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Free radical processes involving electron transfer or producing [gamma]-lactones

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Free radical processes involving electron transfer or producing γ-lactones

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Iowa State University, 1988

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Free radical processes involving electron transfer or producing γ-lactones

by

Steven J. Herron

A Dissertation Submitted to the
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Iowa State University
Ames, Iowa

1988

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GENERAL INTRODUCTION

The thesis is divided into three parts. Part I presents the calculation of the formation constants of isopropylmercurates and their subsequent reaction with bromotrichloromethane. Part II presents data on the reaction of free radicals from the thermolysis of azo compounds in the presence and absence of electron acceptors. Part III presents the reaction of free radicals with *tert*-butyl peroxy-4-pentenoate.

PART I. FREE RADICAL HALOGENATION INVOLVING MERCURATES

INTRODUCTION

Mercurate Formation (Mercury Ate Complexes)

Inorganic anionic complexes of mercury(II) have been known since 1903 when Sherril[1] concluded that HgI_4^{2-} was the predominant species in an aqueous solution of HgI_2 and KI. However, even after the first reports of anionic complexes of alkylmercurials in 1959, it was still believed by many that alkylmercury cations formed only 1:1 complexes with anionic ligands.[2-7] Since then, anionic complexes of alkylmercurials, alkylmercurates, have become accepted, even by one of the original opponents, Goggin et al.[8]

Alkylmercurates were first reported by Emeleus and Lagowski[9] in 1959. From conductometric titrations of $(CF_3)_2Hg$, CF_3HgBr, CF_3HgI and C_3F_7HgI in aqueous solutions of KCl, KBr, KI or KSCN, they observed alkylmercurate formation with one and two anions. Iodide anion complexed all of the perfluoromercurials, bromide complexed all except $(CF_3)_2Hg$ while chloride would complex only CF_3HgI and thiocyanate would not complex any of the perfluoromercurials. Emeleus and Lagowski interpreted these results to indicate that the stability of the perfluormercurates decreased in passing from iodide to chloride as the complexing agent. Emeleus and Lagowski even claim to have isolated the precipitates of the zinc(II), copper(II), cadmium(II) and nickel(II) salts of $[CF_3HgI_3]^{2-}$, $[(CF_3)_2HgI_2]^{2-}$ and $[C_3F_7HgI_3]^{2-}$. Downs[10] disputes the results with $(CF_3)_2Hg$ and claims that raman spectroscopy shows no mercurate formation of $(CF_3)_2Hg$ with chloride, bromide or iodide ions.

Within a short time after the Emeleus and Lagowski's report, Barbieri et al., Rizzardi et al. and Stocco et al. published several reports[11-15] on the formation of mercurates, $[RHgX_n]^{1-n}$ (where n=2,3), of ethyl and 2-butylmercurials where X=Cl, Br, I, and SCN. Polargraphic studies[13] of RHgX in aqueous and 50% aqueous methanol solutions indicated the presence of alkylmercurates when X of the original alkylmercurial was iodide or thiocyanate. In 50% aqueous methanol they observed that $[RHgX_2]^-$ was the favored mercurate while $[RHgX_3]^{2-}$ was favored in aqueous solution.

Later, Toropova and Saikina[16] interpreted their reduction of RHgSCN in aqueous thiocyanate as an increase in the formation constant in the sequence Me < Et < n-Pr < iso-Pr < n-Bu < iso-Bu. However, Plazzogna et al.[17] dispute Toropova and Saikina's results and conclude that mercurate formation is more complete when R = methyl or ethyl than when R = propyl or phenyl. In addition, using Ph_3CCl as the source of chloride ion in acetonitrile, Scheme I, Plazzogna and coworkers concluded, the now held belief, that no higher complex than $[RHgCl_2]^-$ is formed.

Using the variation of the Hg-H coupling constant, J (^{199}Hg-C-^1H), upon the addition of thiocyanate, Relf et al.[18]

Scheme I

$$\begin{aligned}
&RHgCl + Cl^- \rightleftharpoons [RHgCl_2]^- \\
&RHgCl + Ph_3CCl \rightleftharpoons Ph_3C^+\ [RHgCl_2]^- \\
&Ph_3C^+\ [RHgCl_2]^- \rightleftharpoons Ph_3C^+ + [RHgCl_2]^- \\
&Ph_3CCl \rightleftharpoons Ph_3C^+\ Cl^- \\
&Ph_3C^+\ Cl^- \rightleftharpoons Ph_3C^+ + Cl^-
\end{aligned}$$

attempted to describe the structure of alkylmercurates. Relf believes that the small increase in the coupling constant, 7Hz, indicates that there is little change in the hybridization of the mercury and concludes that alkylmercurates are best described as a ion-dipole complex. This conclusion is also supported by raman and IR vibrational studies performed by Goggin et al.[8]

The first attempt to accurately measure the formation constant of the equilibrium between alkylmercury halides and alkylmercurates, Equation (1), was made by Lucchini and

$$RHgX + X^- \rightleftharpoons [RHgX_2]^- \qquad (1)$$

Wells.[19] Using ^{199}Hg and ^{1}H NMR spectroscopies they observed only one methyl proton and one mercury resonance. Realizing that the observed NMR shift was the algebraic sum of the fraction ($f = [RHgX_2^-]/([RHgX_2^-] + [RHgX])$) of the resonance from each species, Equation (2), and utilizing the

$$\delta_{obsd} = f\delta_{RHgX2^-} + (1 - f)\delta_{RHgX} \qquad (2)$$

definition of the equilibrium constant, Equation (3), they

$$K = [RHgX_2^-]/[RHgX][X^-] = f/[(1-f)([X^-]-f) \qquad (3)$$

obtained a linear relationship, Equation (4), from which they

$$1/(\delta_{RHgX} - \delta_{obsd}) = [1/(\delta_{RHgX} - \delta_{RHgX2^-})](1 + 1/K[X^-] \qquad (4)$$

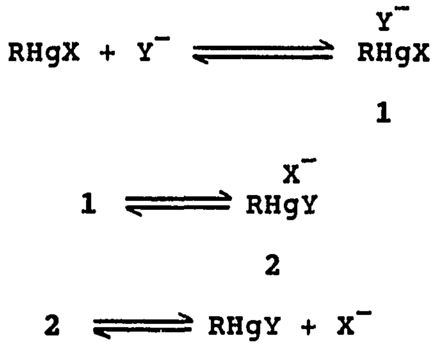
measured the formation constants for $[(CH_3)_2HCHgCl_2]^-$ and $[(CH_3)_2HCHgBr_2]^-$ in ethanol (Table 1). Using a similar procedure with ^{199}Hg NMR and *J*(Hg-H) data, Goggin et al.[8] measured the formation constants for these and other alkylmercurates in methylene chloride and acetonitrile (Table 1).

Table 1. Formation constants for some methylmercurates, $[MeHgX_2]^-$

X^-	solvent	K/dm^3mol^{-1}	reference
Cl	CH_3CH_2OH	0.313	19
Cl	CH_2Cl_2	10.2	8
Cl	CD_3CN	18.2	8
Br	CH_3CH_2OH	0.938	19
Br	CH_2Cl_2	14.8	8
I	CH_2Cl_2	12.2	8
SCN	CH_2Cl_2	31.1	8

Except for these studies, very little is known about the chemistry of alkylmercurates. Although, no study has been performed on the transition state or intermediates of the exchange of the halide ion of an alkylmercurial halide by a free halide ion, these reactions could proceed through mercurate formation, Scheme II, where the first formed ion-dipole complex, 1, equilibrates to a second ion-dipole complex, 2, in which the new anion becomes covalently bonded to the mercury. In addition to this example, Seyferth et al.[20] has observed that iodide ion will displace the trihalomethyl anion in trihalomethylphenylmercurials. The displaced trihalomethyl anion abtracts a proton from protic solvents (i.e., acetone) or undergoes elimination of chloride ion to form dichlorocarbene which reacts with added olefins in aprotic solvents (i.e., benzene). Although Seyferth et al. state that they believe this to be a direct ion exchange,[20] this reaction may actually proceed through Scheme II where X = Cl_3C and Y = I. However, Seyferth's work in this area appeared near the advent of the study of alkylmercurates and

Scheme II



$$\mathrm{RHgX} + \mathrm{Y}^- \rightleftharpoons \underset{\mathbf{1}}{\overset{\mathrm{Y}^-}{\mathrm{RHgX}}}$$

$$\mathbf{1} \rightleftharpoons \underset{\mathbf{2}}{\overset{\mathrm{X}^-}{\mathrm{RHgY}}}$$

$$\mathbf{2} \rightleftharpoons \mathrm{RHgY} + \mathrm{X}^-$$

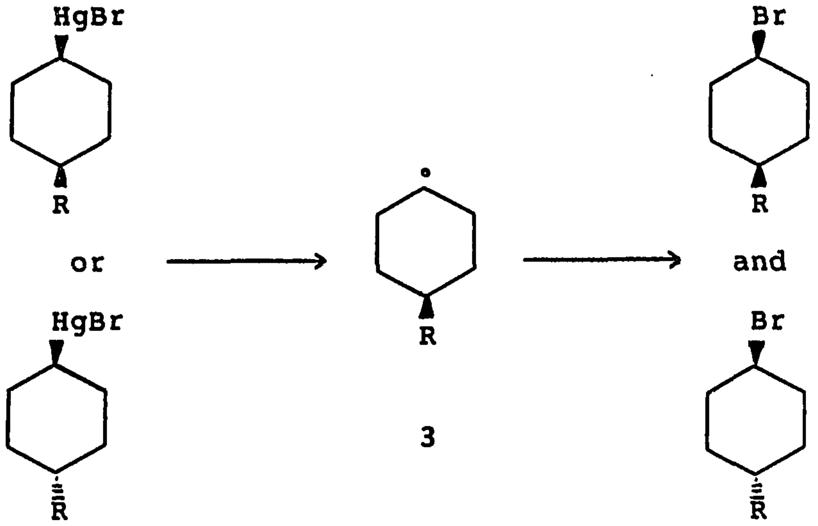
further mechanistic investigations have not been reported.

Free Radical Halogenation Involving Organomercurials

Electrophilic aliphatic substitution reactions of organomercurials have been extensively studied with a number of reviews[21-23] and a book[24] appearing on the subject. Their homolytic substitution counterparts have been studied to a lesser extent. The first recognized homolytic reaction was observed by Winstein and Traylor[25,26] as a side reaction of the electrophilic reaction between iodine and alkylmercury iodides in the work of Keller.[27] The reaction was found to be accelerated by light or the presence of free radical initiators and to be retarded by oxygen. Winstein later showed that alkylmercury bromides react with hydrogen bromide by a free radical mechanism rather than the previously presumed electrophilic pathway.

In an attempt to establish the stereochemistry of an electrophilic substitution reaction, Jensen and coworkers[28,29] observed a total loss of stereochemistry in the cleavage of _cis_- or _trans_-4-methylcyclohexylmercury bromide by bromine. These and similar results obtained in the bromine cleavage of _cis_- or _trans_-_tert_-butylcyclohexylmercury[30] indicate that the reaction, Scheme III, must go through a common intermediate, 3. However, cleavage of _cis_- or _trans_-4-methylcyclohexylmercury bromide by sulfuryl chloride gave a cis:trans ratio of 70:30 for which Jensen developed an

Scheme III R = Me, t-Bu



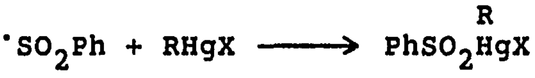
explanation based on torsional effects to account for the non-statistical ratio of products. Later, Jensen and Gale[31] reported the complete racemization of products in the bromine cleavage of optically active sec-butylmercury bromide. These results are supported by kinetic and stereochemical evidence by Reutov et al.[32] and have been interpreted mechanistically as involving a tri-coordinate mercury radical species.

More recently, other halogen compounds have been used to cleave alkylmercurials; bromotrichloromethane, carbon tetrachloride, benzenesulphonyl chloride and alkyl hypohalites. Tashtoush[33] has studied the reaction of alkylmercury halides in the presence of bromotrichloromethane and carbon tetrachloride. He concludes that while the reaction does follow a radical pathway, it does not follow a chain mechanism.

However, reaction with benzenesulphonyl chloride does appear to proceed by the free radical chain mechanism shown in Scheme IV.

Scheme IV

$$R^{\cdot} + ClSO_2Ph \longrightarrow RCl + {}^{\cdot}SO_2Ph$$



$${}^{\cdot}SO_2Ph + RHgX \longrightarrow PhSO_2\overset{R}{Hg}X$$

4

$$4 \longrightarrow R^{\cdot} + PhSO_2HgX$$

Nugent and Kochi[34] have shown that dialkylmercurials, RHgR′ undergo a reductive elimination of an olefins via a free radical chain process with carbon tetrachloride, Scheme V.

Scheme V

$${}^{\cdot}CCl_3 + HC(CH_3)_2CH_2HgR \longrightarrow {}^{\cdot}C(CH_3)_2CH_2HgR + CHCl_3$$

$${}^{\cdot}C(CH_3)_2CH_2HgR \longrightarrow (CH_3)_2C \quad CH_2$$

$$RHg^{\cdot} \longrightarrow R^{\cdot} + Hg^{O}$$

$$R^{\cdot} + CCl_4 \longrightarrow RCl + {}^{\cdot}CCl_3$$

However, Nesmeyanov et al.[35] dispute these results and claim that an alkylmercury chloride and a 1,1,1-trichloroalkane are produced by the chain mechanism depicted in Scheme VI.

Attempting to confirm these results, Jensen and Guard[36] and Tashtoush[33] were unable to reproduce these results with a variety of dialkylmercurials and propose mechanisms similar to Nugent and Kochi's.

Scheme VI

$$(C_6H_5CO_2)_2 \longrightarrow C_6H_5^{\cdot} + C_6H_5CO_2^{\cdot} + CO_2$$

$$C_6H_5^{\cdot} + CCl_4 \longrightarrow C_6H_5Cl + {}^{\cdot}CCl_3$$

$${}^{\cdot}CCl_3 + RHgR' \longrightarrow RCCl_3 + R'Hg^{\cdot}$$

$$R'Hg^{\cdot} + CCl_4 \longrightarrow R'HgCl + {}^{\cdot}CCl_3$$

Statement of Research Problem

Russell et al.[37] have made the observation that the addition of iodide ion to solutions of <u>tert</u>-butylmercury chloride and electron deficient olefins, significantly increased the efficiency of their subsequent photostimulated free radical reactions. The reason for this increased efficiency is still undecided and may be a result of anion exchange, iodide ion reduction of the intermediate radical, Scheme VII, or a result of mercurate formation.

Scheme VII (EWG = electron withdrawing group)

$$R^{\cdot} + H_2C{=}CH(EWG) \longrightarrow RH_2\dot{C}CH(EWG)$$

$$RH_2CCH(EWG) + I^- \longrightarrow RH_2CCH(EWG) + I^{\cdot}$$

$$I^{\cdot} + RHgCl \longrightarrow R\overset{I}{Hg}Cl$$

$$R\overset{I}{Hg}Cl \longrightarrow R^{\cdot} + HgICl$$

In light of the inefficiencies of the reaction of alkylmercury halides with bromotrichloromethane (non-chain mechanism), the effect of iodide ion on the reaction on isopropylmercury halides with bromotrichloromethane was the object of this study. The question we hoped to answer is whether mercurate formation participates in the reaction. At the very least, iodide ion should reduce the intermediate trichloromethyl radical and provide an efficient chain propagation step, Scheme VIII (Seyferth's data indicate that

Scheme VIII

$$(CH_3)_2HC^{\bullet} + BrCCl_3 \longrightarrow (CH_3)_2HCBr + {}^{\bullet}CCl_3$$

$${}^{\bullet}CCl_3 + I^- \longrightarrow {}^-CCl_3 + I^{\bullet}$$

$$I^{\bullet} + (CH_3)_2HCHgX \longrightarrow \quad \longrightarrow (CH_3)_2HC^{\bullet} + HgXI$$

the trichloromethyl anion does not react with iodide anion or alkylmercury halides; it does, of course, readily decompose to form dichlorocarbene and chloride ion).

RESULTS AND DISCUSSION

Isopropylmercurates

Prior to this study, no concerted effort to accurately measure the formation constants of secondary organomercurates in organic solvents had been attempted. The systems studied were isopropylmercury chloride with chloride ion and isopropylmercury iodide with iodide ion. Initial ^{1}H NMR studies on the systems reinforced previous findings[8,18,19] that iodide exchange between RHgX and $[RHgX_2]^-$ is fast on the NMR time scale and thus only one isopropyl heptet and doublet was observed. Therefore, the same technique used by Lucchini and Wells was used to obtain the formation constants of $[(CH_3)_2HCHgCl_2]^-$ and $[(CH_3)_2HCHgI_2]^-$.

The ^{1}H NMR shift of the isopropyl heptet was used because of the greater sensitivity it shows to the increasing concentration of X^-. This variation is shown in Figures 1 and 2 and the ^{1}H NMR shifts are given in Table 2. From plots of $1/(\delta_{RHgX} - \delta_{obsd})$ vs $1/[X^-]$, Figures 3 and 4, formation constants of 8.0×10^{-2} and 8.6 dm^3/mole were calculated for the mercurates $[(CH_3)_2HCHgCl_2]^-$ and $[(CH_3)_2HCHgI_2]^-$, respectively. It should be noted that because of the large formation constant for $[(CH_3)_2HCHgI_2]^-$, the assumption that the concentration of the iodide ion is large in respect to the concentration of $[(CH_3)_2HCHgI_2]^-$ does not strictly hold at low concentrations of iodide ion. This problem was corrected

Table 2. ^1H NMR shifts of the isopropyl heptet with respect to [I^-] at constant ionic strength[a] in DMSO at 25 °C

$(CH_3)_2HCHgCl$		$(CH_3)_2HCHgI$	
[Cl^-]/M	δ/ppm	[I^-]/M	δ/ppm
0	2.281	0	2.407
0.1260	2.265	0.1170	2.276
0.1890	2.257	0.1756	2.242
0.2520	2.248	0.2341	2.233
0.3150	2.243	0.2926	2.217
0.3780	2.235	0.3511	2.209
0.4410	2.256	0.4096	2.198
0.5040	2.219	0.4682	2.192
0.5670	2.209	0.5267	2.184

[a] Ionic strength for [Cl^-] study is 0.632 moles/L while the ionic strenth for the [I^-] is 0.585 moles/L.

by using the first calculated formation constant to calculate a more accurate iodide concentration and then recalculating the formation constant.

These formation constants are in line with the findings of Goggin et al.[8] They also reinforce the observation of several authors that the iodide complexes are easier to form and more stable than the chloride complexes; a fact mirrored by the halide complexes of mercury(II) complexes.

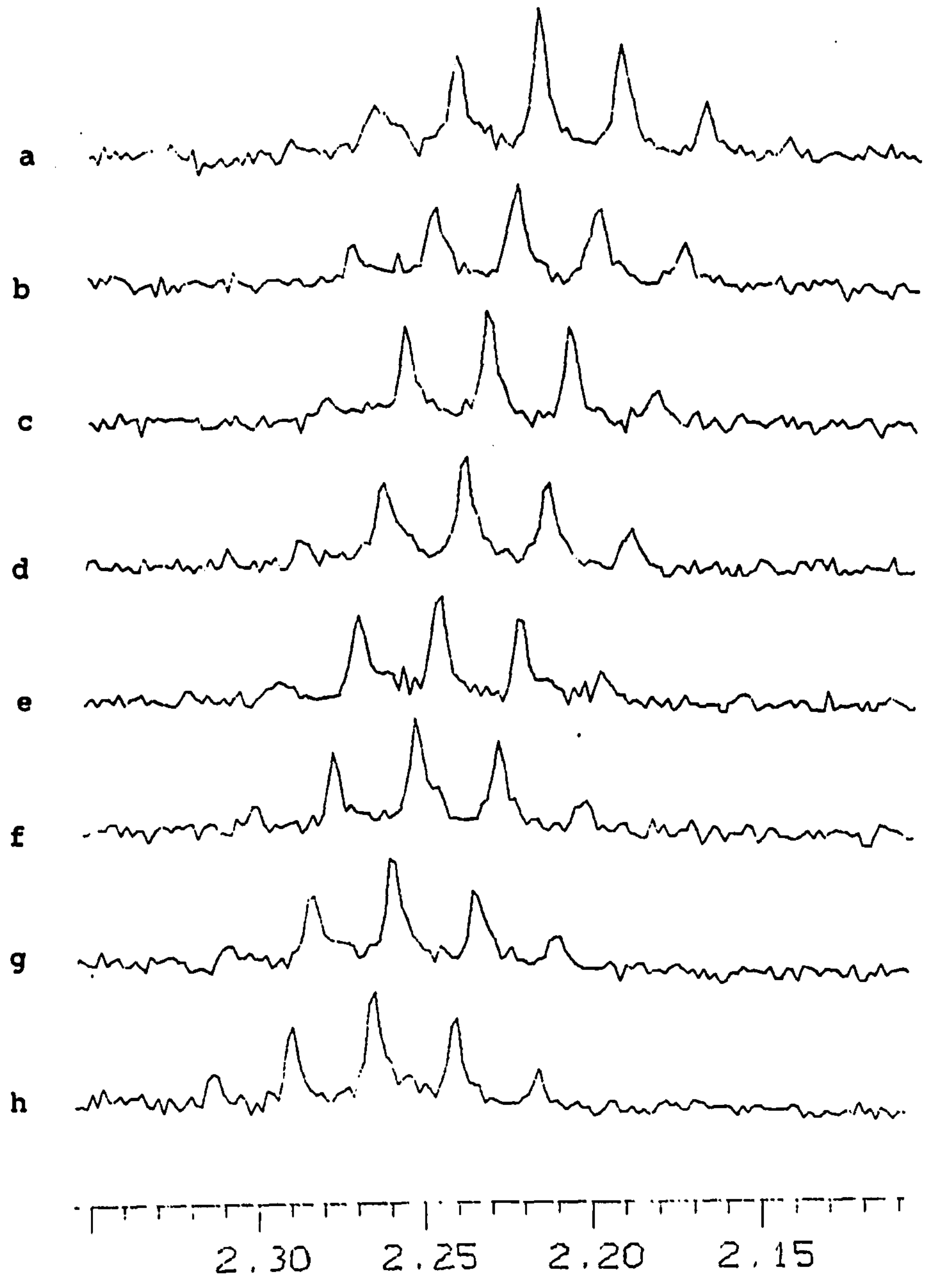


Figure 1. The variation of the ^{1}H NMR shift of the isopropyl heptet of isopropylmercury chloride with increasing [Cl$^-$]. a. [Cl$^-$] = 0.5670 M b. [Cl$^-$] = 0.5040 M c. [Cl$^-$] = 0.4410 M d. [Cl$^-$] = 0.3780 M e. [Cl$^-$] = 0.3150 M f. [Cl$^-$] = 0.2520 M g. [Cl$^-$] = 0.1890 M h. [Cl$^-$] = 0.1260 M

