of CAN at 84°

in 75 per cent aqueous acetonitrile. The results are tabulated in Table 3.

7-MeCHT

$$\text{MeCHT} \xrightarrow[5\ \text{min}]{\text{CAN}} \text{Ph-Ph} + \text{Ph-CH}_3 + \text{Ph-CO-CH}_3 + \underline{o}\text{-CH}_3\text{C}_6\text{H}_4\text{CHO} + \underline{m}\text{-CH}_3\text{C}_6\text{H}_4\text{CHO} + \underline{p}\text{-CH}_3\text{C}_6\text{H}_4\text{CHO}$$

MeC_7H_7^+

Table 3. Products from the oxidations of methylcycloheptatrienes by CAN in 75 per cent aqueous acetonitrile

Substrate	Product Ratios[a,b], %					Yield
		$\text{MeC}_6\text{H}_4\text{CHO}$				
	PhCH_3	o-	m	p	PhCOCH_3	%
7-MeCHT[c]	16	22	27	18	17	35
1-, 2-, 3-, and 7-MeCHT[c]	17	19	29	18	17	27
$\text{MeC}_7\text{H}_8^+\text{BF}_4^-$[d]	17	25	28	18	12	34

[a]Two independent runs.

[b]Two analyses of each run.

[c]Oxidized with four equivalents of CAN.

[d]Oxidized with two equivalents of CAN.

The oxidation of $\text{MeC}_7\text{H}_8^+\text{BF}_4^-$ was carried out by dissolving the tropylium ion in acetonitrile and adding this solution to two equivalents of CAN in 50 per cent aqueous acetonitrile.

The identity of the products was determined by collection of the individual components from an analytical glpc sample and comparison of their spectral properties (nmr and ir) with those of authentic samples.

Phenylcycloheptatrienes

7-PhCHT (21), 1-PhCHT (22, p. 37), and 3-PhCHT (22, p. 38) were prepared by known methods. The 3-PhCHT was greater than 85 per cent pure (see Table 4). Analysis of a routine sample was by nmr and comparison of the integral at δ 2.25 (C_7-H_2) with the integral at δ 7.2 (phenyl protons) allowed accurate determination of the amount of 3-PhCHT present.

Table 4. Purity of 3-phenylcycloheptatriene

	Area	Area/Proton	Per Cent
3-PhCHT (δ 2.25)	38	38/2 = 19.0	88
φ-region (δ 7.2)	108	108/5 = 21.6	--

The 1-PhCHT, also analyzed by nmr, was greater than 95 per cent pure (there was no evidence for other isomers).

2-PhCHT was prepared by the irradiation of a sample of 3-PhCHT in benzene at 3560 Å for ten hours. Analysis by nmr suggests that the only isomers present are the 7-Ph and the 2-Ph and that approximately 15 per cent of the total is the

7-isomer (see Table 5). ter Borg (23) reports the irradiation of 92 per cent 3-PhCHT and 7 per cent 7-PhCHT gave 80

Table 5. Purity of 2-phenylcycloheptatriene[a]

	Area	Area/Proton	Per Cent[b]
2-PhCHT (C_7-H_2; δ 2.2)	42.5	42.5/2 = 21.5	--
7-PhCHT (C_7-H_1; δ 2.7)[c]	3.5	3.5/1 = 3.5	84
C_3-C_4 olefin (δ 6.6)	48	48.0/2 = 24	89
C_2-C_5 olefin (δ 6.2)	31	31.0/1 = 31 (27.5)[d]	77
C_1-C_6 olefin (δ 6.8)	47	47.0/2 = 23.5	90

[a]The phenyl region could not be used for analysis as the residual traces of benzene remained.

[b]Based on each integral value.

[c]The per cent 7-PhCHT is 16 based on the integration at δ 2.2 and 15 based on the integration at δ 6.6.

[d]Correcting for the amount of 7-PhCHT present.

per cent 2-PhCHT, 12 per cent 7-PhCHT, 6 per cent 3-PhCHT and 2 per cent of the 1-PhCHT. No 3-PhCHT was apparent in the nmr spectra. The 7-PhCHT yield may include some 1-PhCHT, however.

7-PhCHT was oxidized in a variety of solvents. In 85 per cent aqueous acetic acid, the products were benzophenone, diphenylmethanol, and diphenylmethyl acetate (see Table 6).

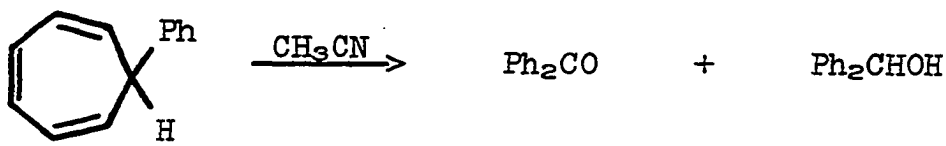
Table 6. Products of the oxidation of 7-PhCHT in 85 per cent aqueous acetic acid by CAN

Run	Reaction Time	Equivalents Cerium(IV)	Relative Yields Ph_2CO	Ph_2CHOH	$Ph_2CHO_2CCH_3$	Yield
1	16 days[a]	4	33	10	57	28
2	38 min	2	--	--	100	--
3	40 min	4	21.2± 2.4[b]	8.2± 2.0	70.2± 3.2	68.6± 9.2

[a]This reaction was run at room temperature; all others were run at 84° ± 2°.

[b]Standard deviations based on four runs are given.

It is interesting to note that with two equivalents of CAN only diphenylmethyl acetate is formed. In 100 per cent acetonitrile the only product was N-diphenylmethyl acetamide. In 50 and 75 per cent acetonitrile, the products were benzophenone and diphenylmethanol.

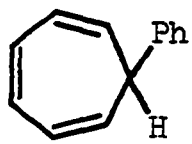


(See Table 7)

Table 7. Products of the oxidation of 7-PhCHT in aqueous acetonitrile by CAN

Solvent	Reaction Temp.	Ph_2CO	Ph_2CHOH	Yield
50%, CH_3CN	84°	53	47	87
75%, CH_3CN	84°	25	75	95

A mixture of isomers of phenylcycloheptatriene was oxidized in 85 per cent aqueous acetic acid. The products were biphenyl, benzophenone, and all three isomeric phenylbenzaldehydes (see Table 8). The composition of the phenyl-



$\longrightarrow$ Ph-Ph + Ph_2CO + o-PhC_6H_4CHO + m-PhC_6H_4CHO + p-PhC_6H_4CHO

Table 8. Products of the oxidation of phenylcycloheptatrienes in 85 per cent aqueous acetic acid by CAN

Reaction Time	Temp	Relative Yields, %				
		Ph-Ph	Ph_2CO	Ph-C_6H_4CHO o	m	p
35 min	85°	28	8	9	25	30

cycloheptatrienes was greater than 85 per cent 3-PhCHT with the ratio of other isomers unknown.

1-PhCHT, 2-PhCHT, and 3-PhCHT were each oxidized in 50 and 75 per cent aqueous acetonitrile (see Tables 9 and 10, respectively). The products were biphenyl, benzophenone, and

Table 9. The products of the oxidation of phenylcycloheptatrienes in 50 per cent aqueous acetonitrile by CAN

Substrate	Temp	Reaction Time	Relative Yield, %					Yield
			Ph-Ph	Ph_2CO	Ph-C_6H_4CHO o	m	p	
3-PhCHT	81°	20 min	30	3	16	25	25	--
2-PhCHT	83°	5 min	18	6	22	32	22	24
1-PhCHT	75°	5 min	28	17	20	35	--	24

Table 10. The products of the oxidation of phenylcycloheptatrienes in 75 per cent aqueous acetonitrile by CAN

Substrate	Run	Time (min)		Relative Yield[a,b]					Yield
		Add'n	Stir	Ph-Ph	Ph_2CO	Ph-C_6H_4CHO o	m	p	
1-PhCHT	1[c]	25	15	49	22	8	9	12	56
	2[c]	1	15	51	13	--	22	16	62
	3[d]	2	15	52	13	--	13	22	66

[a]At least two analyses were made for each run.

[b]The average deviation (σ relative) for each run was less than one per cent.

[c]The temperature was $84 \pm 3°$.

[d]The concentration of 1-PhCHT was one half that in the other runs.

Table 10 (Continued)

Substrate	Run	Time (min) Add'n	Time (min) Stir	Relative Yield[a,b] Ph-Ph	Ph_2CO	Ph-C_6H_4CHO o	m	p	Yield
	4[e]	2	30	52	1	11	16	19	70
	5[f]	5	60	48	13	--	22	17	74
2-PhCHT	1[c]	4	10	40	23	5	13	20	34
	2[c]	17	15	40	20	6	18	16	42
3-PhCHT	1[c]	2	15	42	9	9	17	21	72
	4[c]	24	15	39	10	14	16	21	34

[e]The temperature was 61°.

[f]The temperature was 18°.

mixtures of the phenylbenzaldehydes. In 50 per cent acetonitrile, 1-PhCHT gave all of the above products except p-phenylbenzaldehyde. In at least two runs three aldehydes were observed. Although no analytical results are available for these runs, there is no evidence (except that of a speculative nature) which can discount the (apparent) fact three aldehydes are obtainable from the oxidation of 1-PhCHT. The other isomers gave all three aldehydes in all cases. In 75 per cent aqueous acetonitrile a wide variety of results were obtained for 1- and 3-PhCHT. Either all three aldehydes were obtained or the o-isomer was missing. In all cases there was a wide scatter of the relative yields for each isomer. There was in most cases a wide scatter of absolute

yields also.

Phenylcycloheptatrienylium fluoborate was oxidized in 50 and 75 per cent aqueous acetonitrile with two equivalents in CAN. The products were biphenyl, benzophenone, and m- and p-phenyl benzaldehyde (see Table 11). The salt was dissolved in a reduced CAN solution to reproduce as closely as possible its environment in the reaction.

Table 11. The products of the oxidation of phenylcycloheptatrienylium fluoborate by two equivalents of CAN

Solvent	Temp	Relative Yield, %					Yield
		Ph-Ph	Ph_2CO	Ph-C_6H_4CHO			
				o	m	p	
50% CH_3CN	82°	27	18	--	22	33	56
75% CH_3CN	80°	25	21	--	21	33	56

DISCUSSION

The Cerium(IV) Oxidant Specie

The structure of solid ceric ammonium nitrate determined by Beineke (24) has six nitrates coordinated bidentate to a central cerium atom. The complex has a center of symmetry with the nitrates as blades of two 3-bladed propellers. There is nothing to suggest this structure is fundamentally altered in solution. Miller and Irish (25) have concluded from a study of the ir and raman spectra of aqueous CAN solutions that at least three nitrates are coordinated to each cerium. Henshall (26) has determined from chemical evidence that tetranitratocerium(IV) is the predominant specie in glacial acetic acid solutions of CAN. From an X-ray diffraction study of aqueous CAN solutions Larsen and Brown (27) found evidence for twelve cerium-oxygen interactions but could not tell whether the oxygen atoms were from water or nitrates.

The great weight of evidence for the cerium(IV) species in CAN solutions is that at least one and probably more nitrates are coordinated to each cerium atom.

Although one might speculate at great length upon whether the oxidation proceeds <u>via</u> a ligand (outer sphere) or direct coordination with the metal atom (inner sphere), essentially nothing is known about this question. In fact, very little is known about the coordination of olefins to

lanthanides. Therefore, it is with little if any justification that the oxidation will be visualized as proceeding via a ligand and a "$CeONO_2$" specie will be used to illustrate the oxidant.

One Electron or Two Electron Oxidant

Cerium has two stable oxidation states, cerium(III) and cerium(IV), with electronic configurations of the Xenon core and the Xenon core + $4f^1$, respectively (28, p. 1054). Cerium(IV) should, therefore, be a one-electron oxidant (1). Unfortunately, cerium(IV) has a high tendency to hydrate and polymerize (28, p. 1068). The complexity of the problem may be understood by the fact cerium(IV) in 1 f sulfuric acid and 1 f nitric acid migrates to the anode in an electrolytic cell, in 1.8 f sulfuric acid migrates to the cathode, and in 2 f nitric acid does not migrate at all. Different specie must be involved in each case and it has been suggested (29) that dimers, trimers, and perhaps higher polymers are involved. Indeed, if aggregates of cerium(IV) are possible, transfer of almost any number of electrons is feasible. Dorfman and Gryder (30) have found that Tl(I) may be oxidized in a single step to Tl(III), a two-electron transfer, by aqueous solutions of cerium(IV). Although this work does not confirm that cerium(IV) may accept two electrons, it does confirm cerium(IV) solutions may act as a two-electron oxidant. Some oxidations of organic compounds by cerium(IV)

also appear to involve a two-electron transfer, most notably the oxidation of toluenes (31, 32). Apparently the question of one- or two-electron transfer must be answered for each individual case.

The lack of polymerization of CHT in the CAN oxidations and the fact no radicals could be trapped when CHT or 7-PhCHT were oxidized in the presence of acrylamide suggests radicals are not being formed. However, Hunter (33) and Vincow (34) have found the cycloheptatrienyl radical to be chemically inert to polymerization and reaction with oxygen. Furthermore, if CAN is added to a CHT solution, only polymeric materials are isolated. There is, then, insufficient evidence to conclude the cerium(IV) oxidation of cycloheptatrienes is either a one- or two-electron process.

Unfortunately, a process involving two one-electron transfers cannot in any of the suggested mechanisms make any predictions the single two-electron transfer does. As the burden of proceeding through each mechanism for one-electron and then two-electron transfers would soon become overwhelming, the two-electron process has been chosen for its brevity.

Mechanistic Approaches

Trahanovsky (2) has shown that both cycloheptatriene and tropylium fluoborate yield benzene and benzaldehyde in similar ratios when oxidized by CAN:

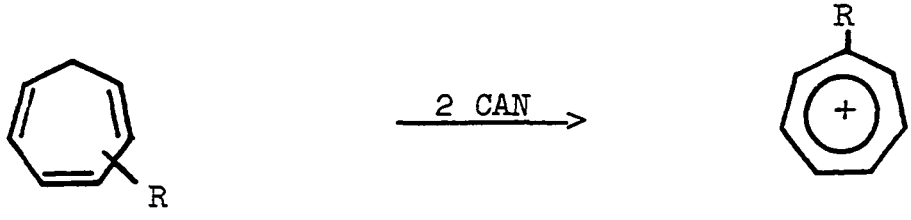
$$CHT + 4\ CAN \longrightarrow \underset{85\%}{C_6H_6} + \underset{15\%}{C_6H_5CHO}$$

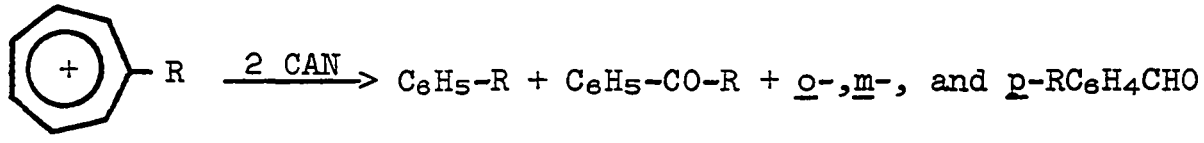
$$C_7H_7^+BF_4^- + 2\ CAN \longrightarrow \underset{86\%}{C_6H_6} + \underset{14\%}{C_6H_5CHO}$$

Along with the other evidence accumulated for the CHT oxidation, this suggested the intermediacy of the tropylium ion:

$$CHT \xrightarrow{2\ CAN} C_7H_7^+ \xrightarrow{2\ CAN} C_6H_6 + C_6H_5CHO$$

The same mechanism can be expanded to mono-substituted cycloheptatrienes. Replacing an R group for a hydrogen atom the predicted products are alkyl benzenes, an alkyl phenyl ketone, and alkyl benzaldehydes:



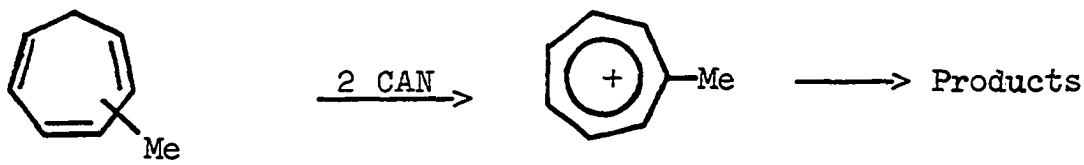


These are exactly the results which are obtained from the methylcycloheptatrienes. 7-MeCHT, a mixture of 1-,2-,3-, and 7-MeCHT, and $MeC_7H_8^+BF_4^-$ all give toluene, acetophenone, and o-, m-, and p-methylbenzaldehyde in approximately the same

amounts, indicating a very similar process is occurring in each case:

		$Ph-CH_3$	+ $Ph-CO-CH_3$	+ $CH_3-C_6H_4CHO$ o	m	p
7-MeCHT	4 CAN →	16%	17%	22%	27%	18%
1-,2-,3- and 7-MeCHT	4 CAN →	17%	17%	19%	29%	18%
$MeC_7H_8^+BF_4^-$	2 CAN →	17%	12%	25%	28%	18%

The slight differences in the MeCHT and $MeC_7H_8^+$ product ratios are probably due to the difficulty of introducing the methyltropylium ion in the same environment as it is generated in during the reaction. It should be noted that for the three examples the ratio of toluene to "oxygenated products" is 17 to 83 as compared to a ratio of 15 to 85 for CHT. The close similarity with the CHT oxidation makes it apparent that the methyl substituent has not altered the course of the reaction and a tropylium ion is an intermediate here also:



Fortunately, the phenyl substituent has greatly altered the course of the reaction. In 50 per cent aqueous acetonitrile 7-PhCHT is oxidized to diphenylmethanol and benzophenone, a set of products not predicted by a tropylium ion mechanism:

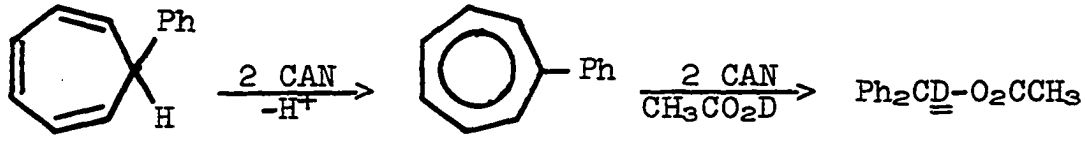
$$\text{7-PhCHT} \xrightarrow{4\ \text{CAN}} Ph_2CHOH + Ph_2CO$$

One important fact is that the proton on the 7-carbon of 7-PhCHT is apparently not lost, a necessary condition for tropylium ion formation. In deuterioacetic acid the diphenylmethyl acetate formed (corresponding to the diphenylmethanol in acetonitrile) contains no deuterium:

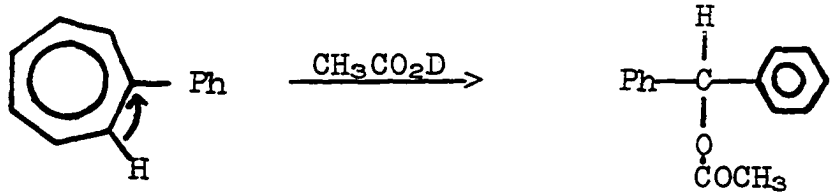
$$\text{7-PhCHT} \xrightarrow[CH_3CO_2D]{4\ \text{CAN}} Ph_2\underline{\underline{C}}H\text{-}O_2CCH_3$$

0% d

The methine hydrogen in the acetate in a tropylium ion mechanism should come from solvent:



This is not sufficient proof for lack of a tropylium ion intermediate, however, as there is the possibility of a migration of hydrogen with ring closure:



The other isomers of PhCHT in 50 per cent aqueous acetonitrile yield products more like MeCHT, biphenyl, benzophenone, and o-, m-, and p-phenylbenzaldehyde. There is an important difference, however, in that none of the product ratios are similar and, in fact, the p-phenylbenzaldehyde is completely missing from 1-PhCHT, suggesting identical processes are not occurring in all cases:

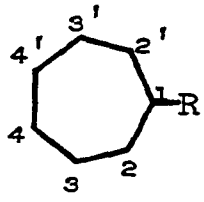
		Ph-Ph	+ Ph_2CO	+ Ph-C_6H_4CHO o	m	p
1-PhCHT	4 CAN →	28%	17%	20%	35%	---
2-PhCHT	4 CAN →	18%	6%	22%	32%	22%
3-PhCHT	4 CAN →	30%	3%	16%	25%	25%

Finally, $PhC_7H_6^+BF_4^-$ does not give all of the products expected for a tropylium ion, the o-phenylbenzaldehyde being missing:

$PhC_7H_6^+BF_4^-$ $\xrightarrow{2\ CAN}$ Ph-Ph + Ph_2CO + m- and p-Ph-C_6H_4CHO

It appears attack is occurring only at the 1- and 4,4'-carbons as attack at the 2,2'- and 3,3'-carbons would give some of the o-phenylbenzaldehyde. The reasons for this are obscure. Simple Hückel molecular orbital calculations indicate there is no excessive charge localized at the 1- and 4,4'-carbons (see Table 12) to cause exclusive attraction of charged cerium(IV) species to those positions. Inspection of models does not suggest the 2,2'- and 3,3'-carbons are particularly

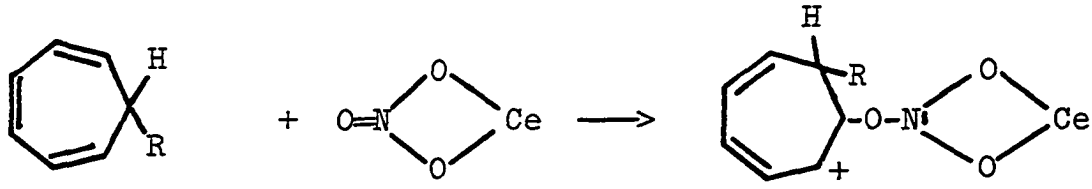
Table 12. Charge distributions of substituted cycloheptatrienyl ions from simple Hückel molecular orbital calculations

Numbering Scheme	R=	1	2,2'	3,3'	4,4'
	H	.8571	.8571	.8571	.8571
	Ph	.8573	.8621	.8692	.8660
	p-$NO_2C_6H_4$	.8797	.8397	.8665	.8529

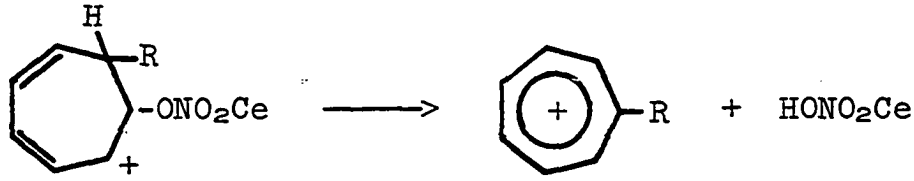
hindered. In any case, the ion should be flat with access of attack from above and below. There does seem to be something "magical" about the 4,4'-carbons. Dewar (8) found only terephthalic acid in his oxidations of cycloheptatriene-7-carboxylic acid. Attack at the 2,3-bonds would have produced some isophthalic acid and hence attack occurred only at the 4,4'-carbons. Nozoe (14) found $PhC_7H_7^+$ is converted only to 4-phenyltropone by chromic acid, again attack at the 4,4'-carbons. Neither author could explain their results (or even attempted to) and neither can we. As inexplicable as the results may be, they are at least available for comparison with those from the parent hydrocarbons.

The oxidation of PhCHT is evidently not proceeding <u>via</u> the phenyltropylium ion. The products from the isomeric PhCHT's are not those obtained from $PhC_7H_7^+$ and the difference in product ratios indicates identical intermediates are not involved in each case. As it is difficult to be-

lieve a completely different reaction than with CHT is occurring here, the answer must lie in the steps leading to the tropylium ion. Waters (35, p. 109) has suggested that "...the first step of an aromatic substitution...is an addition to the organic molecule of a powerful electrophilic reagent and so is, in fact, an oxidation (of olefins)". This is probably the first step in the oxidation of all cycloheptatrienes by CAN:

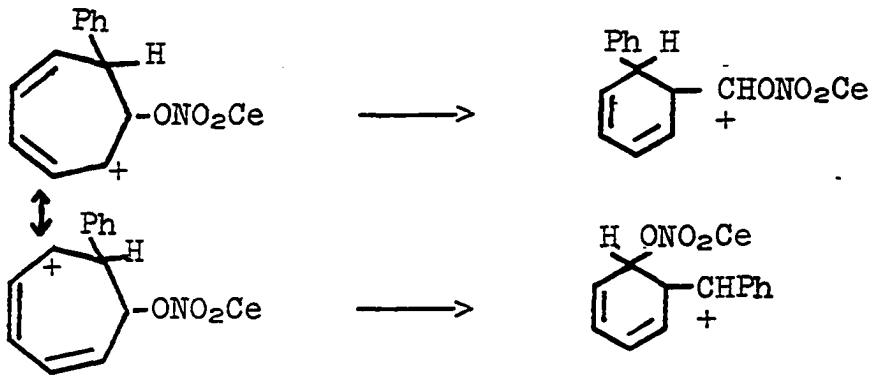


With CHT and MeCHT the adduct apparently dissociates to the tropylium ion:

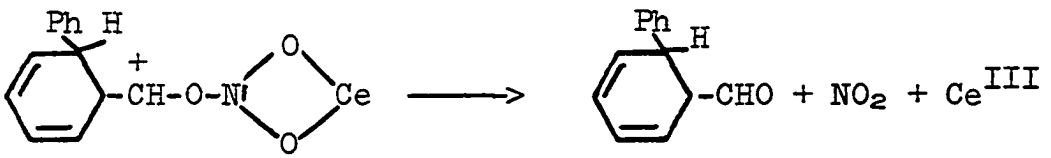


With PhCHT this dissociation does not occur and the adduct must react in another way.