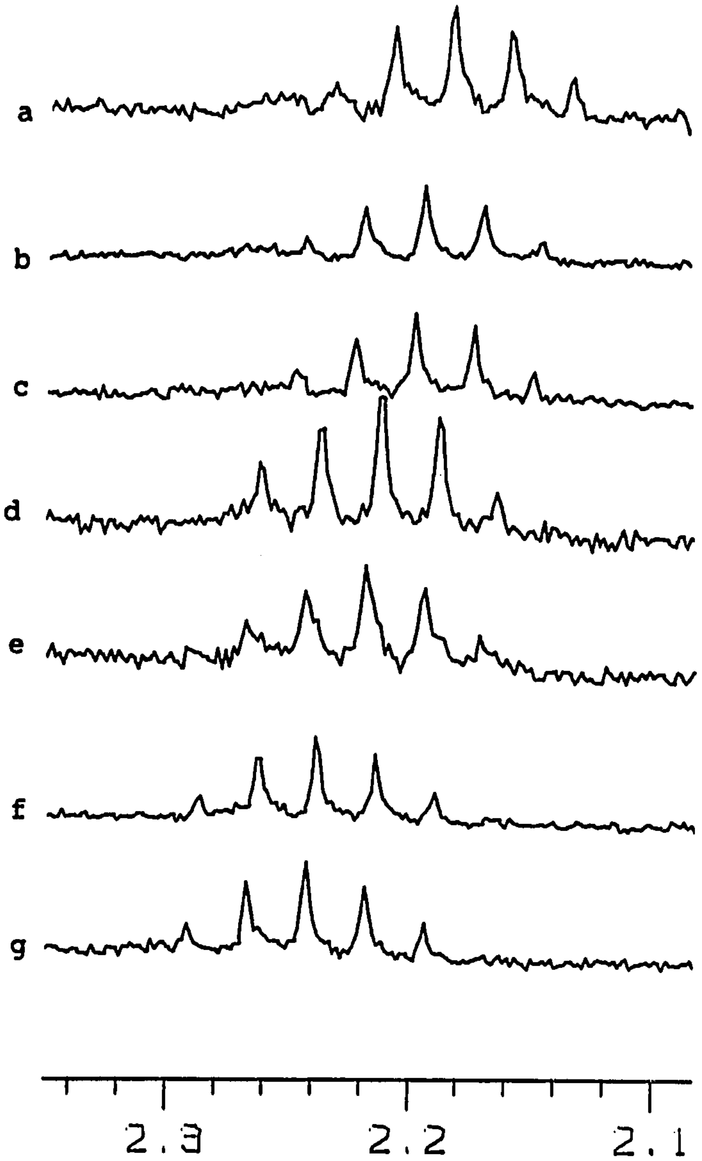


Figure 2. The variation of the ^{1}H NMR shift of the isopropyl heptet of isopropylmercury iodide with increasing $[I^-]$. a. $[I^-]$ = 0.5267 M b. $[I^-]$ = 0.4682 M c. $[I^-]$ = 0.4096 M d. $[I^-]$ = 0.3511 M e. $[I^-]$ = 0.2926 M f. $[I^-]$ = 0.2341 M g. $[I^-]$ = 0.1756 M

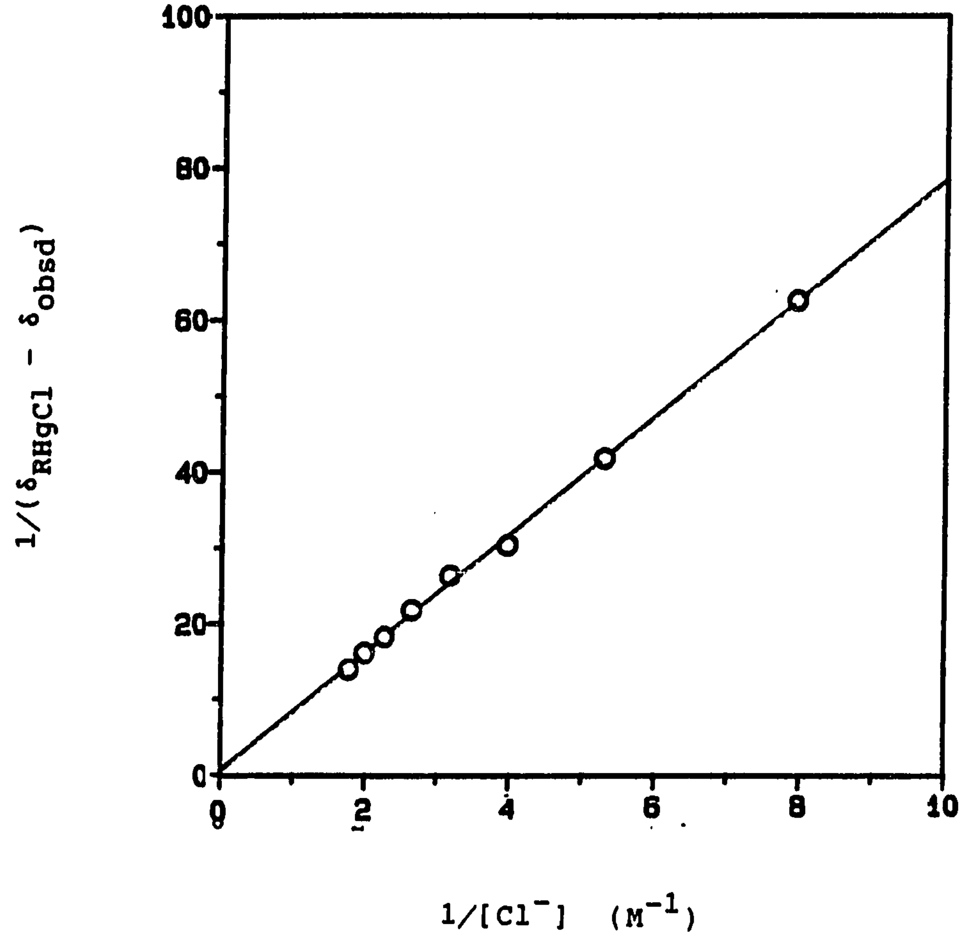


Figure 3. Plot of $1/(\delta_{RHgCl} - \delta_{obsd})$ vs $1/[Cl^-]$ for the calculation of the formation constant of dichloroisopropylmercurate.

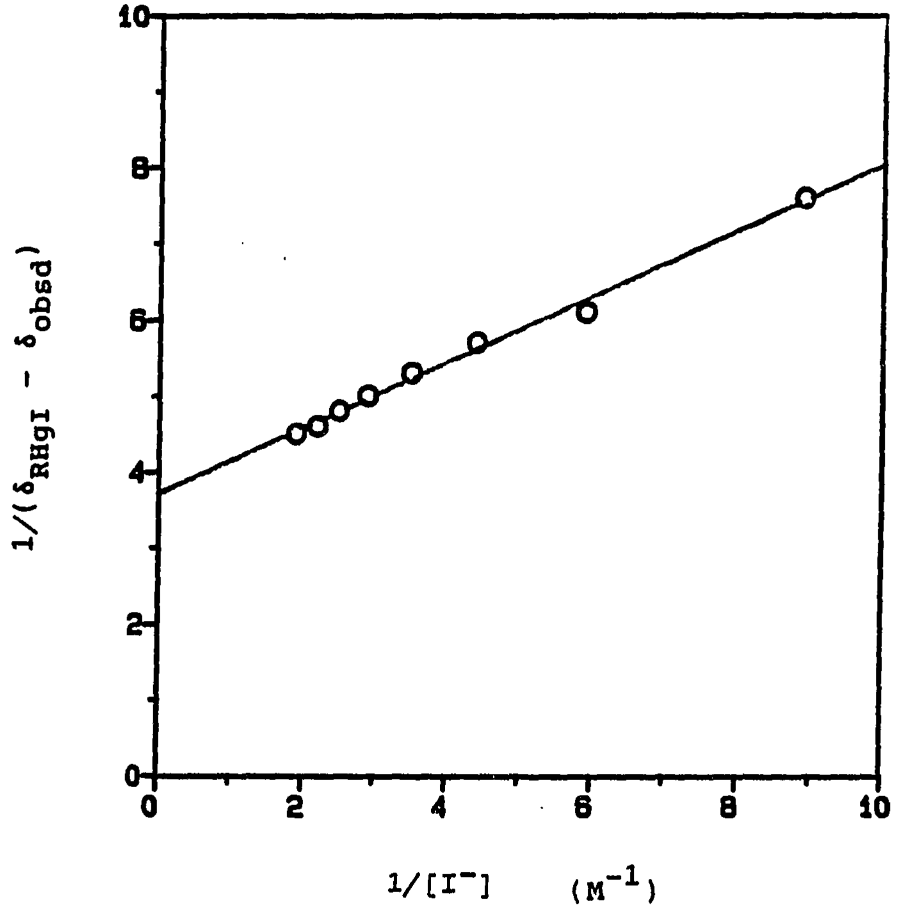


Figure 4. Plot of $1/(\delta_{RHgI} - \delta_{obsd})$ vs $1/[I^-]$ for the calculation of the formation constant of diiodoisopropylmercurate.

Reaction of Isopropylmercury Halides with Bromotrichloromethane

Isopropylmercury chloride and isopropylmercury iodide, 0.1 M, react with two equivalents of bromotrichloromethane in d_6-DMSO under sunlamp photolysis to give 80% and 82% yield of isopropyl bromide respectively. Chloroform (13% and 9% respectively) and isopropyl chloride (9% and 3% respectively) are also produced while no Hg^o is observed. The reaction requires 6 hours of sunlamp irradiation to go to completion and is inhibited by 10 mole % of di-*tert*-butyl nitroxide. In the dark, isopropylmercury chloride does not react with bromotrichloromethane while isopropylmercury iodide produces only 10% of isopropyl bromide after two days in the dark.

These results confirm previous results[33] that indicate that the reaction proceeds by a free radical mechanism in which the isopropyl radical abstracts a bromine atom from bromotrichloromethane. Chloroform results from the abstraction of a β-hydrogen from the isopropylmercury halide reminiscent of Kochi's mechanism with dialkylmercurials.[34] The slow dark reaction of isopropylmercury iodide, forming isopropyl bromide, results from the slow thermolysis of the alkylmercury iodide.

Initial rate studies indicate that isopropyl bromide is produced at a rate 0.5 times the rate of initiation as measured by di-*tert*-butyl nitroxide product inhibition. This fact was at first very disturbing, since the reaction produces an 80% yield of isopropyl bromide and it is known that alkyl radicals react very rapidly with bromotrichloromethane (methyl radicals react with bromotrichloromethane at a rate of 2.2 x 10^6 dm^3/mol-s [38]). This means that the photolytic decomposition of the alkylmercury halide is not the only source of free radicals and that the known photolysis of the bromine-carbon bond in bromotrichloromethane is involved in radical formation, Scheme IX. Measurement of the initial reaction

Scheme IX (X = Cl,I)

$$BrCCl_3 \xrightarrow{h\nu} Br^\cdot + {}^\cdot CCl_3$$

$$Br^\cdot + (CH_3)_2HCHgX \longrightarrow (CH_3)_2CH^\cdot + BrHgX$$

rate also shows that the propagation step, Equation (5), must

$$^\cdot CCl_3 + (CH_3)_2HCHgX \longrightarrow \quad \longrightarrow (CH_3)_2CH^\cdot + Cl_3CHgCl \qquad (5)$$

proceed very slowly or perhaps not at all.

Reaction of Alkylmercury Halide with Bromotrichloromethane in the Presence of Iodide Ion

Non-equilibrated solutions

Isopropylmercury chloride, 0.1 M, reacts with two equivalents of bromotrichloromethane, in the presence of sodium iodide, 0.2 M, in d_6-DMSO under sunlamp irradiation for 2.5 hours, to give isopropyl bromide (79%), chloroform (7%) and isopropyl iodide (11%). Whereas, in the absence of iodide ion the reaction with bromotrichloromethane does not proceed under room fluorescent lights, the solution containing iodide ion now reacts with bromotrichloromethane in 5.5 hours under room fluorescent lighting to give similar yields as sunlamp photolysis and will in fact react in the dark to give a 56% yield of isopropyl bromide (after 6 hours). However, in the dark only 75% of the starting mercurial was consumed after 3 days.

The reaction is inhibited by 10 mole % of di-*tert*-butyl nitroxide under all conditions and thus appears to be a free radical reaction. After a few minutes in the presence of di-*tert*-butyl nitroxide a shift in the isopropyl heptet is observed. This indicates that the equilibrium to form the isopropylmercurate requires a little time to establish its equilibrium concentration values. After long periods of time (in the dark) in the presence of di-*tert*-butyl nitroxide, traces of diisopropylmercury are observed which appears not to form a mercurate as evidenced by the ^{1}H NMR remaining at the same chemical shift values as observed in the absence of iodide ion.

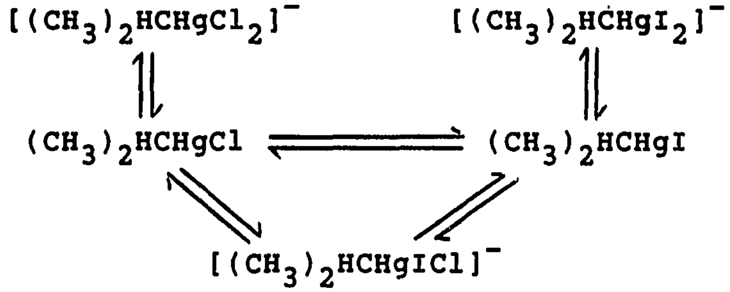
Rate studies indicate that the reaction no longer fits the first order plot as observed in the absence of iodide ion. This suggests that there must be a second radical pathway contributing to the production of isopropyl bromide. In light of mercurate formation, this pathway must be more efficient than in the absence of iodide since mercurate formation should reduce the rate of that radical pathway as a consequence of the reduction in the concentration of free isopropylmercury halide. In fact, a rate increase is observed. However, the participation of the mercurate is not assured since the new radical pathway may only involve a more efficient chain propagation step, as outlined previously in Scheme VIII, in which the trichloromethyl radical, in the presence of iodide ion and isopropylmercury halide, reacts to generate the isopropyl radical.

Equilibrated solutions

In these studies, the solution of alkylmercury halide and two-fold excess of iodide ion were equilibrated for one hour to ensure that the equilibrium concentrations of the alkylmercurial and alkylmercurates had been established.

Isopropylmercury chloride and iodide ion After equilibration of a solution initially 0.1 M in isopropylmercury chloride and 0.2 M in sodium iodide in d_6-DMSO, the ^1H NMR shift of the isopropyl heptet becomes $\delta = 2.247$ ppm compared to the ^1H NMR shift of $\delta = 2.280$ ppm for isopropylmercury chloride in d_6-DMSO. Though the shift is small, 0.033 ppm, the addition of an equal amount of an inert salt, sodium perchlorate, to a solution of isopropylmercury chloride shows that the shift is not due to a change in ionic strength. In actuality, the observed ^1H NMR shift is probably larger due to anion exchange which would produce isopropylmercury iodide (δ = 2.407 ppm). This possibility creates a complex equilibrium, Scheme X, which would lie to the right ($[(CH_3)_2HCHgI_2]^-$

Scheme X



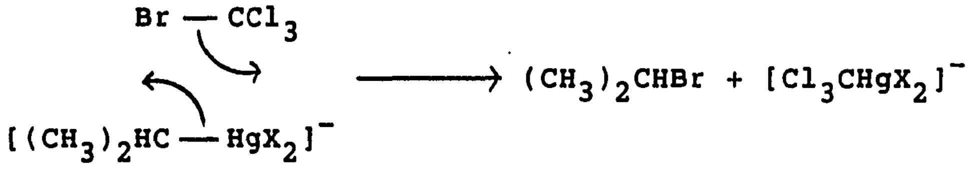
and $(CH_3)_2HCHgI$ as the predominant species) as predicted by the formation constants. However the exact composition of the mixture is not known.

Two equivalents of bromotrichloromethane react with equilibrated solutions of isopropylmercury chloride, 0.1 M, and sodium iodide, 0.2 M, under sunlamp or room fluorescent light photolysis to produce isopropyl bromide (93% and 76% respectively) and chloroform (4% and 16% respectively) while no Hg^0 is observed. The reaction requires 50 minutes under sunlamp photolysis and 1.5 hours under room fluorescent lights. The reaction also proceeds in the dark to give a 49% yield of isopropyl bromide after 6 hours but does not consume all the mercurial, even after 3 days in the dark.

The reaction is inhibited by 10 mole % of di-tert-butyl nitroxide for 12 minutes under sunlamp photolysis, 2.5 days under room fluorescent lights and over 7 days in the dark. The addition of di-tert-butyl nitroxide does not disturb mercurate formation as evidenced by the ^1H NMR of the isopropylmercurial species heptet remaining at $\delta = 2.247$ ppm. However, after a few hours in the dark in the presence of di-tert-butyl nitroxide, measurable amounts of diisopropylmercury are observed (presumably from the action of iodide ion in catalyzing the disproportionation of isopropylmercury halide).

The above facts eliminate ionic mechanisms, shown in Schemes XI and XII, which could account for the formation of

Scheme XI



Scheme XII

$$[(CH_3)_2HCHgX_2]^- \rightleftharpoons (CH_3)_2CH^- + HgX_2$$

$$(CH_3)_2CH^- + BrCCl_3 \longrightarrow (CH_3)_2CHBr + Cl_3C^-$$

isopropyl bromide. If the di-tert-butyl nitroxide had somehow inhibited mercurate formation, these ionic pathways could not be ruled out in favor of a radical mechanism. It should be also be noted, that the dark inhibition study excludes significantly increased initiation rates due to mercurate formation, Scheme XIII. This observation is

Scheme XIII

$$(CH_3)_2HCHgX + X^- \rightleftharpoons [(CH_3)_2HCHgX_2]^-$$

$$[(CH_3)_2HCHgX_2]^- \xrightarrow[\text{or } \Delta]{h\nu} (CH_3)_2CH^{\cdot} + {}^{\cdot}HgX_2^-$$

$${}^{\cdot}HgX_2^- + (CH_3)_2HCHgX \longrightarrow HgX_2 + [(CH_3)_2HCHgX]^-$$

$$[(CH_3)_2HCHgX]^- \longrightarrow (CH_3)_2CH^{\cdot} + Hg^0 + X^-$$

confirmed by di-tert-butyl nitroxide consumption studies by Russell et al.[37] that indicate that the presence of iodide in solutions of tert-butyl or n-butylmercury halides does not increase the rate of their thermal or photolytic decompositions to produce free radicals.

Kinetic data obtained to determine if the reaction proceeded by a chain mechanism, revealed that the reaction occurs in two stages. The first stage occurs in the dark in about 2 minutes (the time it takes to mix the bromotrichloromethane and obtain the ^1H NMR FID) and produces isopropyl bromide (approximately 40%) and a trace of chloroform. In the dark, this corresponds to an initial rate of isopropyl bromide formation at least 20,000 times the rate of initiation. Since the ionic mechanisms have been eliminated, this indicates that the dark reaction is a free radical chain process of considerable length.

The initial fast dark reaction is also accompanied by a shift in the isopropyl heptet of the mercurial species downfield to a value of $\delta = 2.274$ ppm. This observation indicates that the isopropylmercurate is being consumed in the initial fast reaction and provides evidence that eliminates the electron transfer process with free iodide ion indicated in Scheme VIII.

The second stage of the reaction is much slower requiring 48 and 90 minutes for completion under sunlamp and room fluorescent light photolysis, respectively. The dark reaction never does consume all the isopropylmercurial species. After completion of the initial fast dark reaction, the reaction continues to give an additional 9% of isopropyl bromide. At this point the ^{1}H NMR shift of the isopropylmercurial species heptet is $\delta = 2.278$ ppm (near that of isopropylmercury chloride). Thus it appears that most of the iodide ion is consumed by some reaction and can no longer form the isopropylmercurate which, as already shown, reacts quickly in a free radical chain mechanism. A possible source of the consumption may be the exchange of anions in the original isopropylmercury chloride to form isopropylmercury iodide which will then form isopropylmercurates with the released chloride ion and the remaining iodide ion. However, the ^{1}H NMR shift of the isopropylmercurial species heptet at the end of the dark reaction is suspiciously close to the value of isopropylmercury chloride and indicating that the anion exchange may not proceed to any appreciable extent. Additional reactions which could lead to the consumption of iodide ion will be considered in the next section.

Isopropylmercury iodide and iodide ion To reduce the isopropylmercurate compositional problem, Scheme X, isopropylmercury iodide (0.1 M) with two equivalents of soduim iodide was used to reduce the number of mercury species in the equilibrium to two, Equation 6. After equilibration, the

$$(CH_3)_2HCHgI + I^- \rightleftharpoons [(CH_3)_2HCHgI_2]^- \qquad (6)$$

^{1}HNMR shift of the isopropylmercurial species heptet becomes $\delta = 2.268$ ppm compared to a ^{1}H NMR value of $\delta = 2.407$ ppm for isopropylmercury iodide. Using the calculated equilibrium constant at the typical concentrations used in the experiments, the composition of the solution is calculated to be 55% isopropyldiiodomercurate.

Two equivalents of bromotrichloromethane react with this equilibrium solution in the same manner as they do with the mercurate solution of isopropylmercury chloride. The reaction proceeded in a two stage process to give an overall yield of 95% isopropyl bromide (4% chloroform) under sunlamp photolysis in 10 minutes, 91% isopropyl bromide (8% chloroform) in 2 hours under room fluorescent lights and 85% isopropyl bromide (14% chloroform) in the dark after 20 hours.

The yields after the initial fast dark reaction for several runs are given in Table 3 with the calculated initial mercurate percentage for the particular run. The initial fast

Table 3. Yield of isopropyl bromide after the intial dark reaction and the calculated percentage of mercurate formed in the equilibrium

initial $[(CH_3)_2HCHgI]/M$	initial $[I^-]/M$	% mercurate	% yield of isopropyl bromide[a]
0.111	0.244	60	56
0.093	0.162	50	42
0.111	0.202	55	53
0.107	0.203	55	57

[a] Observed by ^1H NMR appoximately 2 minutes after the addition of bromotrichloromethane.

dark reaction is inhibited by 10 mole % of di-*tert*-butylnitroxide for 8 minutes under sunlamp photolysis, 1.75 days under room fluorescent lights and over 7 days in the dark, ruling out the possibility of the ionic reactions shown in Schemes XI and XII. Thus, the fast dark reaction has an initial rate of isopropyl bromide formation at least 27,000 times the rate of initiation.

The initial dark reaction is again accompanied by a shift in the isopropylmercurial species heptet downfield to a value of $\delta = 2.307$ ppm. This indicates that the mercurate is being consumed faster than it can be restored to its equilibrium value and that the iodide ion is not simply effecting the chain transfer indicated in Scheme VIII.

Additional evidence that the chain reaction is being carried by the mercurate rather than the iodide ion may be obtained by observing the effect of iodide ion concentration on the fast dark reaction. If iodide ion reduces the trichloromethyl radical and propagates the chain reaction via Scheme VIII, then an increase in the iodide ion concentration should decrease the percentage of isopropyl bromide produced in the initial fast dark reaction (by decreasing the concentration of isopropylmercury iodide). However, if the mercurate propagates the chain, in any manner, the increase in iodide ion should result in an increase in the percentage of isopropyl bromide produced in the initial fast dark reaction. At a total initial mercurial species concentration ($[(CH_3)_2HCHgI] + [(CH_3)_2HCHgI_2^-]$) of 0.10 M, an increase the iodide ion concentration from 0.2 M to 0.4 M and finally to 0.6 M results in an increase in the initial fast dark reaction yield of isopropyl bromide from 59% to 74% and finally to 80% (resembling closely the % composition of the mercurate in solution). The 0.6 M solution has an initial rate of isopropyl bromide formation >38,000 times the rate of initiation and requires only 5 additional minutes under room fluorescent lights to go to completion.