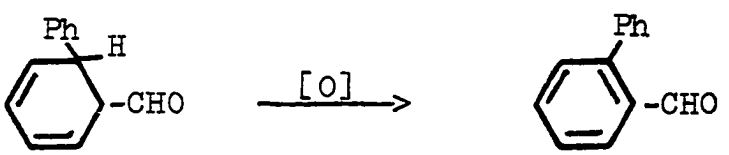
One possible reaction of the PhCHT-ONO_2Ce adduct is a Wagner-Meerwein shift to yield cyclohexadienes in a process similar to that suggested by Dewar (8) in the oxidation of cycloheptatriene-7-carboxylic acid:



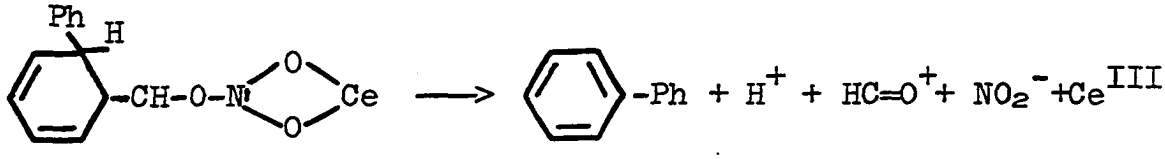
Ring closure can occur to give two cyclohexadienes, one with the cerium specie on the α-carbon and one with it on the ring. As there are six possible sites of attack each isomer of PhCHT should give six adducts with ring closure from each. In all cases, however, only the two general types of cyclohexadienes will be produced. The further reactions of these lead to the products. The cyclohexadiene with the cerium specie on the α-carbon can oxidize very readily to a carbonyl compound:



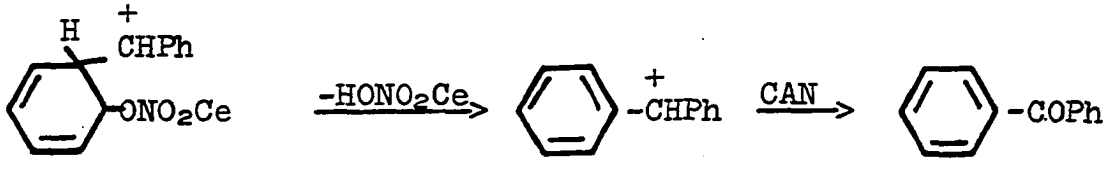
Dehydrogenation of the cyclohexadiene should be quite facile:



If the substituent is on the ring, aryl benzaldehydes will be produced, but if the substituent is on the α-carbon the product will be the aryl phenyl ketone. The α-carbon ring bond can also be broken in an oxidative step to yield an aryl benzene and carbon monoxide:



The other cyclohexadiene can lose the elements of $HONO_2Ce$ to form a benzylic cation. It has been well-established that benzyl cations are oxidized to benzaldehydes by CAN (36):



Again, depending on where the substituent is, the products are aryl benzaldehydes or an aryl phenyl ketone.

Thus, it is possible for a substituted cycloheptatriene to be oxidized to an aryl benzene, aryl benzaldehydes, and an aryl phenyl ketone without proceeding <u>via</u> the tropylium ion:

$$PhCHT \longrightarrow C_6H_5\text{-}Ph + C_6H_5\text{-}CO\text{-}Ph + Ph\text{-}C_6H_4CHO$$

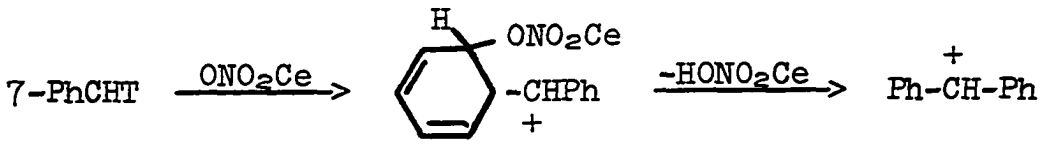
It is obvious that the substitution pattern of the cycloheptatriene will be important in determining the products formed. These results are summarized in Table 13. In

particular one should note that this mechanism predicts exactly the products from 1-, 2-, and 3-PhCHT.

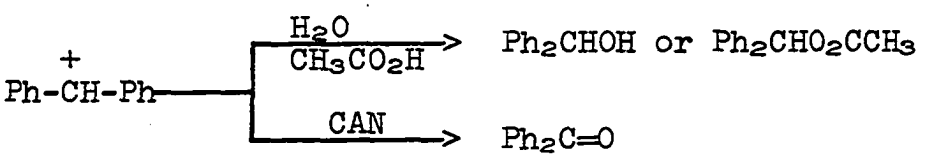
Table 13. Products predicted for the oxidation of substituted cycloheptatrienes by CAN *via* cyclohexadienes

Substrate	C_6H_5-Ph	C_6H_5-CO-Ph	Ph-C_6H_4CHO o	m	p
7-PhCHT	x	x	x		x
1-PhCHT	x	x	x	x	
2-PhCHT	x	x	x	x	x
3-PhCHT	x	x	x	x	x

No *p*-phenylbenzaldehyde is expected from 1-PhCHT and none is found experimentally. As each isomer should give different sets of adducts different product ratios should be obtained for each isomer and this is indeed what is observed, especially with 2- and 3-PhCHT. Unfortunately, the correlation is not as good with 7-PhCHT. Some biphenyl and *o*- and *p*-phenylbenzaldehyde are predicted but none is observed. This may be due to predominate ring closure to give the cyclohexadiene with the cerium specie on the ring and the positive charge on the α-carbon stabilized by the phenyl group, from which the diphenylmethyl cation can very readily be formed:



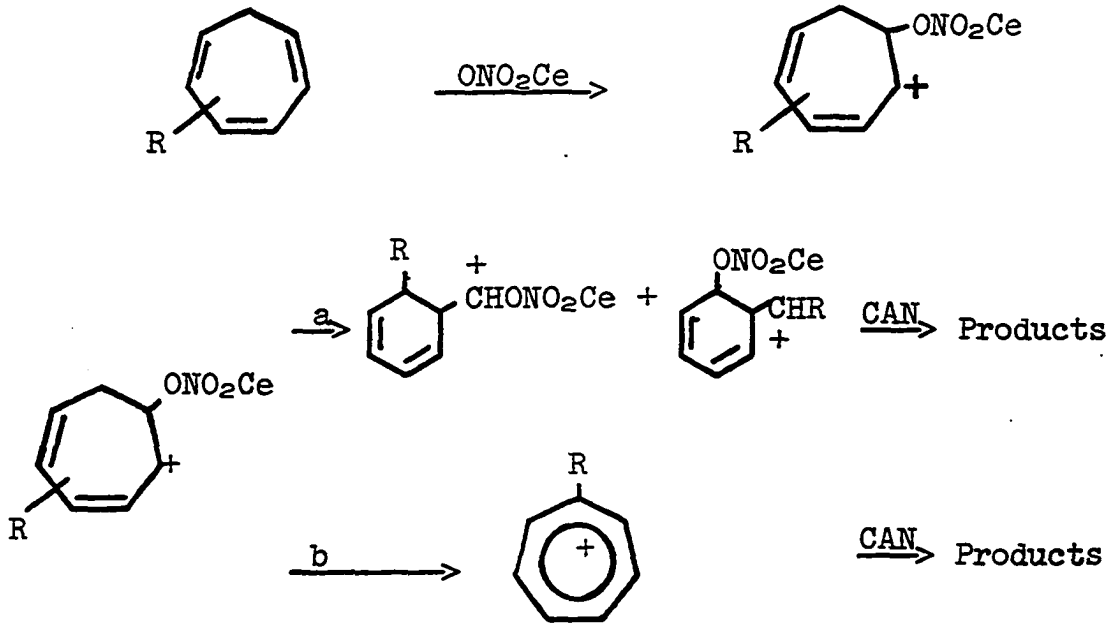
The diphenylmethyl cation can be attacked by solvent, thus the diphenylmethanol and the acetate ester (in acetic acid), or be oxidized to benzophenone:



The other possibilities with 7-PhCHT yield benzylic cations on ring closure, a less energetically favorable situation.

Some consideration must be given as to why the tropylium ion is formed in the CHT and MeCHT oxidations and not in those of PhCHT. There seems to be two competing pathways leading from the first oxidized adduct of cycloheptatrienes. One is dissociation to tropylium ion; the other is immediate ring closure to a cyclohexadiene. It doesn't seem the stability of cations formed can be the deciding factor in the choice between the two as the tropylium ion should greatly overcome any benzylic cations. There may be very little difference between the two pathways but the dissociation is slightly favored. If stabilization could be effected in the adduct, then ring closure may predominate. This appears to be the case with the phenyl substituent. The extra stabilization of the electron deficient center causes the

reaction to swing away from the tropylium ion. Even here the balance is delicate as in 75 per cent aqueous acetonitrile 1-PhCHT appears to be oxidized in some cases via the tropylium ion, evidenced by the formation of p-phenylbenzaldehyde known not to come from a ring closure. These conclusions may be summarized in the following scheme:



Thus, when R is a substituent which will stabilize an electron deficient center, ring closure to cyclohexadienes predominates (path a). In other cases, dissociation to the tropylium ion occurs (path b).

EXPERIMENTAL

Equipment

All nuclear magnetic resonance spectra (nmr) were taken on a Varian A-60 spectrometer. Chemical shifts are measured as δ-values in ppm from tetramethylsilane.

The infrared (ir) spectra were obtained on a Beckman IR-12 instrument.

Mass spectra were measured on an Atlas CH-4 spectrometer.

Gas liquid partition chromatography (glpc) analyses were done on an Aerograph Model 200 instrument with dual thermal conductivity detectors.

Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected.

Methods

Glpc analyses were carried out using either a 7' x ¼" column packed with 20% 1,2,3-tris(cyanoethoxy)propane on Chromosorb P (60/80 mesh) (for the MeCHT oxidations) or on a 6' x ¼" column packed with 20% SE-30 on Chromosorb P (60/80 mesh) (for the PhCHT oxidations). Peak areas were determined by planimetry, cutting and weighing, or disc integration.

Analysis for the o-, m-, and p-methylbenzaldehydes was as follows: Glpc analysis provided the absolute yield of the o- + m-isomers and the p-isomer. Nmr analysis provided the o/(m + p) ratio. The following equations were used to obtain the yields:

$$\underline{o} + \underline{m} = a$$

$$\underline{p} = b$$

$$\underline{o}/(\underline{m} + \underline{p}) = y$$

$$\underline{m} = \frac{a-by}{y+1}$$

Analysis for the o-, m, and p-phenylbenzaldehydes was as follows: Glpc analysis provided the yield of benzophenone + the o-isomer and the m- + p-isomers. Nmr provided the o:m:p ratios and the simple proportions were used to separate the yields of the various components.

The absence or presence of the phenylbenzaldehydes was determined in each case by positive peak enhancement in the nmr spectra by addition of authentic sample.

Absolute yields were determined by adding diphenyl ether as the internal standard for the oxidation of 7-PhCHT and $PhC_7H_7^+BF_4^-$; 1,4-di-t-butylbenzene as internal standard for the oxidation of 1-, 2-, or 3-PhCHT; and mesitylene as internal standard for the oxidation of the MeCHT's and $MeC_7H_7^+BF_4^-$.

Product identifications were made by collection of glpc fractions and comparison of their nmr and ir spectral properties with those of authentic samples.

Thermal conductivity and extraction ratios were determined by subjecting known mole ratios of the products and internal standards to the reaction conditions.

The molecular orbital calculations were performed on an IBM S360 computer using the MOCAO program.

Materials

Reagents and solvents were used as obtained from commercial sources unless purification procedures are noted.

Toluene (Baker Analyzed Reagent), acetophenone (Matheson Coleman and Bell), mesitylene (Matheson Coleman and Bell), diphenyl ether (Matheson Coleman and Bell), 1,4-di-t-butylbenzene (Eastman), and biphenyl (Eastman) were used as received from commercial sources. Ceric ammonium nitrate was used as received from the supplier (G. F. Frederick Smith Chemical Co.) and it was assumed the equivalent weight was 548.

7-Methylcycloheptatriene

7-Methylcycloheptatriene was prepared by the method of Conrow (18), bp 32° (35 mm) (lit. (18) 50° (42 mm)); nmr ($CDCl_3$) δ 6.6 (m, 2, C_3-olefin), 6.0 (m, 2, C_2-olefin), 5.0 (m, 2, C_1-olefin), 1.6 (m, 1, C_7-H), 1.2 (m, 3, C_7-Me).

Tropylium fluoborate

Tropylium fluoborate was prepared by the method of Dauben (37).

Isomerization of 7-methylcycloheptatriene

Isomerization of 7-methylcycloheptatriene was performed by vacuum pyrolysis at 400° (0.3 mm); nmr (Neat) δ 6.5 (m), 5.25 (m), 2.2 (m), and 1.2 (m).

o-Methylbenzaldehyde

o-Methylbenzaldehyde was prepared from 2-methylbenzyl alcohol (obtained from the hydrolysis of 2-methylbenzyl acetate (Aldrich Chemical Co.)) using the oxidative procedure of Trahanovsky (38) to yield a viscous oil (39); nmr ($CDCl_3$) δ 10.15 (s, 1, C<u>H</u>O), 7.2 (m, 4, $MeC_6\underline{H}_4CHO$), 2.5 (s, 3, CH_3-PhC<u>H</u>O).

m-Methylbenzaldehyde

m-Methylbenzaldehyde was prepared from 3-methylbenzyl alcohol (obtained from the hydrolysis of 3-methylbenzyl acetate (Aldrich Chemical Co.)) using the oxidative procedure of Trahanovsky (38) to yield an oil (40); nmr ($CDCl_3$) δ 9.95 (s, 1, C<u>H</u>O), 7.2 (m, 4, $MeC_6\underline{H}_4CHO$), and 2.5 (s, 3, $C\underline{H}_3PhCHO$).

p-Methylbenzaldehyde

p-Methylbenzaldehyde was used as obtained (Aldrich Chemical Co.); nmr ($CDCl_3$) δ 9.90 (s, 1, C<u>H</u>O), 7.3 (q, 4, $MeC_6\underline{H}_4CHO$), and 2.5 (s, 3, $C\underline{H}_3PhCHO$).

7-Phenylcycloheptatriene

7-Phenylcycloheptatriene was prepared by the method of ter Borg (21) and recrystallized from absolute ethanol, mp 31-2° (lit. (21) 30.0-31.5°); nmr (CCl_4) δ 7.2 (m, 5, PhCHT), 6.7 (m, 2, C_3-olefin), 6.2 (m, 2, C_2-olefin), 5.4 (m, 2, C_1-olefin), and 2.7 (m, 1, C_7-H).

3-Phenylcycloheptatriene

3-Phenylcycloheptatriene was prepared by heating 7-PhCHT at 166° for 30 min (22) and distilling the residue through a short path condenser at 75-85° (0.1 mm); nmr (neat) δ 7.2 (m, 5, PhCHT), 6.8 (d, 1, J = 7 Hz, C_3-olefin), 6.3 (m, 2, C_2-olefin), 5.3 (m, 2, C_1-olefin), and 2.25 (t, 2, J = 7 Hz, C_7-H).

2-Phenylcycloheptatriene

2-Phenylcycloheptatriene was prepared by irradiating 1 g of 3-PhCHT in 30 ml of benzene which had been purged with nitrogen for one hour in a Rayonet at 3560 Å for 10 hours (23). The benzene was removed under vacuum and the sample was used without further purification; nmr (neat) δ 7.1 (m, 5, PhCHT), 6.8 (m, 2, C_3-olefin), 6.1 (m, 1, C_2-olefin), 5.3 (m, 2, C_1-olefin), and 2.2 (t, 2, J = 7 Hz, C_7-H).

1-Phenylcycloheptatriene

1-Phenylcycloheptatriene was prepared by the method of Cairncross (22); nmr ($CDCl_3$) δ 7.2 (m, 5, PhCHT), 6.4 (m, 4, C_3- and C_2-olefin), 5.3 (m, 1, C_1-olefin), 2.7 (d, 2, J = 7 Hz, C_7-H).

Phenylcycloheptatrienylium fluoborate

Phenylcycloheptatrienylium fluoborate was prepared using the method of Cairncross (22) and recrystallized from ethyl acetate and acetonitrile, mp 150-6° (lit (22) 154.7-

156.4°); nmr (CD_3CN) δ 9.1 (m, 6, $C_7\underline{H_8}Ph$), 7.8 (m, 5, CHT-$C_8\underline{H_5}$).

Methylcycloheptatrienylium fluoborate

Methylcycloheptatrienylium fluoborate was prepared using the hydride exchange method of Conrow (18). A quantity of 0.8 ml of 7-MeCHT was added to 2.3 g of triphenylmethyl fluoborate in 12.8 ml of acetonitrile in a Dry Ice-acetone bath. The yellow color of the trityl ion was discharged in approximately 10 min and a white precipitate formed. The temperature of the bath was allowed to rise slowly and at -30° the color of the precipitate changed to a dark green. After the temperature of the bath had reached room temperature, the ether was removed under vacuum. Quantities of 25 ml of ethyl acetate were added and removed under vacuum. A final quantity of 15 ml of ethyl acetate was added which caused the precipitation of 1.1 grams of green needles (78%), mp 85-89°; nmr (CD_3CN) δ 9.9 (s, 6, $MeC_7\underline{H_6}$), 3.1 (s, 3, $C\underline{H_3}CHT$).

Anal. Calcd. for $C_8H_9BF_4$: C, 50.06; H, 4.73. Found: C, 49.10; H, 4.71.

o-Phenylbenzaldehyde

A quantity of 1.58 g of lithium aluminum hydride was added to 10 g of 2-phenylbenzoic acid (Aldrich Chemical Co.) in 200 ml of ether and the solution was stirred for one hour. A water-saturated ether solution was added until no

more precipitate formed, followed by sufficient 2 N nitric acid to dissolve the precipitate. The ether layer was separated, washed with water and saturated sodium bicarbonate solution, dried ($MgSO_4$), and the ether was removed in vacuo. The 2-phenylbenzyl alcohol was oxidized to 2-phenylbenzaldehyde using the procedure of Trahanovsky (38). The product was a thick liquid (41); nmr ($CDCl_3$) δ 9.91 (s, 1, PhPhC<u>H</u>O), 7.4 (m, 9, <u>PhPh</u>CHO).

<u>m</u>-Phenylbenzaldehyde

To a Grignard prepared from 0.01 moles of magnesium and 0.01 moles of 3-bromobiphenyl (K & K Laboratories, purified by distillation, bp 138-142 (15 mm)) in 25 ml of ether was added 0.01 moles of N-methylformaline at 0° using the method of Buehler (42). Each drop caused vigorous boiling and a copious white precipitate was obtained. Sixty ml of dilute hydrochloric acid and ice was added and the ether layer separated, washed with water, and dried ($MgSO_4$). The product was an oil; nmr ($CDCl_3$) δ 10.01 (s, 1, PhPhC<u>H</u>O), 7.6 (m, 9, <u>PhPh</u>CHO).

<u>p</u>-Phenylbenzaldehyde

<u>p</u>-Phenylbenzaldehyde was used as obtained (Aldrich Chemical Co.); nmr ($CDCl_3$) δ 9.97 (s, PhPhC<u>H</u>O, 1) and 7.5 (m, <u>PhPh</u>CHO, 9).

Benzophenone

Benzophenone was used as obtained from commercial sources (Matheson Coleman and Bell), mp 48-49° (lit (43) 48.1).

Diphenylmethanol

Diphenylmethanol (Matheson Coleman and Bell) was recrystallized from ethanol, mp 67-69° (lit (43) 69°); nmr ($CDCl_3$) δ 7.3 (m, $\underline{Ph}_2CHOH$, 10), 5.8 (s, $Ph_2C\underline{H}OH$, 1), and 2.3 (s, $Ph_2CHO\underline{H}$, 1).

Diphenylmethyl acetate

Diphenylmethyl acetate was prepared by the method of Harvey and Stinson, mp 41-42° (lit (44) 42°): nmr ($CDCl_3$) δ 7.0 (m, $\underline{Ph}_2CHO_2CCH_3$, 10), 6.85 (s, $Ph_2C\underline{H}O_2CCH_3$, 1), and 2.0 (s, $Ph_2CHO_2CC\underline{H}_3$, 3).

Diphenylmethyl nitrate

Diphenylmethyl nitrate was prepared from diphenylmethyl chloride (b 101° (0.2 mm) (lit (45) 173° (19 mm)) using the method of Cheeseman (46), mp 35-36° (lit (47) 36.2-37.2): nmr (CCl_4) δ 7.3 (s, $\underline{Ph}_2CHONO_2$, 10), 6.8 (s, $Ph_2C\underline{H}ONO_2$, 1); ir (thin film) cm^{-1} 1645 (s), 1290 (s), 860 (s).

Reactions

Cerium(IV) oxidations of methylcycloheptatrienes

7-Methylcycloheptatriene. A quantity of ca. 400 mg of 7-MeCHT in 10 mls of acetonitrile was added dropwise to a

solution of ca. 8.7 g of CAN (4.2 eq) in 50 percent aqueous acetonitrile at 78°. The cerium(IV) color first faded to colorless, then darkened to a deep red. After stirring for 5 min and cooling, ca. 100 mg of mesitylene was added as an internal standard. The mixture was poured into 50 ml of water, extracted twice with 25 ml of ether, washed three times with water, and dried ($MgSO_4$). The ether was removed by fractional distillation. Analysis was by glpc and nmr ($CDCl_3$) δ 10.1 (s, p-$CH_3C_6H_4CHO$), 9.9 (2 lines, o- and m-$CH_3C_6H_4CHO$), 7.6 (m, phenyl hydrogens), 2.7 (s, $PhCOCH_3$), 2.6 (s, o-$CH_3C_6H_4CHO$), 2.4 (s, m- + p-$CH_3C_6H_4CHO$), and 2.3 (s, $PhCH_3$); ir (thin film) cm^{-1} 1680 (s), 1600 (s), and 1240 (s).

1-, 2-, 3-, And 7-methylcycloheptatriene mixture. A weighed quantity of ca. 550 mg of a mixture of MeCHT's in 10 ml of acetonitrile was added dropwise to a solution of 12.3 g of CAN (4 eq) in 50 per cent aqueous acetonitrile at 78°. The color change, work up, and analysis was identical for that for 7-MeCHT; nmr (neat) δ 10.1 (s), 9.9 (2 lines, 7.6 (m), 2.7 (s), 2.6 (s), 2.4 (s), and 2.3 (s).

Methyltropylium fluoborate. A weighed quantity of ca. 200 mg of $MeC_7H_6^+BF_4^-$ in 10 ml of acetonitrile was added to a solution of ca. 1.2 g CAN (2 eq) in 50 per cent aqueous acetonitrile at 82°. The color was discharged immediately

and a flocculent white precipitate formed. A quantity of ca. 30 mg of mesitylene was added as internal standard and the work up and analysis procedure for 7-MeCHT followed: Nmr ($CDCl_3$) δ 10.1 (s), 9.9 (2 lines), 7.6 (m), 2.7 (s), 2.6 (s), 2.4 (s), and 2.3 (s).

Cerium(IV) oxidations of phenylcycloheptatrienes in acetic acid

7-Phenylcycloheptatriene.

Four equivalents. A weighed quantity of ca. 200 mg of 7-PhCHT in 10 ml of glacial acetic acid was added to an equivalent amount of 0.5 N CAN solution in 75 per cent acetic acid (4 eq) at 84°. The solution faded to a light orange and stirring was continued for 7-40 min. A weighed quantity of ca. 40 mg of diphenyl ether was added and the mixture extracted twice with 20 ml of ether, washed three times with 10 ml of water and three times with 10 ml of saturated sodium bicarbonate, and dried ($MgSO_4$). Analysis was by glpc and nmr: ($CDCl_3$) δ 7.6 (m), 7.3 (m), 5.7 (s, $Ph_2C\underline{H}OH$), and 2.0 (s, $Ph_2CHO_2CC\underline{H}_3$); ir ($CCl_4$) cm^{-1} 3500 (w), 174 (s), 1500 (m), 1200 (s), and 1030 (s).

Two equivalents. A quantity of ca. 200 mg of 7-PhCHT in 5 ml of glacial acetic acid was added to 5 ml of 0.5 N CAN in 75 per cent aqueous acetic acid (2 eq). The CAN solution turned colorless after addition of approximately one half of the 7-PhCHT, then darkened to a deep red. After

stirring for 15 min, the mixture was added to 10 ml of water, extracted twice with 15 ml of ether, washed three times with water and two times with 10 ml of a saturated solution of sodium bicarbonate, and dried ($MgSO_4$). Analysis by nmr: ($CDCl_3$) δ 7.3 (m, $\underline{Ph_2}CHO_2CCH_3$), 6.8 (s, $Ph_2C\underline{H}O_2CCH_3$), and 2.0 (s, $O_2CHO_2C\underline{H_3}$).

1-, 2-, 3-, And 7-phenylcycloheptatriene mixture. A weighed quantity of ca. 170 mg of PhCHT's in ca. 8 ml of glacial acetic acid was added to an equal amount of 0.5 N CAN in 75 per cent acetic acid (4 eq) at 85°. After stirring for 3 min and cooling, the mixture was extracted twice with 15 ml of ether, washed three times with 10 ml of water and three times with 10 ml of saturated sodium bicarbonate solution, and dried ($MgSO_4$). Analysis was by glpc and nmr: ($CDCl_3$) δ 10.0 (3 lines, $PhC_6H_4C\underline{H}O$) and 7.4 (m, phenyl).