Two likely free radical chain mechanisms can be drawn for the reaction. One possible mechanism is that the trichloromethyl radical displacement of the isopropyl radical, Equation

(7), is facilitated by mercurate formation. At first this

$$^{\cdot}CCl_3 + [(CH_3)_2HCHgI_2]^- \longrightarrow (CH_3)_2CH^{\cdot} + [Cl_3CHgI_2]^- \qquad (7)$$

seems like a plausible mechanism. However, on a conceptual basis, the trichloromethyl radical would have a difficult time approaching the already crowded mercury atom, especially in light of the evidence that it does not readily replace the isopropyl radical in the less crowded isopropylmercury iodide. Evidence for this mechanism seemed to be provided by the fact that in the presence of a proton source, methanol, no additional chloroform was produced. However, thermolysis of the reaction mixture produced little additional chloroform. Additionally, if 10 equivalents of cyclohexene are added, no dichlorocarbene trapped products are observed as would be expected from the decomposition of the trichloromethyl anion into dichlorocarbene and chloride ion. These results are contrary to the results that would be predicted by Seyferth's observation on the displacement of the trichloromethyl anion in trichloromethylphenylmercury.[20] This indicates that methanol may not be the best choice for a proton source in d_6-DMSO. When ammonium iodide is used as the iodide ion and proton source, chloroform is produced in almost a 1:1 ratio with isopropyl bromide as shown in Figure 5.

Another possible mechanism is that the isopropylmercurate reduces the trichloromethyl radical, Scheme XIV, producing an

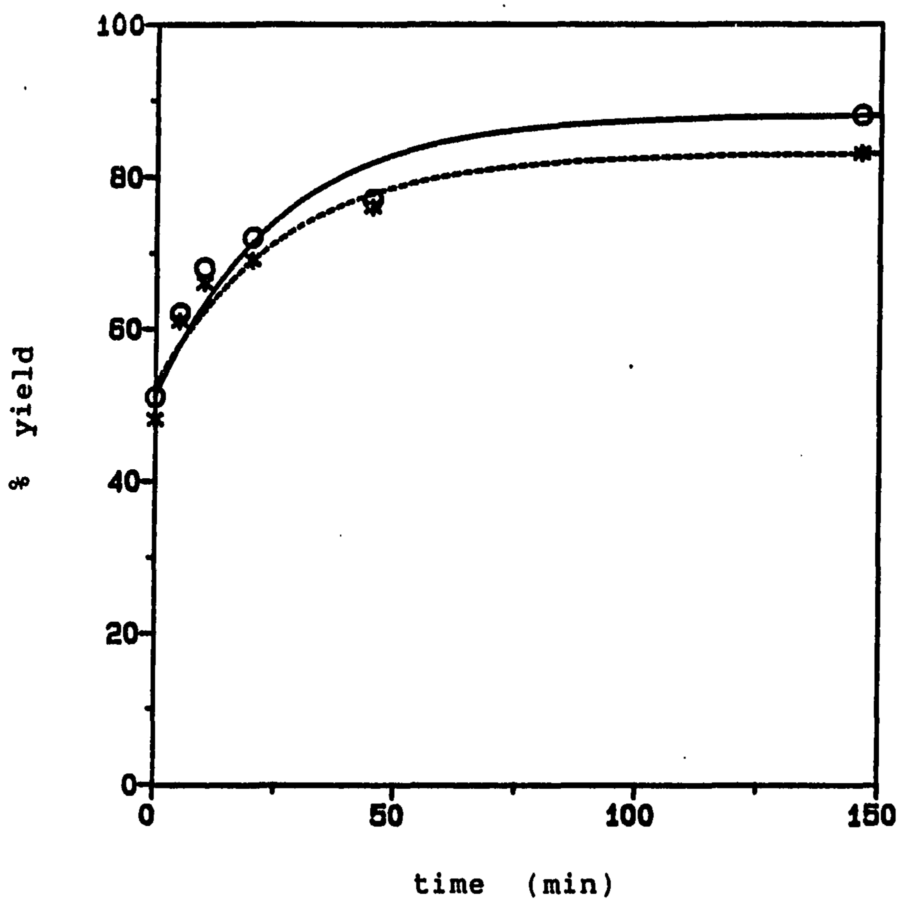


Figure 5. Reaction of equilbrated solutions of isopropyl mercury iodide (0.1 M) and ammonium iodide (0.2 M) with bromotrichloromethane to produce isopropyl bromide (circles) and chloroform (stars)

intermediate/transition state, 5, similar to the intermediate/transition state proposed for the iodine or bromine

Scheme XIV

$$[(CH_3)_2HCHgI_2]^- + {}^\cdot CCl_3 \longrightarrow \underset{5}{(CH_3)_2HCHgI_2} + Cl_3C^-$$

$$5 \longrightarrow (CH_3)_2CH^\cdot + HgI_2$$

atom cleavage of alkylmercurials. Scheme XIV is consistent with the formation of one equivalent of chloroform in the presence of ammonium ion. Apparently, the rate of proton transfer from methanol is too slow to compete with the reaction of the trichloromethyl anion with the isopropylmercury halide, Equation 8, or the elimination of chloride ion to form

$$(CH_3)_2HCHgI + {}^-CCl_3 \longrightarrow (CH_3)_2HCHgCCl_3 \qquad (8)$$

dichlorocarbene (dichlorocarbene would be readily trapped by bromotrichloromethane to yield 1-bromo-1,1,3,3,3-pentachloroethane).

The second stage of the reaction is more complicated. This stage may be a combination of iodide reduction, Scheme VIII, and mercurate reduction with a steady state concentration of the isopropylmercurate approaching the equilibrium concentration only towards the end of the reaction. If reaction (8) is occurring, then the second stage of the reaction must involve the reaction of trichloromethylisopropylmercury with bromotrichloromethane to produce isopropyl bromide at a slow rate. However, the late stages of the reaction may also result from the thermal or photolytic decomposition of isopropylmercury iodide due to the loss of free iodide ion needed for the complexation to form isopropylmercurate by the formation of the triiodo and tetraiodomercurates, Equations (9) and (10), from the mercuric iodide produced by the fast dark reaction.

$$HgI_2 + I^- \rightleftharpoons [HgI_3]^- \qquad (9)$$

$$[HgI_3]^- + I^- \rightleftharpoons [HgI_4]^{2-} \qquad (10)$$

Reaction of Dialkylmercurials with Bromotrichloromethane

Diisobutylmercury (0.050 M) reacts with 2 equivalents of bromotrichloromethane, in d_6-DMSO at 25 °C, under UV and sunlamp photolysis to give isobutyl bromide (74% and 76% respectively, yields based on moles of diisobutylmercurial), chloroform (72% and 60% respectively) and 3-bromo-1,1,1-trichloro-3-methylbutane (62% and 56% respectively). Two equivalents of bromotrichloromethane reacts with diisopropylmercury (0.050 M), in d_6-DMSO at 25 °C, under sunlamp photolysis to give isopropyl bromide (98%), chloroform (52%) and 3-bromo-1,1,1-trichlorobutane (48%). The reactions require 2.5 hours for completion under sunlamp photolysis and

1 hour under UV photolysis, produce Hg^{0}, are inhibited by 10 mole % of di-tert-butyl nitroxide and does not occur in the dark.

These results support Nugent and Kochi's mechanism,[34] Scheme V, in which the trichloromethyl radical propagates the chain by abstracting a β-hydrogen atom to produce a 1:1:1 ratio of bromoalkane, chloroform and alkene (trapped as the 3-bromo-1,1,1-trichloroalkane adduct, see Kharasch et al.[39]). However, there appears to be some dependency on the nature of the β-hydrogen atom to be abstracted. In the case of diisobutylmercury, the ratio of chloroform:isobutyl bromide is 1:1 indicating that the attack of the trichloromethyl radical upon diisobutylmercury yields one molecule of chloroform and a radical which decomposes by a two bond cleavage to form isobutene, Hg^{0} and an isobutyl radical which is coverted to isobutyl bromide and trichloromethyl radical by reaction with bromotrichloromethane. In the case of diisopropylmercury, the ratio of chloroform:isopropyl bromide is 1:2. Thus, there must be another route to the formation of the isopropyl radical besides the β-hydrogen atom abstraction reaction. A possibility is the displacement of the isopropyl radical from diisopropylmercury by the trichloromethyl radical.

Although Kochi did not determine the initial kinetic chain length, he states that the reaction of isobutylneopentylmercury with carbon tetrachloride, initiated with benzoyl peroxide at 95 °C, is an efficient free radical chain mechanism. However, di-tert-butyl nitroxide studies show that the alkyl bromide is produced at a rate 4 times the rate of initiation and might indicate that the chain may not be as efficient as Kochi suggests. However, since bromotrichloromethane has a faster initiation rate (through photolytic homolysis) than benzoyl peroxide, the results may simply reflect a difference in the rates of initiation vs the rates of β-hydrogen atom abstraction for the two different reactions.

Reaction of Dialkylmercurials with Bromotrichloromethane in the Presence of Iodide Ion

Diisobutylmercury and diisopropylmercury, 0.05 M, react with 2 equivalents of bromotrichloromethane in the presence of 4 equivalents of sodium iodide to give isobutyl or isopropyl bromide (126% and 140% respectively, yields based on the number of moles of mercurial), chloroform (40% and 30% respectively) and alkene (26% and 18% respectively, trapped as the 3-bromo-1,1,1-trichlorobutane adduct). The reactions require 50 minutes for completion, produce no Hg^0, are inhibited by 10 mole % of di-tert-butyl nitroxide and do not proceed in the dark. In addition, there is no effect of iodide ion on the ^{1}H NMR shift of the dialkylmercurial protons upon equilibration with iodide ion before reaction with bromotrichloromethane.

The reduced yields of chloroform and alkene (observed as the 3-bromo-1,1,1-trichlorobutane adduct) as well as the absence of Hg^{0}, indicate that the β-hydrogen atom abstraction observed in the absence of iodide ion is no longer the main reaction pathway. As there is no initial mercurate formation, the trichloromethyl radical must be reduced by the iodide ion. However since this reaction should produce alkylmercurial iodides, subsequent reaction of the alkylmercury iodide/alkylmercurate (never observed by ^{1}H NMR, thus indicating that its steady state concentration is low) must be fast, Scheme XV.

Scheme XV

$$R^{\cdot} + BrCCl_3 \longrightarrow RBr + {}^{\cdot}CCl_3$$

$${}^{\cdot}CCl_3 + I^- \longrightarrow {}^{-}CCl_3 + I^{\cdot}$$

$$I^{\cdot} + R_2Hg \longrightarrow R^{\cdot} + RHgI$$

$$RHgI + I^- \rightleftharpoons [RHgI_2]^-$$

$$[RHgI_2]^- + {}^{\cdot}CCl_3 \longrightarrow R^{\cdot} + HgI_2 + {}^{-}CCl_3$$

It should be noted that this mechanism requires that at least one half of the reduction of the trichloromethyl radical occurs by iodide ion reduction. Since a significant amount of chloroform is produced (in relation to the alkylmercury halide with iodide ion experiments) and the alkylmercurate is never observed, it follows that the iodide reduction of the trichloromethyl radical must be slow in comparison to the mercurate reduction. Also, as with the alkylmercury halide studies in the presence of iodide ion, the reaction of the trichloromethyl anion with the alkylmercury halide produced by the reaction of the iodine atom with the dialkylmercurial, can not be ruled out as an additional step in the reaction (Equation (8).

CONCLUSION

Isopropylmercury halides react with bromotrichloromethane to give good yields of isopropyl bromide and small amounts of chloroform. Mechanistically, the reaction has been shown to proceed through free radicals but not in a chain fashion. This mechanism is supported by the observation that the reaction fails to proceed in the dark and is inhibited by di-*tert*-butyl nitroxide under photolysis conditions.

Isopropylmercury halides produce isopropylmercurates in the presence of halide ions and the formation constants of isopropyldichloromercurate and isopropyldiiodomercurate in d_6-DMSO at 25 ^oC have been calculated to be 8.0×10^{-2} and 8.6 dm^3/mole, respectively. These isopropylmercurate solutions react with bromotrichloromethane to produce excellent yields of isopropyl bromide and small amounts of chloroform. Mechanistically, the reaction has been shown to proceed in two stages. The first stage is a fast free radical chain reaction in which the trichloromethyl radical is reduced by the isopropylmercurate to produce a tricovalent mercury species,$(CH_3)_2HCHgI_2{}^\cdot$, which decomposes to give isopropyl radicals and mercuric iodide. This mechanism is supported by the observations that the reaction occurs in the dark in 2 minutes but is inhibited by 10 mole % of di-*tert*-butyl nitroxide for over 7 days in the dark. Proof of the isopropylmercurate reduction of the trichloromethyl radical is that the ^1H NMR shifts observed during the initial fast reaction show that the mercurate is consumed at a rate faster than it is regenerated by the equilibrium between isopropylmercury iodide and iodide ion. Furthermore, an increase in iodide concentration, and thus of the mercurate concentration, increases the extent of the initial fast reaction. Initial kinetic chain lengths have been calculated to be at least 38,000 but are actually larger since the equipment available (300 MHz ^1H NMR) did not allow the isopropyl bromide concentration to be measured for a reaction period less than 2 minutes.

Dialkylmercurials (R_2Hg, R = isopropyl and isobutyl) react with bromotrichloromethane to give good yields of alkyl bromides, chloroform and alkenes (trapped as 3-bromo-1,1,1-trichloro adducts). The mechanism appears to proceed by the β-hydrogen atom abstraction process previously described by Kochi. Evidence indicates that the reaction proceeds in a free radical chain mechanism as evidenced by di-*tert*-butyl nitroxide product inhibition.

Dialkylmercurials (R_2Hg, R = isopropyl and isobutyl) do not form mercurates with iodide ion in DMSO solution. However, in the presence of iodide ion the reaction of dialkylmercurials with bromotrichloromethane undergoes a change in mechanism to give excellent yields of alkyl bromides and only small amounts of chloroform and alkenes (trapped as

3-bromo-1,1,1-trichloro adducts). The reaction no longer proceeds, to a significant extent, by β-hydrogen atom abstraction and now appears to proceed by iodide reduction of the trichloromethyl radical. The iodine atom produced reacts to form an alkyl radical and alkylmercury iodide which can now form the mercurate and reduce the trichloromethyl radical or react with the trichloromethyl anion to yield the mixed organomercurial, trichloromethylisopropylmercury.

EXPERIMENTAL

General Considerations

Instrumentation

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra (300 MHz) were recorded on a Nicolet Magnetics Corp. NMC-1280 spectrometer in d_6-DMSO with the residual nondeuterated solvent peak as the internal chemical shift standard. Product yields were determined by ^{1}H NMR integration comparison with a known amount of 1,3,5-tribromobenzene.

Equipment

Irradiations were carried out 6 inches in front of a 275 W Sylvania sunlamp. Room light irradiations were performed under 40 W Sylvania cool white fluorescent lights.

All glassware and syringes were dried at 150 °C for at least 24 hours and then allowed to cool in a desiccator. Disposable syringe needles were used for all solution transfers of less than or equal to 1 mL.

Materials

Purified Davidson 4A molecular sieves purchased from Fisher Scientific were activated by drying, in vacuo, at 230 °C for 16 hours.

Deuterated dimethyl sulphoxide (d_6-DMSO) purchased from Cambridge Isotope Laboratories was dried with activated 4A molecular sieves and purged with argon to remove traces of oxygen.

Methanol purchased from Fisher Scientific was refluxed over calcium hydride for 12 hours, distilled and stored over activated 4A molecular sieves.

Unpurified Authentic samples of isopropyl bromide, isopropyl iodide, isopropyl chloride, n-butyl bromide, n-butyl chloride, *tert*-butyl bromide and *tert*-butyl chloride were purchased from Aldrich Chemical Company. Sodium iodide, sodium perchlorate and ammonium chloride were purchased from Fisher Scientific. Ammonium perchlorate and ammonium iodide were purchased from J. T. Baker Chemical Company and 1,3,5-tribromobenzene was purchased from Eastman Kodak Company.

Preparation of the Organomercury Compounds

Alkylmercury chlorides

The alkylmercury chlorides were prepared as described by Markarova and Nesmeyanov[40]. Thus by treatment of the appropriate Grignard reagent with a slight excess of mercuric chloride in THF, the following alkylmercury chlorides were prepared and purified by recrystallization from the mixed solvent system of methylene chloride and hexane and have m.p. in good agreement with literature values: *tert*-butylmercury chloride, m.p. 121-122 °C isopropylmercury chloride; m.p. 94-95 °C and n-butylmercury chloride; m.p. 126-127 oC.

Isopropylmercury Iodide

Isopropyllmercury iodide was prepared by anion exchange.[41] Thus the appropriate alkylmercury chloride was treated with a ten-fold excess of sodium iodide in methylene chloride for 24 hours. The reaction mixture was filtered through sintered glass and the solvent removed under reduced pressure. The isopropylmercury iodide was purified by recrystallization from the mixed solvent system of methylene chloride and hexanes to give light yellow crystals with a m.p. in good agreement with literature value: m.p. 122-123 °C.

Symmetrical dialkylmercurials

All dialkylmercurials employed were prepared by W. Jang or N. Preecha. The dialkylmercurials were checked for purity by ^{1}H NMR and purified if necessary by vacuum distillation.

Equilibrium Studies

Procedure for isopropylmercury chloride

A 5 mL volumetric flask was charged with isopropylmercury chloride (0.1375 g, 0.4926 mmole) and fitted with a septum. A second 5 mL volumetric flask was charged with ammonium perchlorate (0.3715 g, 3.162 mmole) and fitted with a septum, while a third 5 mL volumetric flask was charged with ammonium chloride (0.1658 g, 3.150 mmole) and fitted with a septum. Each volumetric flask was purged with argon and 4 mL of d_6-DMSO was syringed into each flask. The flasks were swirled to dissolve their respective contents and diluted with d_6-DMSO to bring the total volume to 5 mL.

Nine NMR tubes were fitted with septa, flushed with argon and charged with 0.1 mL of the 9.852×10^{-2} M isopropylmercury chloride solution. Each NMR tube was charged with varying amounts of the ammonium perchlorate and ammonium chloride solutions to keep a constant ionic strength of 0.632 moles/L and a total volume of 1 mL. The samples were allowed to equilibrate for one hour and then were analyzed by ^1H NMR.

Procedure for Isopropylmercury Iodide

A 5 mL volumetric flask was charged with isopropylmercury iodide (0.1882 g, 0.5079 mmole) and fitted with a septum. A second 5 mL volumetric flask was charged with sodium perchlorate (0.3580 g, 2.924 mmole) and fitted with a septum, while a third 5 mL volumetric flask was charged with sodium iodide (0.4386 g, 2.926 mmole) and fitted with a septum. Each volumetric flask was purged with argon and 4 mL of d_6-DMSO was syringed into each flask. The flasks were swirled to dissolve their respective contents and diluted with d_6-DMSO to bring the total volume to 5 mL.

Nine NMR tubes were fitted with septa, flushed with argon and charged with 0.1 mL of the 0.1016 M isopropylmercury iodide solution. Each NMR tube was the charged with varying amounts of the sodium perchlorate and sodium iodide solutions to keep a constant ionic strength of 0.585 moles/L and a total volume of 1 mL. The samples were allowed to equilibrate for one hour and then were analyzed by ^1H NMR.

Reaction of Alkylmercurials with Bromotrichloromethane

Typical Preparation of a di-tert-butyl nitroxide Solution

A 5 mL volumetric flask was charged with di-*tert*-butyl nitroxide (0.0747 g, 0.518 mmole) and fitted with a septum. The volumetric flask was purged with argon, and 4 mL of d_6-DMSO was syringed into the flask. The flask was swirled to mix its contents and diluted with d_6-DMSO to bring the total volume to 5 mL.

Typical procedure for the photolysis of alkylmercury halides with bromotrichloromethane

This procedure was followed for isopropylmercury chloride, isopropylmercury iodide, *ter*t-butylmercury iodide and n-butylmercury iodide under photolysis conditions. A NMR tube was charged with an alkylmercury halide (0.100 mmole) and the quantification standard (0.0100 g, 0.0318 mmole), 1,3,5-tribromobenzene, and fitted with a septum. The NMR tube was purged with argon and 1 mL of d_6-DMSO was syringed into the NMR tube. After the alkylmercury halide and 1,3,5-tribromobenzene had disolved, bromotrichloromethane (0.0200 mL, 0.203 mmole) was syringed into the NMR tube. The NMR tube was inverted a few times to mix its contents and then analyzed by ^1H NMR. The NMR tube was the photolyzed 6 inches in front of a 275 W sunlamp or under 40 W room fluorescent lights and analyzed by ^{1}H NMR at predetermined times.

Typical procedure for the photolysis of alkylmercury halides with bromotrichloromethane in the presence of di-tert-butyl nitroxide

This procedure was followed for isopropylmercury chloride and isopropylmercury iodide under photolysis conditions. A NMR tube was charged with an alkylmercury halide (0.100 mmole) and the quantification standard (0.0100 g, 0.0318 mmole), 1,3,5-tribromobenzene, and fitted with a septum. After the NMR tube was purged with argon, 0.9 mL of d_6-DMSO and 0.1 mL of the 0.104 M (0.0204 mmole) di-*tert*-butyl nitroxide solution was syringed into the NMR tube. After the alkylmercury halide and 1,3,5-tribromobenzene had dissolved, bromotrichloromethane (0.0200 mL, 0.203 mmole) was syringed into the NMR tube. The NMR tube was inverted a few times to mix its contents and then analyzed by ^{1}H NMR. The NMR tube was the photolyzed 6 inches in front of a 275 W sunlamp or under 40 W room fluorescent lights and analyzed by ^{1}H NMR at predetermined times.

Typical procedure for the dark reaction of the alkylmercury halides with bromotrichloromethane

This procedure was followed for isopropylmercury chloride and isopropylmercury iodide under photolysis conditions. A NMR tube was charged with an alkylmercury halide (0.100 mmole) and the quantification standard (0.0100 g, 0.0318 mmole), 1,3,5-tribromobenzene, and fitted with a septum. The NMR tube was purged with argon and 1 mL of d_6-DMSO was syringed into the NMR tube. After the alkylmercury halide and 1,3,5-tribromobenzene had dissolved, the NMR tube was tightly wrapped in aluminum foil and bromotrichloromethane (0.0200 mL, 0.203 mmole) was syringed into the NMR tube. The NMR tube was inverted a few times to mix its contents and analyzed immediately and at other predetermined times by ^{1}H NMR. All transfers to the NMR tube to the spectrophotometer were performed in a darkened room.

Photolysis of diisobutylmercury with bromotrichloromethane

A 5 mL volumetric flask was charged with diisobutylmercury (0.1964 g, 0.6238 mmole) and the quantification standard (0.0814 g, 0.259 mmole), 1,3,5-tribromobenzene and fitted with a septum. The volumetric flask was purged with argon, and 4 mL of d_6-DMSO was syringed into the flask. The flask was swirled to mix its contents and diluted with d_6-DMSO to bring the total volume to 5 mL.

Into an argon purged NMR tube, fitted with a septum, was syringed 0.4 mL of the 0.1248 M diisobutylmercury solution, 0.6 mL d_6-DMSO and bromotrichloromethane (0.0200 mL, 0.203 mmole). The NMR tube was inverted a few times to mix its contents and analyzed by ^{1}H NMR. The NMR tube was then photolyzed 6 inches in front of a 275 W sunlamp and analyzed by ^1H NMR at predetermined times.