Cerium(IV) oxidation in deuteroacetic acid

7-Phenylcycloheptatriene. To a solution of 2.61 g CAN (4 eq) in 9.52 ml of 75 per cent deuteroacetic acid (in deuterium oxide) at 82° was added a solution of 200 mg of 7-PhCHT in 9.52 ml of deuteroacetic acid. After stirring for 15 min, the mixture was added to 5 ml of deuterium oxide, extracted twice with 20 ml of ether, washed three times with 10 ml of water and three times with 10 ml of saturated sodium bicarbonate, and dried ($MgSO_4$). Analysis by nmr in-

dicated no evidence for deuterium in the diphenylmethanol or diphenylmethyl acetate: nmr ($CDCl_3$) δ 7.7 (m, o-Ph_2CO, 15), 7.2 (m, 135), 6.85 (s, $Ph_2C\underline{H}O_2CCH_3$, 7), 5.7 (s, $Ph_2C\underline{H}OH$, 2), and 2.0 (s, $Ph_2CHO_2CC\underline{H}_3$, 21). Diphenylmethyl acetate was separated by glpc and analyzed by mass spectrometry: Parent (226) 599; Parent + 1 (227) 99; P = 100, P+1 = 16.5. Calcd. for $C_{15}H_{14}O_2$ P = 100, P+1 = 16.51.

Cerium(IV) oxidations in 50% acetonitrile

7-Phenylcycloheptatriene. A quantity of ca. 200 mg of 7-PhCHT in 10 ml of acetonitrile was added to ca. 2.7 g CAN (4 eq) in 10 ml water at 84°. After stirring for 5 min and cooling, ca. 70 mg of mesitylene was added as an internal standard. The mixture was poured into 50 ml of water, extracted twice with 25 ml of ether, washed twice with 25 ml of water and once with 25 ml of saturated sodium bicarbonate solution, and dried ($MgSO_4$). Analysis was by nmr: ($CDCl_3$) δ 7.8 (m, o-Ph_2CO, 24), 7.2 (m, phenyl, 201), 6.7 (s, $C_6\underline{H}_3(CH_3)_3$, 18), 5.7 (s, $Ph_2C\underline{H}OH$, 14), and 2.2 (s, $C_6H_3(C\underline{H}_3)_3$, 52).

1-Phenylcycloheptatriene. A weighed quantity of ca. 250 mg of 1-PhCHT in 10 ml of acetonitrile was added dropwise to 3.30 g CAN (4 eq) in 10 ml of water at 75°. After cooling, the solution was poured into 5 ml of water, extracted twice with 25 ml of ether, washed thrice with 25 ml

of water, and dried ($MgSO_4$). Analysis was by nmr and glpc. After glpc analysis, a quantity of ca. 95 mg of 1,1,2,2-tetrachloroethane was added as internal standard and the nmr repeated. The total yield was based on the aldehyde and tetrachloroethane integrals; nmr ($CDCl_3$) δ 10.0 and 9.91 (2 lines, o- and m-Ph-C_6H_4C<u>H</u>O, 9), 7.4 (m, phenyl), and 5.8 (s, C_2Cl_4<u>H_2</u>, 30).

2-Phenylcycloheptatriene. A quantity of ca. 230 mg of 2-PhCHT was oxidized in a manner identical to that for 1-PhCHT. Analysis was by the same procedure: nmr ($CDCl_3$) δ 10.0 (3 lines, o-, m- and p-PhC_6H_4CHO) and 7.3 (m, phenyl).

3-Phenylcycloheptatriene. A quantity of ca. 200 mg 3-PhCHT in 10 ml of acetonitrile was added dropwise to a solution of 2.61 g CAN (4 eq) in 10 ml of water at 81°. A white precipitate was formed. After stirring for 20 min, the mixture was poured into 50 ml of water, extracted twice with 25 ml of ether, washed thrice with 25 ml of water, and dried ($MgSO_4$). Analysis was by glpc and nmr: ($CDCl_3$) δ 10.0 (3 lines) and 7.3 (m).

Phenylcycloheptatrienylium fluoborate. A weighed quantity of 300 mg of $PhC_7H_7^+BF_4^-$ in 10 ml of acetonitrile was added to ca. 1.34 g CAN (2 eq) in 10 ml of 50 per cent aqueous acetonitrile at 80°. The reaction was instantaneous and a flocculent white precipitate formed. A quantity of

ca. 60 mg of diphenyl ether was added as a standard and the mixture added to 50 ml of water, extracted twice with 50 ml of ether, washed twice with 25 ml of water, and dried ($MgSO_4$). Analysis was by glpc and nmr ($CDCl_3$) δ 9.97 (2 lines, m- and p-$PhC_6H_4C\underline{H}O$) and 7.3 (m, phenyl).

Cerium(IV) oxidations in 75% acetonitrile

7-Phenylcycloheptatriene. A weighed quantity of ca. 200 mg of 7-PhCHT in 10 ml of acetonitrile was added dropwise to a solution of ca. 3.0 g CAN (4 eq) in 10 ml of 50 per cent acetonitrile at 83°. The solution darkened upon the addition. After stirring for 15 min and cooling, ca. 60 mg of mesitylene was added as internal standard. The mixture was poured into 50 ml of water, extracted twice with 25 ml of ether, washed thrice with 25 ml of water, and dried ($MgSO_4$). Analysis was by glpc and nmr ($CDCl_3$) δ 7.8 (m, o-phenyl, 16), 7.3 (m, phenyl, 216, 6.8 (s, $C_6\underline{H}_3(CH_3)_3$, 6.5), 5.7 (s, $Ph_2C\underline{H}OH$, 15.5), and 2.2 (s, $C_6H_3(C\underline{H}_3)_3$, 6); ir ($CDCl_3$) cm^{-1} 3500 (s), 1740 (s), 1680 (s), 1600 (m), 1500 (m), 1440 (m), and 1200 (s).

1-Phenylcycloheptatriene.

Slow addition. A quantity of ca. 150 mg of 1-PhCHT in 10 ml of acetonitrile was added to ca. 2.1 g CAN (4 eq) in 10 ml of 50 per cent acetonitrile at 87° over a period of 35 min. After stirring for 15 min and cooling, ca. 26 mg of 1,4-di-tert-butylbenzene was added as an internal standard.

The work up and analysis was identical to that for 1-PhCHT in 50% acetonitrile: nmr ($CDCl_3$) δ 10.0 (3 lines, o-, m-, and p-PhC_6H_4CHO) and 7.3 (m, phenyl).

Fast addition. A quantity of ca. 200 mg of 1-PhCHT in 10 ml of acetonitrile was added all at once to ca. 2.6 g CAN (4 eq) in 10 ml of 50 per cent acetonitrile at 83°. After stirring for 15 min, ca. 40 mg of 1,4-di-tert-butylbenzene was added as internal standard and the mixture worked up and analyzed in a manner identical for that for 1-PhCHT: nmr ($CDCl_3$) δ 9.91 and 9.97 (2 lines, m- and p-PhC_6H_4CHO) and 7.3 (m).

Reaction at 60°. A quantity of ca. 200 mg of 1-PhCHT and ca. 2.5 g CAN were reacted in the same manner as for the slow addition but at a bath temperature of 60°: nmr ($CDCl_3$) δ 10.0 (3 lines) and 7.3 (m).

Reaction at 18°. A quantity of 300 mg of 1-PhCHT and 3.7 g CAN were reacted at room temperature in the same manner as for the slow addition. Stirring was continued for one hour: nmr ($CDCl_3$) δ 9.97 and 9.91 (2 lines, m- and p-PhC_6H_4CHO) and 7.3 (m).

2-Phenylcycloheptatriene. A quantity of ca. 200 mg of 2-PhCHT in 10 ml of acetonitrile was added to ca. 2.5 g CAN (4 eq) in 10 ml of 50 per cent acetonitrile at 82°. After

stirring, a quantity of ca. 40 mg of 1,4-di-tert-butylbenzene was added as internal standard. The work up and analysis procedure was the same as that for 1-PhCHT: nmr ($CDCl_3$) δ 9.95 (3 lines, o-, m-, and p-PhC_6H_4CHO) and 7.3 (m).

3-Phenylcycloheptatriene. A quantity of ca. 200 mg of 3-PhCHT in 10 ml of acetonitrile was added to ca. 2.7 g CAN (4 eq) in 10 ml of 50 per cent aqueous acetonitrile. After stirring, ca. 40 mg of 1,4-di-tert-butylbenzene was added as standard. The work up and analysis as for 1-PhCHT was followed: nmr ($CDCl_3$) δ 10.0 (3 lines) and 7.3 (m).

Phenylcycloheptatrienylium fluoborate. A quantity of ca. 300 mg of $PhC_7H_6^+BF_4^-$ in 10 ml of 50 percent acetonitrile 0.5 N in cerium(III) (prepared by reducing the CAN solution with pinacol) was added to ca. 1.3 g CAN (2 eq) in 10 ml of 50 per cent aqueous acetonitrile at 82°. A flocculent white precipitate formed. After cooling, ca. 30 mg of diphenyl ether was added as internal standard and the work up and analysis procedure for 1-PhCHT followed: nmr ($CDCl_3$) δ 10.0 and 9.91 (2 lines, m- and p-PhC_6H_4CHO) and 7.3 (m).

7-Phenylcycloheptatriene plus acrylamide. A solution of ca. 200 mg of 7-PhCHT in 22 ml of glacial acetic acid was added all at once to a solution of ca. 2.5 g CAN in 22 ml of 75 per cent acetic acid to which had been added 4.4 g of acrylamide and the mixture heated at 80° for 15 min. The

mixture was poured into 50 ml of water, extracted twice with 25 ml of ether, washed thrice with 20 ml of water, and thrice with 10 ml of saturated sodium bicarbonate solution, and dried ($MgSO_4$). There was never any sign of polymer formation. The nmr was identical to the reaction with no added acrylamide: ($CDCl_3$) δ 7.4 (m, phenyl, 116), 6.8 (s, $Ph_2C\underline{H}O_2CCH_3$, 6), 5.7 (s, $Ph_2C\underline{H}OH$, 3), and 2.0 (s, $Ph_2CHO_2CC\underline{H}_3$, 19).

Reaction of phenyltropylium fluoborate and nucleophiles

Sodium borohydride. To approximately 1 g $PhC_7H_8^+$ in 5 ml of water covered with 5 ml of pentane was added 2 g sodium borohydride. After stirring for approximately 30 min, the pentane layer was separated, washed with a saturated ammonium chloride solution, dried ($MgSO_4$), and concentrated on a rotary evaporator. Nmr analysis of the residue was identical to that of a thermally equilibrated mixture (23).

Lithium aluminum hydride tri-tert-butoxide. A suspension of 0.2 g of $PhC_7H_8^+$ in diglyme was added to a solution of 0.2 g $LiAlH(O\text{-}\underline{t}\text{-}Bu)_3$ in ether at room temperature. After stirring for 30 min, the reduced material was extracted with 25 ml of ether: nmr ($CDCl_3$) δ 7.4 (m), 6.8 (m), 6.2 (m), 5.6 (m), and 3.5 (m).

Sodium methoxide. A solution of approximately 0.1 g of PhDiHO in 10 ml of water was treated with 0.1 g of sodium methoxide in 5 ml of water. After stirring for 15 min, the

mixture was extracted with ether and dried ($MgSO_4$): nmr (CCl_4) δ 7.2 (m, 5), 6.8 (m, 2), 6.2 (m, 2), 5.6 (m, 2), 3.2 (s, 40), 3.0 (s, 0.5).

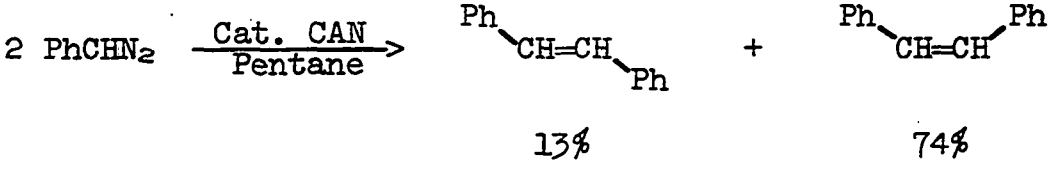
Potassium t-butoxide. A solution of 0.1 g of $PhC_7H_6^+$ in 10 ml of t-butanol was treated with 0.3 g potassium t-butoxide in 5 ml of t-butanol at room temperature. The mixture was extracted with methylene chloride, washed four times with 25 ml of water and 2 ml of deuterium oxide, and dried ($MgSO_4$): nmr ($CDCl_3$) δ 7.3 (m), 6.8 (m), 6.3 (m), 5.6 (m), and 1.1 (s).

PART II. REACTIONS OF CERIC AMMONIUM NITRATE WITH DIAZOALKANES

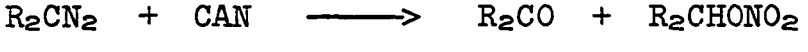
INTRODUCTION

The reactions of diazoalkanes with metal ions and in particular with oxidants has not been well studied. Previously, most reactions have been rationalized on the basis of carbene or metal-carbene complexes. Very little attention has been given to the possibility of radical cation intermediates. Evidence presented here indicates that the radical chemistry of diazoalkanes is much more general than had been reported.

Phenyldiazomethanes are decomposed by catalytic amounts of ceric ammonium nitrate to high yields of stilbenes. Noteworthy is the high cis/trans ratio:



With diazoalkanes whose radical cations are expected to be more stable than those of phenyldiazomethane coupling does not occur. Instead either the parent carbonyl or alkyl nitrate is obtained.



These results are readily explained by the formation of a radical cation which can undergo a chain reaction to yield the olefins or be trapped by nucleophiles present to yield the alkyl derivatives.

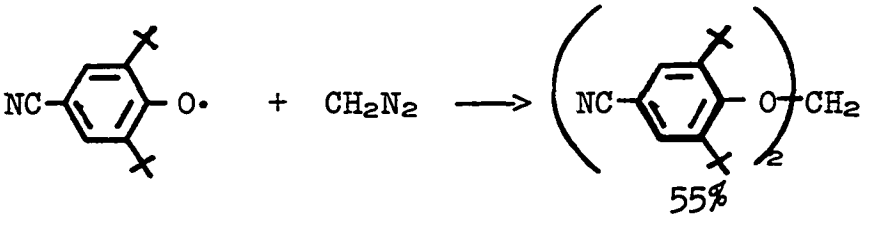
HISTORICAL

In general, diazoalkanes have been decomposed thermally, photolytically, or with a Lewis acid. The use of metals to form carbenes or polymers with diazoalkanes has also been the object of a great deal of study in previous years. These areas have been extensively covered in reviews (48-56) and will not be discussed here. Very little, however, is known about the reactions with oxidants or with metal ions not involving free carbenes.

The earliest reported oxidation is that of 9-diazofluorene to fluorenone with peroxybenzoic acid (57) in 1951. Hensel (58) found the same conversion could be affected with lead tetraacetate. In 1962 Wittig and Schlosser (59) observed stilbene formation from the triphenylphosphine-cuprous chloride oxidation of phenyldiazomethane:

$$PhCHN_2 + Ph_3P + Ph_2CO + CuCl \longrightarrow \underset{28\%}{PhCH{=}CHPh} + PhCH{=}N{-}N{=}CHPh$$

Very little of the expected 1,1,2-triphenylethene was found and no attempt was made to explain the formation of stilbene. Müller (60) in 1963 reported diazomethane could be oxidized with aroxyl radicals:



In 1966 Yoshida *et al.* (61) found stilbenes are formed when phenyldiazomethane is treated with benzoyl peroxide:

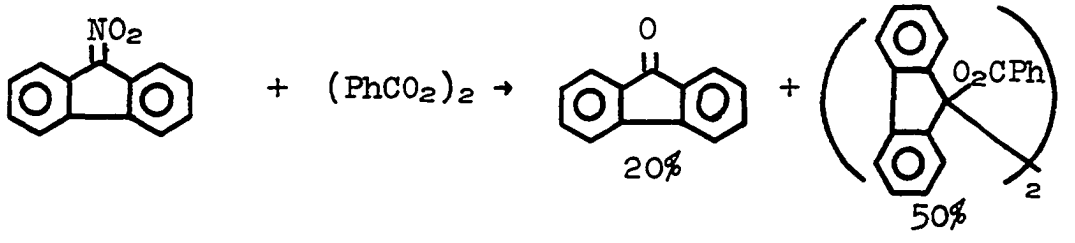
$$(PhCO_2)_2 + PhCHN_2 \xrightarrow[10\ days]{Et_2O} \underset{42\%}{PhCH{=}CHPh} + \underset{37\%}{PhCH{=}CHPh} + \underset{4\%}{PhCH_2O_2CPh}$$

Under similar conditions, diphenyldiazomethane gave dibenzoyloxydiphenylmethane and 1-phenyldiazoethane led to acetophenone, its azine, and 1-phenylethyl benzoate:

$$(PhCO_2)_2 + Ph_2CN_2 \longrightarrow Ph_2C(O_2CPh)_2$$

$$(PhCO_2)_2 + Ph(CH_3)CN_2 \longrightarrow PhCOCH_3 + (Ph(CH_3)C{=}N{-})_2 + Ph(CH_3)CHO_2CPh$$

Due to the formation of stilbenes, it was suggested carbenes were involved. Lind and Fahr (62) have presented further examples of the reaction of diazoalkanes with peroxides. Some coupling products were found from 9-diazofluorene and phenyldiazomethane but the majority of products were benzoates:



$PhCOCHN_2 + (PhCO_2)_2 \longrightarrow PhCO_2CH_2O_2CPh$

$PhCHN_2 + (PhCO_2)_2 \longrightarrow PhCHO + PhCH(O_2CPh)_2 + PhCH(OCOPh)-CH(OCOPh)Ph$

'etwas' 'etwas'

$Ph_2CN_2 + (PhCO_2)_2 \longrightarrow Ph_2C(O_2CPh)_2$

A radical cation intermediate was proposed:

$$R_2CN_2 + (PhCO_2)_2 \longrightarrow R_2C(N_2^+)-OCOPh + PhCO_2\cdot$$

$$R_2C(N_2^+)-OCOPh \xrightarrow{-N_2} R_2\overset{+}{C}-OCOPh$$

$$R_2\overset{+}{C}-OCOPh + R_2CN_2 \longrightarrow R_2C(R_2C-N_2^+)-OCOPh$$

$$R_2C(R_2C-N_2^+)-OCOPh + PhCO_2^- \xrightarrow{-N_2} R_2C(R_2C-OCOPh)-OCOPh$$

$$R_2\overset{+}{C}-OCOPh + PhCO_2^- \longrightarrow R_2C(OCOPh)_2$$

Baganz and May (63) have reported that α-diazocarbonyl compounds yield α-ketoacetals when treated with tert-butyl hypochlorite in alcohols:

$$N_2CH-CO-R \xrightarrow[R'OH]{t\text{-}BuOCl} (R'O)_2CH-CO-R$$

R = $-CO_2Et$, $-OMe$, $-Ph$

No explanation was suggested.

Saegusa et al. (64) have observed the oxidation of ethyl diazoacetate with cupric chloride to ethyl chloroacetates and diethyl dichlorofumarate and maleate:

$$N_2CH\text{-}CO_2Et + CuCl_2 \xrightarrow[CH_3CN]{15^\circ} \underset{40\%}{EtO_2C\text{-}CHCl_2} + \underset{16\%}{EtO_2C\text{-}CH_2Cl} + CuCl$$

$$+ \underset{30\%}{EtO_2C\text{-}CH{=}CH\text{-}CO_2Et} + \underset{3\%}{EtO_2C\text{-}CCl{=}CCl\text{-}CO_2Et}$$

The diethyl fumarate and maleate were shown to arise from the cuprous chloride catalyzed decomposition of ethyl diazoacetate:

$$N_2CH\text{-}CO_2Et + CuCl \longrightarrow EtO_2C\text{-}CH{=}CH\text{-}CO_2Et$$

Diphenyldiazomethane was oxidized to dichlorodiphenylmethane, benzophenone azine, and tetraphenylethene:

$$Ph_2CN_2 + 2\ CuCl_2 \longrightarrow \underset{48\%}{Ph_2CCl_2} + \underset{34\%}{(Ph_2C{=}N\text{-})_2} + \underset{9\%}{Ph_2C{=}CPh_2}$$

It was believed organometallics of the type $Cu(CClR_2)_2$ were involved but radical cations could not be ruled out for the olefins obtained. No attempt was made to determine if the reaction proceeded via ligand transfer or metal ylides.

The electrooxidation of diazoalkanes has been extensively studied by Jugelt and Pragst. In general, aryldiazoalkanes can be converted to olefins (65, 66) using only 5 to 14 per

cent of the current necessary for a one electron transfer (see Table 14):

$$2\ R_2CN_2 \xrightarrow[-e]{CH_3CN} R_2CH{=}CHR_2 + 2\ N_2$$

Table 14. Yield of olefins from the electrooxidation of aryldiazoalkanes[a]

Diazoalkanes	Half-Wave Potential $E_{1/2}$	Absolute Yield ArCR=CRAr
Ph_2CN_2	+0.95	80%
(p-$NO_2C_6H_4$)$PhCN_2$	+1.14	60%
(p-$NO_2C_6H_4$)CH_3CN_2	+1.16	30%
(p-$NO_2C_6H_4$)CHN_2	+1.33	40% trans 30% cis
9-Diazofluorene	+1.22	45%
CH_2N_2	+1.70	--
EtO_2C-CHN_2	+2.10	--

[a]Data from reference 66.

A chain mechanism with radical cation intermediates was proposed:

Initiation:

$$R_2CN_2 \xrightarrow[+e^-]{-e^-} R_2\dot{C}\text{-}N_2^+$$

I II

Propogation:

$$II + I \xrightarrow{N_2} R_2C(N_2^+)-\dot{C}R_2$$

III

$$III + I \xrightarrow{-N_2} R_2C{=}CR_2 + R_2\dot{C}-N_2^+$$

Termination:

$$II + H_2O \xrightarrow{-N_2} R_2\dot{C}OH$$

IV

$$IV + III \longrightarrow R_2C{=}CR_2 + R_2CO + H^+$$

$$IV + II \longrightarrow R_2C(N_2^+)-CR_2(OH) \xrightarrow{-N_2} R_3C-CO-R$$

It was possible to suppress the coupling by running the reaction in a large excess of n-propyl amine. They suggested the radical cation was trapped by the nucleophilic amine:

$$R_2\dot{C}-N_2^+ + n\text{-}C_3H_7NH_2 \xrightarrow{-N_2} R_2\dot{C}-NH-C_3H_7\text{-}n$$

$$R_2\dot{C}-NH-C_3H_7\text{-}n \xrightarrow[-H^+]{-e^-} R_2C{=}N-C_3H_7\text{-}n$$

Later, polarographic evidence was presented confirming the radical cation (66-69) and half-wave potentials were obtained for a wide range of diazoalkanes. It is interesting to note that while half-wave potentials could be obtained for diazomethane and ethyl diazoacetate neither yielded olefins. In fact, Pragst, Hübner, and Jugelt (70) have re-

ported α-phenyl-α-carbonyl diazoalkanes do not couple when electrooxidized. Azibenzils undergo the Wolff rearrangement or couple via the phenyl rings:

$$Ph\text{-}C(N_2)\text{-}CO\text{-}Ph \longrightarrow Ph_2C{=}C{=}O$$

$$\underline{p}\text{-}Z\text{-}C_6H_4CO\text{-}C(N_2)C_6H_5 \longrightarrow (\underline{p}\text{-}Z\text{-}C_6H_4CO\text{-}C(N_2)\text{-}C_6H_4)_2$$

The mechanisms of these reactions were not discussed.

The role of metal ions reacting with diazoalkanes has been studied in very few instances, the most notable of which is the copper catalyzed decomposition. Kirmse (71) has reported that cuprous halides generally lead to carbenes and then to olefins or cyclopropanes, e.g.,

The only exception is tert-butyldiazomethane which yields among the usual products trans-di-tert-butylethylene and 2,2-dimethylpropanol azine:

$$(CH_3)_3C\text{-}CHN_2 \xrightarrow{CuCl} (CH_3)_3C\text{-}CH{=}CH\text{-}C(CH_3)_3 + ((CH_3)_3C\text{-}CH{=}N)_2$$

70% 30%

Werner and Richards (72) have observed the formation of diethyl maleate and fumarate with nickel(0) complexes, copper metal, or copper(I) or (II) salts. In the presence

of cyclohexene appreciable amounts of ethyl norcarane-carboxylate were obtained (see Table 15).

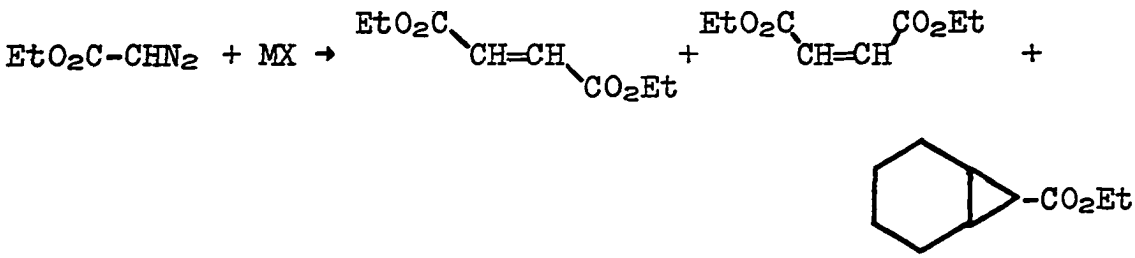


Table 15. Relative yields of products from the metal-catalyzed decomposition of ethyl diazoacetate in the presence of cyclohexene[a]

	Relative Yields		
Metal Salt	Diethyl Fumarate	Diethyl Maleate	Ethyl Norcaranecarboxylate
$NiCp_2$	1.4	2.6	1.0
$Ni(CO)_4$	6.0	---	1.0
Cu	0.57	0.67	1.0
CuBr	0.5	0.5	1.0
$CuSO_4$	0.7	0.5	1.0
ZnI_2	1.4	0.6	1.0
$CrCp_2$	1.5	0.6	1.0

[a]Data from reference 72.