Photolysis of diisobutylmercury with bromotrichloromethane in the presence of di-tert-butyl nitroxide

Into an argon purged NMR tube, fitted with a septum, was syringed 0.4 mL of the the previously described 0.1248 M diisobutylmercury solution, 0.5 mL d_6-DMSO, 0.1 mL of a 0.104 M di-tert-butyl nitroxide solution and bromotrichloromethane (0.0200 mL, 0.203 mmole). The NMR tube was inverted a few times to mix its contents and analyzed by ^1H NMR. The NMR tube was then photolyzed 6 inches in front of a 275 W sunlamp and analyzed by ^1H NMR at predetermined times.

Photolysis of diisopropylmercury with bromotrichloromethane

A 5 mL volumetric flask was charged with diisopropylmercury (0.1274 g, 0.4443 mmole) and the quantification standard (0.0646 g, 0.205 mmole), 1,3,5-tribromobenzene and fitted with a septum. The volumetric flask was purged with argon, and 4 mL of d_6-DMSO was syringed into the flask. The flask was swirled to mix its contents and diluted with d_6-DMSO to bring the total volume to 5 mL.

Into an argon purged NMR tube, fitted with a septum, was syringed 0.6 mL of the 8.885×10^{-2} M diisopropylmercury solution, 0.4 mL d_6-DMSO and bromotrichloromethane (0.0200 mL, 0.203 mmole). The NMR tube was inverted a few times to mix its contents and analyzed by ^1H NMR. The NMR tube was then photolyzed 6 inches in front of a 275 W sunlamp and analyzed by ^1H NMR at predetermined times.

Photolysis of diisopropylmercury with bromotrichloromethane in the presence of di-tert-butyl nitroxide

Into an argon purged NMR tube, fitted with a septum, was syringed 0.6 mL of the the previously described 8.885×10^{-2} M diisopropylmercury solution, 0.3 mL d_6-DMSO, 0.1 mL of a 0.104 M di-*tert*-butyl nitroxide solution and bromotrichloromethane (0.0200 mL, 0.203 mmole). The NMR tube was inverted a few times to mix its contents and analyzed by ^1H NMR. The NMR tube was then photolyzed 6 inches in front of a 275 W sunlamp and analyzed by ^1H NMR at predetermined times.

Reaction of Alkylmercurates with Bromotrichloromethane

Typical Preparation of a Sodium Iodide Solution

A 5 mL volumetric flask was charged with sodium iodide (0.5000 g, 3.336 mmole) and the quantification standard (0.0500 g, 0.159 mmole), 1,3,5-tribromobenzene and fitted with a septum. The volumetric flask was purged with argon, and 4 mL of d_6-DMSO was syringed into the flask. The flask was swirled to dissolve its contents and diluted with d_6-DMSO to bring the total volume to 5 mL.

Typical procedure for the photolysis of non-equilibrated solutions of alkylmercurates with bromotrichloromethane

This procedure was followed for non-equilibrated solutions of sodium iodide with isopropylmercury chloride. A NMR tube was charged with isopropylmercury chloride (0.100 mmole) and fitted with a septum. The NMR tube was purged with argon and 0.7 mL of d_6-DMSO was syringed into it. The NMR tube was inverted a few times to dissolve the isopropylmercury chloride and wrapped tightly with aluminum foil. Into the darkened NMR tube was syringed, 0.3 mL of a 0.6720 M sodium iodide solution and bromotrichloromethane (0.0200 mL, 0.203 mmole). The NMR tube was inverted a few times to mix its contents and immediately analyzed by ^1H NMR (tranfer to the NMR spectrometer took place in a darkened room). The NMR tube was the photolyzed 6 inches in front of a 275 W sunlamp or under 40 W room fluorescent lights and analyzed by ^1H NMR at predetermined times.

Typical procedure for the photolysis of equilibrated solutions of alkylmercurates with bromotrichloromethane

This procedure was followed for equilibrated solutions of sodium iodide with isopropylmercury chloride or isopropylmercury iodide. A NMR tube was charged with isopropylmercury halide (0.100 mmole) and fitted with a septum. The NMR tube was purged with argon and 0.7 mL of d_6-DMSO was syringed into it. The NMR tube was inverted a few times to dissolve the isopropylmercury halide and wrapped tightly with aluminum foil. Into the darkened NMR tube was syringed, 0.3 mL of a 0.6720 M sodium iodide solution. The darkened NMR tube was inverted a few times to mix its contents which were allowed to equilibrate for one hour. After equilibration, bromotrichloromethane (0.0200 mL, 0.203 mmole) was added into the darkened NMR tube which was inverted a few times to mix its contents and immediately analyzed by ^1H NMR (tranfer to the NMR spectrometer took place in a darkened room). The NMR tube was the photolyzed 6 inches in front of a 275 W sunlamp or under 40 W room fluorescent lights and analyzed by ^1H NMR at predetermined times.

Typical procedure for the dark reaction of equilibrated solutions alkylmercurates with bromotrichloromethane

This procedure was followed for equilibrated solutions of sodium iodide with isopropylmercury chloride or isopropylmercury iodide. A NMR tube was charged with isopropylmercury halide (0.100 mmole) and fitted with a septum. The NMR tube was purged with argon and 0.7 mL of d_6-DMSO was syringed into it. The NMR tube was inverted a few times to dissolve the isopropylmercury halide and wrapped tightly with aluminum foil. Into the darkened NMR tube was syringed, 0.3 mL of a 0.6720 M sodium iodide solution. The darkened NMR tube was inverted a few times to mix its contents which were allowed to equilibrate for one hour. After equilibration, bromotrichloromethane (0.0200 mL, 0.203 mmole). The darkened NMR tube was inverted a few times to mix its contents and analyzed immediately and at other predetermined times by ^1H NMR. All tranfers to the NMR spectrometer were performed in a darkened room.

Typical procedure for the photolysis of equilibrated solutions alkylmercurates with bromotrichloromethane in the presence of di-tert-butyl nitroxide

This procedure was followed for equilibrated solutions of sodium iodide with isopropylmercury chloride or isopropylmercury iodide. A NMR tube was charged with isopropylmercury halide (0.100 mmole) and fitted with a septum. The NMR tube was purged with argon and 0.6 mL of d_6-DMSO was syringed into it. The NMR tube was inverted a few times to dissolve the isopropylmercury halide and wrapped tightly with aluminum foil. Into the darkened NMR tube was syringed, 0.3 mL of a 0.6720 M sodium iodide solution and 0.1 mL of a 0.104 M di-*tert*-butyl nitroxide solution. The darkened NMR tube was inverted a few times to mix its contents which were allowed to equilibrate for one hour. After equilibration, bromotrichloromethane (0.0200 mL, 0.203 mmole) was added to the darkened NMR tube which was inverted a few times to mix its contents and immediately analyzed by ^1H NMR (tranfer to the NMR spectrometer took place in a darkened room). The NMR tube was the photolyzed 6 inches in front of a 275 W sunlamp or under 40 W room fluorescent lights and analyzed by ^{1}H NMR periodically.

Typical procedure for the dark reaction of equilibrated solutions alkylmercurates with bromotrichloromethane in the presence of di-tert-butyl nitroxide

This procedure was followed for equilibrated solutions of sodium iodide with isopropylmercury chloride or isopropylmercury iodide. A NMR tube was charged with isopropylmercury halide (0.100 mmole) and fitted with a septum. The NMR tube was purged with argon and 0.6 mL of d_6-DMSO was syringed into it. The NMR tube was inverted a few times to dissolve the isopropylmercury halide and wrapped tightly with aluminum foil. Into the darkened NMR tube was syringed, 0.3 mL of a 0.6720 M sodium iodide solution and 0.1 mL of a 0.104 M di-*tert*-butyl nitroxide solution. The darkened NMR tube was inverted a few times to mix its contents which were allowed to equilibrate for one hour. After equilibration, bromotrichloromethane (0.0200 mL, 0.203 mmole) was added to the darkened NMR tube which was then inverted a few times to mix its contents and analyzed immediately and periodically by ^{1}H NMR. All tranfers to the NMR spectrometer were performed in a darkened room.

Photolysis of equilibrated solutions of alkylmercurates with bromotrichloromethane in the presence of methanol

A NMR tube was charged with isopropylmercury iodide (0.0386, 0.104 mmole) and fitted with a septum. The NMR tube was purged with argon and 0.7 mL of d_6-DMSO was syringed into it. The NMR tube was inverted a few times to dissolve the isopropylmercury halide and wrapped tightly with aluminum foil. Into the darkened NMR tube was syringed, 0.3 mL of a 0.6720 M sodium iodide solution. The darkened NMR tube was inverted a few times to mix its contents which were allowed to equilibrate for one hour. After equilibration, methanol (0.017 mL, 0.42 mmole) bromotrichloromethane (0.0200 mL, 0.203 mmole) was syringed into the NMR tube. The darkened NMR tube was inverted a few times to mix its contents and analyzed immediately by ^{1}H NMR (tranfers to the NMR spectrometer were performed in a darkened room). The NMR tube was then photolyzed under room fluorescent lights for 5 hours, analyzed by ^{1}H NMR, thermolized in a water bath at 80 °C for 5 hours and once again analyzed by ^{1}H NMR.

Photolysis of equilibrated solutions of ammonium iodide-alkylmercury iodide solutions with bromotrichloromethane

A 5 mL volumetric flask was charged with diisopropylmercury (0.2570 g, 1.773 mmole) and the quantification standard (0.0411 g, 0.131 mmole), 1,3,5-tribromobenzene and fitted with a septum. The volumetric flask was purged with argon, and 4 mL of d_6-DMSO was syringed into the flask. The flask was swirled to mix its contents and diluted with d_6-DMSO to bring the total volume to 5 mL.

A NMR tube was charged with isopropylmercury iodide (0.100 mmole) and fitted with a septum. The NMR tube was purged with argon and 0.3 mL of d_6-DMSO was syringed into it. The NMR tube was inverted a few times to dissolve the isopropylmercury halide and wrapped tightly with aluminum foil. Into the darkened NMR tube was syringed 0.6 mL of a 0.3546 M ammonium iodide solution. The darkened NMR tube was inverted a few times to mix its contents which were allowed to equilibrate for one hour. After equilibration, bromotrichloromethane (0.0200 mL, 0.203 mmole). The darkened NMR tube was inverted a few times to mix its contents and immediately analyzed by ^{1}H NMR (tranfer to the NMR spectrometer took place in a darkened room). The NMR tube was the photolyzed under 40 W room fluorescent lights and analyzed by ^{1}H NMR at predetermined times.

Reactions of Dialkylmercurials in the Presence of the Iodide Ion

Photolysis of equilibrated solutions of diisobutylmercury and sodium iodide with bromotrichloromethane

A 5 mL volumetric flask was charged with diisobutylmercury (0.1964 g, 0.6238 mmole) and fitted with a septum. A second 5 mL volumetric flask was charged with sodium iodide (0.5175 g, 3.452 mmole) and the quantification standard (0.0592 g, 0.188 mmole), 1,3,5-tribromobenzene and fitted with a septum. The volumetric flasks were purged with argon, and 4 mL of d_6-DMSO was syringed into each flask. The flasks were swirled to mix and dissolve their contents and diluted with d_6-DMSO to bring the total volume to 5 mL.

Into an argon purged NMR tube, fitted with a septum, was syringed 0.4 mL of the 0.1248 M diisobutylmercury solution, 0.3 mL of the 0.6905 M sodium iodide solution and 0.3 mL of d_6-DMSO. The NMR tube was inverted a few times to mix its contents, wrapped tightly with aluminum foil and allowed to equilibrate for one hour. After equilibration, bromotrichloromethane (0.0200 mL, 0.203 mmole) was syringed into the darkened NMR tube. The NMR tube was inverted a few times to mix its contents and immediately analyzed by ^1H NMR (transfer to the NMR spectrometer was performed in a darkened room. The NMR tube was then photolyzed 6 inches in front of a 275 W sunlamp and analyzed by ^1H NMR at predetermined times.

Photolysis of equilibrated solutions of diisobutylmercury and sodium iodide with bromotrichloromethane in the presence of di-tert-butyl nitroxide

Into an argon purged NMR tube, fitted with a septum, was syringed 0.4 mL of the previously described 0.1248 M diisobutylmercury solution, 0.3 mL of the 0.6905 M sodium iodide solution, 0.2 mL of d_6-DMSO and 0.1 mL of a 0.104 M di-tert-butyl. The NMR tube was inverted a few times to mix its contents, wrapped tightly with aluminum foil and allowed to equilibrate for one hour. After equilibration, bromotrichloromethane (0.0200 mL, 0.203 mmole) was syringed into the darkened NMR tube. The NMR tube was inverted a few times to mix its contents and immediately analyzed by ^1H NMR (transfer to the NMR spectrometer was performed in a darkened room). The NMR tube was then photolyzed 6 inches in front of a 275 W sunlamp and analyzed by ^1H NMR at predetermined times.

Photolysis of equilibrated solutions of diisopropylmercury and sodium iodide with bromotrichloromethane

A 5 mL volumetric flask was charged with diisopropylmercury (0.1274 g, 0.4446 mmole) and the quantification standard (0.0646 g, 0.205 mmole), 1,3,5-tribromobenzene and fitted with a septum. The volumetric flask was purged with argon, and 4 mL of d_6-DMSO was syringed into the flask. The flask was swirled to mix its contents and diluted with d_6-DMSO to bring the total volume to 5 mL.

Into an argon purged NMR tube, fitted with a septum, was syringed 0.6 mL of the 8.885×10^{-2} M diisopropylmercury solution, 0.3 mL of a 0.6744 M sodium iodide solution and 0.1 mL of d_6-DMSO. The NMR tube was inverted a few times to mix its contents, wrapped tightly with aluminum foil and allowed to equilibrate for one hour. After equilibration, bromotrichloromethane (0.0200 mL, 0.203 mmole) was syringed into the darkened NMR tube. The NMR tube was inverted a few times to mix its contents and immediately analyzed by ^{1}H NMR (transfer to the NMR spectrometer was performed in a darkened room). The NMR tube was then photolyzed 6 inches in front of a 275 W sunlamp and analyzed by ^{1}H NMR at predetermined times.

Photolysis of equilibrated solutions of diisopropylmercury and soduim iodide with bromotrichloromethane in the presence of di-tert-butyl nitroxide

Into an argon purged NMR tube, fitted with a septum, was syringed 0.6 mL of the 8.885 x 10^{-2} M diisopropylmercury solution, 0.3 mL of a 0.6744 M sodium iodide solution and 0.1 mL of a 0.104 M di-*tert*-butyl nitroxide solution. The NMR tube was inverted a few times to mix its contents, wrapped tightly with aluminum foil and allowed to equilibrate for one hour. After equilibration, bromotrichloromethane (0.0200 mL, 0.203 mmole) was syringed into the darkened NMR tube. The NMR tube was inverted a few times to mix its contents and immediately analyzed by ^{1}H NMR (transfer to the NMR spectrometer was performed in a darkened room). The NMR tube was then photolyzed 6 inches in front of a 275 W sunlamp and analyzed by ^{1}H NMR at predetermined times.

PART II. ADDITION OF FREE RADICALS TO VINYL ETHERS AND ELECTRON TRANSFER REACTIONS OF THE ADDUCT RADICALS

INTRODUCTION

General Considerations

It has long been known that radicals will add to double bonds and participate in free radical chain reactions (i.e., free radical halogenations and polymerizations). It has even been shown that, carbon centered radicals may be oxidized.[42] The Meerwein,[43,44] Kharasch,[45,46] and Minisci[47] processes, Schemes XVI - XVIII, have shown that the oxidation of the carbon centered radical may participate in a chain reaction if the metal cation is capable of existing in several oxidation states with the proper oxidation-reduction potentials.

Scheme XVI

$$ArN_2{}^{+}Cl^{-} + CuCl \longrightarrow CuCl^{+} + ArN_2{}^{\cdot} \longrightarrow Ar^{\cdot} + N_2$$

$$Ar^{\cdot} + H_2C \quad CHPh \longrightarrow ArCH_2CHPh$$

$$ArCH_2CH(Ph)^{\cdot} + CuCl^{+} \longrightarrow CuCl + ArCH_2CH(Ph)^{+}$$

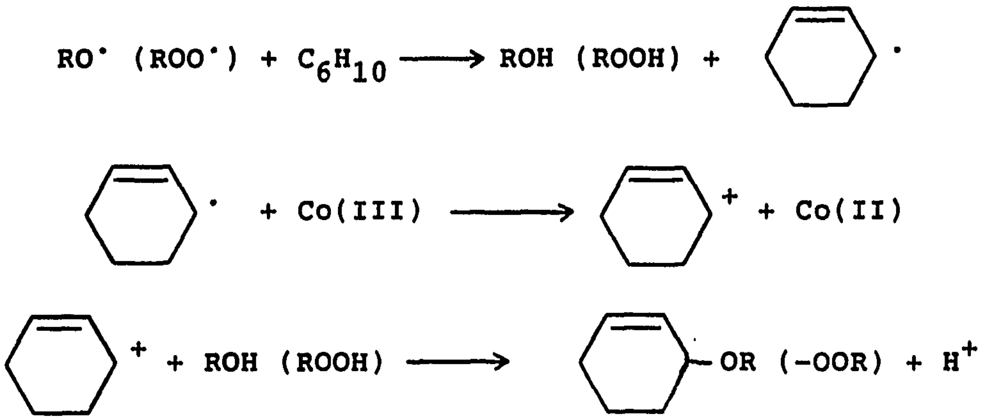
$$ArCH_2CH(Ph)^{+} \xrightarrow{Cl^{-}} ArCH_2CH(Ph)Cl$$

Jagannadham and Steenken[48] have shown that radicals adjacent to an electron rich center, such as α-hydroxyalkyl radicals, may be oxidized in aqueous solution by para-substituted nitrobenzenes. The oxidation process proceeds best when the nitrobenzene contains a para-electron withdrawing group with rates approaching diffusion control when subtituents on the α-hydroxyalkyl radical can stabilize a

Scheme XVII

$$\mathrm{ROOH\ Co(II)} \longrightarrow \mathrm{RO^{\bullet} + HO^{-} + Co(III)}$$

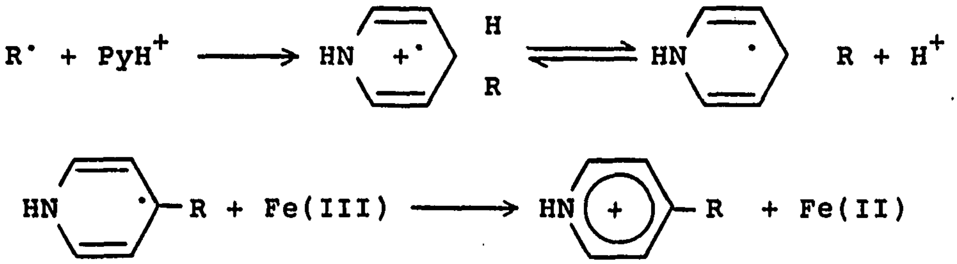
$$\mathrm{RO^{\bullet} + ROOH} \longrightarrow \mathrm{ROH + ROO^{\bullet}}$$



Scheme XVIII

$$\mathrm{RC(O)OOH + Fe(II)} \longrightarrow \mathrm{Fe(III) + HO^{-} + RCO_2^{\bullet}}$$

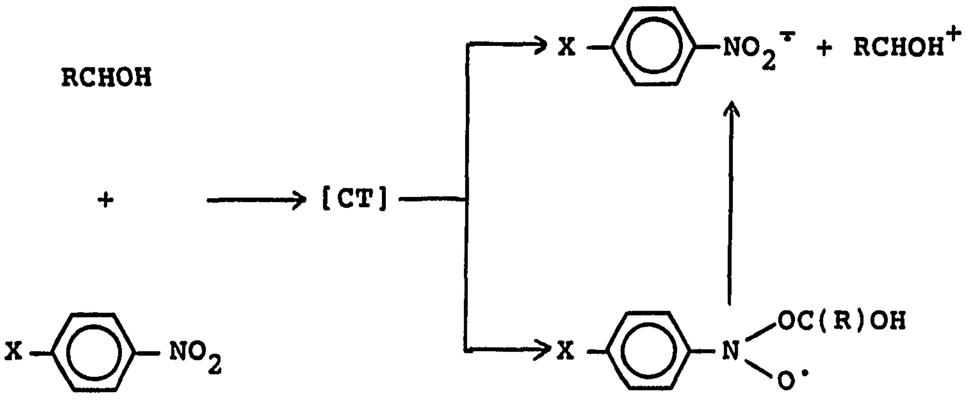
$$\mathrm{RCO_2^{\bullet}} \longrightarrow \mathrm{R^{\bullet} + CO_2}$$



developing positive charge.

The results show that, at pH < 6, the one electron oxidation occurs through both an inner sphere electron transfer and an outer sphere electron transfer,[49,50,51] Scheme XIX. The

Scheme XIX



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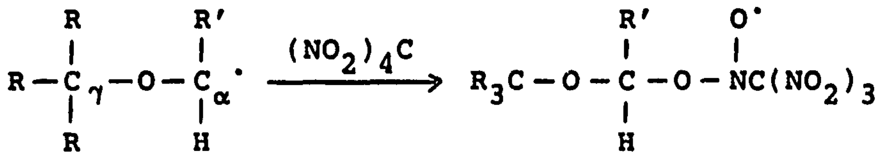
outer sphere electron transfer proceeds via a direct transfer of an electron to produce the radical anion of the para-substituted nitrobenzene and an aldehyde after deprotonation. On the other hand, the inner sphere electron transfer proceeds through the formation of the nitroxyl adduct (observed by ESR), 6, which then undergoes an unimolecular heterolysis to give the same products. The fraction of outer sphere electron transfer was found to increase with increasing electron withdrawing power of X and the electron donating ability of R.

Though no study of the one electron oxidation of α-mono-alkoxyalkyl radicals by nitrobenzenes has been made, Steenken and coworkers have, in a previous study,[52] oxidized α-mono-alkoxy radicals in aqueous solutions of tetranitromethane. In this study they observed a striking structure dependence upon the alkyl portion of the alkoxy group. It was found that, in addition to the dependence on substitution at C_α of structure 7, Equation 11, that substitution for H at C_α with electron donating groups significantly decreases the lifetime



$$R-\overset{R}{\underset{R}{C_\gamma}}-O-\overset{R'}{\underset{H}{C_\alpha^{\bullet}}} \xrightarrow{(NO_2)_4C} R_3C-O-\overset{R'}{\underset{H}{C}}-O-\overset{O^{\bullet}}{N}C(NO_2)_3 \qquad (11)$$

7 8

of the inner sphere electron transfer complex 8. Although no concerted effort was made to prove the mechanism in those cases where the inner sphere electron transfer complex was not observable by ESR, it is conceivable that some of these may have proceeded by outer sphere electron transfer. Nonetheless, the products of the oxidation were always the nitroform anion and a hemiacetal or hemiketal produced by the attack of water on the cation formed.

Steenken and coworkers' observations that tetranitromethane can be reduced by radicals to a radical anion which will decompose are in line with the observation on nitroalkanes by numerous other authors[53-59] and have been used in free radical chain reactions, Schemes XX and XXI.