Because of the formation of the norcarane and with nickelocene, there was no evidence for any type of a free radical intermediate, it was suggested a metal ylide of the type popularized by Yates (73) and Takebayashi *et al.* (74) with

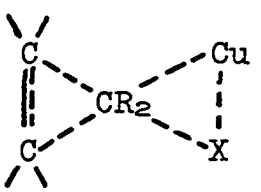
α-diazocarbonyls was involved:

$$M = CR_2, \quad \underline{e.g.}, \quad Cu{=}CH\text{-}CO_2Et$$

No reaction occurred with diphenyldiazomethane or 9-diazofluorene and diazomethane gave only polymethylene. Nozai *et al.* (75) found that diphenyldiazomethane could be decomposed to tetraphenylethane by several copper salts but that yields were best with bis(2,4-pentanedionato)copper(II):

$$Ph_2CN_2 \xrightarrow[Cu(acac)_2]{\text{Benzene}} \underset{60\%}{Ph_2C{=}CPh_2} + \underset{30\%}{Ph_2C{=}N\text{-}N{=}CPh_2}$$

Here again the intermediacy of a copper-carbene ylide was proposed. D'yakonov (76) has suggested a similar intermediate in the reaction of ethyl diazoacetate with cupric stearate. Moser (77) has confirmed the presence of such ylides by detailed kinetic studies with ethyl diazoacetate with the further conclusion that the olefin may be involved in the complex:



Copper metal itself has been found to be an active catalyst in reactions with diazoalkanes. Copper-bronze was used to convert α-diazocarbonyls to olefins by Quintana (78):

$$2\ (CH_3)_3C\text{-}CO\text{-}CHN_2 \xrightarrow{Cu} (CH_3)_3C\text{-}CO\text{-}CH{=}CH\text{-}CO\text{-}C(CH_3)_3$$

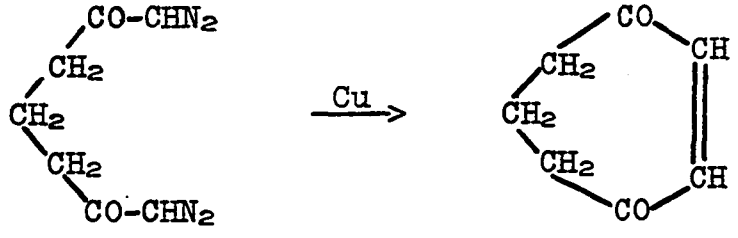
70%

by Grundmann (79):

$$2\ Ph\text{-}CO\text{-}CHN_2 \xrightarrow{Cu} Ph\text{-}CO\text{-}CH{=}CH\text{-}CO\text{-}Ph$$

65%

and by Font (80):



20%

Zinc halides have also been utilized to decompose diazoalkanes. Bethell and Brown (81) report that 9-diazofluorene is converted to bifluorenylidene, fluorenone, and 9-halofluorenes by zinc halides. They believe organometallics are involved but do not elaborate. Goh et al. (82) have found that phenyldiazoalkanes may be readily decomposed with lithium and zinc halides in the presence of olefins to yield cyclopropanes. Presumably the reaction proceeds via carbenes.

Finally, the carbonium ion catalyzed decomposition of diazoalkanes reported by Whitlock (83) should be noted. If phenyldiazomethane was treated with the trityl carbonium ion, an 11 per cent yield of trans-stilbene and a 6% yield of

tetraphenylethylene was obtained:

$$PhCHN_2 + Ph_3C^+ \xrightarrow{-N_2} Ph_3C\text{—}\overset{+}{C}HPh$$

$$PhC(+)\text{-}CHPh \longrightarrow Ph_2\overset{+}{C}\text{-}CHPh_2 \longrightarrow Ph_2C{=}CPh_2$$

$$PhC(+)\text{-}CHPh \xrightarrow[-N_2]{PhCHN_2} Ph_3C\text{-}CHPh\text{-}\overset{+}{C}HPh \longrightarrow PCH{=}CHPh + Ph_3C^+$$

Diphenyldiazomethane gave tetraphenylethene:

$$Ph_2CN_2 + Ph_3C^+ \xrightarrow{-N_2} Ph_3C\text{-}\overset{+}{C}Ph_2 \xrightarrow[-N_2]{Ph_2CN_2} Ph_3C\text{-}CPh_2\text{-}\overset{+}{C}Ph_2$$

$$Ph_3C\text{-}CPh_2\text{-}\overset{+}{C}Ph_2 \longrightarrow Ph_2C{=}CPh_2 + Ph_3C^+$$

A similar reaction occurs with diphenyldiazomethane and the tropylium ion (56).

$$C_7H_7^+ + Ph_2CN_2 \longrightarrow C_7H_7\text{-}CPh_2\text{-}N_2^+ \xrightarrow[-N_2]{Ph_2CN_2} C_7H_7\text{-}CPh_2\text{-}CPh_2\text{-}N_2^+$$

$$C_7H_7\text{-}CPh_2\text{-}CPh_2\text{-}N_2^+ \xrightarrow{-N_2} Ph_2C{=}CPh_2 + C_7H_7^+$$

In these cases the carbonium ion acts as a site of reaction and is both an electrophile and a leaving group.

RESULTS

A series of para-substituted phenyldiazomethanes was decomposed with catalytic amounts of ceric ammonium nitrate at -5°. The diazoalkanes were in pentane and the CAN in acetonitrile. Reaction time was of the order of 15 to 60 seconds and at most required one third of an equivalent of CAN. Only cis- and trans-stilbenes were isolated (see Table 16):

$$2\ ArCHN_2 \xrightarrow[Pentane]{Cat.\ CAN} ArCH{=}CHAr + 2\ N_2$$

Table 16. Yields of stilbenes from the decomposition of aryldiazoalkanes, $ArCHN_2$, with ceric ammonium nitrate

Ar-	$ArCHN_2$ used, mmol	CAN used, mmol	cis-Stilbene[a] trans-Stilbene	Yield[a], %
C_6H_5	3.81[b]	0.1	5.49±0.12[b]	88 ± 3
p-$CH_3C_6H_4$-	0.52[c]	0.15	3.2 ±0.30[d]	80 ± 2
p-ClC_6H_4-	0.39[c]	0.15	2.33±0.12[d]	98 ± 2

[a]Standard deviations are based on at least three runs.

[b]Concentration was analyzed by nmr using 1,1,2,2-tetrachloroethene.

[c]Concentration was analyzed by adding benzoic acid and back titrating the excess acid (84).

[d]Yield determined by glpc analysis using diphenylmethane as standard.

Table 16 (Continued)

Ar-	$ArCHN_2$ used, mmol	CAN used, mmol	cis-Stilbene[a] trans-Stilbene	Yield[a], %
p-$O_2NC_6H_4$-	No reaction			
p-$CH_3OC_6H_4$-	Complicated reaction with no stilbenes produced			

No reaction occurred when phenyldiazomethane was treated with a reduced CAN solution. The oxidation of p-methoxyphenyldiazomethane gave some azine and at least five other products, none of which were the stilbenes. Phenyldiazomethane was also oxidized with ceric sulfate in acetonitrile. Reaction was much slower than with CAN but cis- and trans-stilbene were observed in the usual ratio (4/1).

A CAN reaction with phenyldiazomethane was run in an nmr probe. Although no CIDNP effect was noted, the formation of cis-stilbene could be followed by observing the increase of a peak at δ 6.5 and the concomitant decrease of the α-hydrogen of phenyldiazomethane at δ 6.1. No peaks were observed which could not be attributed to stilbene or phenyldiazomethane.

p-Methylphenyldiazomethane was decomposed by CAN in the presence of trans-stilbene at various concentrations. There did not seem to be any appreciable change in the cis/trans ratio (see Table 17). It is significant that the ratio does not vary and that no other products were observed. p-Chloro-

Table 17. Ratio of p-substituted stilbenes from the decomposition of aryldiazomethanes, $ArCHN_2$, by CAN in the presence of trans-stilbene

$ArCHN_2$	Concentration[a] $ArCHN_2$	Solvent	Concentration[a] trans-Stilbene	Relative Yield, % ArCH=CHAr cis	trans
p-$CH_3C_6H_4CHN_2$	0.0933	Pentane	0.506[b]	78	22
			0.212[b]	82	18
			0.109	72	27
			0.0591	69	31
			0.0163	78	22
p-$ClC_6H_4CHN_2$	0.0699	Benzene	0.0000	89	11
			0.1103	40	60

[a]Concentration is moles per liter.

[b]The solution was saturated in trans-stilbene.

phenyldiazomethane was also decomposed in the presence of trans-stilbene (see Table 17). The p,p'-dichlorostilbene cis/trans ratio changed drastically but no cis-stilbene was found.

Phenyldiazomethane was oxidized at three concentrations and no effect was observed on the cis/trans ratio (see Table 18).

Table 18. Relative yields of stilbenes from the decomposition of phenyldiazomethane by CAN at various concentrations.

Concentration[a] $C_6H_5CHN_2$	Relative Yield, % PhCH=CHPh	
	cis	trans
0.349	84	16
0.0697	86	14
0.0349	86	14

[a]Concentration is moles per liter.

The o-substituted phenyldiazomethanes yielded only minor amounts of stilbenes on oxidation with CAN. The products from o-methyl- and o-chlorophenyldiazomethane were the stilbenes and the diphenylethanediols and their dinitrates (see Table 19):

$$ArCHN_2 \xrightarrow{CAN} ArCH{=}CHAr + \underset{OH\ OH}{ArCH{-}CHAr} + \underset{O_2NO\ \ ONO_2}{ArCH{-}CHAr}$$

Table 19. Yields of products from the oxidation of o-substituted phenyldiazomethanes by CAN

Diazoalkane	-ArCH=CHAr- cis	trans	Relative Yields, %[a] ArCHOH-CHOHAr	ArCH(ONO_2)CH(ONO_2)Ar
o-$CH_3C_6H_4CHN_2$	10	--	25	65
o-$ClC_6H_4CHN_2$[b]	24	18	33	24

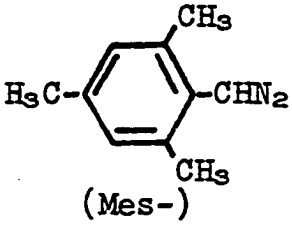
[a]Determined by nmr analysis.

[b]The p-chlorophenyldiazomethane required approximately 1/7 of an equivalent of CAN.

2,4,6-Trimethylphenyldiazomethane gave a more complex set of products. Glpc collection afforded two products, one containing nitrate groups and having only one α-hydrogen by nmr analysis. The other product had only ring and methyl hydrogens in the nmr and may be mesitoic acid. It is known that the nitrate ester of benzoin cleaves under glpc conditions similar to the above to benzaldehyde and benzoic acid:

$$PhCH(ONO_2)\text{-}CO\text{-}Ph \xrightarrow[glpc]{180^\circ} PhCHO + PhCO_2H$$

Thus the products are probably the ethanediol and its dinitrate but the ready cleavage of the dinitrate precluded further product studies:



$$\xrightarrow{CAN} Mes\text{-}CH(OH)\text{-}CH(OH)\text{-}Mes + Mes\text{-}CH(O_2NO)\text{-}CH(ONO_2)\text{-}Mes$$

The 1- and 2-naphthyldiazomethanes were also oxidized with CAN. Again a very complex mixture of products was obtained and although some of the products were identified, problems with apparent oxidation of the naphthyl rings made further work undesirable:

$$1\text{-}NpCHN_2 \xrightarrow{CAN} (1\text{-}Np)_2CH\text{-}CH(1\text{-}Np)_2 + 1\text{-}NpCH_2CO\text{-}1\text{-}Np + 1\text{-}NpCH_2ONO_2 + \text{"X"}$$

$$2\text{-}NpCHN_2 + \xrightarrow{CAN} (2\text{-}Np)_2CH\text{-}CH(2\text{-}Np)_2 + 2\text{-}NpCH_2\text{-}CO\text{-}2\text{-}Np + 2\text{-}NpCH_2ONO_2$$

The ethylenes were identified by comparison with an authentic sample prepared from the photolysis and the bis(2,4-pentanedionato)copper(II) decomposition of 1-naphthyldiazomethane, both of which are known to yield trans-ethylenes. The nitrates were identified by comparison with authentic samples and the deoxybenzoins were identified from their nmr, ir, and mass spectrums.

Two cross experiments were run. Equimolar amounts of p-methyldiazomethane and phenyldiazomethane was decomposed by CAN. All possible stilbenes were produced, stilbene, p-methylstilbene, and p,p'-dimethylstilbene (see Table 20) in approximately a statistical ratio. The reaction between

Table 20. Relative amounts of stilbenes from the decomposition of p-methylphenyldiazomethane and phenyldiazomethane by CAN

Stilbene	p-Methylstilbene	p,p'-Dimethylstilbene
1.16 ± 0.06	1.62 ± 0.08	1.000

phenyldiazomethane and 1-phenyldiazoethane led to none of the expected 1,2-diphenylpropene. Stilbenes and benzyl nitrate were the products from phenyldiazomethane and acetophenone was the product from 1-phenyldiazoethane:

$PhCHN_2$ + $Ph(CH_3)CN_2$ $\xrightarrow{2.2\ \text{mmoles CAN}}$ PhCH=CHPh + $PhCH_2ONO_2$ + $Ph\text{-}CO\text{-}CH_3$

1.76 mmoles; 1.4 mmoles

	cis	trans		
Absolute Yield, %	24	24	15	80

A wide variety of diazoalkanes was oxidized with one equivalent of CAN in acetonitrile and gave the parent carbonyl or the alkyl nitrate (see Table 21):

$$R_2CN_2 + CAN \xrightarrow{CH_3CN} R_2CO + R_2CHONO_2$$

Table 21. Yields of products from the oxidation of diazoalkanes by CAN

Diazoalkane	Absolute Yield, % R_2CO	R_2CHONO_2	R_2CHOH
EtO_2CCHN_2	--	100	--
$Ph(CH_3)CN_2$	80	--	--
$Ph(CF_3)CN_2$	No reaction		
$PhCOCHN_2$	No reaction		
$PhCO(Ph)CN_2$	--	94	--
$Ph((CH_3)_3C)CN_2$	65	12	23
9-Diazofluorene	80	--	--
Ph_2CN_2	55	45	--

No olefins were noted in any of these reactions.

Cerium(IV) is rapidly consumed by diphenyldiazomethane and the quantity of cerium(IV) may be followed by a titration-like blue coloration formed as each drop of CAN is added to the diazoalkane. At the end of the addition of one equivalent of CAN the red color of the diphenyldiazomethane has disappeared and further addition causes no more blue coloration. Furthermore, one equivalent of a gas was evolved (43.7 ml (at STP) vs. 43.0 expected) which was collected and analyzed by mass spectrum showing signals at m/e 28 (nitrogen), 32 (oxygen, background), 40 (argon was used to flush the system) and 44 (background). Diphenyldiazomethane could also be decomposed to diphenylmethyl nitrate and diphenylmethanol in a ratio of 7:1 (nmr analysis), but the reaction was much slower than with CAN and no blue coloration was noted.

One equivalent of CAN was necessary to decompose ethyl diazoacetate and if a sufficient amount was not used starting diazoalkane was recovered. With one equivalent of CAN a little more than one equivalent of a gas was evolved (115 ml vs. 98 calculated). Ethyldiazoacetate could also be decomposed by cerium(III) solution to ethyl nitratoacetate.

The other diazoalkanes all required one equivalent of cerium(IV) for complete decomposition. Gas evolution was observed in some cases but not measured.

The oxidation of diazomethane yielded no olefin that could be trapped by bromine in carbon tetrachloride. One

product appears to be N-methylacetamide.

Both phenyldiazomethane and 2-methylphenyldiazomethane were decomposed by bis(2,4-pentanedionato)copper(II) and only cis- and trans-stilbenes isolated (see Table 22):

$$2\ ArCHN_2 \xrightarrow{\text{Cat. } Cu(acac)_2} ArCH{=}CHAr + 2\ N_2$$

Table 22. Relative yields from the bis(2,4-pentanedionato)-copper(II) decomposition of phenyldiazoalkanes

Diazoalkane	Solvent	Relative Yield, % ArCH=CHAr cis	trans	Absolute Yield, %
$C_6H_5CHN_2$	Benzene	60	40	46
	Acetonitrile	60	40	46
o-$CH_3C_6H_4CHN_2$	Benzene	46	54	--

DISCUSSION

The reactions of CAN with diazoalkanes is obviously very complex. The most perplexing aspect is the coupling of phenyldiazoalkanes to yield stilbenes. Dimerization of the alkyl portion of diazoalkanes has never been easy to explain and many alternatives are possible.

Historically, one must always consider that the photolysis, thermolysis, or acid catalyzed decomposition of diazoalkanes can lead to high yields of ethylenes (85). With diazomethane itself it is believed that a carbene intermediate is involved which reacts with another diazomethane to form ethylene:

$$CH_2N_2 \longrightarrow :CH_2 + N_2$$

$$CH_2N_2 + :CH_2 \longrightarrow CH_2{=}CH_2 + N_2$$

Stilbene has been observed from the decomposition of phenyldiazomethane by Bethell (86, 87) with acids:

$$PhCHN_2 \xrightarrow{H^+} \underset{49\%}{PhCH{=}CHPh} + \underset{42\%}{PhCH{=}N{-}N{=}CHPh}$$

$$\frac{cis}{trans} = 0.89$$

The relative yields were dependent on concentration of the diazoalkane and added stilbene or azine. With diphenyldizaomethane the carbene could be trapped by olefins to yield cyclopropanes (88). Both Gutsche (89) and Nozaki (90)

have observed stilbenes from the photolysis of phenyldiazomethanes:

$$2\ PhCHN_2 \xrightarrow{h\nu} PhCH{=}CHPh$$

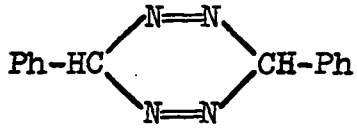
Gutsche reported only cis-stilbene and was able to trap an intermediate with benzene to yield 7-phenylcycloheptatriene. Nozaki reported only trans-stilbene in non-aromatic solvents and obtained no stilbene in the presence of cyclohexene. In benzene cis-stilbene was found along with significant yields of 7-phenylcycloheptatriene. Furthermore, the o-methylphenyldiazomethane gave a 41 per cent yield of o,o'-dimethylstilbene. In all cases because reactions typical of carbenes (addition to double bonds) were found, it was assumed the stilbenes arose via carbenes. In the CAN decompositions, the product ratio is invariant over concentration changes or added stilbene. In the presence of cyclohexene, no norcarane products were observed and stilbenes were found in the usual ratio (75/25). Also, when the oxidation was carried out in benzene, phenylcycloheptatrienes were not observed but stilbenes were in an 80/20 ratio. These results are not compatible with a carbene intermediate such as proposed by the above authors.

It is possible that the carbene is not free but complexed with the metal similar to the ylides generally believed present in the reactions of diazoalkanes with copper

salts. Although bis(2,4-pentanedionato)copper(II) does react with phenyldiazomethanes to yield stilbenes, the reaction is much slower and the cis/trans ratio is much less than that with CAN. More importantly, o-methylphenyldiazomethane yields stilbenes with the copper complex and not with CAN. The metal ylides are also known to react with olefins to yield cyclopropanes, a reaction which does not occur in the CAN decomposition. Thus, it seems a metal complexed carbene may be excluded as a possibility.

Organometallic derivatives such as the mercuric and lithium salts of diazomethane (91) are known. As cerium(IV) is not known to bond readily to carbon, similar intermediates are most likely not involved.

There is the possibility of an intermediate being formed which reacts further to yield stilbenes. Two conceivable ones are azines and azo compounds. Benzalazine can be quantitatively recovered from the reaction conditions at room temperature and although it is oxidized rapidly at 74°, the major product is benzaldehyde and no stilbenes are observed. A bis-azo compound has been suggested by Bethell



(86) in the reaction of phenyldiazomethane with acids. There was no evidence for such an intermediate in his case.

When phenyldiazomethane was oxidized in the nmr probe, the decrease of the diazoalkane and increase of stilbene could be followed with no spurious signals. In addition, nothing but stilbenes has ever been isolated from the reaction. This, of course, does not answer the question but lack of supporting evidence makes conjecture unattractive.

The catalytic role of cerium(IV) and the high yields suggest a chain reaction, perhaps analogous to that of Jugelt and Pragst (65):

$$PhCHN_2 + ONO_2Ce^{IV} \longrightarrow PhCH(N_2^+)-ONO_2Ce^{IV}$$

$$PhCH(N_2^+)-ONO_2Ce^{IV} \longrightarrow Ph\dot{C}H-N_2^+ + ONO_2Ce^{III}$$

$$Ph\dot{C}H-N_2^+ + PhCHN_2 \longrightarrow Ph\dot{C}H-\overset{+}{C}HPh + 2\ N_2$$

$$Ph\dot{C}H-\overset{+}{C}HPh + PhCHN_2 \longrightarrow PhCH{=}CHPh + Ph\dot{C}H-N_2^+$$

The formation of the radical cation is reasonable considering cerium(IV) is a one-electron oxidant and sufficient precedent exists in the electrooxidation of Jugelt and Pragst (65), the benzoyl peroxide oxidation of Lind and Fahr (62), and the cupric chloride oxidations of Saegusa (64). The benzoyl peroxide oxidation of Yoshida (61) probably also involves radical cations. Lack of reaction by p-nitrophenyldiazomethane can be explained by the powerful electron withdrawing nitro group causing the α-carbon to be too electron deficient to be attacked by the electrophilic cerium species.

The complicated reaction of p-methoxyphenyldiazomethane may be due to the formation of a stable p-methoxyaryl radical cation and not a function of the diazo group.

Unfortunately, it has not been possible to observe any radical intermediates. Acrylamide, a known radical trap (36), did not affect the reaction and cis- and trans-stilbene were obtained in a 70/30 ratio. This may have been due to the low solubility of acrylamide in pentane. When oxygen was bubbled through the reaction mixture, only cis- and trans-stilbene (80/20) were found. No benzaldehyde or benzyl alcohol was observed. Using a flow apparatus, no esr signal could be observed. Both very slow and very fast flow rates were used as well as completely stopped. The speed of the reaction may reflect a very short lifetime for any radicals involved and thus render trapping or spectral observation very difficult.

In conjunction with the chain mechanism, there was no concentration effect, a highly reasonable observation. No other oxidant was found which would generate the chain reaction. Phenyldiazomethane did not react with potassium ferricyanide. It did react with tris(p-bromophenyl)aminium hexachloroantimonate but no stilbenes were formed. Benzyl and benzal chlorides are among the products. This reaction is very reminiscent of the cupric chloride oxidation of Saegusa (64) where ligand transfer predominated over coupling.

One of the greatest failures of the radical chain mechanism is the lack of a ready explanation for the high cis/trans ratio. In part this may be due to the belief that as trans-stilbene is thermodynamically more stable it should predominate in the products. In fact, in many reactions the cis isomer is formed in equal or greater amounts. Only where the starting material has a cisoid configuration, however, has the cis/trans ratio been greater than 5 (92). Thus, it seems some exceptional process is occurring. In the final electron transfer to afford stilbene, a high energy moiety bearing close resemblence to the "phantom" intermediate in the photochemistry of stilbenes (93) could be produced:

$$PhC\dot{H}-\overset{+}{C}HPh + PhCHN_2 \longrightarrow (PhCH{=}CHPh)^* + PhC\dot{H}-N_2^+$$

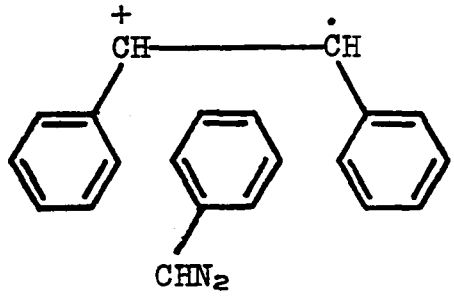
$$(PhCH{=}CHPh)^* \longrightarrow PhCH{=}CHPh \quad \underline{cis} > \underline{trans}$$

cis-Stilbene predominates in the photochemical mixture at the photostationary state about 92/8. Several problems exist about such an intermediate. There is considerable question (94) as to the spin multiplicity of the "phantom" and it is not advisable to argue that particular aspect here. It is not of the greatest importance as electron transfer can conceptually be accomplished to afford either triplet or singlet states. There is consensus that the "phantom" is approximately 40 to 50 kcal above the ground state and that decay from the "phantom" to ground state

should yield a cis/trans ratio of 1.5. These facts apparently conflict with the cerium(IV) decomposition. The cis/trans ratio of 5 is much closer to the photostationary state than the natural decay ratio. The photostationary state is obtained because of unequal rates of excitation from the stilbene ground states and a similar process is not available thermally. The 40 to 50 kcal necessary to produce the "phantom" would be difficult to attain at room temperature. Even though the reduction of cerium(IV) is a potential source of energy it cannot be sufficient because of its catalytic nature. Electron transfer alone seems unlikely to afford an excess 40 kcal. If a high energy intermediate is present, it should be quenched as in the photochemical process. Most quenchers of reasonable energy are polyaromatics which react with cerium(IV) and rule out their use. However, one of the stilbenes should act as an efficient quencher as observed by Hammond (93). When p-methylphenyldiazomethane was decomposed by CAN in the presence of trans-stilbene, no change in the cis/trans ratio was observed over a large concentration range. With p-chlorophenyldiazomethane, there was a drastic increase in the amount of trans-p,p'-dichlorostilbene produced, but there was no corresponding increase in cis-stilbene formed from the trans-stilbene. It seems that if energy transfer had occurred sufficient high energy "phantom" would have been formed to yield some cis-stilbene.

As none was observed, it is difficult to rationalize a high energy stilbene intermediate similar to the one in the photochemical cis-trans transformation.