Statement of Research Problem

The observation that nitroalkanes may be reduced and that the resulting radical anions can decompose to give radicals

Scheme XX $X = Br, Cl, NO_2$

$$[XRNO_2]^{\cdot -} \longrightarrow X^- + RNO_2^{\cdot}$$

$$RNO_2^{\cdot} + A^- \longrightarrow [ARNO_2]^{\cdot -}$$

$$[ARNO_2]^{\cdot -} + XRNO_2 \longrightarrow ARNO_2 + [XRNO_2]^{\cdot -}$$

Scheme XXI

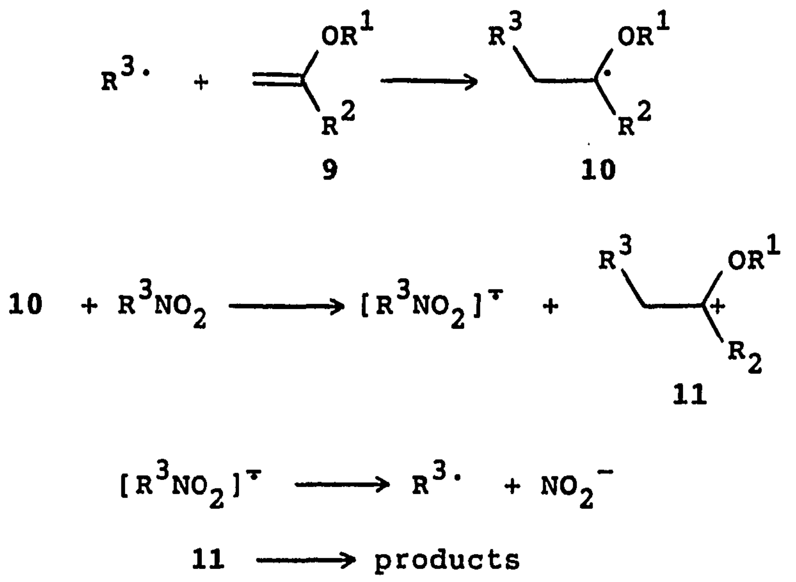
$$[NCRNO_2]^{\cdot -} \longrightarrow NO_2^- + NCR^{\cdot}$$

$$NCR^{\cdot} + A^- \longrightarrow [ARCN]^{\cdot -}$$

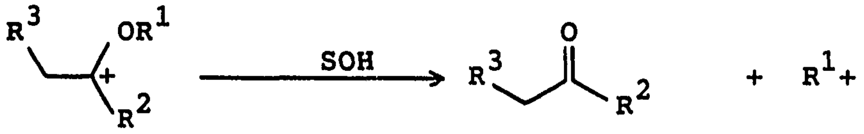
$$[ARCN]^{\cdot -} + NCRNO_2 \longrightarrow ARCN + [NCRNO_2]^{\cdot -}$$

when coupled with Steenken and coworkers' observation that nitrobenzenes and tetranitromethane can oxidize carbon-centered radicals adjacent to an oxygen atom, suggests that a free radical chain mechanism such as Scheme XXII may be implemented. Steenken never carried out a concerted effort with a single reducing agent to determine what the effect of solvent or the groups attached to the oxygen atom would have on the products formed by the reaction. However, his two studies do suggest that different groups do affect the direction the reaction takes after electron transfer. This suggests that by changing R^1 the products of the reaction can be altered. If R^1 can form a stable cation or undergo a solvolytic attack in a chosen solvent, ketones or aldehydes may be formed, Equation (12). However, if R^1 cannot form a stable cation, vinyl ethers may be formed, Equation (13), or if an alcohol is also added, ketals may be formed, Equation (14).

Scheme XXII



A convenient source of 9 would be enol silyl or methyl ethers which should show the range of cation stabilities desired. The electronic nature of these reactants restrict the radicals that may be used to electrophilic radicals since



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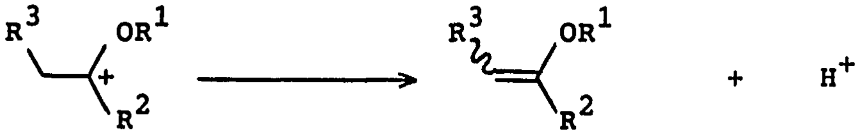

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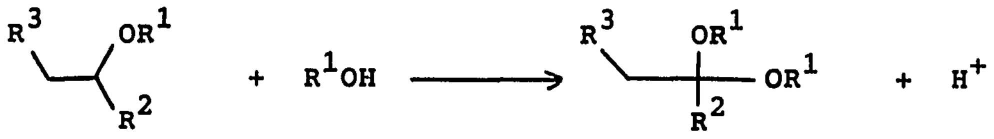
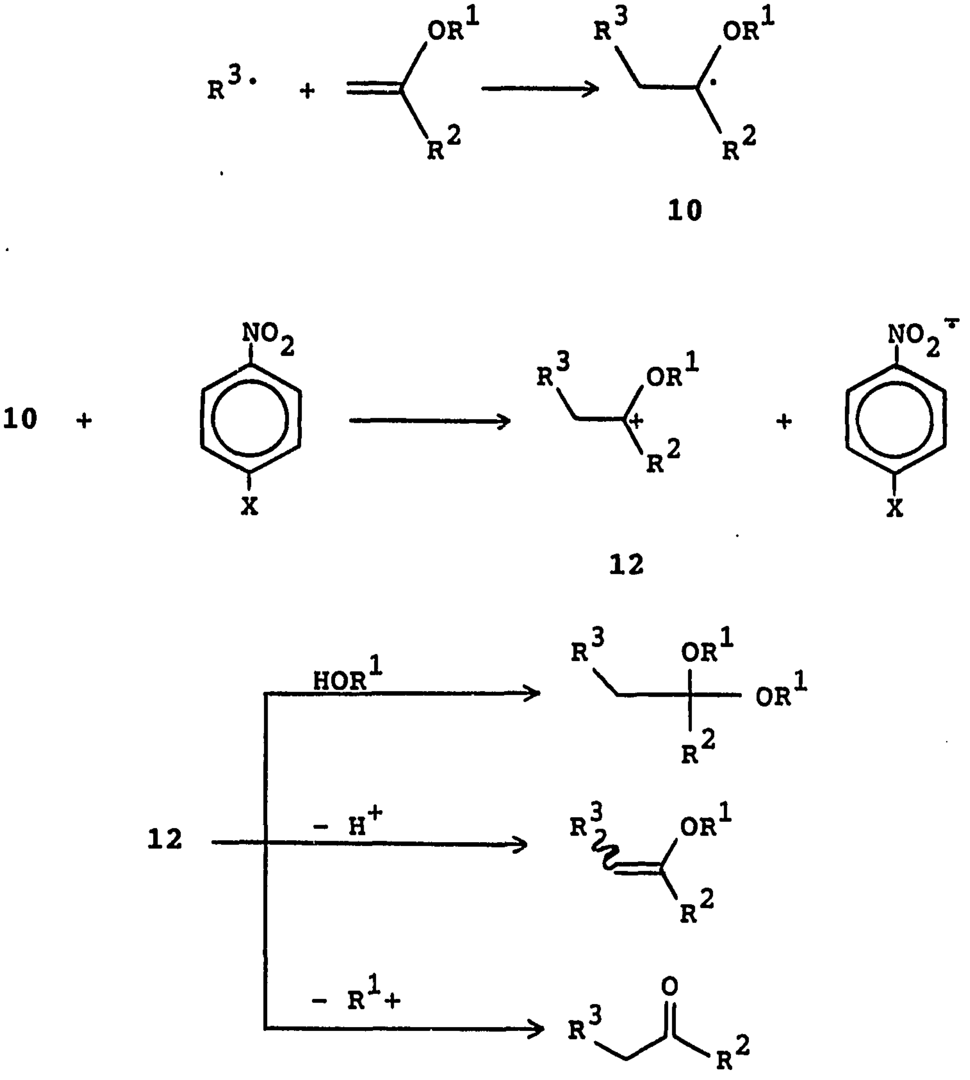


(14)

the double bond is electron rich. One such radical is the 1-cyano-1-methylethyl radical which has been shown to add to enol silyl ethers to form a complicated product mixture.[60] This radical can be produced easily from 2,2′-azobis[2-methylpropanenitrile] (AIBN). In addition, the 2-methyl-2-cyano-2-nitropropane radical anion has been shown to decompose to the 1-cyano-1-methylethyl radical and thus could possibly participate in a chain sequence such as Scheme XXII.

In light of these facts, we hoped to add the 1-cyano-1-methylethyl radical to vinyl ethers via a chain mechanism, Scheme XXII ($R^3 = (CH_3)_2C(CN)$), and show product control by the appropriate choice of R^1 ($R^1 = SiMe_3$, Me). At the very least, the 1-cyano-1-methylethyl radical could be generated from the thermal decomposition of AIBN and products formed by the oxidation of the intermediate radical 10 by added electron transfer reagents (i.e. nitrobenzenes), Scheme XXIII. In addition, we hoped to be able to extend the reaction to the phenyl radical by the thermolysis of phenylazotriphenylmethane (PAT).

Scheme XXIII $R^3 = (CH_3)_2C(CN)$



RESULTS AND DISCUSSION

Reaction of Vinyl Ethers with 2-methyl-2-nitropropanenitrile

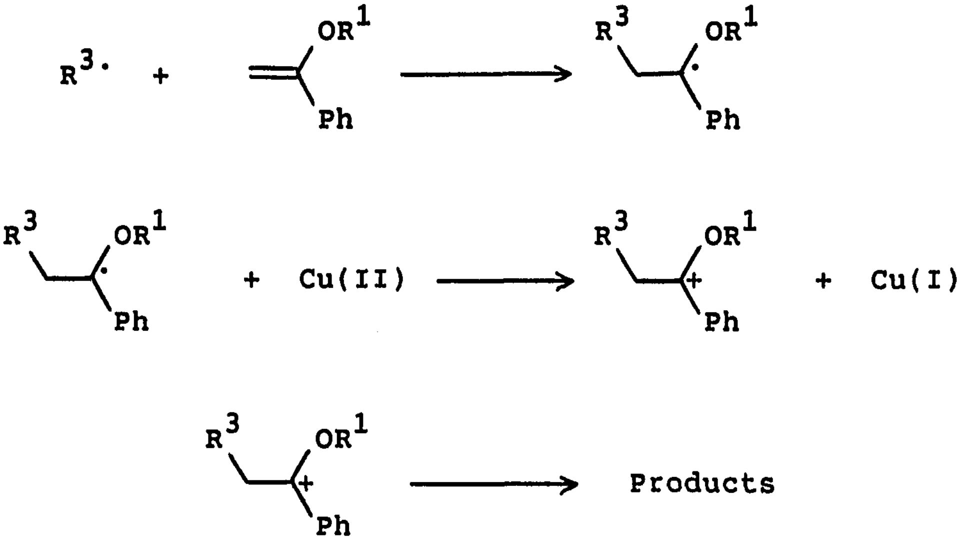
Trimethyl[(1-phenylethenyl)oxy]silane (0.67 M) reacts with 2-methyl-2-nitropropanenitrile (1.33 M), in the presence of 10 mole % of AIBN, in DMSO at 60 °C for 18 hours to produce 85% acetopheneone, 95% unreacted 2-methyl-2-nitropropanenitrile, traces of radical addition products to trimethyl[(1-phenylethenyl)oxy]silane and traces of the 1-cyano-1-methylethyl radical dimers. In a similar manner, (1-methoxyethenyl)benzene reacts with 2-methyl-2-nitropropanenitrile to produce traces of the radical addition products to (1-methoxyethenyl)benzene, traces of the 1-cyano-1-methylethyl radical dimers, 85% unreacted (1-methoxyethenyl)benzene and 97% unreacted 2-methyl-2-nitropropanenitrile. Presumably, the 1-cyano-1-methylethyl radical products result from the thermolysis of the initiator, AIBN, and indicate that 2-methyl-2-nitropropanenitrile must not be able to oxidize the intermediate radical produced by the addition of the 1-cyano-1-methylethyl radical to the vinyl ether and propagate the chain reaction depicted in Scheme XXII.

The fact that the 2-methyl-2-nitropropanenitrile can be reduced by copper(I) salts offered a possible way to circumvent the failure of the nitroalkane to oxidize the intermediate radical by allowing the produced copper(II) salt to oxidize the intermediate radical, Scheme XXIV. However, the reaction of trimethyl[(1-phenylethenyl)oxy]silane or (1-methoxyethenyl)benzene in acetone or <u>tert</u>-butyl alcohol in the presence of catalytic amounts of copper(II) and copper(I)

Scheme XXIV $R^1 = SiMe_3$, Me $R^3 = (CH_3)C(CN)$

$$R^3NO_2 + Cu(I) \longrightarrow [R^3NO_2]^{\cdot-} + Cu(II)$$

$$[R^3NO_2]^{\cdot-} \longrightarrow R^3\cdot + NO_2^{-}$$



salts produced only a trace of the radical addition products, 96% unreacted 2-methyl-2-nitropropanenitrile and gave 90% acetopheneone in the case of trimethyl[(1-phenylethenyl)-oxy]silane and 93% unreacted vinyl ether in the case of (1-methoxyethenyl)benzene.

The production of acetophenone in the reaction of 2-methyl-2-cyano-2-nitropropane with trimethyl[(1-phenyl ethenyl)oxy]silane under all conditions employed is perplexing. Trimethyl[(1-phenylethenyl)oxy]silane is stable to the solvents at the temperatures used, stable to the work-up conditions and stable to the copper salts. However, it has been found that it is unstable to strong bases under the reaction conditions employed.

Reaction of Vinyl Ethers with AIBN

In light of the previous results, 1-cyano-1-methylethyl radicals were generated by the thermal decomposition of AIBN and oxidation of the intermediate adduct radical attempted by the addition of known electron transfer agents.

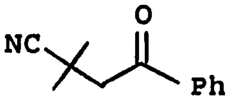
Since the 1-cyano-1-methylethyl radicals generated in the thermolysis of AIBN can dimerize in the solvent cage, 1.5 equivalents of AIBN were used to ensure that enough 1-cyano-1-methylethyl radicals would be produced to provide adequate reaction. Nonetheless, some of the starting vinyl ether remained and even 5 equivalents of AIBN did not consume all traces of the vinyl ether.

It should also be noted that, AIBN decomposes in a first order process.[61] From the activation parameters of AIBN,[61] a half life of approximately 7 hours, at 69 °C can be calculated. The usual time of thermolysis employed was 24 hours. This corresponds to approximately 91% decomposition of AIBN into 1-cyano-1-methyl radicals.

Thermolysis of AIBN in the presence of trimethyl[(1-phenylethenyl)oxy]silane

Trimethyl[(1-phenylethenyl)oxy]silane (0.67 M) reacts with 1-cyano-1-methylethyl radicals, generated from the thermolysis of AIBN at 69 + 1 °C, to produce a mixture predominating in one or two of the frequently observed products; α,α-dimethyl-γ-oxo-benzenebutanenitrile, 13, trimethyl[(3-cyano-3-methyl-1-phenyl-1-butenyl)oxy]silane, 14, α,α-dimethyl-γ-oxo-p-(2-cyano-2-propyl)benzenebutanenitrile, 15, and 2,5-dicyano-2,5-dimethyl-3-trimethylsiloxy-3-phenylhexane, 16. The product yields are given for various solvents in Table 4. Acetophenone is also produced in the reaction and has been shown to form rapidly by the hydrolysis of trimethyl[(1-phenylethenyl)oxy]silane at 69 °C by traces of water present in the solvent[62] and thus its yield will not be given. Mass balances based on the vinyl ether were better than 90% in all cases with the remainder of the unreported mass belonging to acetophenone or unreacted trimethyl[(1-phenylethenyl)oxy]silane.

Each of the four products may be formed by two mechanisms. The first mechanism, requires further reaction of the 1-cyano-1-methylethyl radical with the intermediate radical, 17, via hydrogen atom or trimethylsilyl abstractions and radical radical couplings, Scheme XXV. The second



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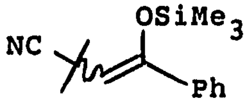

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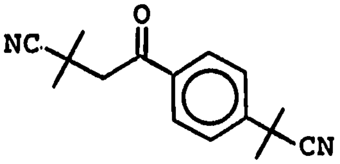

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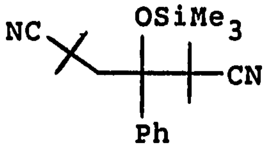

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Table 4. Percent yield of the products of the reaction of 1-cyano-1-methylethyl radicals with trimethyl[(1-phenylethenyl)oxy]silane at 69 + 1 °C for 24 hours[a]

solvent	13	14	15	16
DMSO	9	54	2	8[b]
PhH	2	5	-	60
THF	32	2	34	8[c]
tert-butyl alcohol	34	2	30	9
PhH + DABCO[d]	2	4	-	63

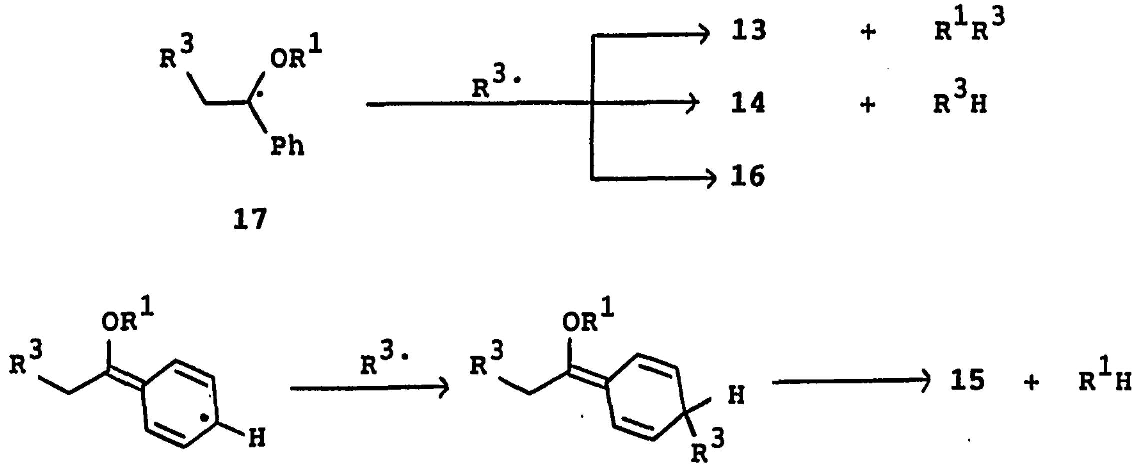
[a] Mass balance for the reaction exceeds 90% in all cases with the unreported mass belonging to acetopheneone and unreacted trimethyl[(1-phenylethenyl)oxy]silane.

[b] A product with the molecular wieght of 256 is observed in approximately 16% yield.

[c] A product with the molecular wieght of 256 is observed in approximately 10% yield.

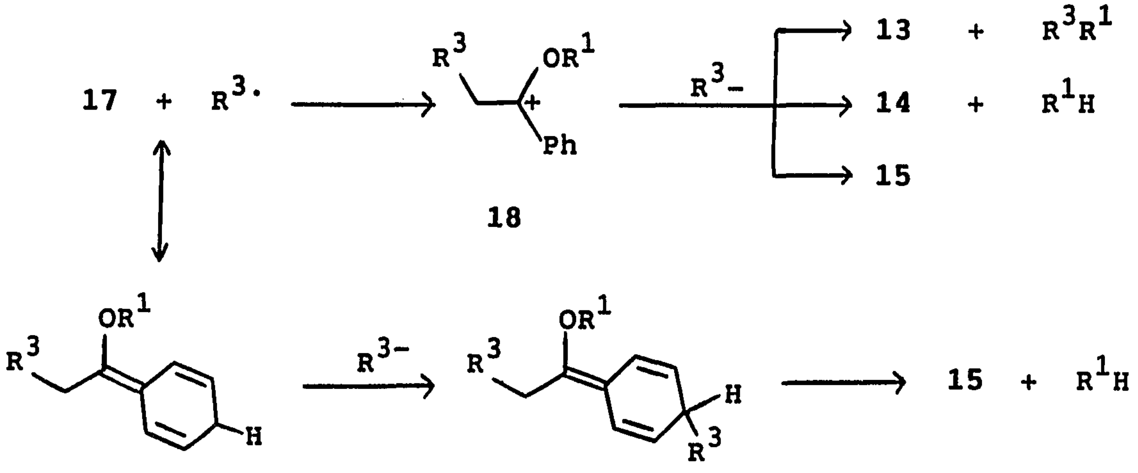
[d] 5 equivalents of DABCO ([2.2.2]-1,4-diazabicyclooctane was used.

Scheme XXV R^1 = $SiMe_3$ R^3 = $(CH_3)_2C(CN)$



mechanism requires the oxidation of 17 by the 1-cyano-1-methylethyl radical to produce the resonance stabilized cation 18, followed by proton or trimethylsilyl abstraction or ionic coupling, Scheme XXVI.

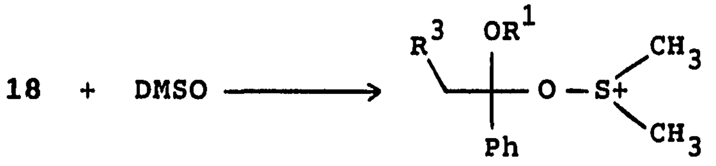
Scheme XXVI R^1 = $SiMe_3$ R^3 = $(CH_3)_2C(CN)$



The product variation observed for the change in solvent provided a valuable mechanistic probe. The fact that 16 is observed in the solvent least likely to support charged species, benzene, suggests that this product is formed by the coupling of the 1-cyano-1-methylethyl radical and the intermediate radical 17. The addition of 5 equivalents of the base DABCO to the reaction confirms this fact. If the free cation had been formed, the addition of the strong base should result in a significant increase in the formation of the substituted vinyl ether 14. This was not observed (Table 4). The possibility that, in benzene solution, the electron transfer proceeds by a very tight ion pair that cannot be intercepted by DABCO and collapses exclusively to give 16 can not be ruled out.

Table 4 indicates a dramatic solvent effect upon the reaction products formed by the interaction of two radicals. Such a large solvent effect is unprecedented in radical-radical interactions. The products suggest that electron transfer, Scheme XXVI, may be the dominant mechanism of interaction in polar solvents. In DMSO, THF or *tert*-butyl alcohol there is little formation of 16, the major product observed in benzene and tentatively assigned as the radical coupling product. If 13, 14 and 15 do indeed form via ion pairs or free ion intermediates why does DMSO form the substituted vinyl ether 14 almost exclusively while THF and tert-butyl alcohol produce almost equal amounts of ketones 13 and 15 and little vinyl ether 14?

One explanation may be the fact that DMSO is known to effectively stabilize cations by the formation of complexes such as 19, Equation (15). This would the give



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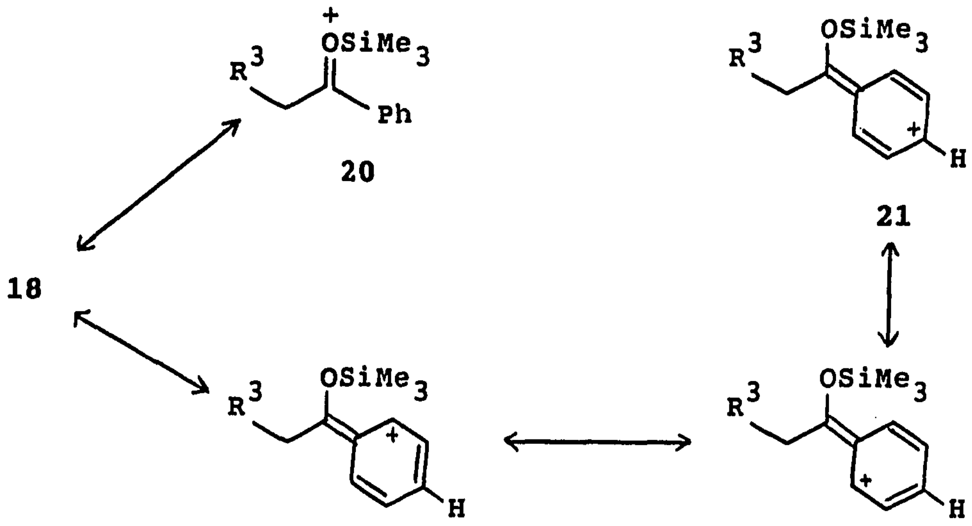
the 1-cyano-1-methylethyl anion time to selectively abstract the proton and convert complex 19 to the vinyl ether 13. Alternately, DMSO may itself serve as the proton acceptor. The THF and tert-butyl alcohol would be weaker solvating agents for cation 18 which in the absence of strong solvation must rely upon resonance with the oxygen atom and the phenyl ring for stabilization, Equation (16). The products could then form by the loss of the trimethyl silyl group from resonance form 20, to form ketone 13, or attack of the 1-cyano-1-methylethyl anion upon resonance form 21 followed by the formal loss of trimethylsilyl hydride, to form ketone 15. Since 15 was only observed to be a significant product when the ketone 13 was also formed, the possibility exists that 15 is also formed by further attack of 1-cyano-1-methylethyl radicals upon 13.