However, it is possible the intermediate is configurationally close to the "phantom". It is only necessary that the stilbene precursor twist so that the phenyl rings are gauche or nearly so as the final electron transfer is made. One particular possibility is that the phenyl rings are sandwiched around a diazoalkane molecule and that electron transfer occurs through the π-clouds:



The non-polar pentane solvent may make this pairing likely.

More information was needed to answer the cis/trans question and an apparent way to obtain it was to substitute groups on the α-carbon of the diazoalkane and observe the changes in the cis/trans ratio. From the cross experiment with phenyldiazomethane and p-methylphenyldiazomethane it appeared that mixed stilbenes could be prepared. Phenyldiazomethane and 1-phenyldiazoethane then should yield stilbenes, 1,2-diphenylpropene, and 2,3-diphenyl-2-butene:

$$PhCHN_2 + Ph(CH_3)CN_2 \xrightarrow{\text{Cat. CAN}} PhCH{=}CHPh + PhCH{=}CPh\text{-}CH_3 + CH_3\text{-}CPh{=}CPh\text{-}CH_3$$

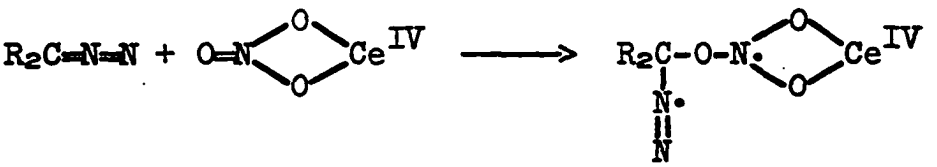
When the mixed reaction was run, only stilbenes, benzyl nitrate, and acetophenone were formed:

$$PhCHN_2 + Ph(CH_3)CN_2 \xrightarrow{1\ CAN} PhCH{=}CHPh + PhCH_2ONO_2 + PhCO\text{-}CH_3$$

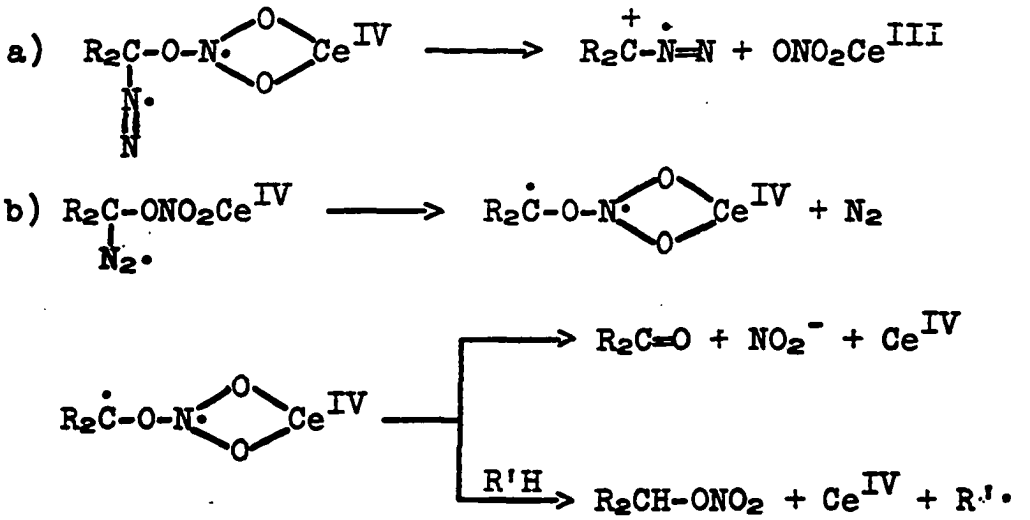
None of the expected propene or butene were found. Thus, not only does 1-phenyldiazoethane itself not yield coupled products but neither can the chain reaction be induced by phenyldiazomethane radical cations. There are several possible explanations for this. The reactions of phenyldiazomethane radicals may be very rapid and all electron transfer is effectively accomplished by them. Stilbenes are formed immediately and then the 1-phenyldiazoethane is oxidized. Corollary to this, the 1-phenyldiazoethane radical cation may be more stable and its lifetime such that trapping by a nucleophile may predominate. Yoshida (61) has noted in the reactions of diazoalkanes with benzoyl peroxide a very similar phenomenon, although Pragst (66) has observed some coupling of 1-(p-nitrophenyl)diazoethane. (Here the nitro group may have destabilized the radical cation sufficiently to permit reaction.) However, it does not seem obvious that such an explanation can be applied to the observation that either a methyl group or a chlorine atom in the o-position of phenyldiazomethane can so drastically alter

reaction away from the stilbenes. The electronic effects of groups ortho and groups para to a benzylic position are not significantly different. An ortho effect could be invoked, but this usually requires participation of the group in the reaction and no disturbance of the ortho groups was noted.

Evidently the reaction is much more sensitive to substituents than the simple chain mechanism would predict. Remembering that many oxidations of CAN proceed via ligands, the first step in which the radical cation is formed can be visualized as involving a prior intermediate:

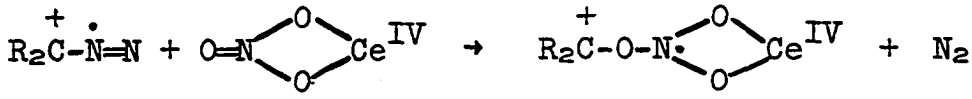


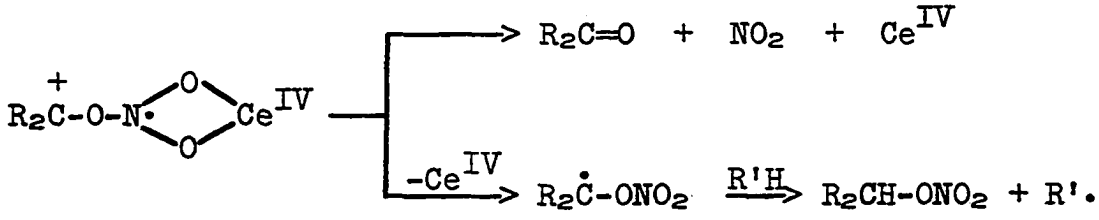
This intermediate may dissociate to yield the radical cation, oxidize at this stage, or couple with another molecule of diazoalkane:



c) $R_2C(N_2\cdot)-ONO_2Ce^{IV} + R_2CN_2 \xrightarrow{-N_2} R_2C(R_2C-N_2\cdot)-ONO_2Ce^{IV}$

The radical cation a) can participate in the chain mechanism to yield stilbenes. It can also be oxidized to the parent carbonyl or be converted to the alkyl nitrates:



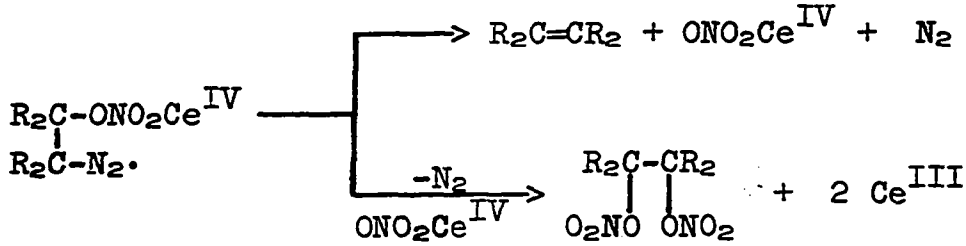


The hydrogen source could be radical abstraction from the hydrocarbon solvent although there is no evidence of any products derived from the solvent. Apparently, cerium(IV) is consumed in the reactions leading to carbonyls or alkyl nitrates (cf. diphenyldiazomethane and ethyl diazoacetate) but the formation of the nitrate is not formally an oxidation. The nitrate can be formed from reaction of the diazoalkane with nitric acid (53) and is probably the reaction occurring with cerium(III), but it appears to be much slower than the radical cation formation, particularly with diphenyldiazomethane. Nitrogen is the only gaseous product and no nitrogen oxides are observed. Furthermore, the reactions are run in anhydrous media so water cannot be oxidized.

Thus, we are left with the quandary of an equivalent of cerium(IV) reduced but no concomitant oxidized specie. There seems to be no answer at present.

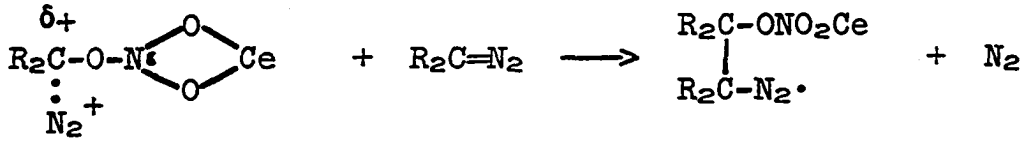
The loss of nitrogen followed by oxidation b) is probably only a special case of the radical cation oxidation. Timing of the different steps and which moiety is actually oxidized can only be speculative and this has been added for completeness.

The rather complex coupled product c) can yield olefins or be further oxidized to the ethanediol dinitrate. (The ethanediol itself probably comes from hydrolysis of the dinitrate during work up.):



The coupling without proceeding <u>via</u> the radical cation seems to be a rather odd reaction although precedent exists in the carbonium ion catalyzed decompositions of Whitlock (83) and Cowell (56). It is difficult to rationalize this pathway with electronic effects. The most reasonable explanation may be that the <u>ortho</u> groups of the phenyldiazomethanes force the timing of loss of nitrogen and the cerium specie to change so that radical cations never form. A positively charged inter-

mediate is then attacked by the nucleophilic diazoalkane with loss of the best leaving group, nitrogen:



Loss of the cerium specie and a second molecule of nitrogen yields the olefin. As no reduction occurs, the cerium(IV) is available for recycling and hence its catalytic nature. Further oxidation of the coupled product yields the ethanediol- dinitrates.

It is not surprising that a scheme such as this would require a very sensitive balance of all factors and minor substituent changes could produce significant changes in products. The stability of the radical cation is very important in determining whether coupling occurs. Except for the electrooxidations, radical cations from the more stable diazoalkanes do not couple; for example, with benzoyl peroxide the dibenzoates are major products. In the electrooxidations, diphenyldiazomethane couples but apparently the radical cation must be destabilized in other cases by nitro groups to achieve coupling. In addition, azibenzils couple only through the phenyl rings leaving the diazo group intact. Therefore, the more stable radical cations should be rapidly trapped by nucleophiles, a process Jugelt (65) has shown to predominate over coupling even with diphenyldiazomethane.

It seems then that phenyldiazomethanes are the limit of stability from which coupling can be expected.

Unfortunately, none of the added details of the chain mechanism offers an alternative to explain the high cis/trans ratio of the stilbenes. As very nearly the scope of diazoalkanes has been surveyed and no other coupling was found, it does not seem possible to arrive at any definitive answer to this problem.

EXPERIMENTAL

Equipment

Esr spectra were obtained on a Varian Model V-4500 instrument. The other equipment used was described on page 40.

Methods

Phenyldiazomethane concentration in Table 16 was determined by comparing the integral at δ 5.8 of 1,1,2,2-tetrachloroethane with the integral at δ 5.1 of the α-hydrogen of phenyldiazomethane. The stilbene yields were obtained by comparing the integral at δ 5.8 of tetrachloroethane with the integral at δ 6.5 of cis-stilbene and at δ 7.3 for the phenyl protons. Stilbenes were identified from their nmr spectra and by glpc retention times and positive peak enhancement with authentic samples.

In all other cases the diazoalkane concentration was determined by adding a known quantity of benzoic acid in benzene to a 10 ml aliquot of the diazoalkane solution and back titrating the excess acid with standardized sodium hydroxide (84). The diazoalkane reacted rapidly with the benzoic acid as evidenced by the evolution of nitrogen and fading of color. The sodium hydroxide was standardized initially with potassium hydrogen phthalate and then with benzoic acid blanks at every analysis. Phenolphthalein was the indicator used.

The products from diphenyldiazomethane were analyzed by nmr using diphenylmethane as standard and comparing the integral at δ 3.9 (s, $Ph_2C\underline{H}_2$) with the integrals at δ 6.8 (s, $Ph_2C\underline{H}ONO_2$) and δ 7.6 (m, $\underline{o}$-Ph_2CO). Product identification was made by comparison of nmr and ir spectra of the mixtures with authentic samples. The products from azibenzil and ethyl diazoacetate were assayed with mesitylene as internal standard and those of 2,2-dimethylphenyldiazopropane, 1-phenyldiazoethane, and 9-diazofluorene with 1,1,2,2-tetrachloroethane.

The stilbene yields were determined by glpc analysis using diphenylmethane as internal standard. Analysis was on a ¼" by 5' 20% by weight SE-30 Chromosorb P or a ¼" by 5' 10% by weight UCON water soluble on Chromosorb P column. Peak areas were determined by disc integration. Extraction ratios were determined by resubjecting the samples to the extraction procedure. In most cases thermal conductivities were not determined.

Materials

Solvents were used as obtained from commercial sources. Acetonitrile was Baker 'Analyzed' reagent and pentane was Baker Grade. Ceric ammonium nitrate was used as obtained from G. Frederick Smith or was Baker 'Analyzed' reagent. 1,1,2,2-Tetrachloroethane (Mallinckrodt OR) was distilled and bibenzyl (Eastman) was used as received. Ethyl diazo-

acetate (Aldrich) was used as supplied. The tosylhydrazones of the benzaldehydes were prepared by the method of Closs (95) and recyrstallized from methanol. The bis(2,4-pentanedionato)copper(II) was used as obtained from Alfa Inorganics. cis- and trans-Stilbene (J. T. Baker) were used as supplied without further purification.

trans-Di-1-naphthylethene

The ethylene was prepared by two methods, the copper(II) decomposition and the photolysis of 1-naphthyldiazomethane.

Bis(2,4-pentanedionato)copper(II) decomposition. A quantity of 1 g of 1-naphthyldiazomethane in 25 ml of pentane was treated with 0.3 g of bis(2,4-pentanedionato)copper(II) suspended in 10 ml of benzene. After 3 hours the copper salt was filtered off and the green solution concentrated on a rotary evaporator. Separation on tlc (silica gel with pentane) yielded two components:

1) nmr (CCl_4) δ 7.5 (m) and 7.0 (d, $J = 7$ Hz).

2) nmr (CCl_4) δ 7.5 (m, 7) and 7.0 (m, 1).

Photolysis. A quantity of 1 g of 1-napthyldiazomethane in 200 ml of pentane was irradiated in Pyrex with a medium pressure Hg lamp for 4 hours. The pentane was removed on a rotary evaporator and two components separated on tlc (silica gel with pentane):

1) nmr (CCl_4) δ 7.5 (m, 7), 2.7 (m, 2), and 1.2 (m, 11).

2) nmr (CCl_4) δ 7.5 (m, 7), and 6.95 (d, J = 7 Hz, 1).

Pivalophenone

Using the method of Ford (96) pivalophenone was prepared from the Grignard from bromobenzene and magnesium and 2,2-dimethylpropanoic acid: nmr ($CDCl_3$) δ 7.8 (m, o-PhCOC$(CH_3)_3$, 2), 7.3 (m, m- and p-PhCOC$(CH_3)_3$, 3), and 1.0 (s, PhCOC$(CH_3)_3$, 9).

Tris(p-bromophenyl)aminium hexachloroantimonate

The aminium salt was prepared by the method of Beresford (97) from 2.4 g tris(p-bromophenyl)amine in methylene chloride and 1 ml of antimony pentachloride. The mixture was poured into 60 ml of ether and the dark blue crystals were collected by filtration. The salt decomposed when a melting point was attempted.

Benzalazine

A quantity of 10.6 g benzaldehyde and 1.5 g 95% hydrazine hydrate was mixed at 0°. The resulting yellow solid was recrystallized from ethanol to yield 10 g of yellow needles: mp 92° (lit. (86) mp 92-93°): nmr ($CDCl_3$) δ 8.0 (s, PhCH=N)$_2$, 1), 7.8 (m, (o-PhCH=N)$_2$, 2), and 7.3 (m, (m- and p-PhCH=N)$_2$, 1), 7.8 (m, (o-PhCH=N)$_2$, 2), and 7.3 (m, (m- and p-PhCH=N)$_2$, 3).

1,2-Diphenyl-1,2-ethanediol

The diol was prepared according to the method of Fieser (98) from benzil and sodium borohydride, m.p. (134-136°) (lit. (98) m.p. 136-137°); nmr ($CDCl_3$) δ 7.2 (m, PhCHOHCHOHPh 5), 4.7 (s, PhCHOHCHOHPh, 1) meso, and 2.2 (s, PhCHOHCHOHPh, 1).

meso-1,2-Diphenyl-1,2-ethanediol dinitrate

The dinitrate was prepared from the ethanediol with fuming nitric acid in acetic anhydride using the method of Hayward (99), mp 133-135° (lit. (99) mp 148°): nmr ($CDCl_3$) δ 7.3 (m, PhCH(ONO_2)CH(ONO_2)Ph, 5) and 6.1 (s, PhCH(ONO_2)CH(ONO_2)Ph, 1); ir ($CHCl_3$) cm^{-1} 1650 (s), 1540 (w), 1290 and 1275 (s), 980 (s), and 850 (s).

Ethyl nitratoacetate

Ethyl nitratoacetate was prepared by refluxing 2 ml of ethyl chloroacetate and 3 g of silver nitrate in 20 ml of acetonitrile for 2 days using the method of White (100). The silver salts were filtered off and the solution poured into 250 ml of ice water, extracted twice with 50 ml of ether, dried ($MgSO_4$) and concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 4.8 (s, $O_2NOCH_2CO_2Et$, 3, 2 on addition of deuterium oxide), 4.3 (q, $O_2NOCH_2CO_2CH_2CH_3$, $J = 7$ Hz, 4, 2 on addition of deuterium oxide), and 1.25 (t, $O_2NOCH_2CO_2CH_2CH_3$, $J=7$ Hz, 6, 3 on addition of deuterium oxide); ir ($CHCl_3$) cm^{-1}

1665 (vs), 1290 (vs), 1070 (m), 1030 (m), and 845 (s).

1-Naphthylmethyl nitrate

The nitrate was prepared by adding 2 ml of 1-naphthylmethyl chloride to a solution of 5 g of silver nitrate in 20 ml of acetonitrile following the general procedure of Ferris (101). The mixture was extracted with ether, dried ($MgSO_4$), and the solvent removed on the rotary evaporator to yield 2 g of a liquid: nmr ($CDCl_3$) δ 7.6 (m, $C_{10}\underline{H}_7CH_2ONO_2$, 7) and 5.65 (s, $C_{10}H_7C\underline{H}_2ONO_2$, 2); ir ($CHCl_3$) cm^{-1} 1645 (s), 1290 (s), and 860 (s).

2,4,6-Trimethylbenzaldehyde hydrazone

The hydrazone was prepared by stirring 0.5 ml of 2,4,6-trimethylbenzaldehyde in 10 ml of absolute ethanol with 5 ml of 95% hydrazine hydrate at room temperature for one hour. The solution was then cooled to 0° and filtered, yielding 0.5 g of white crystals, mp 88-90°.

1-Naphthaldehyde hydrazone

Using the method of Nakaya (102) the hydrazone was prepared from 1-naphthaldehyde and 95+% hydrazine hydrate yielding white crystals, mp 90-92° (lit (102) mp 91-92°).

2-Naphthaldehyde hydrazone

The hydrazone was prepared from 2-naphthaldehyde using the method of Nakaya (102), mp 147-149 (lit. (102) 149-151°).

Phenyldiazomethane

The diazoalkane was prepared from benzaldehyde tosylhydrazone and sodium methoxide in triethylene glycol using the method of Closs (95), affording a wine red solution in pentane; nmr (pentane) δ 7.1 (m, $\underline{Ph}CHN_2$, 5) and 5.1 (s, $PhC\underline{H}N_2$, 1). For solutions in other solvents the pentane was removed by vacuum distillation at 0°, never allowing all of the pentane to be removed to avoid benzalazine formation. The amount of pentane in the solutions did not exceed 1 ml. p-Methyl- and p-chlorophenyldiazomethane were prepared in an identical manner.

o-Methylphenyldiazomethane

The diazoalkane was prepared from o-methylbenzaldehyde tosylhydrazone using the method of Closs (95) yielding an orange-red solution: nmr (pentane) δ 7.1 (m, $o\text{-}CH_3C_6\underline{H}_4CHN_2$, 4), 5.1 (s, $o\text{-}CH_3C_6H_4C\underline{H}N_2$, 1), and 2.3 (s, $o\text{-}CH_3C_6H_4CHN_2$, 3). For the solutions in benzene, the pentane was removed by vacuum distillation at 0° leaving at least 1 ml of pentane to avoid azine formation. o-Chlorophenyldiazomethane was prepared in an identical manner.

p-Nitrophenyldiazomethane

The diazoalkane was prepared by stirring 2 g of p-nitrobenzaldehyde tosylhydrazone, 0.5 g of sodium methoxide, and 20 ml of triethylene glycol at room temperature for 20 min

after the method of Closs (95). The mixture was poured into ice water and a deep red solution was obtained which could not be readily extracted with organic solvents (pentane, ether, chloroform, carbom tetrachloride, etc.). The triethylene glycol solution was then used for the CAN decomposition. A very pale yellow solution of the p-nitrophenyldiazomethane could be obtained in benzene but it was too dilute for quantitative analysis.

p-Methoxyphenyldiazomethane

The p-methoxyphenyldiazomethane was prepared by stirring an ether solution of p-methoxybenzaldehyde hydrazone with excess silver oxide at 0° for 20 min. Further stirring caused some decomposition of the p-methoxyphenyldiazomethane. The silver oxide was removed by filtration and the ether evaporated carefully at 0°, leaving a deep red residue. This residue was taken up in 50 ml of pentane and used immediately due to the instability of the diazoalkane. This procedure is patterned after the method of Closs (95) substituting silver oxide for mercuric oxide. Silver oxide makes addition of base unnecessary and leads to a smoother reaction and higher yield in the preparation of most diazoalkanes from the hydrazones.

2,4,6-Trimethylphenyldiazomethane

The diazoalkane was prepared by stirring 2,4,6-trimethylbenzaldehyde hydrazone with silver oxide in ether at 0° for

5 min. The pale orange solution (90) was filtered and the ether removed under vacuum at room temperature. The diazoalkane was dissolved in pentane and used immediately.

1-Naphthyldiazomethane

Using the method of Schroeder and Katz (103) for the preparation of diphenyldiazomethane, 1-naphthyldiazomethane was prepared by stirring 1-naphthaldehyde hydrazone with silver oxide in ether, affording deep red crystals as reported by Nakaya (102): nmr (CCl_4) δ 7.4 (m, $C_{10}\underline{H}_7CHN_2$, 7) and 5.2 (s, $C_{10}H_7C\underline{H}N_2$, 1).

2-Naphthyldiazomethane

The diazoalkane was prepared by the silver oxide oxidation of 2-naphthaldehyde hydrazone after the method of Schroeder and Katz (103), affording the red crystals reported by Nakaya (102).

1-Phenyldiazoethane

Using the method of Farnum (104), 1-phenyldiazoethane was prepared from acetophenone tosylhydrazone and sodium methoxide in pyridine, yielding a deep pink pentane solution.

1-Phenyl-2,2,2-trifluorodiazoethane

The diazoalkane was prepared from 2,2,2-trifluoroacetophenone tosylhydrazone and sodium methoxide in pyridine according to Shepard (105), yielding an orange pentane solu-

tion: ir (CCl_4) cm^{-1} 2048 (s), 1728 (m), 1680 (m), and 1400 (b).

α-Diazoacetophenone

α-Diazoacetophenone was prepared according to Hauptmann (106) by stirring 10 g of α-bromoacetophenone and 10 ml of 95+% hydrazine hydrate in 20 ml of absolute ethanol (it is essential the ethanol be anhydrous) while raising the temperature to 60° (it is important that addition be made at room temperature) and stirring for 20 min. The mixture was poured into 200 ml of ice water and cooled to 0° for 30 min and the precipitate collected by filtration. Then 1.5 g of the phenylglyoxal hydrazone was stirred with 3.0 g manganese dioxide (unactivated commercial grade will suffice) in 50 ml of chloroform. The manganese dioxide was filtered off and the chloroform solution used without further work up: ir ($CHCl_3$) cm^{-1} 2117 (vs), 1610 (m), and 1370 (s), identical to that reported by Yates (107) from a more tedious preparation.

p-Methyl-α-diazoacetophenone

p-Methyl-α-diazoacetophenone was used as obtained from J. Stam, prepared by the method of Newman (108).

Azibenzil

Azibenzil was prepared by stirring benzil monohydrazone and silver oxide in ether after the procedure of Nenitzescu

(109), affording red crystals: ir (CCl_4) cm^{-1} 2190 (s) and 1700 (s).

9-Diazofluorene

9-Diazofluorene was obtained from J. Stam, prepared by the method of Nenitzescu (109), and used without further purification.

Diphenyldiazomethane

Diphenyldiazomethane was obtained from J. Stam, prepared after the method of Miller (110), and purified by dissolving in pentane, filtering off insoluble white material and removing the pentane under vacuum: ir (CCl_4) cm^{-1} 2050 (s), 1600 (w), and 1500 (m).

2,2-Dimethyl-1-phenyldiazopropane

The diazoalkane was prepared from pivalophenone tosylhydrazone and sodium methoxide in pyridine following the method of Farnum (104) for the preparation of 1-phenyldiazoethane, yielding a deep red pentane solution: ir (pentane) cm^{-1} 2060 (s).

Diazomethane

Diazomethane was prepared from 7.1 g of bis(n-methyl-N-nitroso)terephthalate (ESR-101, E. I. du Pont du Nemours & Company) using exactly the procedure of Moore and Reed (111) and yielding a pale yellow ether solution.

Reactions of Cerium(IV)

Phenyldiazomethane

The pentane solution of phenyldiazomethane from a typical preparation from 5 g of benzaldehyde tosylhydrazone was placed in a bath at -10° (acetone/ice) and two 2 ml aliquots were added to flasks containing weighed quantities of 1,1,2,2-tetrachloroethane. The resulting solutions were placed in nmr tubes and stored over Dry Ice. Ten ml aliquots of the pentane solutions were transferred to flasks immersed in a bath at -10°. Approximately 1 ml of a 0.1 N CAN solution in acetonitrile was added. The pentane layer turned colorless immediately and a gas was vigorously evolved, ceasing after 60 seconds. The pentane layer was poured into a flask containing 50 ml of saturated sodium bicarbonate solution covered with 50 ml of pentane. The pentane layer was separated, dried ($MgSO_4$) and the pentane removed on a rotary evaporator. Accurately weighed amounts of 1,1,2,2-tetrachloroetahen were then added and analysis of the stilbenes and the diazoalkane was accomplished by nmr: Spectra of products without standard, nmr ($CDCl_3$) δ 7.2 (m, PhCH=CHPh and trans-PhCH=CHPh) and 6.55 (s, cis-PhCH=CHPh); ir ($CDCl_3$ cm^{-1} 1650 (m), 1620 (m), 1500 (m), 1460 (m), and 1280 (m); only two peaks were observed on the glpc trace on SE-30 at 180° corresponding to cis-stilbene and trans-stilbene by retention times and peak enhancement by authentic samples.

Control. To 2 ml of a 10% phenyldiazomethane solution in acetonitrile at -5° was added approximately 6 ml of a pinacol reduced 0.1 N CAN solution. No reaction was evident and no gas was evolved. The solution was poured into 20 ml of ether and 20 ml of a saturated sodium bicarbonate solution. The ether layer was separated, washed with 20 ml of water, and concentrated on the rotary evaporator, yielding a red residue: nmr ($CDCl_3$) δ 7.2 (m, 95), 5.3 (s, 13), 4.6 (s, 5), 1.9 (s, CH_3CN, 40) and 1.2 (s, 25).

At three concentrations. The pentane was removed from a typical preparation of phenyldiazomethane and the diazoalkane diluted to 10 ml, one ml of which was diluted 10 ml again, one ml of which was diluted to 5 ml, yielding three solutions of phenyldiazomethane of different concentrations. The concentration was analyzed by treating a 1 ml aliquot of the first solution with benzoic acid and back titrating the excess acid with sodium hydroxide. The contents of each flask was oxidized as normal. The pentane layer was separated and added to weighed quantities of diphenylmethane and the products analyzed by glpc.

CIDNP experiment. A solution of ca. 200 mg of phenyldiazomethane in pentane was placed in an nmr probe. One drop of CAN (0.1 N in acetonitrile) was added and the spectrum scanned. After two drops, the peak corresponding to phenyl-

diazomethane at δ 5.0 became broad and a peak appeared at δ 6.5 corresponding to cis-stilbene. After about 4 drops the peak at δ 5.0 became fuzzy and the peak at δ 6.5 quite sharp. The multiplet around δ 7.1 had compacted from the broad multiplet of phenyldiazomethane. After about 10 min no diazoalkane was noted and the spectrum was that of cis-stilbene. No peaks were noted except those at δ 7.3 (m) and 6.5 (s).

ESR experiment. Equal volumes of a 0.05 M phenyldiazomethane solution in pentane and a 0.02 N CAN solution in acetonitrile were flowed through an efficient mixing chamber and then through an esr probe. Spectra were run for both flow rates fast, both slow, one alternately slow and the other fast, and both stopped. Bubbling did not interfere although reaction was obvious by evolution of a gas and by disappearance of the red color of the diazoalkane. No signal was observed on any of the spectra.

In the presence of acrylamide. To a usual preparation of phenyldiazomethane in pentane was added 5 g of acrylamide (only approximately one fourth dissolved) and oxidized and worked up as usual: nmr ($CDCl_3$) δ 7.3 (m, 47) and 6.5 (s, 6). No polymer was observed.

In solutions saturated with oxygen. Oxygen was bubbled through a typical preparation of phenyldiazomethane and the solution was oxidized as usual: nmr ($CDCl_3$) δ 7.3 (m, 120), 6.5 (s, 16), and 5.3 (s, 5).

At -80°. A usual preparation of phenyldiazomethane was oxidized in a Dry Ice-acetone bath. Reaction was slow due to freezing of the acetonitrile solutions of CAN. A gas was evolved and the diazoalkane color faded to yield a colorless pentane solution. The pentane layer was separated, dried ($MgSO_4$), and concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 7.3 (m, 137) and 6.5 (s, 20).

With added cyclohexene. To a usual preparation of phenyldiazomethane in pentane was added 1 g of cyclohexene and the solution oxidized with 1 ml of a 10% solution of CAN in acetonitrile. The oxidation proceeded as usual. The mixture was extracted with ether, washed with water, dried ($MgSO_4$) and concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 7.3 (m, 187), 6.5 (s, 11), 6.1 (s, 3.5), 5.6 (m, 9), 5.2 (s, 8), 2.3 (m, 4), and 1.8 (m, 70); ir ($CDCl_3$) cm^{-1} 2750 (w), 1710 (w), 1650 (s), 1500 (w), 1460 (w), 1280 (s), and 860 (s). A maximum of four products was observed by glpc on SE-30 at 75°. The mixture was separated on tlc (silica gel and carbon tetrachloride):

1) nmr ($CDCl_3$) δ 10.0 (s) and 7.5 (m)—benzaldehyde.

2) nmr ($CDCl_3$) δ 7.3 (m, 56.4), 7.1 (s, 4.5), and 6.5 (s, 6)—*cis*- and *trans*-stilbene, the only appreciable quantities of material.

3) nmr ($CDCl_3$) δ 7.3 (m, 55), 6.0 (m, 5.5), 4.3 (m, 5), 3.5 (m, 4), 2.5 (m, 8), and 1.5 (m, 250).

With added 9,10-dibromoanthracene. The pentane solution of phenyldiazomethane was evaporated under vacuum at room temperature and 50 ml of benzene was added. To 10 ml aliquots of the benzene solution was added *ca.* 160 mg of 9,10-dibromoanthracene and 1.5 ml of a 0.1 N solution of CAN in acetonitrile. A deep purple color was noted that slowly faded to a light yellow-green (when 100 mg of 9,10-dibromoanthracene in 10 ml of benzene was treated with 1.5 ml of the CAN solution a deep purple color formed that slowly faded to pale yellow). The contents of the flask were washed with 10 ml of water and 3 ml of ether. The organic layer was separated, dried ($MgSO_4$) and concentrated on a rotary evaporator. The products were dissolved in perdeuteriobenzene and the insoluble dibromoanthracene filtered off: nmr (C_6D_6) δ 7.5 (m) and 7.1 (s). Glpc analysis showed only one peak with the retention time of *trans*-stilbene.

Phenyldiazomethane and 1-phenyldiazoethane

Phenyldiazomethane and 1-phenyldiazoethane were prepared as usual and each diluted to 50 ml of pentane. A 10 ml

aliquot of each was added to benzoic acid to determine concentrations and 20 ml aliquots (1.76 mmoles of phenyldiazomethane and 1.4 mmoles of 1-phenyldiazoethane) of each were mixed and 6 ml of a 20% solution of CAN (2.2 mmoles) in acetonitrile added. The pentane layer was separated, dried ($MgSO_4$), and the pentane removed on a rotary evaporator. A weighed quantity of 1,1,2,2-tetrachloroethane was added and the mixture analyzed by nmr: nmr ($CDCl_3$) δ 7.3 (m, 176.5), 6.5 (s, 9.2), 5.95 (s, 35), 5.3 (s, 12), 2.5 (s, 23); ir ($CHCl_3$), without added standard cm^{-1} 1700 (s), 1640 (s), 1450 (m), 1380 (m), and 1290 (s). The products were identified by comparing their retention times on the glpc with those of authentic samples.

Phenyldiazomethane and p-methylphenyldiazomethane

Solutions of phenyldiazomethane and p-methylphenyldiazomethane in pentane were cooled in an ice-acetone bath and 10 ml aliquots were removed from each and added to weighed quantities of benzoic acid in benzene. The normality of each solution was calculated and appropriate volumes were then taken so that the mixture would contain equimolar amounts of each diazoalkane. Approximately one half of an equivalent of CAN in acetonitrile was added and after 1 min, 1 ml of acetic acid and then 10 ml of water. Not all of the diazoalkane had reacted when the acetic acid was added. The pentane layer was separated, washed with water, dried ($MgSO_4$),

and concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 7.2 (m), 6.4 (3 lines), and 2.2 (3 lines); mass spectrum m/e 208 (13%), 194 (52%), 180 (100%), 120 (28%), 108 (13%), and 106 (13%). Analysis was by glpc on a Ucon water soluble column at 200° with the injection port at 280°. Apparently, cis/-trans isomerization occurred during glpc analysis but the proportions of the three stilbenes remained constant.

p-Methylphenyldiazomethane

The pentane solution of the diazoalkane was cooled in an ice bath and decanted. If solid particles were evident, the solution was also filtered. Two 10 ml aliquots were added to flasks containing weighed quantities of benzoic acid and 10 ml aliquots were placed in flasks in an ice-acetone bath and 1.5 ml of a 0.1 N CAN solution in acetonitrile added with stirring. After the reaction was over, a quantity of ca. 10 mg of 1,2-diphenylethane was added. The contents of the flask was washed out with 10 ml of water and 3 ml of ether. The organic layer was separated, dried ($MgSO_4$), and concentrated on a rotary evaporator; without added standard, nmr (CCl_4) δ 7.7 (m), 7.3 (m), 6.5 (s), 2.3 (3 lines); ir (CCl_4) cm^{-1} 1710 (w), 1690 (w), 1640 (s), 1610 (w), 1520 (w), 1285 (s), 1050 (m), 910 (m), and 850 (m). Analysis was by glpc on a Se-30 column at 180°.

With added trans-stilbene. The diazoalkane was prepared as usual and the solution diluted to 75 ml with pentane (the same reaction was run in benzene under the same conditions). A 10 ml aliquot was added to benzoic acid for determination of concentration. Then 10 ml aliquots were added to weighed samples of trans-stilbene (in pentane, all of the stilbene did not dissolve in the two most concentrated solutions but in benzene all of the stilbene dissolved). Approximately, 1 ml of a 10% solution of CAN in acetonitrile was added. The pentane layer was decanted and analyzed by glpc using a UCON water soluble column at 195°. It was necessary to use this column to achieve complete separation of all the stilbenes even though isomerization is known to occur with it.

p-Chlorophenyldiazomethane

The diazoalkane was decomposed, worked up, and analyzed exactly as was p-methyldiazomethane using diphenylmethane as the standard: without added standard, nmr ($CDCl_3$) δ 7.3 (m), 7.0 (s), 6.5 (s), and 5.3 (s); ir (CCl_4) cm^{-1} 1650 (s), 1600 (w), 1500 (s), 1405 (w), 1290 (w), 1100 (s), 1010 (m), 910 (s), and 835 (m).

With added trans-stilbene. The pentane solution of p-chlorophenyldiazomethane was evaporated at room temperature and 50 ml of benzene added. A 10 ml aliquot was added to benzoic acid and 10 ml aliquots were added to flasks containing weighed amounts of trans-stilbene and 1.5 ml of a 0.1 N solu-

tion of CAN in acetonitrile was added. The contents of the flask were washed out with 10 ml of water and 3 ml of ether. The organic layer was separated, dried ($MgSO_4$) and concentrated on the rotary evaporator. Glpc analysis revealed peaks only for trans-stilbene and the dichlorostilbenes.

p-Methoxyphenyldiazomethane

To 10 ml aliquots of the pentane solution of p-methoxyphenyldiazomethane in an ice-acetone bath was added 1.5 ml of a 0.1 N solution of CAN in acetonitrile. There was evolution of a gas and the color faded from deep red to pale yellow. The contents of the flask were washed out with 10 ml of water and 3 ml of ether. The organic phase was separated, dried ($MgSO_4$), and concentrated on a rotary evaporator: nmr ($CDCl_3$) δ 8.5 (s, 3), 7.7 (m, 12), 6.85 (m, 136), 5.3 (s, 4.5), 4.2 (m, 11), and 3.7 (m, 104); ir ($CHCl_3$) cm^{-1} 2440 (w), 1610 (m), 1520 (m), 1220 (vs), 1040 (m), 750 (b). Glpc analysis on SE-30 at 245° showed 6 peaks, 4 of which were major.

p-Nitrophenyldiazomethane

To a deep red solution of the diazoalkane in triethylene glycol was added 10 ml of a 10% solution of CAN in water. A yellow precipitate formed but no gas was evolved. The color of solution deepened slightly.

Extraction of an original triethylene glycol solution with benzene afforded very dilute pale yellow solutions of

the diazoalkane. Treatment of these solutions with a 10% solution of CAN in water caused the benzene layer to become colorless and the water layer deep red. There was no evidence of evolution of a gas.

Control. Phenyldiazomethane was prepared in 20 ml of triethylene glycol and 10 ml of 10% CAN in water was added. A gas was evolved and the red color of the diazoalkane faded to a pale yellow.

o-Methylphenyldiazomethane

To a typical preparation of o-methylphenyldiazomethane in pentane was added 2 ml of a 10% solution of CAN in acetonitrile. There was the usual evolution of bubbles and fading of color. The mixture was extracted with ether, washed with water, and dried ($MgSO_4$), and concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 7.2 (m, 160), 6.7 (s, 4), 5.4 (s, 26), 4.6 (s, 10) and 2.5 (m, 115); ir ($CHCl_3$) cm^{-1} 1640 (s), 1280 (s), 910 (s), and 860 (s); mass spectrum m/e 209 (10%), 208 (50%), 207 (10%), 193 (30%), 178 (30%), 165 (9%), 150 (11%), 120 (100%), and 119 (100%), on silica gel, 251, 249, 247 (15%), 193, 191, 189 (15%), 167 (12%), 135, 133, 131 (10%), 120 (off scale), 105 (85%), 91 (100%). Glpc on SE-30 indicated three components and these were collected:

1) 2-methylbenzaldehyde

2) nmr ($CDCl_3$) δ 7.3 (m, 4), 4.7 (s,1), and 2.4 (s, 3); ir (CCl_4) cm^{-1} 3610 (w), 1740 (m), 1710 (m), 1390 (s).

3) nmr ($CDCl_3$) δ 7.2 (m, 4), 5.5 (s, 1), and 2.4 (s, 3); ir ($CHCl_3$) cm^{-1} 1640 (s), 1290 (s), 910 (s); Anal. Found: C, 64.06; H, 7.21; N, 5.96.

The product mixture was reduced with lithium aluminum hydride: nmr ($CDCl_3$) δ 7.0 (m, 120), 5.1 (s, 8), 4.5 (s, 32), and 2.3 (s, 95).

o-Chlorophenyldiazomethane

To a typical preparation of the diazoalkane (7.4 mmoles in 40 ml of pentane) was added 5.5 ml of a 10% solution of CAN in acetonitrile (1.02 mmoles of CAN) just until the pentane layer was perfectly colorless and no further gas evolution was noted. The mixture was extracted with 50 ml of ether, washed twice with 20 ml of water, dried ($MgSO_4$), and concentrated on the rotary evaporator; nmr ($CDCl_3$) δ 7.5 (m, 189), 7.1 (s, 11), 5.5 (s, 15) and 4.5 (s, 11); ir (CCl_4) cm^{-1} 3460 (w), 1707 (w), 1650 (s), 1450 (m), 1285 (s), 1050 (m), and 850 (s). Four components could be isolated on tlc (silica gel with carbon tetrachloride):

1) nmr ($CDCl_3$) δ 7.3 (m, 5) and 4.5 (s, 1)
2) nmr ($CDCl_3$) δ 10.5 (s) and 6.95 (m)
3) nmr ($CDCl_3$) δ 7.1 (m), 6.9 (m), and 6.68 (s)
4) nmr ($CDCl_3$) δ 6.9 (m, 4) and 5.5 (s, 1); ir (CCl_4) cm^{-1} 1650 (s), 1370 (b), 1285 (s), and 850 (w)

Ceric sulfate oxidation. To a typical preparation of o-chlorophenyldiazomethane in pentane was added a catalytic amount of ceric sulfate in acetonitrile. There was a vigorous evolution of bubbles. The pentane layer was separated and concentrated on a rotary evaporator: nmr ($CDCl_3$) δ 7.1 (m, 100), 4.7 (d, 31, J = 6.5 Hz), and 2.66 (t, 18, J = 6.5 Hz); ir ($CHCl_3$) cm^{-1} 3610 (m), 3460 (b), 130 (shoulder), 1700 (m), 1670 (m), 1600 (m), 1480 (m), 1450 (s), 1400 (b), 1270 (b), and 1130 (m). A repeat of the same reaction gave an nmr ($CDCl_3$) δ 7.2 (m, 170), 4.7 (s, 58), and 3.1 (s, 32).

Ceric ammonium sulfate oxidation. To a typical preparation of o-chlorophenyldiazomethane was added a slurry of 1 g ceric ammonium sulfate in 10 ml of acetonitrile and the mixture stirred in excess of 24 hours. There was no evolution of a gas but the color of the diazoalkane faded. The pentane layer was separated and concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 7.2 (m), 5.3 (s), 5.1 (s), 4.4 (m), 3.5 (m), and 1.9 (m).

2,4,6-Trimethylphenyldiazomethane

To approximately 500 mg of the diazoalkane in pentane was added 1 g of CAN in 10 ml of acetonitrile. There was an immediate evolution of bubbles and fading of the orange color. The mixture was extracted with ether, washed with water, dried ($MgSO_4$), and concentrated on a rotary evaporator: nmr

($CDCl_3$) δ 10.5 (s, 3), 9.0 (s, 5), 6.8 (s, 35), 5.5 (s, 16), and 2.5 and 2.3 (m, 209); ir ($CHCl_3$) cm^{-1} 1785 (m), 1635 (s), 1285 (s), and 915 (s). Two products were separated by tlc (silica gel with pentane).

1) nmr ($CDCl_3$) δ 6.8 (m, 50), 5.5 (s, 3), 4.5 (s, 5), and 2.3 (m, 220); ir ($CHCl_3$) cm^{-1} 1680 (s), 1610 (s), 1440 (b), 1280 (s), and 1150 (m).
2) nmr ($CDCl_3$) δ 9.3 (s, 1), 6.8 (s, 2), and 2.5 (s and 2, 9); mass spectrum m/e 292, 278, and successive loss of 15.

Two products were separated by glpc:

1) nmr ($CDCl_3$) δ 6.69 (s, 2) and 2.3 (5 lines, 9); mass spectrum m/e 164 and 147.
2) nmr ($CDCl_3$) δ 6.68 (s, 2), 5.5 (s, 1), and 2.4 (m, 9); ir ($CHCl_3$) cm^{-1} 1635 (s), 1360 (vs), 1285 (s), and 915 (s).

Reduction of the product mixture with lithium aluminum hydride gave nmr ($CDCl_3$) δ 6.68 (s, 2), 4.6 (s, 1), and 2.3 (3 lines, 10); mass spectrum m/e 264, 196, 178, 151. Two products could be separated by glpc:

1) nmr ($CDCl_3$) δ 6.7 (s) and 2.3 (m); mp 120°.
2) nmr ($CDCl_3$) δ 6.7 (m, 2), 4.6 (s, 1), and 2.3 (3 lines, 10).

1-Naphthyldiazomethane

A quantity of ca. 1 g of the diazoalkane in 10 ml of pentane was treated with 1.2 ml of a 10% solution of CAN in acetonitrile. There was a rapid evolution of bubbles and the formation of a green slime on the bottom of the flask. The pentane layer was removed and concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 7.5 (m), 6.5 (m), 5.5 (s), 5.15 (s), 4.55 (s), and 3.8 (s); ir ($CHCl_3$) cm^{-1} 1700 (m), 1645 (m), 1520 (m), 1390 (b), 1290 (m), 1235 (m), and 910 (vvs). Glpc analysis on SE-30 at 160° afforded three sets of compounds:

1) nmr ($CDCl_3$) δ 9.28 and 9.18 (s and s, 1), and 7.7 (m, 10); ir ($CDCl_3$) cm^{-1} 1680 (w), 1400 (b), 1250 (s), and 1000 (m),
2) nmr ($CDCl_3$) δ 7.5 (m, 4) and 4.1 (s, 1),
3) nmr ($CDCl_3$) δ 7.5 (m, 10) and 4.15 (s, 1).

Four products were separated by tlc (silica gel with 50:50 hexane-benzene):

1) nmr ($CDCl_3$) δ 7.7 (m, 7) and 7.0 (m, 1); ir ($CDCl_3$) cm^{-1} 1640 (w), 1590 (w), and 865 (s); mass spectrum m/e 280 (base), 221 (small), 203 (trace), and 177 (trace),
2) nmr ($CDCl_3$) δ 9.2 (s, 1), 7.5 (m, 12), and 4.6 (s, 2); ir ($CHCl_3$) cm^{-1} 1740 (shoulder), 1700 (s), 1510 (s), 1280 (w), and 1090 (w); mass spectrum m/e 296, 282,

187, 159, 158 (base), 157, and 156.

3) nmr ($CDCl_3$) δ 7.5 (m, 7) and 5.5 (s, 2); ir ($CHCl_3$) cm^{-1} 1645 (s) and 1290 (s).

4) nmr ($CDCl_3$) δ 7.5 (m, 11), 6.65 (m, 2), and 3.8 (s, 3); ir ($CHCl_3$) cm^{-1} 1700 (w), 1600 (m), 1515 (m), 1365 (m), 1170 (m), and 1110 (m); mass spectrum m/e 296, 281, 218, 205, 158, 156 (base); Anal. Found: C, 88.27 or 85.82; H, 6.23, or 6.42; N, 2.72 or 2.32.

In water. A quantity of ca. 500 mg of 1-naphthyldiazomethane in 20 ml of pentane was treated with 0.5 g CAN in 10 ml of water. A brown emulsion formed that was soluble in ether. The water layer was extracted with ether, dried ($MgSO_4$) and concentrated on the rotary evaporator; nmr ($CDCl_3$) δ 10.2 (s, 14), 9.6 (m, 16), 7.6 (m, 207), and 5.8 (s, 12); ir ($CHCl_3$) cm^{-1} 1680 (s), 1640 (s), 1510 (m), 1280 (s), 1170 (m), 1060 (m), and 860 (s). Glpc analysis on SE-30 showed only two components.

Control. To 1 g of 1-naphthyldiazomethane in pentane was added to a solution of 0.5 g CAN in 90% aqueous acetonitrile which had been reduced with pinacol. The color faded rapidly from red to colorless, but there was no evolution of bubbles. The mixture was extracted with ether, washed with water, dried ($MgSO_4$), and concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 10.2 (s, 3.5), 7.5 (m, 211), 5.7 (s, 36), and 5.0 (s, 8); ir (CCl_4) cm^{-1} 3500 (b), 3000 (s), 2240 (w),

1700 (s), 1650 (s), 1520 (m), 1390 (m), 1290 (s), 1110 (m), and 890 (vs).

2-Naphthyldiazomethane

A quantity of ca. 500 mg of 2-naphthyldiazomethane in pentane was treated with 1 ml of a 0.1 N solution of CAN in acetonitrile. There was a vigorous evolution of a gas and a rapid fading of the red color to a pale yellow. The mixture was extracted with ether, dried ($MgSO_4$), and concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 10.1 (s), 7.8 (m), 6.7 (s), 5.5 (s), and 4.5 (s).

Diazomethane

An ether solution of diazomethane was placed in a 200 ml round bottom flask immersed in an ice bath. A solution of 10% CAN in acetonitrile was added until the yellow color of the diazomethane disappeared. A huge volume of a gas was evolved. The gas was directed through a solution of 5 g of bromine in 10 ml of carbon tetrachloride. (This reaction has been used for qualitative and quantitative analysis for ethylene, even in the presence of other olefins (112). The excess bromine was removed by washing with sodium bisulfate and the carbon tetrachloride concentrated on the rotary evaporator. No signals were observed in the nmr. The ether layer was then distilled leaving a residue: nmr ($CDCl_3$) δ 8.0 (m), 3.9 (s), 3.3 (s), 2.8 (s), 2.4 (m), 2.2 (s), 1.5 (m),

and 1.0 (m). The multiplets at 1.5 and 1.0 may be the mineral oil stabilizer of the diazomethane precursor.

α-Diazoacetophenone

To approximately 100 mg of the diazoalkane was added 1 g CAN in 10 ml of acetonitrile. No appreciable amount of gas was evolved and no color change was noted. The mixture was extracted with ether, dried ($MgSO_4$), and concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 7.5 (m, 152), 6.0 (s, 6), and 5.65 (s, 11).

p-Methyl-α-diazoacetophenone

To 0.6 mmoles of the substrate in 10 ml of acetonitrile was added 1 eq of CAN in 10 ml of acetonitrile. There was no indication of any reaction after 35 min. The mixture was extracted with ether, washed with water, dried ($MgSO_4$), and concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 7.5 (q, 117), 6.2 (s, 9), 5.75 (s, p-$CH_3C_6H_4$-$COCHN_2$, 28), 4.8 (s, 3), and 2.4 (d, 86); ir (CCl_4) cm^{-1} 2120 (s), 1695 (m), 1410 (m), 1280 (s), 1240 (m), and 860 (s). Glpc analysis on SE-30 at 120° indicated only one component.

Azibenzil

To ca. 700 mg of azibenzil in ether was added 2.3 g CAN in 10 ml acetonitrile. After evolution of gas had ceased, the mixture was extracted with ether, washed twice with 25 ml of water, dried ($MgSO_4$), and concentrated on the rotary

evaporator. A weighed quantity of *ca.* 150 mg of mesitylene was added and analysis was by nmr ($CDCl_3$) δ 8.0 (m, 35), 7.5 (m, 131), 6.8 (s, 22), 5.5 (s), and 2.4 (s). Quantitative analysis was made by comparing the integrals of the aromatic protons of the product with those of mesitylene.