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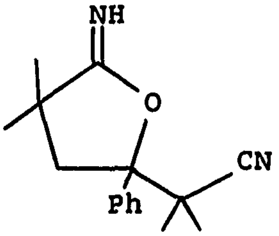
The identity of a minor product 22 observed in DMSO and THF (Table 4) is still a matter of conjecture. On the basis of mass spectral data, the product has a molecular weight of 256 (observed as the M + 1 ion in a chemical ionization experiment, inert gas CH_4). It is believed that it is either the iminoether 23 or the lactam 24. The significant NMR and IR spectral lines for the compound lie in the overlap region of the iminoethers and lactams, Table 5. The unknown, 22,



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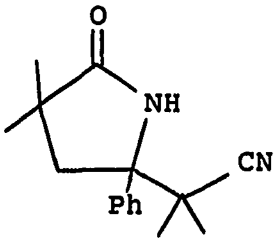

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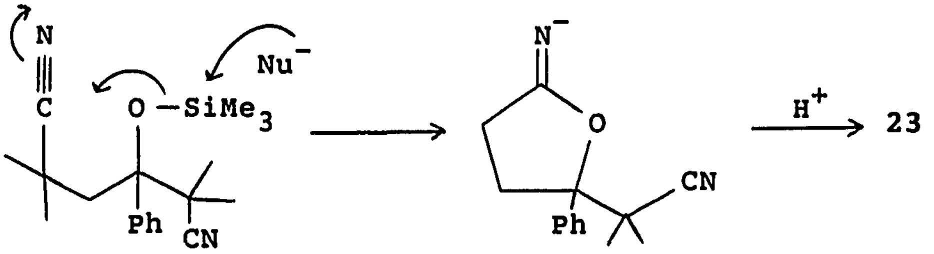
Table 5. NMR and IR spectral data for iminoethers, lactams and 22

compound	NMR shift(ä)	IR wavelenth(cm^{-1})	
	C N H	N H	C X
imino ethers	none reported	3500 - 3400	1675 - 1625
lactams	8.5 - 5.0	3100 - 3000	1725 - 1625
22	7.1 broad	3300	1690

readily formed an insoluble hydrochloride when exposed to anhydrous HCl in diethyl ether. This suggests that it is the imino ether 23 since amides are notoriously hard to protonate. However, a clean IR specrum of the hydrochloride salt of 22 could not be obtained to give a definitive answer.

Mechanistically, it is not known how 22 forms in the reaction but it is most likely derived from 16, Equation (17).



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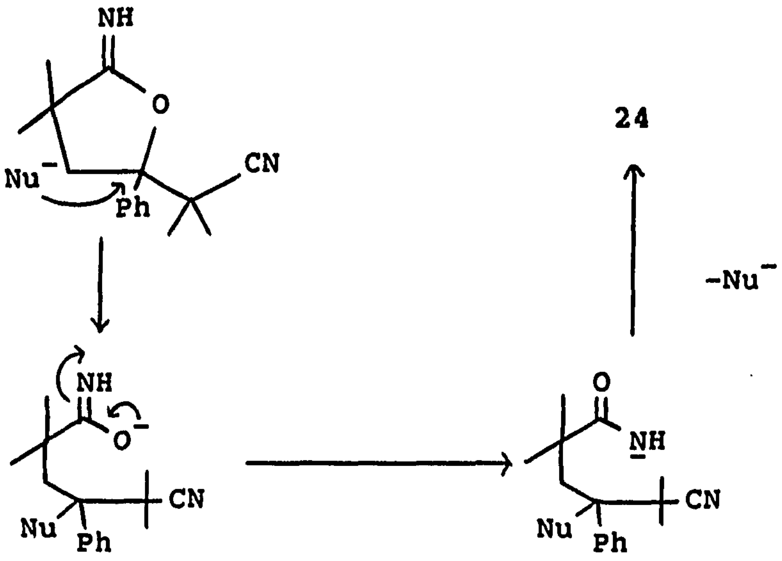
Deprotonated alcohols are known to attack nitriles to form iminoethers however, this example is complicated by the isomerization depicted in Equation (18).



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<u>Thermolysis of AIBN with trimethyl[(1-phenylethenyl)oxy]silane in the presence of para-dinitrobenzene</u>

Trimethyl[(1-phenylethenyl)oxy]silane (0.67 M) reacts with 1-cyano-1-methylethyl radicals, generated from the thermolysis of AIBN at 69 + 1 °C for 18 hours, in the presence of one equivalent of the electron transfer reagent para-dinitrobenzene (DNB), to produce mainly α,α-dimethyl-γ-oxo-benzenebutanenitrile, Table 6. A 10% yield of dimethyl(4-nitrophenyl)ethanenitrile is also produced in all cases from the attack of the 1-cyano-1-methylethyl radical on DNB. Acetopenone is also produced in the reaction and has been shown to form rapidly from the hydrolysis of the starting trimethyl[(1-phenylethenyl)oxy]silane, at 69 °C, with traces of water present in the solvent and AIBN and thus its yield will not be reported.

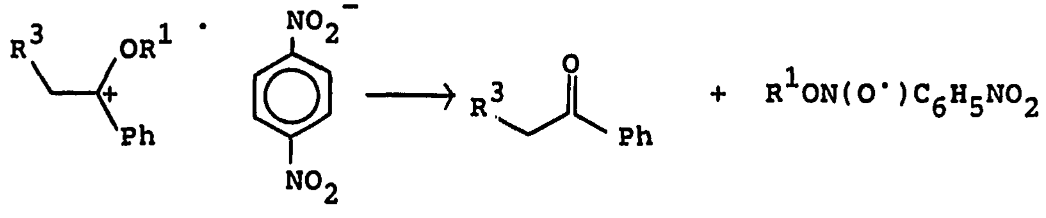
Table 6. Percent yield of the products of the 1-cyano-1-methylethyl radical reaction with trimethyl[(1-phenylethenyl)oxy]silane in the presence of one equivalent of DNB at 69 + 1 °C for 24 hours[a]

solvent	13	14	15	16
DMSO	74	trace	2	3
PhH	35	7	18	12
THF	63	2	4	-
<u>tert</u>-butyl alcohol	60	3	6	-

[a] Mass balance for the reaction exceeds 90% in all cases with the unreported mass beloning to acetopheneone and unreacted trimethyl[(1-phenylethenyl)oxy]silane.

It was hoped that the addition of DNB would produce the free cation by an outer sphere electron transfer. Jagannadham and Steenken's results with α-hydroxyalkyl radicals indicated that this para-substituted nitrobenzene gave the largest fraction of outer sphere electron transfer which approached unity when substituents on the alkyl fragment could stabilize a developing positive charge.

The results in Table 6 indicate that para-dinitrobenzene is intimately involved in the reaction. In benzene solution it greatly reduced the yield of the radical coupling product 16 while in THF or <u>tert</u>-butyl alcohol it greatly reduced the yield of the aromatic substitution product 15. In DMSO the major product is no longer the substituted enol silyl ether 14 but instead the ketone 13 (the solvolysis product of 14). If an outer sphere electron transfer mechanism is involved, the ion pair 25 must react by the attack of the para-dinitrobenzene radical anion upon the trimethylsilyl group, Equation (19). Abstraction of a proton by 1-cyano-1-methylethyl anion,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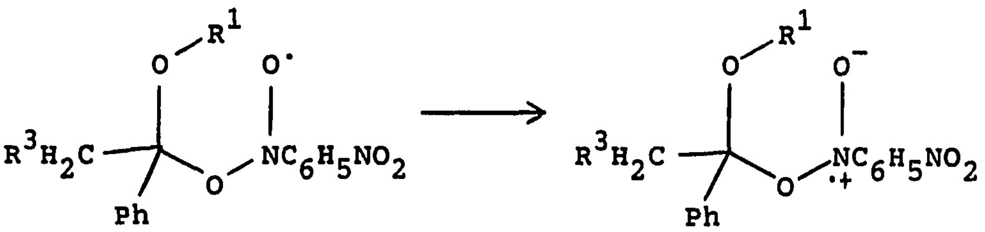
from 18, to give 14 would be an irreversible reaction. However, abstraction of a proton by para-dinitrobenzene, a much weaker proton acceptor, could be a reversible process. This could lead to the solvolysis of the initially formed substituted enol silyl ether 14 to yield the observed ketone 13. Alternatively, an inner shell electron transfer process may be involved to yield 26 (R = $SiMe_3$). The nitroxide 26 could undergo a unimolecular decomposition to form ketone 13 and a siloxynitroxide which could capture another 1-cyano-

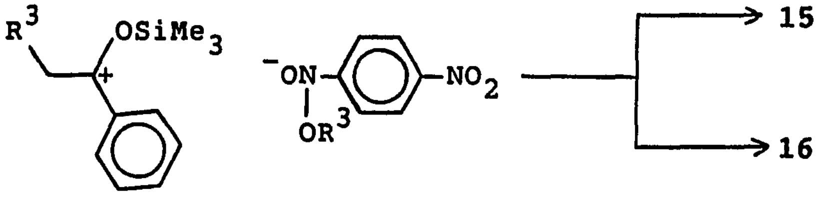


26

1-methyl-ethyl radical to yield an unstable product, Reaction (20), which is destroyed upon hydrolytic workup.

$$26 \longrightarrow 13 + R^3ON(O^\cdot)C_6H_5NO_2 \xrightarrow{R^1} \begin{array}{c}\text{unstable}\\ \text{product}\end{array} \qquad (20)$$

The fact that the radical coupling product 16 is formed in low yield in benzene solution indicates that DNB may not be an efficient electron transfer agent in this solvent. This seems most consistent with a outer shell electron transfer mechanism whose rate increases with the polarity of the solvent. In benzene solution a small amount of the aromatic substitution product 15 is observed in the presence of DNB but not in its absence. Perhaps 15 is derived from the initially formed 13, however, it is not obvious why benzene promotes this reaction; only small amounts of 14, 15 and 16 were formed in DMSO, THF and <u>tert</u>-butyl alcohol solutions. Other possible routes to 15 and 16 are attack of the 1-cyano-1-methylethyl radical upon 26 or the tight ion pair formed by outer sphere electron transfer. The resulting 27 might be able to transfer



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the 1-cyano-1-methylethyl group to the para position of the benzene ring or to the benzylic carbon atom.

Thermolysis of AIBN in the presence of (1-methoxyethenyl)-benzenes

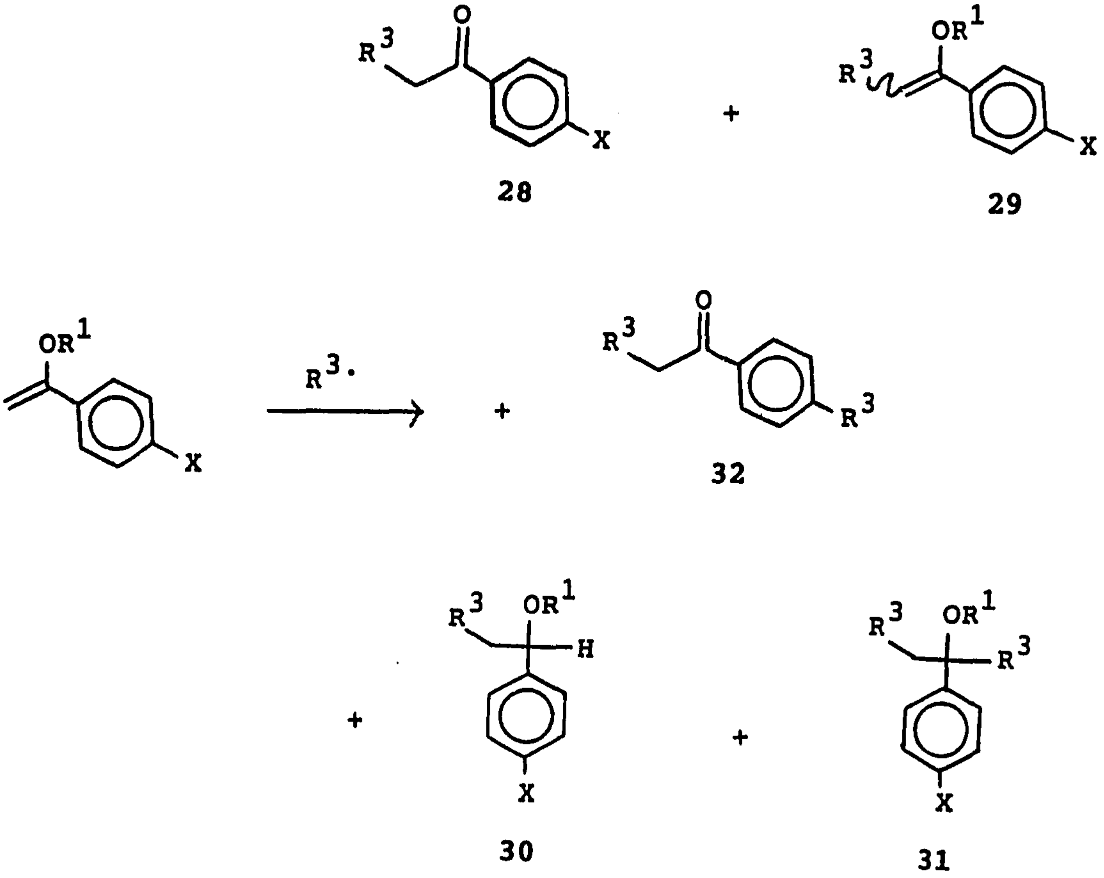
The reaction of para substituted (1-methoxyethenyl)-benzenes (0.67 M) with 1-cyano-1-methylethyl radical, generated from the thermolysis of AIBN at 69 + 1 °C for 18 hours, produced products similar in structure to those produced in the reaction of AIBN with trimethyl[(1-phenylethenyl)oxy]silane, Scheme XXVII. However, the change in product ratios, Table 7, indicates that a change of mechanism may have accompanied the change in R^1 from

Table 7. Percent yield of the products of the reaction of 1-cyano-1-methylethyl radicals with (1-methoxy-ethenyl)benzenes at 69 + 1 °C for 24 hours[a]

para substituent, solvent	28	29	30	31	32
H, DMSO	5	10	8	41	3
H, PhH	4	3	5	58	trace
OMe, DMSO	8	8	25	28	9
OMe, PhH	4	6	4	60	trace
NO_2, DMSO	17	36	-	18	18

[a] Mass balance for the reaction exceeds 90% in all cases with the unreported mass belonging to the unreacted (1-methoxyethenyl)benzenes.

Scheme XXVII R1 = Me, R^3 = $(CH_3)_2C(CN)$, X = H, OMe, NO_2



trimethylsilyl to methyl. With the unsubstituted vinyl ether the effect of the solvent upon the product ratio is much smaller than observed for the enol silyl ether.

It appears that the switch in R^1 from trimethylsilyl has increased the oxidation potential of the intermediate radical 17 (R^1 = Me) to the point that the 1-cyano-1-methylethyl radical can no longer oxidize it. This possibility is supported by the observation that both DMSO and benzene as the solvent give similar product distributions when the para substituent is hydrogen; the expected radical coupling product 31 is the major product in both solvents. The possibility of electron transfer followed by the coupling of the 2-cyano-propan-2-yl anion and cation 18 (R = Me) was ruled out by theobservation that the addition of methanol (solvent to methanol ratio of 14:1) did not significantly affect the product distributions, Table 8. The small amounts of ketal formed, Scheme XXVIII, are produced at the expense of ketones 28 and 32, which are expected to form via cation 18.

Table 8. Percent yield of the products of the reaction of 1-cyano-1-methylethyl radicals with (1-methoxyethenyl)benzenes at 69 ± 1 °C for 24 hours in the presence of methanol[a-c]

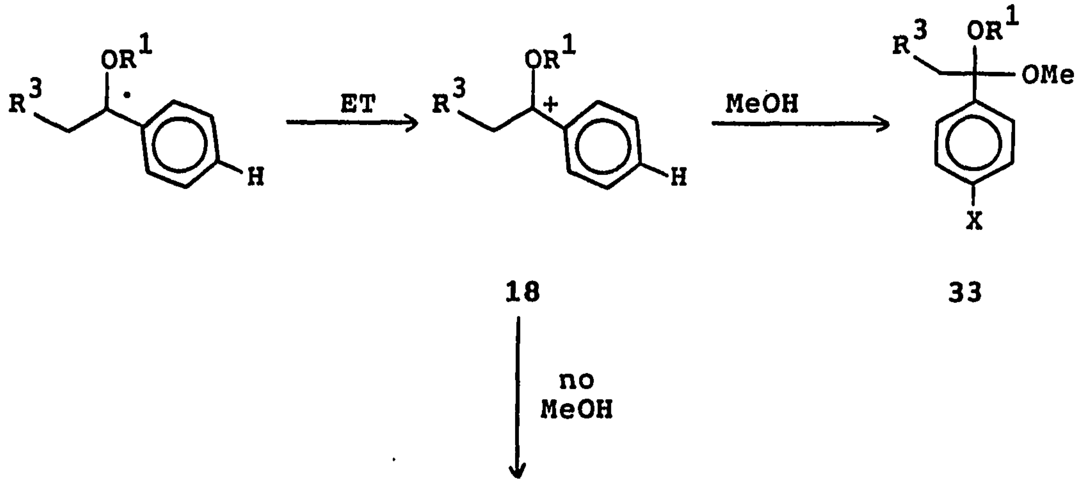
para substituent, solvent	28	29	30	31	33
H, DMSO	2	8	8	53	10
H, PhH	-	3	trace	57	2
OMe, DMSO	2	4	3	56	6
OMe, PhH	3	23	7	30	12
NO_2, DMSO	-	2	8	68	5

[a] Solvent to methanol ratio is 14:1.

[b] Mass balance for the reaction exceeds 90% in all cases with the remaining unreported mass being the unreacted (1-methoxyethenyl)benzenes.

[c] 32 is observed in only trace amounts in all cases.

Scheme XXIII R^1 = Me, R^3 = $(CH_3)C(CN)$, X = H, OMe



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33

28 + 32

The results with the X = NO_2 are particularly perplexing. On the basis of the previous results, it would be expected that only the radical coupling products would be observed. However, the formation of the substituted vinyl ether 29 (X = NO_2) and ketone 32 suggests that electron transfer is occurring. This is probably a result of the para-nitrophenyl substituent which can oxidize the first formed adduct radical.

Thermolysis of AIBN in the presence of (1-methoxyethenyl)-benzene and electron transfer reagents

para-dinitrobenzene The reaction of para substituted (1-methoxyethenyl)benzenes (0.67 M) with 1-cyano-1-methylethyl radical, generated from the thermolysis of AIBN at 69 + 1 °C for 18 hours, in the presence of one equivalent of the electron transfer agent DNB, produced the same products observed in the absence of DNB, Table 9. However, the product distribution now indicates that an electron transfer has occurred because, the yield of the radical coupling product, 31, is drastically decreased and the substituted vinyl ether, 29, is now the major product in either benzene or DMSO.

Table 9. Percent yield of the products of the reaction of 1-cyano-1-methylethyl radicals with (1-methoxyethenyl) benzenes, in the presence of one equivalent of DNB, at 69 + 1 °C for 24 hours[a]

para substituent, solvent	28	29	31	32
H, DMSO[b]	24	47	2	2
H, PhH	8	37	12	3
OMe, DMSO[c]	4	62	2	3
OMe, PhH	3	47	11	trace
NO_2, DMSO	13	39	12	10
H, DMSO[d]	3	40	30	trace

[a] Mass balance for the reaction exceeds 90% in all cases with the remaining unreported mass belonging to the unreacted (1-methoxyethenyl)benzenes.

[b] 10% yield of 33 is observed.

[c] 17% yield of 33 is observed.

[d] Only 0.1 equivalent of DNB was used.

The result that ketone 32 is not formed to any significant extent seems to indicate that the free cation is not formed. However, in the mixed solvent DMSO/methanol(14:1 by volume) the reaction forms the dimethyl ketal 33 in benzene and methanol but not DMSO, Table 10. This appears to indicate that the electron transfer in DMSO proceeds through the inner sphere electron transfer complex 26. The fact that the product ratio in DMSO is not affected by the addition of methanol appears to demand it. With this evidence it is hard to conceive that the electron transfer can be outer sphere,

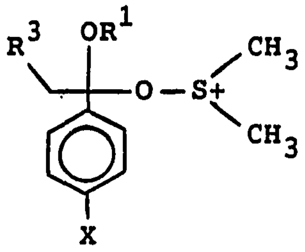
Table 10. Percent yield of the products of the reaction of 1-cyano-1-methylethyl radicals with (1-methoxy ethenyl)benzenes at 69 + 1 °C for 24 hours in the presence of one equivalent of DNB and methanol[a,b]

para substituent, solvent	28	29	31	32	33
H, DMSO	33	39	2	2	13
H, PhH	7	9	9	3	51
H, MeOH	2	2	5	2	69
OMe, DMSO	5	63	3	2	17
OMe, PhH	4	6	-	-	65

[a] Solvent to methanol ratio is 14:1.

[b] Mass balance for the reaction exceeds 90% in all cases with the unreported mass belonging to the unreacted (1-methoxyethenyl)benzenes.

even with the possibility that DMSO could stabilize the resulting cation via the formation of complex 19. Significant amounts of methanol should interfere with the formation of complex 19 and form the substituted ketal 33. In addition, the lack of preference between the loss of a proton, to form 29, and loss of a methyl group, to form 28 is suspicious.



R^1 = Me
R^3 = $(CH_3)C(CN)$
X = H, OMe

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The stability and solvation effects alone should favor the loss of a proton from cation 18.[48] The fact that no preference is seen suggests that a bond is formed between the departing cation and the para-dinitrobenzene radical ion.

The presence of one equivalent of DNB in the reaction of 1-cyano-1-methylethyl radicals with 4-nitro-(1-methoxyethenyl)benzene had no significant effect on the product distribution. This fact confirms the previous observation that the oxidation probably occurs via electron transfer with the para-nitrophenyl group of the reactants or products.

Other electron transfer reagents It was disappointing that the change in R^1 from trimethylsilyl to methyl did not change the reaction product, in the reaction of 1-cyano-1-methylethyl radicals with vinyl ethers, to exclusively the substituted vinyl ether 29. In an attempt to perform this transformation, other electron transfer reagents were used, Table 11. Particular hope was held for organic oxidants which when oxidized could also pick up protons. However, anthraquinone would not oxidize the intermediate radical, DDQ was complicated by the immediate formation of a charge transfer complex and benzoquinone reacted with the 1-cyano-1-methylethyl radical.