2,2-Dimethylphenyldiazomethane

A 10 ml aliquot of a pentane solution of the diazoalkane was added to benzoic acid to determine the concentration and 40 ml aliquots were oxidized with CAN. A gas was evolved and the color faded to a pale yellow. The pentane layer was separated and concentrated on the rotary evaporator. A weighed quantity of 1,1,2,2-tetrachloroethane was added and absolute yields were determined by nmr: without added standard; nmr ($CDCl_3$) δ 7.3 (m) and 1.2 and 0.9 (m); ir ($CHCl_3$) cm^{-1} 1670 (s), 1625 (s), 1485 (m), 1380 (m), 1275 - (s), 1175 (m). The products were identified by comparison of their retention times on the glpc with those of authentic samples. The relative yields were determined by glpc.

1-Phenyldiazoethane

A 10 ml aliquot of a pentane solution of the diazoalkane was added to benzoic acid and 40 ml aliquots were oxidized with 2 ml of a 20% solution of CAN in acetonitrile. No rapid evolution of a gas was noted. The pentane layer was separated and concentrated on the rotary evaporator. A

weighed quantity of 1,1,2,2-tetrachloroethane was added and analysis was by nmr ($CDCl_3$) δ 7.5 (m, 34), 7.3 (m, 115), and 2.3 (s, 49.5). Product identification was by glpc retention times.

Ethyl diazoacetate

To a quantity of 0.5 ml of ethyl diazoacetate in 40 ml of pentane was added 2.4 g CAN in 10 ml of acetonitrile and the solution stirred for 2 hours. If one equivalent of CAN were not added, some ethyl diazoacetate could be recovered. Approximately 130 ml of gas was evolved and collected over water. Ten ml of water was added, the pentane layer separated, dried ($MgSO_4$), and concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 4.8 (s, 49), 4.3 (q, 63), and 1.2 (t, 96), on addition of deuterium oxide, 4.8 (s, 49), 4.3 (q, 52), and 1.2 (t, 87); ir ($CHCl_3$) cm^{-1} 1760 (s), 1660 (s), 1415 (m), 1385 (m), 1295 (s), 1140 (m), and 1065 (m); Anal. Found: C, 32.47 or 33.65; H, 4.70 or 4.85; N, 8.27 or 8.95; Calc. C, 37.43; H, 4.05; N, 9.46.

As no mass spectrum could be obtained, a molecular weight was determined by nmr. A typical oxidation was run. The product was isolated and a portion accurately weighed (975.8 mg). Then a weighed amount of mesitylene (362 mg) was added and the nmr obtained ($CDCl_3$) δ 6.8 (s, 43.5), 4.8 (s), 4.3 (q), 2.25 (s, 136), and 1.25 (t, 103.6). By comparing the integrals for mesitylene and the integral for the triplet at

δ 1.25 a molecular weight of 135 ± 15 was obtained. The molecular weight of ethyl nitratoacetate is 149.

A yield was obtained by the same method using mesitylene as standard. Re-extraction gave an extraction ratio of 1.38.

Control. A quantity of 2.4 CAN in 5 ml of water was reduced with acetone. The solution was diluted with 5 ml of acetonitrile and added to 0.5 ml of ethyl diazoacetate in 10 ml of acetonitrile. A gas was evolved and the yellow color of the diazoalkane faded. Work up was as with the CAN oxidation: nmr ($CDCl_3$) δ 4.8 (s, 3), 4.3 (q, 4), and 1.2 (t, 6).

1-Phenyl-2,2,2-trifluorodiazoethane

To the red-orange pentane solution of the diazoalkane was added 0.95 g CAN in 5 ml of acetonitrile. There was no color change in the pentane layer after 6 days. The pentane layer was separated, filtered, and concentrated on the rotary evaporator: ir (CCl_4) cm^{-1} 2040 (s), 1728 (m), and 1680 (m). In another preparation, the mixture was stirred 16 hours and had the same ir spectrum.

Diphenyldiazomethane

To a weighed quantity of diphenyldiazomethane (0.3715 g) in 15 ml of pentane was added 1 eq of CAN (1.05 g) in acetonitrile in a system previously flushed with argon. Each drop of CAN caused a deep blue color like a titration indicator and the evolution of a gas under diphenyldiazomethane. The

gas was collected over water at 23° (48.8 ml) and analyzed by mass spectrum (m/e; background, 28 (45 units), 32 (1 unit), and 44 (5 units); sample, 28 (99 units), 32 (1 unit), and 44 (5 units). The solution was extracted with ether, washed with water, dried ($MgSO_4$), and concentrated on the rotary evaporator. A weighed quantity of diphenylmethane was added and analysis was by nmr: without added standard; nmr (CCl_4) δ 7.6 (m, 26.66), 7.3 (m, 68.8), 6.7 (s, 4.1); ir (CCl_4) cm^{-1} 1665 (s), 1645 (s), 1600 (m), 1445 (m), 1320 (s), 1280 (s), 850 (s), and 700 (s). Glpc analysis showed only one component with the retention time of benzophenone.

Control. To a quantity of 0.15 g diphenyldiazomethane in 10 ml of acetonitrile was added a solution of 0.549 g CAN in 80% aqueous acetonitrile which had been reduced with acetone. There was no color change when the cerium(III) was added and the diazoalkane color faded in about 20 min. Work up was as above: nmr ($CDCl_3$) δ 7.3 (s, 88), 7.0 (s, 4), 6.8 (s, 7), and 5.7 (s,1); ir (CCl_4) cm^{-1} 1650 (s), 1280 (s), 850 (s), and 700 (s).

9-Diazofluorene

To 0.1 g of 9-diazofluorene in 10 ml of pentane were added 0.29 g CAN in 10 ml 80% acetonitrile and the mixture stirred at room temperature. The color slowly faded to pale yellow but no evolution of a gas was noted. The mixture was extracted with 50 ml of ether, washed thrice with 25 ml of

water, dried ($MgSO_4$), and concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 7.4 (m, 189), 6.8 (s, 14), and 5.3 (s, 3); ir ($CHCl_3$) cm^{-1} 1650 (vs), 1460 (m), 1280 (vs), 1110 (m), and 1030 (vs).

Benzalazine

At room temperature. To 100 mg of benzalazine in 10 ml of pentane was added 1 ml of a 10% solution of CAN in 80% aqueous acetonitrile and the mixture stirred for 30 min. The mixture was extracted with ether, washed with water, dried ($MgSO_4$), and concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 8.5 (s, $(PhC\underline{H}{=}N)_2$, 34), 7.7 (m, $(\underline{o}\text{-}\underline{Ph}CH{=}N)_2$, 76), and 7.3 (m, ($\underline{m}$- and $\underline{p}$-$\underline{Ph}CH{=}N)_2$, 121).

At 74°. To 2 eq of CAN in 10 ml of water at 74° was added approximately 2.3 mmoles of benzalazine in 10 ml of acetonitrile. Each drop of azine caused a red coloration and a vigorous evolution of a gas. A quantity of ca. 0.9 mmoles of mesitylene was added as internal standard and the mixture was extracted with ether, washed with water, dried ($MgSO_4$), and concentrated on the rotary evaporator: nmr without added standard ($CDCl_3$) δ 10.0 (s, 32), 7.2 (m, 211), and 6.2 (s, 8).

Reactions of phenyldiazomethane with other oxidants

Potassium ferricyanide

A pentane solution of phenyldiazomethane was stirred with solid potassium ferricyanide for 30 min. Then sufficient acetone was added to dissolve the oxidant. No reaction occurred by evidence of the red color of the diazoalkane. The color persisted for at least 10 days.

Tris(p-bromophenyl)aminium hexachloroantimonate

To a pentane solution of phenyldiazomethane was added a few crystals of the solid salt. After 3 hours no more gas was evolved and the red color of the diazoalkane had disappeared. The salts were filtered off and the pentane concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 9.8 (s, 2), 7.2 (m, 176), 6.5 (s, 2), 4.4 (m, 43), 4.0 (m, 18), and 3.4 (m, 6). Glpc analysis showed at least 5 products, none of which had a retention time corresponding to stilbenes.

Bis(2,4-pentanedionato)copper(II)

The pentane was removed from a typical preparation of phenyldiazomethane and the diazoalkane dissolved in 20 ml of benzene and 20 ml of ether to which was added 2 g of the copper salt. The solution was stirred for 80 min. The copper salts were filtered off and the solvents removed on the rotary evaporator: nmr ($CDCl_3$) δ 7.3 (m, 172) and 6.5 (s, 15); ir ($CDCl_3$) cm^{-1} 1960 (w), 1815 (w), 1680 (s).

Analysis was by glpc on SE-30 at 180°. The same reaction was run with o-methylphenyldiazomethane: nmr ($CDCl_3$) δ 10.1 (s, 2), 7.0 (m, 142), 6.7 (s, 15), and 2.4 (m, 100). Analysis was also by glpc on SE-30 at 180°.

PART III. REACTIONS OF CERIC AMMONIUM NITRATE WITH SODIUM AZIDE AND OLEFINS

INTRODUCTION

The oxidation of sodium azide by CAN usually leads to evolution of stochiometric amounts of nitrogen:

$$2\ Ce^{IV} + 2\ N_3^- \longrightarrow 2\ Ce^{III} + 3\ N_2$$

However, the addition of an olefin completely suppresses gas evolution and α-azido-β-nitratoalkanes are isolated:

$$NaN_3 + 2\ ONO_2Ce^{IV} + R_2C{=}CR_2 \longrightarrow \underset{N_3\ \ ONO_2}{R_2C{-}CR_2} + 2\ Ce^{III}$$

The formation and characterization of these compounds is discussed along with some observations on the scope and nature of the reaction.

HISTORICAL

The evidence for the oxidation of azide ion to nitrogen has been collected (113, 114) for many years. Potassium chlorate (113), manganese dioxide (113), potassium permanganate (113), hypohalous acids (113), nitrous acid (113, 115, 116), iodine (113, 117, 118), peroxides (119), nitrosyl ion (120), chromate ion (121), and ceric salts (113, 122-126) have been shown to decompose metallic azides to nitrogen. Of these, ceric salts affect decomposition most completely and the oxidation in fact has been used as an analytical method for the determination of azide ion (122). The mechanisms of the decompositions have not in general been studied in great detail (except for iodine, which is not an oxidation at all) but for ceric salts the azido radical has been suggested as an intermediate (113):

$$Ce^{IV} + N_3^- \longrightarrow Ce^{III} + N_3\cdot$$

$$2\ N_3\cdot \longrightarrow 3\ N_2$$

The electrolysis of sodium azide solutions has been well studied (127) and from polarographic data (128, 129) the loss of an electron from azide ion to yield the azido radical has been established as the first step:

$$N_3^- \longrightarrow N_3\cdot$$

Characteristically, the second step is represented as:

$$N_3\cdot \longrightarrow 3/2\ N_2$$

There seems little doubt that the azido radical exists as it has been observed spectroscopically (130-132) during flash photolysis of aqueous sodium azide solutions.

The addition of the azido radical to olefins (133) to yield stable alkyl azides (134) was first noted by Minisci and Galli in 1962 (135). tert-Butyl hydroperoxide in the presence of ferric and ferrous sulfate, sodium azide, and styrene yielded a variety of products, among them 1,2-diazido-1-phenylethane:

$$(CH_3)_3COOH + Fe^{+2} + Fe^{+3} + N_3^- + PhCH{=}CH_2 \rightarrow PhCH(OC(CH_3)_3){-}CH_2N_3 + PhCH(N_3){-}CH_2N_3$$

Minisci suggested the route for formation of the azides was the reaction of azide ion with an alkoxy radical to give the azido radical which then added to the olefin:

$$(CH_3)_3COOH + Fe^{+3} \longrightarrow Fe^{+2} + OH^- + (CH_3)_3CO\cdot$$

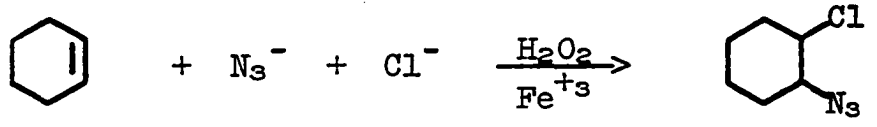
$$(CH_3)_3CO\cdot + N_3^- \longrightarrow (CH_3)_3CO^- + N_3\cdot$$

$$PhCH{=}CH_2 + N_3\cdot \longrightarrow Ph\dot{C}H{-}CH_2{-}N_3$$

$$Ph\dot{C}H{-}CH_2N_3 + FeN_3^{+2} \longrightarrow PhCH(N_3){-}CH_2N_3 + Fe^{+2}$$

$$\dot{\text{PhCH}}\text{-CH}_2\text{N}_3 + (\text{CH}_3)_3\text{CO}\cdot \longrightarrow \text{PhCH}(\text{OC}(\text{CH}_3)_3)\text{-CH}_2\text{N}_3$$

In 1963 the yield was improved and the reaction extended to other olefins with the use of hydrogen peroxide (136). In 1964 the preparation of azidochlorides was reported (137):



In 1965, in yet another elaboration, Minisci reported the preparation of several azido ketones using hydrogen peroxide and ferric salts (138):

$$\text{PhCH=CH}_2 + \text{NaN}_3 \xrightarrow[\text{O}_2]{\text{H}_2\text{O}_2,\ \text{Fe}^{+3}} \text{PhCO-CH}_2\text{-N}_3$$

$$\text{PhCH=CHPh} + \text{NaN}_3 \xrightarrow[\text{O}_2]{\text{H}_2\text{O}_2,\ \text{Fe}^{+3}} \text{PhCO-CHPh-N}_3$$

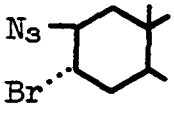
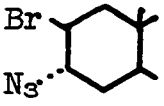
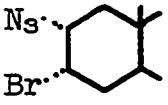
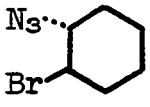
$$\underline{n}\text{-C}_4\text{H}_9\text{-CH=CH}_2 + \text{NaN}_3 \xrightarrow[\text{O}_2]{\text{H}_2\text{O}_2,\ \text{Fe}^{+3}} \underline{n}\text{C}_4\text{H}_9\text{-CO-CH}_2\text{-N}_3$$

Finally, the stereochemistry of the addition to cyclohexene was reported to be trans (139, 140):

In 1968 Hassner and Boerwinkle (141) showed that bromoazide would add to olefins <u>via</u> a radical pathway (see Table 23). Haloazides usually add via heterolytic cleavage of the

halogen-nitrogen bond (142) but it was found that solvents of low polarity, the presence of light and the absence of oxygen could facilitate the homolytic cleavage (143). It is interesting to note that the halonium ion leads to products with azide ion going to the α-carbon with styrene and the radical leads to the azide ion at the β-carbon.

Table 23. Ionic and radical products from olefins and haloazides

Olefin	Haloazide	Pathway	Product	Yield, %
$PhCH{=}CH_2$	BrN_3 [a]	Ionic	$PhCH(N_3)CH_2Br$	95
		Radical	$PhCH(Br)CH_2N_3$	100
	ClN_3 [b]	Ionic	$PhCH(N_3)CH_2Cl$	92
		Radical	$PhCH(Cl)CH_2N_3$	100
2-Cholestene	BrN_3 [a]	Ionic		52
		Radical		37
				27
Cyclohexene	BrN_3 [a]	Ionic		47

[a]Data from reference 141.

[b]Data from reference 143.

Zbiral and Kischa have treated olefins with a lead tetraacetate-trimethylsilyl azide mixture to obtain azido-acetates and di-azides (144):

$$Pb(OAc)_4 + Me_3SiN_3 \longrightarrow Pb(OAc)_{4-x}(N_3)_x$$

$$\underset{\sim}{1}$$

$$PhCH{=}CH_2 + \underset{\sim}{1} \longrightarrow \underset{39\%}{PhCH(N_3)CH_2N_3} + \underset{31\%}{PhCH(OAc)CH_2N_3}$$

$$PhCH{=}CHPh + \underset{\sim}{1} \longrightarrow \underset{42\%}{PhCH(N_3)CH(N_3)Ph} + \underset{42\%}{PhCH(OAc)CH(N_3)Ph}$$

$$\underline{n}\text{-}C_4H_9CH{=}CH_2 + \underset{\sim}{1} \longrightarrow \underset{43\%}{\underline{n}\text{-}C_4H_9CH(N_3)CH_2N_3} + \underset{8\%}{\underline{n}\text{-}C_4H_9CH(OAc)CH_2N_3} + \underset{29\%}{\underline{n}\text{-}C_4H_9CH(N_3)CH_2OAc}$$

Heathcock (145) has noted the addition of azide ion to olefins using mercuric azide, although the mechanism is probably ionic:

$$R_2C{=}CH_2 + Hg(N_3)_2 \rightarrow R_2C(N_3)CH_2HgN_3 \xrightarrow{NaBH_4} \underset{60\text{-}90\%}{R_2C(N_3)CH_3}$$

The reaction apparently proceeds only with terminal olefins.

In 1970 Schäfer (146) reported that the presence of olefins during the electrolysis of sodium azide completely suppressed the evolution of nitrogen and that 1,2-diazido-alkanes were isolated in fair yields:

$$PhCH{=}CH_2 + NaN_3 \longrightarrow \underset{55\%}{PhCH(N_3)\text{-}CH_2\text{-}N_3}$$

RESULTS AND DISCUSSION

The oxidation of sodium azide by CAN in acetonitrile has been shown to yield quantitatively stochiometric amounts of nitrogen (127):

$$\underset{1.56\ \text{mmoles}}{2\ NaN_3} + \underset{1.56\ \text{mmoles}}{2\ CAN} \xrightarrow{CH_3CN} \underset{\substack{50\ \text{ml (50.5 ml}\\ \text{theoretical)}}}{3\ N_2}$$

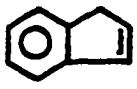
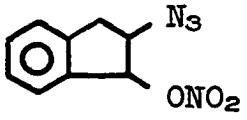
The addition of an olefin causes a complete cessation of gas evolution and the products isolated have azido and nitrato groups as inferred from the ir spectrum (2110 cm^{-1} (147) and 1645 cm^{-1}, respectively):

$$R_2C{=}CR_2 + NaN_3 + 2\ CAN \longrightarrow R_2C(N_3)C(ONO_2)R_2$$

Cyclohexene, 1-methylcyclohexene, 1,3,5-cycloheptatriene, norbornene, α-pinene, α-methylstyrene, stilbene, 2,4-dihydropyran, 1,5-cyclooctadiene, 1,5-hexadiene, 2,3-dimethylbutadiene, and 1,4-diphenylbutadiene are some of the olefins which suppress gas evolution. Gas evolution is not suppressed by diethyl fumarate, maleic anhydride, 4,4-dimethylcyclohexenone, phenylacetylene, 2-methyl-3-butyn-2-ol, trans-cinnamic acid, or cholesterol (perhaps due to low solubility in the reaction mixture). These unsaturated compounds can be recovered intact.

In Table 24 are listed several olefins for which the products have been characterized and absolute yields deter-

Table 24. Absolute yields of products from the oxidation of sodium azide by ceric ammonium nitrate in the presence of olefins

Substrate (mmoles)	NaN_3 mmoles	CAN mmoles	Product	Yield, %[a,b]
 (4.4)	4.7	10		70 ± 1
trans-PhCH=CHCH$_3$ (4.3)[c]	4.5	9.2	Ph-CH(ONO$_2$)-CH(N$_3$)-CH$_3$	76 ± 1
PhCH=CH$_2$ (4.9)	5.3	10.0	Ph-CH(ONO$_2$)-CH$_2$-N$_3$	73 ± 1
n-C$_4$H$_9$CH=CH$_2$ (6.0)	6.1	12.8	n-C$_4$H$_9$-CH(ONO$_2$)-CH$_2$-N$_3$	56 ± 7[d]
n-C$_3$H$_7$(CH$_3$)C=CH$_2$ (6.0)	6.0	12.8	n-C$_3$H$_7$(CH$_3$)C(ONO$_2$)-CH$_2$-N$_3$	49 ± 3

[a]Yield of unpurified products determined by nmr using dibenzyl ether as internal standard.

[b]Standard deviations are based on at least two runs.

[c]Both erythro and threo isomers were formed.

[d]The large deviation is due to problems with emulsion formation in the work up. .

mined. Two equivalents of CAN in acetonitrile is added to a solution of one equivalent each of the olefin and sodium azide in acetonitrile and the reaction is complete as soon

as addition is over. No gas is evolved. The products are isolated by flooding the reaction mixture with water and extracting with pentane. A known amount of standard, dibenzyl ether, was added and the yields determined by nmr analysis. As no starting olefin remains the pentane extracts yield only the azide nitrates. Further purification was accomplished by tlc or by distillation and the products were identified by their nmr, ir, and mass spectra. Only the single isomers reported in Table 24 were observed. In no case was the opposite order of substitution noted. Also, no diazides were ever found.

The characterization of the indan and hexane derivatives will be described in detail.

The spectra of 2-azido-1-nitratoindan is presented on Figure 1. The single proton signal at δ 6.1 is assigned to the proton at carbon 1 which bears the nitrato group. The shift is compatible with those observed for benzylic nitrates with strong electron withdrawing groups on the β-carbon (see, for example, 1,2-diphenyl-1,2-ethanediol dinitrate, δ 6.8, page 98, or 1-naphthylmethyl nitrate, δ 5.7, page 99). The single proton signal at δ 4.2 is assigned to the proton at carbon 2 bearing the azido group, a shift very similar to that reported by Fenical (148) for 2-azido-1-hydroxyindan of δ 3.92. The ir spectrum is presented on Figure 2. The ir bands of 2114 and 1652 cm^{-1} are exactly those of azido

Figure 1. Nmr spectra of 2-azido-1-nitratoindan

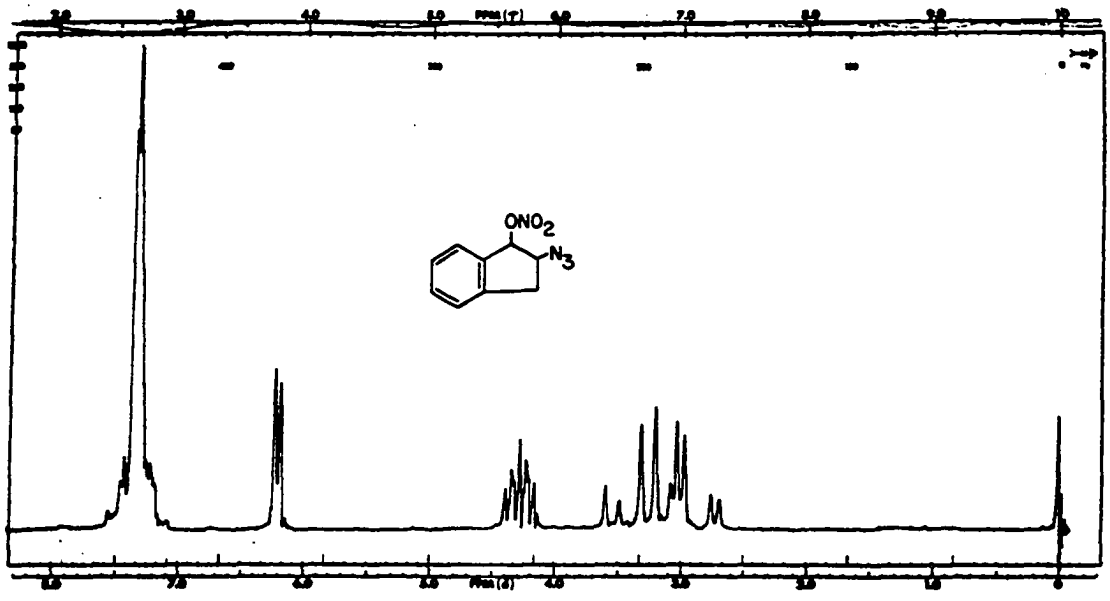
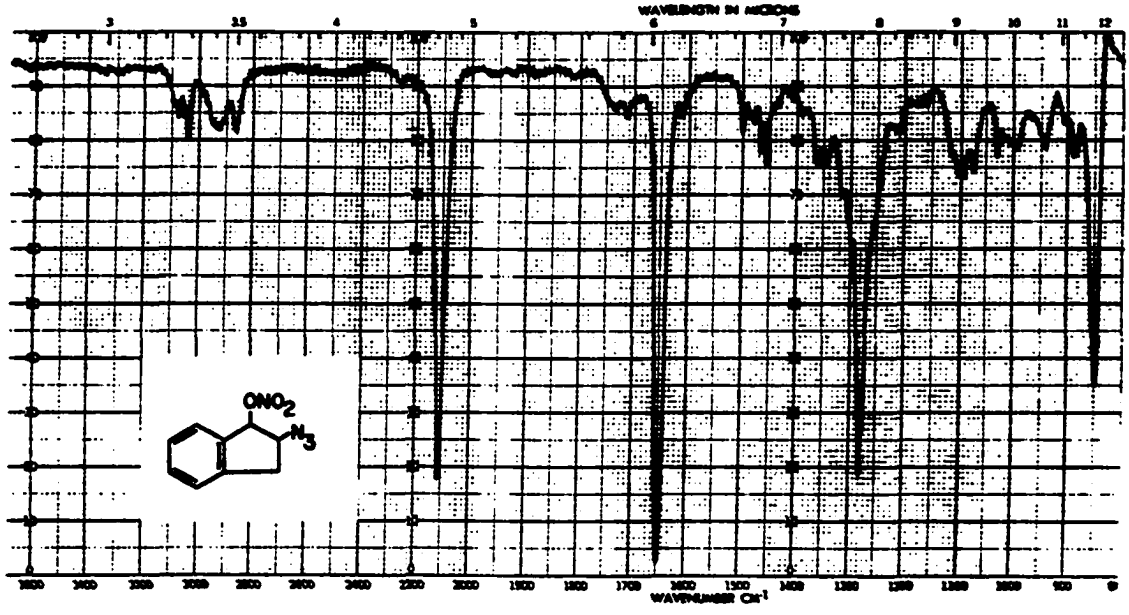

ONO2
N3

Figure 2. Ir spectra of 2-azido-1-nitratoindan


WAVELENGTH IN MICRONS
WAVENUMBER CM⁻¹
ONO2
N3

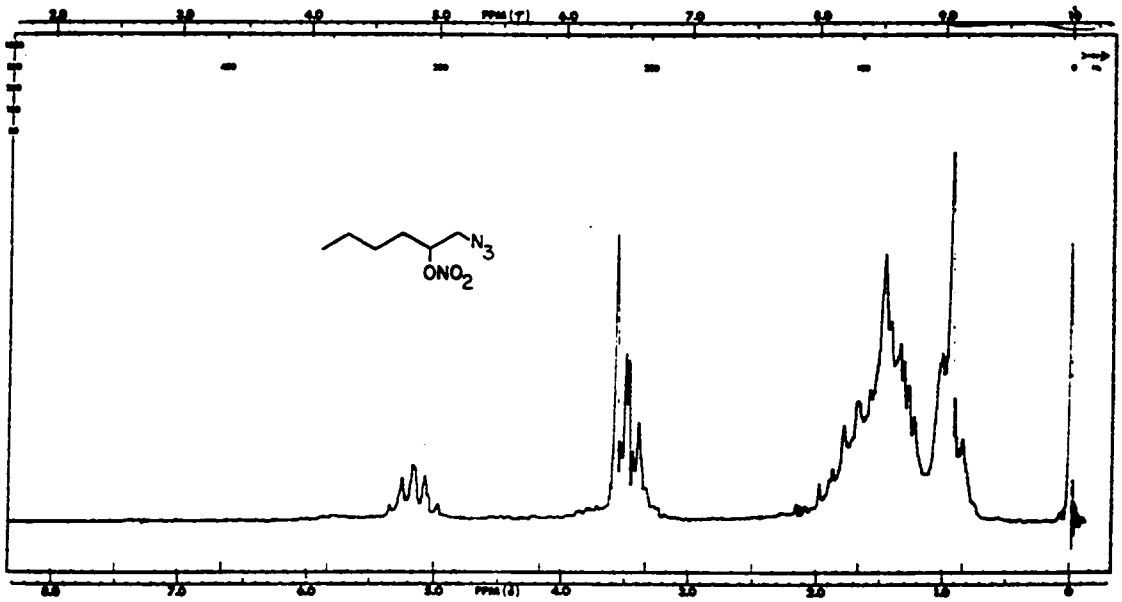
groups and nitrato groups, respectively. An acceptable CHN analysis was obtained for $C_9H_8N_4O_3$. Finally, the mass spectrum provides unequivocal evidence. At 16 eV, a small peak appears at 220 ($M^{+\cdot}$ for $C_9H_8N_4O_3$). Among other fragmentations are noted peaks at 178 (trace, loss of N_3), 145 (co-base, loss of HNO_2 and N_2), and 129 (co-base, loss of HNO_3 and N_2). This confirms the azido and nitrato groups.

The nmr spectra for 1-azido-2-nitratohexane is presented on Figure 3. The single proton signal at δ 5.2 is assigned to the proton at carbon 2 bearing the nitrate ester. The two proton signal at δ 3.5 is assigned to the protons at carbon 1 bearing the azido group, a shift quite compatible with those observed for other alkyl azides (125). Again, there are bands in the ir at 2110 and 1640 cm^{-1} suggesting the azido and nitrato groups. Unfortunately, no acceptable CHN analysis could be obtained for $C_6H_{12}N_4O_3$ (or any other combination of C, H, N, or O):

	C	H	N
Found	41.19	6.63	33.16
Calculated	38.29	6.42	29.77

However, in the mass spectrum a fragmentation peak at 132 m/e was noted. On a high resolution instrument, the exact mass of this fragment was determined to be 132.06614, corresponding to $C_5H_{10}NO_3$ (calculated mass is 132.06606). Thus

Figure 3. Nmr spectrum of 1-azido-2-nitratohexane

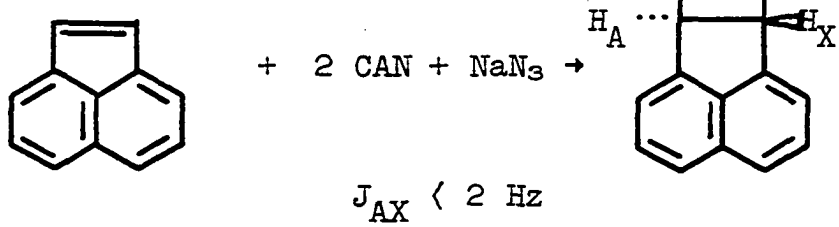

N3
ONO2

there is apparently cleavage between carbon 1 and carbon 2 to yield a n-pentyl nitrate fragment:

$$\underline{n}\text{-}C_4H_9\underset{\underset{ONO_2}{|}}{CH}\text{-}CH_2N_3^{+\bullet} \rightarrow \underline{n}\text{-}C_5H_{10}\text{-}ONO_2^{+} + CH_2N_3\bullet$$

This confirms the presence of a nitrato group. A molecular weight was determined by an nmr analysis. Carefully weighed quantities of purified 1-azido-2-nitratohexane and dibenzyl ether were placed in an nmr tube and the spectrum obtained. From the integrals of the benzyl protons and the protons on the carbon bearing the azido group, the molecular weight of dibenzyl ether, and the weights of the samples a molecular weight of 183 $\pm$ 1 (two attempts) was obtained. The molecular weight of the azide nitrate is calculated to be 188.

The stereochemistry of addition was determined by adding across the double bond of acenaphthylene:



$J_{AX} < 2$ Hz

The reaction proceeded as for the olefins in Table 24 and the product characterized by its nmr and ir spectrum. The observed coupling constant between H_A and H_X was less than 2 Hz. Dewar (149) has shown that in trans-1,2-disubstituted

acenaphthenes J_{AX} is of the order of 2 Hz while in cis-isomers J_{AX} is greater than 6 Hz. Thus, a trans stereochemistry is assigned to the reaction.

The stability of the azide nitrates must be quite high. 1-Azido-2-nitratohexane was refluxed in benzene, toluene, or glacial acetic acid for 16 hours and only starting material recovered. Furthermore, 2'-azido-1'-nitratoethylbenzene and 1-azido-2-nitratohexane may both be molecularly distilled around 100° at 0.1 mm without significant decomposition. Also, 2'-azido-1'-nitratoethylbenzene was photolyzed for five hours and only starting material recovered. In general, organic azides are not readily decomposed photolytically (150).

Sufficient evidence has not been accumulated to allow clear elucidation of a mechanism for the formation of the azide nitrates. However, some observations are possible. The most striking aspect of the reaction is the regiospecificity of the addition of the azido group. No other isomers have ever been noted. This suggests the azide portion adds to the olefin first as in the examples reported by Hassner (141). Because azido radicals are thought to be formed in the CAN oxidation of sodium azide, the first reaction is probably radical addition:

$$Ce^{IV} + N_3^- \longrightarrow Ce^{III} + N_3\cdot$$

$$N_3\cdot + R_2C{=}CR_2 \longrightarrow R_2\dot{C}\text{-}CR_2\text{-}N_3$$

The most stable radical would be expected and, hence, the regiospecificity of the reaction with the nitrate going either to the most substituted carbon or to a benzylic position. The final step would simply be oxidation of the carbon radical by ligand transfer:

$$R_2\dot{C}\text{-}CR_2\text{-}N_3 + ONO_2Ce^{IV} \longrightarrow R_2C(ONO_2)\text{-}CR_2\text{-}N_3 + Ce^{III}$$

This mechanism has considerable precedent. In the reactions of azide ion and peroxides reported by Minisci (140), parallel regiospecificity is observed. Furthermore, Hassner (141) has shown that in the radical additions of haloazides, the azide group goes to the β-carbon while in halonium ion additions the halide goes to the β-carbon. Similar results are observed by Zbiral (144), but the oxidant is so complex strong comparisons are difficult.

One serious problem with radical addition is the lack of reaction with α,β-unsaturated carbonyl compounds. This hints some positive character exists on the α-carbon. Boyer (151) has reported that sodium azide in acetic acid will add to olefins but not to trans-cinnamic acid, a reaction generally thought to proceed via carbonium ions. The addition to bicyclic olefins (norbornene and α-pinene) seems to lead to some rearrangement. Unfortunately, lack of other evidence makes further discussion only speculation.

EXPERIMENTAL

Equipment

The high resolution mass spectrum was determined on an Associated Electronics Industries MS-902 instrument. The other equipment used was described on page 40.

Methods

The yields of the azide nitrates from indene, 1-phenylpropene, styrene, 1-hexene, and 2-methylpentene were all determined by adding dibenzyl ether to the reaction mixture prior to work up. Analysis was by nmr and performed by comparing the integral of the four benzyl protons of dibenzyl ether at δ 4.5 with the integral for the protons on the carbon bearing the nitrato group or the azido group in the products.

Elemental analyses were performed by Chemalytics, Inc.

Materials

Solvents were used as obtained from commercial sources. Fisher purified sodium azide was used directly. 2-Methyl-1-pentene (K & K Laboratories), 1-hexene (Columbia), styrene (Aldrich), and trans-1-phenylpropene (Aldrich) showed no impurities in the nmr spectra and were not further purified. Indene (Columbia) and dibenzyl ether (Aldrich) were distilled prior to use. Acenaphthylene (Aldrich) was used as obtained. The other compounds were used as obtained and their sources

are listed in Table 25.

Table 25. Chemicals

Chemicals	Source
Diethyl fumarate	Aldrich
Maleic anhydride	Fisher Scientific
4,4-Dimethyl-2-cyclohexenane	Aldrich
Phenylacetylene	Aldrich
2-Methyl-3-butyn-2-ol	Aldrich
trans-Cinnamic acid	Eastman
Cholesterol	Matheson Coleman and Bell
Cyclohexene	Aldrich
1-Methylcyclohexene	Aldrich
1,3,5-Cycloheptatriene	Aldrich
Bicyclo(2.2.1)-2-heptene	Aldrich
α-Pinene	Columbia
α-Methylstyrene	Aldrich
trans-Stilbene	J. T. Baker
cis-Stilbene	Aldrich
3,4-Dihydropyran	Eastman
1,5-Cyclooctadiene	Columbian Carbon Company
1,5-Hexadiene	Aldrich
2,3-Dimethylbutadiene	Aldrich
1,4-Diphenylbutadiene	Aldrich

Oxidations of Sodium Azide with CAN

With no olefin added

To a quantity of 100 mg of sodium azide in 15 ml of 0.1 N nitric acid was added 3 ml of a 0.5 N CAN solution. A vigorous frothing was noted and 55 ml of a gas was collected over water at 23°, 50 ml corrected to STP (theoretical, 50.5 ml).

With diethyl fumarate

To 0.3 g sodium azide and 0.8 g diethyl fumarate in 10 ml acetonitrile and 1 ml water was added 5.5 g CAN in 10 ml acetonitrile. A huge evolution of gas was noted (>> 50 ml). The mixture was poured into water and extracted with pentane. Nmr analysis showed only diethyl fumarate present ($CDCl_3$) δ 6.8 (s, 1), 4.3 (q, J = 6 Hz, 2) and 1.3 (t, J = 6 Hz, 3).

With maleic anhydride

Using 0.4 g maleic anhydride, the same reaction as with diethyl fumarate was run with similar results (>>50 ml of gas): nmr ($CDCl_3$) δ 7.1 (s).

With 4,4-dimethyl-2-cyclohexenone

To 0.5 g 4,4-dimethyl-2-cyclohexenone and 0.4 g sodium azide in 10 ml acetonitrile was added 5 g CAN in 10 ml acetonitrile. A large evolution of a gas was noted (>>50 ml). Only starting material was extracted with pentane: nmr ($CDCl_3$)δ 6.65 (d, J = 10 Hz, 1), 5.75 (d, J = 10 Hz, 1), 2.4

(m, 2), 1.8 (m, 2), and 1.2 (s, 6).

With phenylacetylene

To 1 g phenylacetylene and 0.7 g sodium azide in 30 ml of acetonitrile, 1 ml of acetone and 1 ml of water was added 11 g CAN in 10 ml acetonitrile. The color turned brown and a gas was evolved. The mixture was poured into water and extracted with pentane: nmr ($CDCl_3$) δ 7.5 (m, 5), and 3.1 (s, 1); ir (CCl_4) cm^{-1} 2140 (m), 1680 (s), 1610 (s), and 1510 (s).

With 2-methyl-3-butyl-2-ol

To 0.5 g of the acetylene and 0.4 g of sodium azide in 10 ml of water was added 6.9 g of CAN in 10 ml of water. A gas was evolved and the final color was yellow. The mixture was extracted three times with ether, dried ($MgSO_4$), and concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 6.0 (s, 1), 2.45 (s, 1), and 1.5 (s, 6).

With trans-cinnamic acid

To 500 mg of trans-cinnamic acid and 500 mg of sodium azide in either 10 ml acetonitrile and ½ ml acetone (a suspension) or 10 ml acetic acid (a solution) was added 8 g CAN in either 10 ml acetonitrile or 10 ml acetic acid. A large evolution of gas was noted in either case. The mixture was poured into water, extracted with ether, dried ($MgSO_4$), and concentrated on the rotary evaporator: nmr ($CDCl_3$) δ 7.5 (m, 184), 6.5 (d, J = 7 Hz, 12), 5.8 (d, J = 7 Hz, 14), and

4.5 (m, 20).

With cholesterol

To 1 g cholesterol and 500 mg sodium azide in either 10 ml acetonitrile or 10 ml acetic acid (suspensions) and 2 ml water was added 3 g CAN in 10 ml acetonitrile or acetic acid. Two layers were evident immediately with a large evolution of a gas. The mixture was poured into water, extracted with pentane, and concentrated on the rotary evaporator, yielding only crystals of cholesterol: ir ($CHCl_3$) cm^{-1} 3600 (w) and 3300 (s).

With cyclohexene

To a solution of ca. 300 mg of sodium azide and 500 mg of cyclohexene in 10 ml of acetonitrile and 1 ml of water was added 2 g CAN in 10 ml acetonitrile slowly and dropwise. The yellow color of the CAN solution disappeared and no gas was evolved. The mixture was poured into 50 ml of water and extracted with 50 and 25 ml of pentane. After drying ($MgSO_4$) the solvent was removed on the rotary evaporator to yield a pale yellow residue: nmr ($CDCl_3$) δ 5.8 (m), and 2.0 (m); ir ($CHCl_3$) cm^{-1} 2110 (vs), 1720 (m), 1640 (vvs), 1290 (vvs), and 875 (vvs).

With 1-methylcyclohexene

The reaction was identical with that of cyclohexene. The residue was pale yellow with a very pungent odor: nmr

($CDCl_3$) δ 5.5 (m), 4.8 (m), 3.8 (m), and 1.5 (m); ir (CCl_4) cm^{-1} 2115 (vvs), 1720)m), 1640 (vvs), 1290 (vvs), and 875 (vvs).

With 1,3,5-cycloheptatriene

To 0.2 g sodium azide and 0.35 g cycloheptatriene in 10 ml acetonitrile and 1 ml water was added 3.4 g CAN in 10 ml acetonitrile. No frothing or evolution of a gas was noted. Work up was identical as that for cyclohexene: nmr ($CDCl_3$) δ 6.0 (m, 58), 4.2 (m, 17), and 2.3 (m, 31).

With bicyclo(2.2.1)-2-heptene

The reaction and results were observed as with CHT: nmr ($CDCl_3$) δ 4.85 (m, 7), 3.85 (m, 15), and 1.9 (m, 137).

With α-pinene

To 0.6 g α-pinene and 0.3 g sodium azide in 10 ml acetonitrile and 1 ml water was added 5.5 g CAN in 10 ml acetonitrile. No gas was evolved and the mixture was worked up as for cyclohexene: nmr ($CDCl_3$) δ 4.6 (s), 3.8 (m), 2.9 (m), and 1.5 (m).

With α-methylstyrene

To 0.3 g α-methylstyrene and 0.2 g sodium azide in 10 ml acetonitrile and 1 ml water was added 3.4 g CAN in 10 ml acetonitrile. No gas was evolved. After work up as for cyclohexene, a pale yellow residue was obtained: nmr ($CDCl_3$)

δ 7.2 (m, 5), 3.3 (m, 2), and 1.6 (m, 3). This material decomposed to a white insoluble solid after sitting overnight.

With trans-stilbene

To 0.5 g trans-stilbene and 0.2 g sodium azide in 15 ml of acetonitrile and 0.5 ml of water at 75° was added .5 g CAN in 15 ml of acetonitrile. No gas was evolved. After the usual work up, a colorless residue remained: nmr ($CDCl_3$) δ 7.0 (m, J = 8 Hz, 10), 6.0 (d, J = 8 Hz, 1), and 4.8 (m, 1).

With cis-stilbene

The reaction as for trans-stilbene was run but at room temperature. Twenty ml of a gas was evolved: nmr ($CDCl_3$) δ 7.2 (m, 200), 6.6 (s, 9), 5.9 (d, J = 8 Hz), and 4.7 (m, 15).

With 3,4-dihydropyran

To 0.5 g 3,4-dihydropyran and 0.4 g sodium azide in 10 ml acetonitrile and 1 ml water was added 6 g CAN in 10 ml acetonitrile. Twenty ml of a gas were evolved. The mixture was poured into 50 ml water and extracted with dichloromethane: nmr ($CDCl_3$) δ 5.0 (d, J = 7 Hz), 4.6 (d, J = 7 Hz), and 3.5 (m, 43.2) and 1.9 (m, 43.1).

With 1,5-cyclooctadiene (COD)

To ca. 500 mg of 1,5-cyclooctadiene and 400 mg of sodium azide in 10 ml of acetonitrile and 2 ml of water was added 7 g CAN in 10 ml of acetonitrile. No gas was evolved. The mixture was poured into water and extracted with 50 and 25 ml of pentane. After drying ($MgSO_4$), the pentane layer was concentrated on the rotary evaporator. A pale yellow residue was obtained: Nmr ($CDCl_3$) δ 5.5 (m, 36.5), 4.0 (m, 11.5), and 2.0 (m, 188).

With 1,5-hexadiene

To 0.5 g 1,5-hexadiene and 0.4 g sodium azide in 10 ml acetonitrile was added 7 g CAN in 10 ml acetonitrile. No gas was evolved and the mixture worked up as for COD: nmr ($CDCl_3$) δ 5.8 (m), 5.0 (m, 19), 3.5 (m, 11), and 2.0 (m, 32.5).

With 2,3-dimethylbutadiene

The reaction was similar to COD and the product purified on the tlc using pentane: nmr ($CDCl_3$) δ 5.0 (m, 54), 4.0 (s, 41), and 2.0 (s, 154).

With 1,4-diphenylbutadiene

The reaction was the same as with COD: nmr ($CDCl_3$) δ 7.3 (m, 200), 6.2 (m, 52), and 4.5 (m, 14).

With acenaphthylene

To 0.5 g crude acenaphthylene in 10 ml acetonitrile was added 0.4 g sodium azide in 2 ml of water and to this mixture was added 4.5 g CAN in 15 ml acetonitrile. No gas was evolved and the final color was deep brown. The mixture was poured into 50 ml of water, extracted with 50 ml of pentane, dried ($MgSO_4$), and concentrated on the rotary evaporator. The brown oil was purified on tlc (silica gel with pentane) to yield a light yellow oil: nmr ($CDCl_3$) δ 7.5 (m, 5.6), 6.5 (d, J = 1.5 Hz, 1), and 5.3 (d, J = 1.5 Hz, 1); ir ($CHCl_3$) cm^{-1} 2110 (vs), 1645 (vs), and 1290 (s).

With indene

To 0.5 g indene and 0.3 g sodium azide in 10 ml acetonitrile was added 3.4 g CAN in 10 ml acetonitrile. No gas was evolved. The mixture was poured into 50 ml of water and extracted twice with 50 ml of pentane. After drying ($MgSO_4$), the pentane was removed on a rotary evaporator. The residue was purified on tlc (silica gel with pentane), b.p. 80-100° (0.01 mm): nmr ($CDCl_3$) δ 7.1 (m, 5), 6.1 (d, J = 4 Hz, 1), 4.2 (m, 1), and 3.0 (m, 2); ir (CCl_4) cm^{-1} 2115 (vvs), 1652 (vvs), 1283 (vvs) and 850 (vvs); Anal. for $C_9H_8N_4O_3$, Found: C, 49.30; H, 3.76; N, 25.44. Calc. C, 49.09; H, 3.66; N, 25.45. To determine the yield, after the reaction was run a weighed quantity of dibenzyl ether was added and work up performed as usual. Analysis

was by nmr comparing the benzylic protons of dibenzyl ether with the protons on the carbon bearing the nitrato group. An extraction ratio of 1.02 was obtained by resubjecting the analysis mixture to the extraction procedure.

With trans-1-phenylpropene

To 0.5 g trans-1-phenylpropene and 0.3 g sodium azide in 10 ml of acetonitrile was added 5.1 g CAN in 10 ml acetonitrile. No gas was evolved. The extraction procedure for indene was followed and purification was by tlc (silica gel with pentane), b.p. 80-120° (0.01 mm): nmr ($CDCl_3$) δ 7.3 (m, 5), 5.7 (4 lines, 1), 3.9 (m, 1), and 1.2 (m, 3); Anal. for $C_9H_{10}N_4O_3$, Found: C, 51.49; H, 4.88; N, 26.64; Calc. C, 38.29; H, 6.42; N, 29.77. Quantitative analysis was the same as for indene. No extraction ratio was obtained.

Photolysis. Ca. 500 mg of 2'-azido-1'-nitratoethylbenzene in 400 ml of cyclohexane was irradiated with a 450 watt Hg lamp for 5 hours. A brown residue had collected on the walls of the photolysis vessel. The solvent was removed on a rotary evaporator: nmr ($CDCl_3$) δ 7.5 (m, 42), 5.9 (4 lines, 4), 3.5 (m, 8.5), 2.0 (s, 22.5, acetone) and 1.2 (m, 60, cyclohexane).

With styrene

To 500 mg of styrene and 350 mg of sodium azide in 10 ml acetonitrile was added 5.30 g CAN in 10 ml acetonitrile.

Ca. 10 ml of gas was evolved. The mixture was poured into 50 ml of pentane. After drying ($MgSO_4$), the pentane was removed on a rotary evaporator. The residue was purified on tlc (silica gel with pentane): nmr ($CDCl_3$) δ 7.3 (s, 5), 5.9 (4 lines, 2) and 3.5 (m, 2); ir ($CHCl_3$) cm^{-1} 2115 (s), 1640 (s), and 1290 (s); Anal. for $C_8H_8N_4O_3$, Found: C, 47.70; H, 4.10; N, 27.45; Calc. C, 46.16; H, 3.87; N, 29.95. The yield was determined exactly as for indene.

With 1-hexene

To 0.4 g 1-hexene and 0.3 g sodium azide in 10 ml of acetonitrile was added 7.0 g CAN in 10 ml acetonitrile dropwise. No gas was evolved. The extraction (an emulsion was formed) and purification procedure for indene was followed; b.p. 70-80° (0.01 mm): nmr ($CDCl_3$) δ 5.2 (m, 1), 3.5 (m, 2) and 1.5 (m, 9); ir (CCl_4) cm^{-1} 2110 (s), 1640 (s), 1290 (s); Anal. for $C_6H_{12}N_4O_3$; Found; C, 41.19 and 42.03; H, 6.63 and 7.10; N, 33.16 and 33.55; Calc. C, 38.29; H, 6.42; N, 29.77. For an absolute yield, after the reaction was complete a weighed quantity of dibenzyl ether was added. The nmr integrals for the benzyl protons of dibenzyl ether and for the protons on the carbon bearing the azido group of 1-azido-2-nitratohexane were compared for the quantitative analysis. No extraction ratio was obtained.

Molecular weight determination. The product was obtained and purified as usual. Then a known amount (ca. 120 mg) was weighed into an nmr tube. A weighed quantity of dibenzyl ether (ca. 90 mg) was added as the standard. The nmr integrals for the benzyl protons and for the azidomethylene protons were compared for the result. The following equations were used to determine the molecular weight:

$$\text{Moles Standard} \times \frac{\text{Area Product}}{\text{Area Standard}} = \text{Moles Product}$$

$$\text{Molecular Weight Product} = \frac{\text{Grams Product}}{\text{Moles Product}}$$

The result was 183 ± 1 (two runs). The molecular weight of $C_8H_{12}N_4O_3$ is 188.

Thermal decomposition. Ca. 500 mg of 1-azido-2-nitratohexane was refluxed in either benzene, toluene, or glacial acetic acid for 16 hours. The solutions discolored badly. After cooling, the solution was poured into water and extracted into pentane. The nmr was identical with that of the starting material.

With 2-methyl-1-pentene

To 0.3 g 2-methyl-1-pentene and 0.3 g sodium azide in 10 ml acetonitrile was added 5.1 g CAN in 10 ml acetonitrile. Approximately 35 ml of gas were evolved. The extraction procedure for indene was followed and the residue purified

by tlc (silica gel with pentane): nmr ($CDCl_3$) δ 3.5 (s, 2) and 1.5 (m, 10); ir (CCl_4) cm^{-1} 2110 (vvs), 1650 (vvs), and 1290 (vvs); Anal. for $C_6H_{12}N_4O_3$; Found: C, 39.42; H, 6.25; N, 32.09; Calc. C, 38.29; H, 6.42; H, 29.77. Quantitative analysis was as for 1-hexene. An extraction ratio of 1.01 was obtained as for indene.

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