In fact, the only electron transfer agent that worked was 2-bromo-2-nitropropane. The fact that it produced the substituted vinyl ether was particularly pleasing. However, it was perplexing that no 2-nitro-propan-2-yl radicals were trapped by the vinyl ether. It is known that 2-bromo-2-nitropropane radical anions decompose to give 2-nitropropan-2-yl radicals which then react with nucleophiles. However, the 2-nitropropan-2-yl radical has never been directly observed and these data suggest that the radical anion may react with nucleophiles by a $S_{RN}2$ mechanism rather than a $S_{RN}1$ mechanism. Alternatively, the reaction of 2-bromo-2-nitropropane may induce bromine atom transfer followed by dehybrobromination of the unstable α-bromo benzyl ether.

It is also perplexing that no other aromatic nitro compounds would oxidize the intermediate radical. This is

Table 11. Percent yield of the products of the reaction of 1-cyano-1-methylethyl radicals with (1-methoxyethenyl)benzene in DMSO at 69 + 1 °C for 24 hours, in the presence of three equivalents of electron transfer reagents[a]

oxidant	28	29	30	31	32[b]
2-bromo-2-nitro propane	4	61	-	3	3
nitrobenzene	5	8	8	50	3
nitromethane	5	12	6	48	5
1,5-dinitro napthalene	2	4	6	56	3
DDQ[c,d]	-	-	-	trace	-
4-chloronitro benzene	3	2	4	48	4
benzoquinone[e]	-	-	-	10	-
anthraquinone	6	2	8	55	6
persulphate	6	4	8	58	7
nitrobenzene[f]	trace	trace	-	trace	15
nitromethane[f]	6	9	5	51	4

[a] Mass balance for the reaction exceeds 90% in all cases with the unreported mass belonging to the unreacted (1-methoxyethenyl)benzene.

[b] X = H.

[c] Dicyanodichlorobenzoquinone.

[d] A purple charge transfer complex was formed.

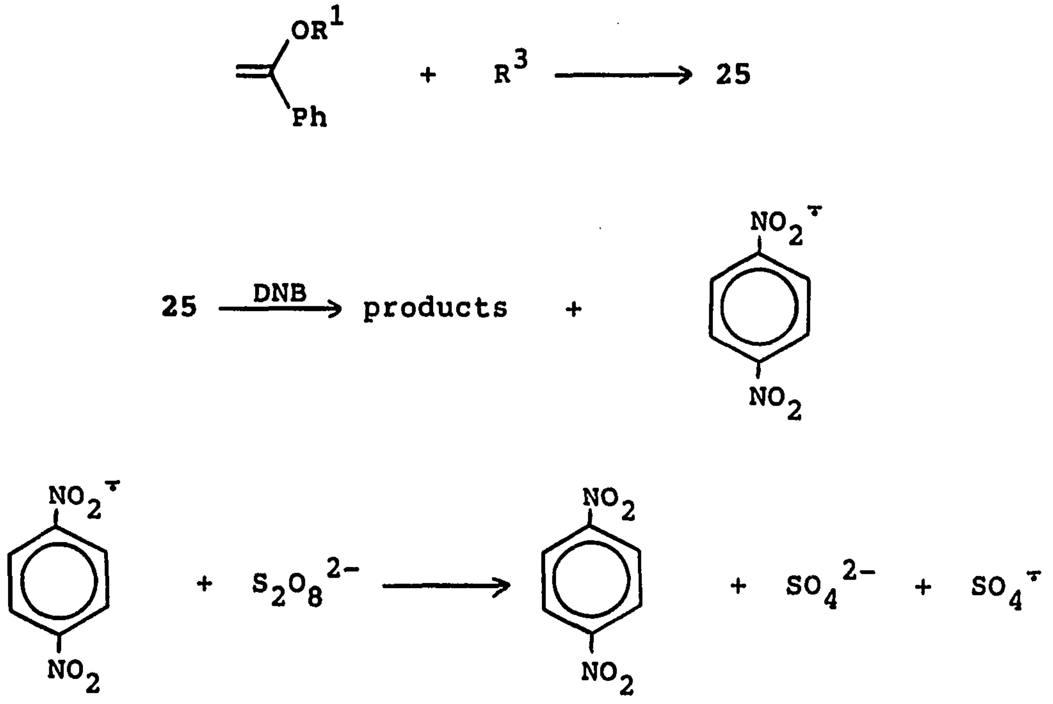
[e] Poor reaction due to the 1-cyano-1-methylethyl radicals reacting with the oxidant.

[f] As the solvent.

confusing since most aromatic nitro compounds have similar reduction potentials. In particular, nitrobenzene and 4-chloronitrobenzene have been shown by Steenken to oxidize α-hydroxyalkyl radicals.

In an attempt to use less of the expensive DNB, catalytic amounts of DNB with three equivalents of sodium persulphate were used in the hope that once the inner sphere electron transfer complex **26** had dissociated, the persulphate anion would oxidize the dinitrobenzene radical anion, Scheme XXIX. However, little effect was observed. This supports the previously discussed observation that as the inner sphere

Scheme XXIX R^1 = Me R^3 = $(CH_3)_2C(CN)$



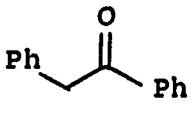
electron transfer complex dissociates that the leaving group bonds to the nitro group of the departing para-dinitrobenzene radical anion. This would the prohibit oxidation by the stronger persulphate to regenerate the DNB.

Reactions of Vinyl Ethers with Phenylazotriphenylmethane

In an attempt to extend the reaction to less electrophilic radicals, phenyl radicals were prepared by the thermolysis of phenylazotriphenylmethane (PAT). This particular system also produces the triphenylmethyl radical which may oxidize the intermediate radical produced by the attack of phenyl radicals on the vinyl ethers.

Thermolysis of PAT in the presence of trimethyl[(1-phenylethenyl)oxy]silane

Trimethyl[(1-phenylethenyl)oxy]silane (0.67 M) reacts with phenyl radicals, generated from the thermolysis of PAT at 40 + 1 °C, in various solvents to produce acetophenone (34), deoxybenzoin (35), E and Z trimethyl[(1,2-diphenylethenyl)-oxy]silane (36), triphenylmethane (90-100% in all cases), biphenyl (5-10%) and traces of benzophenone in poor to moderate yield, Table 12. Mass balances based on the vinyl ether were better than 90% with the remainder of the unreported mass belonging to the unreacted vinyl ether. The low substituted product yield can be accounted for by the low



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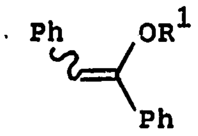

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Table 12. Percent yield of the products of the reaction phenyl radicals with trimethyl[(1-phenylethenyl) oxy]silane at 40 + 1 °C for 24 hours[a]

solvent	34	35	36
DMSO	50	22	7
PhH[b]	10	10	22
THF	21	11	30
tert-butyl alcohol	6	11	44
CH$_3$CN	4	10	25

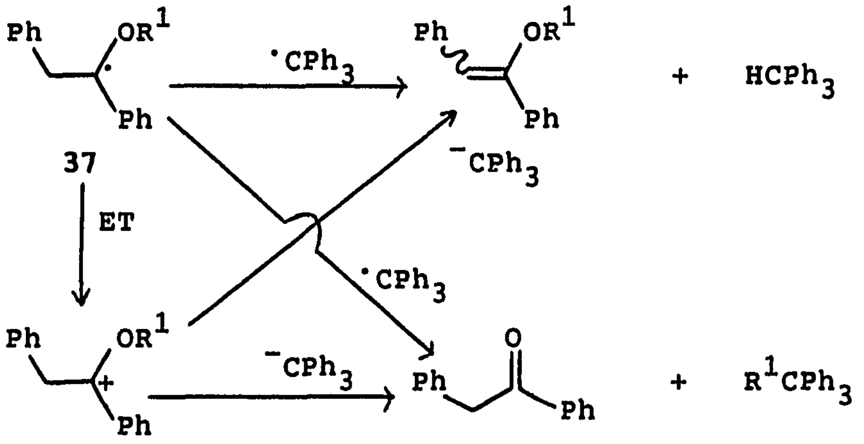
[a] Mass balance for the reaction exceeds 90% in all cases with the unreported mass belonging to unreacted trimethyl[(1-phenylethenyl)oxy]silane.

[b] 60% yield of biphenyl (yield based on PAT).

electrophilicity of the phenyl radical and suggests that only electron acceptor radicals will add effectively to vinyl ethers.

Mechanistically, each of the phenylated products may be formed from the intermediate radical 37 via free radical abstractions or electron transfer to the trityl radical followed by loss of a proton or the trimethylsilyl group, Scheme XXX. The fact that large amounts of acetophenone were

Scheme XXX $R^1 = SiMe_3$



produced in some solvents was perplexing when it was found that all the acetophenone produced could not be accounted for by the hydrolysis of the trimethyl[(1-phenylethenyl)oxy]silane by water in a blank experiment in DMSO. However, it was found that the trimethyl[(1-phenylethenyl)oxy]silane and trimethyl(1,2-diphenylethenyl)oxy]silane are unstable to the dimsyl anion in all solvents and unstable to the trityl anion in DMSO or THF. It was also found that Me_3SiCPh_3 was unstable to sodium triphenylmethane in all solvents. This appears to explain the nearly quantitative yields of triphenylmethane and the lack of formation of Me_3SiCPh_3 even though it is stable in all the solvents and work up conditions employed.

These results suggest that the products are being produced in DMSO or THF by electron transfer. As for other solvents, it could be not be determined if the trimethyl[(1,2-diphenylethenyl)oxy]silane and deoxybenzoin are being formed via hydrogen atom or trimethylsily abstraction or by electron transfer followed by loss of a proton or nucleophilic attack upon the trimethyl silyl group. However it is difficult to imagine that the trityl radical can approach the silicon atom of the trimethyl silyl group close enough to abstract it in a free radical manner. This suggests that a electron transfer mechanism is operating at least for the formation of 35. The formation of 36 could still occur by the electron transfer mechanism or by disproportionation between the adduct radical and the persistent triphenylmethyl radical.

Thermolysis of PAT in the presence of trimethyl[(1-phenylethenyl)oxy]silane and para-dinitrobenzene

Trimethyl[(1-phenylethenyl)oxy]silane (0.67 M) reacts with phenyl radical, generated by the thermolysis of PAT at 40 + 1 °C, in the presence of one equivalent of DNB in various solvents to produce the same products observed in the absence of DNB, but in different ratios, Table 13. A nearly quantitative yield of triphenylmethane were produced in all solvents, along with 5-10% of biphenyl and traces of benzophenone.

Based upon the results with AIBN, the addition of DNB to the reaction should have produced 35 almost exclusively. Indeed, the presence of DNB increased the yield of 35 in all experiments (compare Tables 12 and 13). However, the fact that significant amounts of 36 were also produced suggests

Table 13. Percent yield of the products of the reaction phenyl radicals with trimethyl[(1-phenylethenyl)oxy]silane in the presence of one equivalent of DNB at 40 + 1 °C for 24 hours[a]

solvent	34	35	36
DMSO	35	29	11
PhH[b]	12	21	19
THF	16	35	9
tert-butyl alcohol	20	43	18
CH_3CN	5	26	10

[a] Mass balance for the reaction exceeds 90% in all cases with the unreported mass beloning to unreacted trimethyl[(1-phenylethenyl)oxysilane.

[b] 60% yield of biphenyl (yield based on PAT).

that the persistent triphenylmethyl radical somehow converts the adduct radical 37 to 35, either by electron transfer or by hydrogen atom abstraction and that this process can compete with the reaction of 37 with DNB leading to the desilylated product 35. The fact that acetophenone is produced suggests that the triphenylmethyl radical must be doing some electron transfer since it has already been shown that trimethyl[(1-phenylethenyl)oxy]silane is unstable to the triphenylmethyl anion but stable to the reaction and workup conditions employed.

Thermolysis of PAT in the presence of (1-methoxyethenyl)benzene

The reaction of (1-methoxyethenyl)benzene (0.67 M) with phenyl radicals, generated from the thermolysis of PAT at 40 + 1 °C in DMSO or benzene solvents, produces deoxybenzoin, 35 (2% and 1% respectively), E and Z-(1-methoxy-2-phenylethenyl)benzene, 38 (total yield 44% and 16% respectively), traces of acetophenone, biphenyl (5% and 70% respectively, based on PAT) and nearly quantitative yields of triphenylmethane. Mass balances based on the vinyl ether were better than 90% with the remainder of the unreported mass belonging to unreacted (1-methoxyethenyl)benzene.

As with trimethyl[(1-phenylethenyl)oxy]silane, benzene is a poor solvent for the reaction since the phenyl radical is more prone to attack the solvent to produce biphenyl than it is to attack the vinyl ether. However in DMSO, the change of the R^1 group from trimethylsilyl to methyl increases the yield of phenylated products due to the decrease in the hydrolysis and side reactions of the starting vinyl ether.

Mechanistically, it is believed that, as in the case of the trimethylsilyl vinyl ether, the trityl radical oxidizes the intermediate radical, followed by the nearly quantitative loss of a proton. In an attempt to show that the electron transfer was occurring by an outer sphere mechanism, the mixed solvent system of DMSO/MeOH (14:1 by volume) was used to trap the intermediate cation as the dimethyl ketal. However the only phenylated products observed were 38% of 38 and 3% of 35. This suggests that there must be close contact between the intermediate radical 37 (R =Me) and the trityl radical for the oxidation to occur, followed by the preferential fast abstraction of a proton. However, this observation is also consistent with a hydrogen atom abstraction process in which vinyl ether 38 would be produced.

Thermolysis of PAT in the presence of (1-methoxyethenyl)-benzene and para-dinitrobenzene

The reaction of (1-methoxyethenyl)benzene with phenyl radicals, generated from the thermolysis of PAT at 40 + 1 ^{o}C, in DMSO or DMSO/MeOH (14:1 by volume) in the presence of one equivalent of DNB produced, deoxybenzoin (13% and 15% respectively, (1-methoxy-2-phenylethenyl)benzene (43% and 42% respectively, traces of acetophenone, biphenyl (5% and 6% respectively) and nearly quantitative yields of triphenylmethane. In addition to these products, in DMSO/MeOH, triphenyl methyl ether was produced in significant amounts. Mass balances based on the vinyl ether were better than 90% with the remainder of the unreported mass belonging to unreacted vinyl ether.

Mechanistically, the increase in deoxybezoin indicates that some oxidation by DNB is occurring. The fact that no dimethyl ketal is observed in the mixed solvent of DMSO/MeOH again indicates that this electron transfer proceeds by an inner sphere electron transfer complex. The fact that the ratio of substituted vinyl ether to substituted ketone is not near 1:1 as would be expected from the AIBN studies, again indicates that either a significant amount of oxidation of the intermediate radical is occurring via the trityl radical or that the hydrogen atom abstraction process is much faster than the oxidation by DNB. The significant amount of triphenylmethyl methyl ether indicates that the oxidation of the trityl radical by DNB is also occurring. This produces the triphenylmethyl cation which is subsequently trapped by methanol.

CONCLUSION

The vinyl ethers, trimethyl[(1-phenylethenyl)oxy]silane and (1-methoxyethenyl)benzene react with 1-cyano-1-methylethyl radicals to produce substituted products. Mechanistically, it appears that the intermediate adduct radical may be oxidized by the 1-cyano-1-methylethyl radicals when trimethyl[(1-phenylethenyl)oxy]silane is used but mainly radical-radical coupling is observed when (1-methoxyethenyl)benzenes are used as the substrates.

In the presence of the electron acceptor para-dinitrobenzene, the reactions of both substrates appear to proceed via the oxidation of the intermediate adduct radical to produce mainly substituted ketone in the case of trimethyl[(1-phenylethenyl)oxy]silane or approximately a 1:1 mixture of substituted ketones and substituted vinyl ethers in the case of (1-methoxyethenyl)benzenes.

With DMSO as the solvent and in the presence of methanol the reaction of 1-cyano-1-methylethyl radicals with (1-methoxyethenyl)benzene and in the presence of the electron acceptor para-dinitrobenzene, little dimethyl ketal was produced. This is taken as evidence that the one electron oxidation must be proceeding through an inner sphere electron transfer complex. However, in benzene, the dimethyl ketal was formed suggesting that the mechanism of electron transfer may be solvent dependent.

The vinyl ethers react with phenyl radical to produce phenylated vinyl ether and deoxybenzoin in low to moderate overall yields. Mechanistically, the products appear to be formed by the oxidation of the intermediate adduct radical by the trityl radical (produced simultaneously with the phenyl radical by the thermolysis of PAT). Additions of an electron transfer acceptor, para-dinitrobenzene, increased the yield of deoxybenzoin from the enol silyl ether but had little effect with the methyl vinyl ether. The moderate overall yield of phenylated products indicates that only good electron acceptor radicals such as the 1-cyano-1-methylethyl radical, will add effectively to vinyl ethers.

EXPERIMENTAL

General Considerations

Instrumentation

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra (300 MHz) were recorded on a Nicolet Magnetics Corp. NMC-1280 spectrometer in $CDCl_3$ with the residual nondeuterated solvent peak as the internal chemical shift standard. Infrared spectra (IR) were recorded on a Beckman 4250 spectrophotometer. GC analyses were carried out on a Varian 3700 equipped with a thermal conductivity detector and a Hewlett-Packard 3390A integrator.

Equipment

Thermolyses were carried out in a thermostated mineral oil bath to within 1 °C of the stated temerature while irradiations were carried out 6 inches in front of a 275 W Sylvania sunlamp.

All glassware and syringes were dried at 150 °C for at least 24 hours and then allowed to cool in a desiccator. Disposable syringe needles were used for all solution transfers of less than or equal to 1 mL.

Materials

Purified Davidson 4A molecular sieves purchased from Fisher Scientific were activated by drying, in vacuo, at 230

^{o}C for 16 hours.

Benzene purchased from Fisher Scientific was dried by refluxing with sodium for 14 hours. The dry benzene was then distilled, stored over activated 4A molecular sieves and purged of oxygen by passing argon through the solvent for one hour.

Dimethyl sulfoxide (DMSO), purchased from Fisher Scientific, was purified by refluxing for 16 hours, at 0.5 torr, over calcium hydride. Sodium amide was added just before vacumm distillation (<50 ^{o}C). The DMSO was stored over activated 4A molecular sieves and purged of oxygen by passing argon through the solvent for one hour.

Methanol and tert-butyl alcohol, purchased from Fisher Scientific, was dried by refluxing over cacium hydide for 16 hours. The solvent was then distilled, stored over activated 4A molecular sieves and purged of oxygen by passing argon through the solvent for one hour.

Tetrahydrofuran (THF), purchased from Fisher Scientific, was distilled from litium aluminum hydride. The dry THF was stored over activated 4A molecular sieves and purged of oxygen by passing argon through the solvent for one hour.

Acetonitrile, purchased from Fisher Scientific, was purified by refluxing over anhydrous aluminum chloride for one hour, distilled, refluxed over alkaline potassium permaganate, distilled and then refluxed over calcium hydride for 2 hours.

The acetonitrile was then distilled, stored over activated 4A molecular sieves and purged of oxygen by passing argon through the solvent for one hour.

Unpurified Diisopropyl amine, chlorotrimethylsilane, *para*-methoxyacetophenone, *para*-nitroacetopheneone, *para*-dinitrobenzene, trimethyl orthoformate, bezoquinone, *para*-chloronitrobenzene, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and 1,5-dinitronaphthalene were purchased from Aldrich Chemical Company. Sodium chloride sodium bicarbonate, magnesium sulfate, calcium hydride, sodium persulphate, sodium sulfate and acetophenone were purchased from Fisher Scientific. Nitromethane and anthraquinone were purchased from Eastman Kodak. Alumina was purchased from J. T. Baker Chemical Company while *n*-butyllitium was purchased from Morton Thiokol.

Preparation of Starting Materials

Preparation of trimethyl[(1-phenylethenyl)oxy]silane

Trimethyl[(1-phenylethenyl)oxy]silane was prepared as described by House et al.[63] A dry 500 mL flask, equipped with a magnetic stirrer, addition funnel and an argon line, was charged with 200 mL of dry THF and 145 mL (0.305 moles) of a 2.1 M *n*-butyllithium solution and cooled to -78 °C. The addition funnel was then charged with 44 mL (0.314 moles) of diisopropylamine which was added dropwise, with stirring, to the reaction flask over a period of one hour. Once the addition was complete, the flask was allowed to attain room temperature and then cooled to -78 °C. Into the addition funnel was syringed 35 mL (0.299 moles) of acetophenone which was then added dropwise, with stirring, to the reaction flask over the period of one hour. The flask was then allowed to attain room temperature for one hour and then cooled to -78 °C. The addition funnel was then charged with 45 mL of purified chlorotrimethylsilane (0.355 moles) which was added dropwise, with stirring, over a period of one hour. The reaction mixture was then allowed to stand at room temperature for two hours, cooled to 0 °C, poured into 500 mL of pentane and washed twice with cold saturated sodium bisulphate solution. The organic layer was then dried over sodium sulphate, filtered and the solvent removed under reduced pressure. Vacuum distillation of the residue gave 50 g (87%) of trimethyl[(1-phenylethenyl)oxy]silane as a colorless liquid with a b.p., ^{1}H NMR spectra and mass spectra in good agreement with the literature values.

b.p. 83 °C at 10 torr.

^{1}H NMR ($CDCl_3$) δ 7.61-7.59 (m, 2H), 7.36-7.30 (m, 3H), 4.441 (d, 1H, *J* = 1.8 Hz), 5.043 (d, 1H, *J* = 1.8 Hz), 0.250 (s, 9H).

GCMS, m/e (relative intensity) 192 (36, M^+), 191 (62), 177 (50), 135 (28), 105 (13), 75 (100).

Preparation of (1-methoxyethenyl)benzene

The (1-methoxyethenyl)benzene was prepared by a method adapted from Loudon et al.[64] A 500 mL flask, equipped with a magnetic stirrer, condenser and argon line, was charged with 50 g (0.476 moles) of trimethyl orthoformate, 48 g (0.40 moles) of acetophenone, 0.25 g *para*-toluenesulfonic acid and 200 mL of dry methanol. The contents of the flask were refluxed for 16 hours and then cooled to room temperature. The condenser was replaced with a Vigreux column and the methyl formate, methanol and excess trimethyl orthoformate were distilled. The reaction mixture was then heated to approximately 150 °C and allowed to remain there until methanol was no longer produced. The reaction mixture was cooled and distilled under vacuum to give 37 g (69%) (1-methoxyethenyl)benzene as a colorless liquid with a b.p., ^{1}H NMR spectra and mass spectra in good agreement with the literature values.

b.p. 87-88 °C at 13 torr.

^{1}H NMR δ 7.65-7.25 (m, 5H), 4.650 (d, 1H, *J* = 2.7 Hz), 4.209 (d, 1H, *J* = 2.7 Hz), 3.732 (s, 3H).

GCMS, m/e (relative intensity) 134 (87), 133 (100), 104 (68), 103 (62), 91 (52), 78 (52), 77 (48), 65 (20), 51 (46).

Preparation of para-methoxy(1-methoxyethenyl)benzene

The *para*-methoxy(1-methoxyethenyl)benzene was prepared by a method adapted from Loudon et al.[64] A 500 mL flask, equipped with a magnetic stirrer, condenser and argon line, was charged with 50 g of (0.476 moles) trimethyl orthoformate, 60 g (0.40 moles) of *para*-methoxyacetophenone, 0.25 g *para*-toluenesulfonic acid and 200 mL of dry methanol. The contents of the flask were refluxed for 16 hours and then cooled to room temperature. The condenser was replaced with a Vigreux column and the methyl formate, methanol and excess trimethyl orthoformate were distilled. The reaction mixture was then heated to approximately 150 °C and allowed to remain there until methanol was no longer produced. The reaction mixture was cooled and distilled under vacuum to give 41 g (62%) *para*-methoxy(1-methoxyethenyl)benzene as a clear light yellow liquid with a b.p., ^{1}H NMR spectra and mass spectra in good agreement with the literature values.

b.p. 101-103 °C at 13 torr.

^{1}H NMR δ 7.543 (d, 2H, *J* = 9.0 Hz) 6.849 (d, 2H *J* = 9.0 Hz), 4.540 (d, 1H, *J* = 2.7 Hz), 4.124 (d, 1H, *J* = 2.7 Hz), 3.797 (s, 3H).

GCMS, m/e (relative intensity) 164 (98), 163 (100), 135 (58), 119 (44), 91 (44), 77 (35), 63 (21), 51 (15).

Preparation of para-nitro(1-methoxyethenyl)benzene

The *para*-nitro(1-methoxyethenyl)benzene was prepared by a method adapted from Loudon et al.[64] A 500 mL flask, equipped with a magnetic stirrer, condenser and argon line, was charged with 50 g (0.476 moles) of trimethyl orthoformate, 33 g (0.20 moles) of para-nitroacetophenone, 0.25 g para-toluenesulfonic acid and 200 mL of dry methanol. The contents of the flask were refluxed for 16 hours and then cooled to room temperature. The condenser was replaced with a Vigreux column and the methyl formate, methanol and excess trimethyl orthoformate were distilled. The reaction mixture was then heated to approximately 150 °C and allowed to remain there until methanol was no longer produced. The solution was allowed to cool and solidify. The crude para-nitro(1-methoxyethenyl)benzene was recrystalized from hexane to give 24 g (67%) of a light yellow crystals with a m.p., ^{1}H NMR spectra and mass spectra in good agreement with the literature values.

m.p 83-84 °C.

^{1}H NMR δ 8.172 (d, 2H, J = 9.3 Hz), 7.751 (d, 2H, J = 9.3 Hz), 4.831 (d, 1H, J = 3.3 Hz), 4.413 (d, 1H, J = 3.3 Hz), 3.732 (s, 3H).

GCMS, m/e (relative intensity) 179 (79), 162 (34), 132 (100), 119 (20), 103 (37), 91 (38), 77 (60), 63 (25), 51 (46).

Preparation of 2-methyl-2-nitropropanenitrile

The 2-methyl-2-nitropropanenitrile was prepared as described by Kornblum et al.[57] A 1.0 L flask, equipped with a magnetic stirrer and an argon line, was charged with 3.3 g (0.083 moles) of sodium hydroxide and 25 mL of water. Into the flask was added 2-nitropropane, dropwise with stirring. When the solution had once again turned clear 49 g (0.75

moles) of potassium cyanide dissolved in 130 mL of water and 300 mL of benzene was added to the reaction flask over a period of 1.5 hour. To the resulting mixture was added,with stirring, 63 g (0.19 moles) of potassium ferricyanide dissolved in 160 mL of water over a period of one hour. The aqueous phase was separated from the organic layer and washed twice with 100 mL of ether. The benzene and ether layers were combined, washed with 50 mL of cold water and dried over magnesium sulphate. Removal of the solvent under reduced pressure and recrystallization from hexane afford white crystals with a m.p., ^{1}H NMR spectra and mass spectra in good agreement with the literature values.

m.p. 82-83 ^{o}C.

^{1}H NMR δ 1.995 (s, 6H).

GCMS m/e (relative intensity) 104 (M$^+$, .02), 68 (45), 41 (100).

Procedures

GC analysis

The GC analyses were carried out on a 1/8 in x 10 ft 7% OV-3 on Chromsorb W. A temperature program of 3 min at 120 ^{o}C, 120 to 310 ^{o}C at 15 ^{o}C/min was used for all product analyses. The product yields were determined by use of internal standards and are corrected for molar response for the reactions of the enol silyl ether with the 1-cyano-1-methylethyl radical only. In all other reactions the molar response factors were assumed to be unity.

General work-up procedure

The following work-up procedure was used for all the reactions in this section. The reaction mixture was poured into 30 mL of distilled water. Diphenyl ether (0.020mL, 0.126 mmole) was added as an internal standard. The distilled water was then extracted three times with 30 mL of ethyl ether. The ether extracts were combined and washed once with distilled water and once with saturated sodium chloride solution. The ether layer was the dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was then dissolved in chloroform and analyzed by GC as described above.

Reaction of 2-methyl-2-nitropropanenitrile with vinyl ethers

This procedure was followed for trimethyl[(1-phenylethenyl)oxy]silane and (1-methoxyethenyl)benzene. An 18 x 150 mm test tube was charged with 1 mmole of the vinyl ether, 2 mmoles of 2-methyl-2-nitropropanenitrile and 10 mole % of AIBN and test tube was fitted with a septum. The test tube was purged with argon and 15 mL of DMSO was syringed into the test tube. After the contents of the test tube had dissolved, the test tube was purged with argon for and additional 10 minutes. The test tube was then set up with an argon pressure equalization line, placed in a constant temperature bath at 60 ^{o}C and thermolyzed for 24 hours. After thermolysis, the contents of the test tube were allowed to cool for one hour, worked-up and analyzed as described previously.

Reaction of 2-methyl-2-nitropropanenitrile with vinyl ethers

This procedure was followed for trimethyl[(1-phenylethenyl)oxy]silane and (1-methoxyethenyl)benzene. An 18 x 150 mm test tube was charged with 1 mmole of the vinyl ether, 2 mmoles of 2-methyl-2-nitropropanenitrile and 10 mole % of AIBN and test tube was fitted with a septum. The test tube was purged with argon and 15 mL of DMSO was syringed into the test tube. After the contents of the test tube had dissolved, the test tube was purged with argon for and additional 10 minutes. The test tube was then set up with an argon pressure equalization line, placed in a constant temperature bath at 60 °C and thermolyzed for 24 hours. After thermolysis, the contents of the test tube were allowed to cool for one hour, worked-up and analyzed as described previously.

Reaction of 2-methyl-2-nitropropanenitrile with vinyl ethers

This procedure was followed for trimethyl[(1-phenylethenyl)oxy]silane and (1-methoxyethenyl)benzene. An 18 x 150 mm test tube was charged with 1 mmole of the vinyl ether, 2 mmoles of 2-methyl-2-nitropropanenitrile and 10 mole % of AIBN and test tube was fitted with a septum. The test tube was purged with argon and 15 mL of DMSO was syringed into the test tube. After the contents of the test tube had dissolved, the

test tube was purged with argon for and additional 10 minutes. The test tube was then set up with an argon pressure equalization line, placed in a constant temperature bath at 60 °C and thermolyzed for 24 hours. After thermolysis, the contents of the test tube were allowed to cool for one hour, worked-up and analyzed as described previously.

Reaction of 2-methyl-2-nitropropanenitrile with vinyl ethers in the presence of copper salts.

This procedure was followed for trimethyl[(1-phenylethenyl)oxy]silane and (1-methoxyethenyl)benzene in both acetone and *tert*-butyl alcohol as solvent. An 18 x 150 mm test tube was charged with 1 mmole of the vinyl ether, 2 mmoles of 2-methyl-2-nitropropanenitrile, 0.01 g of cupric chloride and 0.01 g of cuprous chloride and fitted with a septum. The test tube was purged with argon and 15 mL of DMSO was syringed into the test tube. After the contents of the test tube had dissolved, the test tube was purged with argon for and additional 10 minutes. The test tube was then set up with a pressure equalization line, placed 6 inches in front of a 275 W sunlamp and photolyzed for 24 hours. The contents of the test tube were then worked-up and analyzed as described previously.

Reaction of AIBN with vinyl ethers

This procedure was followed for trimethyl[(1-phenylethenyl)oxy]silane, (1-methoxyethenyl)benzene, *para*-methoxy(1-methoxyethenyl)benzene and *para*-nitro(1-methoxyethenyl)-benzene with DMSO, benzene, THF or *tert*-butyl alcohol as solvent. An 18 x 150 mm test tube was charged with 1 mmole of the vinyl ether and 1.5 mmoles of AIBN. The test tube was fitted with a septum, purged with argon and 15 mL of solvent was syringed into the test tube. After the contents of the test tube had dissolved, the test tube was purged with argon for an additional 10 minutes. The test tube was then set up with an argon pressure equalization line, placed in a constant temperature bath at 69 °C and thermolyzed for 24 hours. After thermolysis, the contents of the test tube were allowed to cool for one hour, worked-up and analyzed as described previously.

Reaction of AIBN with vinyl ethers

This procedure was followed for trimethyl[(1-phenylethenyl)oxy]silane, (1-methoxyethenyl)benzene, *para*-methoxy(1-methoxyethenyl)benzene and *para*-nitro(1-methoxyethenyl)-benzene with DMSO, benzene, THF or *tert*-butyl alcohol as solvent. An 18 x 150 mm test tube was charged with 1 mmole of the vinyl ether and 1.5 mmoles of AIBN. The test tube was fitted with a septum, purged with argon and 15 mL of solvent was syringed into the test tube. After the contents of the

test tube had dissolved, the test tube was purged with argon for and additional 10 minutes. The test tube was then set up with an argon pressure equalization line, placed in a constant temperature bath at 69 °C and thermolyzed for 24 hours. After thermolysis, the contents of the test tube were allowed to cool for one hour, worked-up and analyzed as described previously.

Reaction of AIBN with trimethyl[(1-phenylethenyl)oxy]silane in the presence of DABCO

An 18 x 150 mm test tube was charged with 1 mmole of the trimethyl[(1-phenylethenyl)oxy]silane, 1.5 mmoles of AIBN and 5 mmoles of DABCO. The test tube was fitted with a septum, purged with argon and 15 mL of benzene was syringed into the test tube. After the contents of the test tube had dissolved, the test tube was purged with argon for an additional 10 minutes. The test tube was then set up with an argon pressure equalization line, placed in a constant temperature bath at 69 °C and thermolyzed for 24 hours. After thermolysis, the contents of the test tube were allowed to cool for one hour, worked-up and analyzed as described previously.

Reaction of AIBN with vinyl ethers in the presence of para-dinitrobenzene

This procedure was followed for trimethyl[(1-phenylethenyl)oxy]silane, (1-methoxyethenyl)benzene, *para*-methoxy(1-

methoxyethenyl)benzene and para-nitro(1-methoxyethenyl)-benzene with DMSO, benzene, methanol, nitromethane, nitrobenzene, DMSO/methanol or benzene/methanol as solvents. An 18 x 150 mm test tube was charged with 1 mmole of the vinyl ether and 1.5 mmoles of AIBN. The test tube was fitted with a septum, purged with argon and 15 mL of solvent was syringed into the test tube. After the contents of the test tube had dissolved, the test tube was purged with argon for an additional 10 minutes. The test tube was then set up with an argon pressure equalization line, placed in a constant temperature bath at 69 °C and thermolyzed for 24 hours. After thermolysis, the contents of the test tube were allowed to cool for one hour, worked-up and analyzed as described previously.

Reaction of AIBN with (1-methoxyethenyl)benzene in the presence of other electron acceptors

This procedure was followed for the thermolysis of (1-methoxyethenyl)benzene in the presence of 2-bromo-2-nitropropane, nitrobenzene, nitromethane, 1,5-dinitronaphthalene, DDQ, 4-chloronitrobenzene, benzoquinone, anthraquinone and sodium persulphate. An 18 x 150 mm test tube was charged with 1 mmole of (1-methoxyethenyl)benzene, 1.5 mmoles of AIBN and 3 mmoles of the oxidant. The test tube was fitted with a septum, purged with argon and 15 mL of solvent was syringed into the test tube. After the contents of the test tube had dissolved, the test tube was purged with argon for an additional 10 minutes. The test tube was then set up with an argon pressure equalization line, placed in a constant temperature bath at 69 °C and thermolyzed for 24 hours. After thermolysis, the contents of the test tube were allowed to cool for one hour, worked-up and analyzed as described previously.

Reaction of AIBN with (1-methoxyethenyl)benzene in the presence of sodium persulphate and a catalytic amount of para-dinitrobenzene

An 18 x 150 mm test tube was charged with 1 mmole of (1-methoxyethenyl)benzene, 1.5 mmoles of AIBN, 0.1 mmole DNB and 3 mmoles of sodium persulphate. The test tube was fitted with a septum, purged with argon and 15 mL of DMSO was syringed into the test tube. After the contents of the test tube had dissolved, the test tube was purged with argon for an additional 10 minutes. The test tube was then set up with an argon pressure equalization line, placed in a constant temperature bath at 69 °C and thermolyzed for 24 hours. After thermolysis, the contents of the test tube were allowed to cool for one hour, worked-up and analyzed as described previously.

Reaction of PAT with vinyl ethers

This procedure was followed for trimethyl[(1-phenylethenyl)oxy]silane and (1-methoxyethenyl)benzene with DMSO, benzene, THF, acetonitrile or *tert*-butyl alcohol as solvent. An 18 x 150 mm test tube was charged with 1 mmole of the vinyl ether and 1.5 mmoles of AIBN. The test tube was fitted with a septum, purged with argon and 15 mL of solvent was syringed into the test tube. After the contents of the test tube had dissolved, the test tube was purged with argon for an additional 10 minutes. The test tube was then set up with an argon pressure equalization line, placed in a constant temperature bath at 40 °C and thermolyzed for 24 hours. After thermolysis, the contents of the test tube were allowed to cool for one hour, worked-up and analyzed as described previously.

Reaction of PAT with vinyl ethers in the presence of para-dinitrobenzene

This procedure was followed for trimethyl[(1-phenylethenyl)oxy]silane and (1-methoxyethenyl)benzene DMSO, benzene or DMSO/methanol as solvent. An 18 x 150 mm test tube was charged with 1 mmole of the vinyl ether and 1.5 mmoles of AIBN. The test tube was fitted with a septum, purged with argon and 15 mL of solvent was syringed into the test tube. After the contents of the test tube had dissolved, the test tube was purged with argon for an additional 10 minutes. The test tube was then set up with an argon pressure equalization line, placed in a constant temperature bath at 40 °C and thermolyzed for 24 hours. After thermolysis, the contents of the test tube were allowed to cool for one hour, worked-up and analyzed as described previously.

Isolation and Assignment of the Products

The products of the previous reactions were all assigned with GCMS, Tables 14 and 15. In addition, the products of the reaction of the 2-cyano-2-propyl and phenyl radical with trimethyl[(1-phenylethenyl)oxy]silane were also identified by ^{1}H NMR Table 14. In the cases where the product was also assigned by ^{1}H NMR, the products of the reaction were isolated from scaled-up reactions (10 - 20 times) and isolated by separation on an alumina column using a solvent system of hexane(90%)/ethyl acetate(10%). The two major products from the reaction of radicals with trimethyl[(1-phenylethenyl)oxy]silane that were not isolated were the substituted enol silyl ethers 14, and 35. However, after column chromatography these products were always observed as the substituted ketones 13 and 34 respectively. Products 15 and 16, being unreported to date, were also identified by G.C. exact mass.

Product 15; Calculated mass 254.14192, measured mass 254.14339, error -5.8 ppm

Product 16 (observed as the $M^{+} - CH_3$ ion); Calculated mass 313.17363, measured mass 313.17493, error +4.2 ppm

Table 14. ^{1}H NMR and GCMS data for the products of the reaction between trimethyl[(1-phenylethenyl)oxy]silane and 1-cyano-1-methylethyl or phenyl radicals

product	GCMS m/e (relative intensity)	^{1}H NMR[a] δ ppm
13	187 (M^+, 5), 120 (13), 105 (100), 77 (39), 51 (19)	7.930-7.920 (m, 2H), 7.480-7.465 (m, 3H), 3.240 (s, 2H), 1.537 (s, 6H)
14	259 (M^+, 7), 244 (40), 217 (14), 191 (13), 154 (25), 73 (100)	7.930-7.920 (m, 2H), 7.480-7.465 (m, 3H), 3.240 (*s*, 2H), 1.537 (s, 6H)[b]
15	254 (M^+, 0.11), 187(100), 172 (14), 129 (50), 115 (7)	7.959 (d, 2H, *J* = 8.4 Hz), 7.586 (d, 2H, *J* = 8.4 Hz), 3.224 (s, 2H), 1.743 (s, 6H), 1.537 (s, 6H)
16	313 (M^+ - 15, 7), 260 (73), 244 (19), 105 (100), 100 (17), 84 (12), 75 (32), 73 (53)	7.600-7.500 (m, 2H), 7.450-7.300 (m, 2H), 2.664 (d, 1H, *J* = 15 Hz), 2.447 (d, 1H, *J* = 15 Hz), 1.350 (s, 3H), 1.286 (s, 3H), 1.228 (s, 3H), 1.078 (s, 3H), 0.444 (s, 9H)
22	188[c] (M^+ - 68, 57), 105 (100), 77 (24)	7.400-7.200 (m, 5H), 7.016 (broad, 1H), 2.660 (s, 1H), 2.592 (s, 1H), 1.299 (s, 3H), 1.225 (s, 3H), 1.181 (s, 3H), 0.745 (s, 3H)

[a] $CDCl_3$ solutions.

[b] 14 was isolated as the substituted ketone 13.

[c] A CI experiment with methane as the inert gas shows the M^+ + 1 peak as 257.

Table 14. continued.

product	GCMS m/e (relative intensity)	^{1}H NMR[a] δ ppm
34	196 (M^+, 3), 105 (100), 91 (5), 77 (34), 51 (9)	8.200-7.200 (m, 10H), 4.288 (s, 2H)
35	269 (M+, 22), 268(100), 253 (27), 235 (20), 178 (25), 177 (26), 118 (15), 73 (82)	8.200-7.200 (m, 10H), 4.288 (s, 2H)[d]

---

[d] 35 was isolated as the substituted ketone 34.

Table 15. GCMS data for the product of the reaction of 1-cyano-1-methylethyl or phenyl radicals with *para*-subtituted (1-methoxyethenyl)benzenes.

product	X	GCMS m/e (relative intensity)
27	OMe	217 (M^+, 9), 150 (13), 135 (100), 107 (6), 92 (8), 77 (15)
27	NO_2	232 (M+, 1), 215 (4), 165 (36), 150 (100), 104 (23), 96 (19)
28	H	201 (M^+, 23), 186 (100), 154 (20), 105 (14), 94 (16), 77 (32), 51 (15)
28	OMe	231 (M^+, 25), 216 (100), 184 (9), 135 (22), 94 (20), 77 (15)
28	NO_2	246 (M^+, 16), 231 (100), 199 (8), 185 (14), 170 (27), 150 (16), 115 (11)
29	H	203 (M^+, 0.3), 172 (0.2), 121 (100), 105 (5), 91 (10), 77 (12)
29	OMe	233 (M^+, 3), 202 (2), 151 (100), 135 (9)
30	H	255 (M^+ - 15, 0.02), 202 (100), 188 (3), 135 (12), 133 (15), 103 (28), 91(7), 77 (16)
30	OMe	261 (M^+ - 31, 0.11), 232 (100), 164 (31), 163 (36), 135 (12), 133 (18)
30	NO_2	268 (M^+ - 47, 2), 247 (26), 196 (100), 180 (9), 159 (8), 150 (20)

Table 15. continued

product	X	GCMS m/e (relative intensity)
32	H	202 (M^+ - 31, 38), 186 (3), 151 (100), 133 (9), 105 (20), 91 (10), 77 (18)
32	OMe	263 (M+, 2), 232 (33), 216 (10), 181 (100), 164 (13), 163 (17), 135 (42), 91 (10), 77 (15)
40	H	210 (M^+, 100), 167 (49), 165 (52), 105 (33), 91 (57), 77 (18), 51 (15)

PART III. LACTONE FORMATION BY THE ADDITION OF FREE RADICALS TO *tert*-BUTYL PEROXY-4-PENTENOATE

INTRODUCTION

General considerations

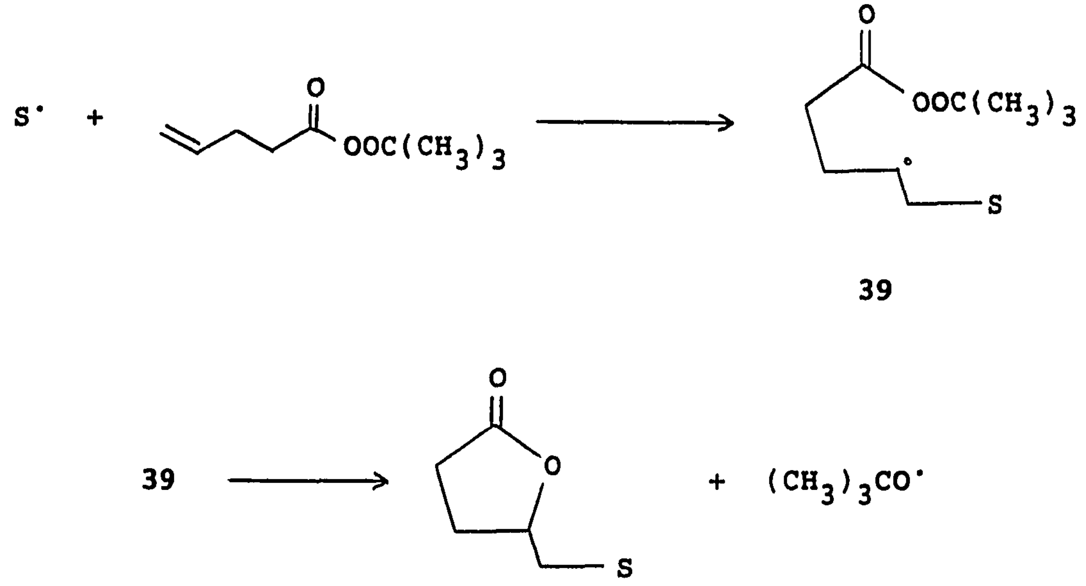
The utility of free radical chemistry has recently blossomed in synthetic organic chemistry. Most free radical syntheses have centered around the formation of 5-membered rings via the cyclization of 5-hexenyl radicals. Based upon the pioneering work of Julia,[65,66] Beckwith[67] and others[68,69] these cyclizations have become prominent in synthetic organic chemistry.[70] In particular, the formation of γ-lactones by free radical methods has become an area of active research because a free radical route provides mild and neutral reaction conditions.

Many free radical methods of producing γ-lactones have focused on preparing a precursor to the γ-lactone via a free radical cyclization followed by a transformation of the precursor to the γ-lactone. Examples of these methods have been reported by Stork et al.,[71] Ladlow and Pattenden[72] and Barton et al.[73] However, most of these methods require transformations that include the same non-neutral and reactive conditions that the free radical cyclization was meant to avoid. However, Heiba et al.[74] and Corey and Kang[75] have recently incorporated lactone formation with non-chain free radical cyclization. Clive and Beaulieu,[76] Kraus and Landgrebe,[77,78] Maillard et al.[79] and Kharrat et al.[80] have demonstrated γ-lactone formation concurrent with free radical chain reactions.

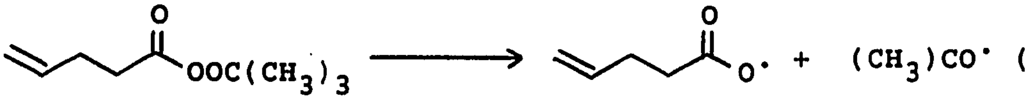
Maillard et als.' work, Scheme XXXI, is interesting in that it generates the γ-lactone in the absence of organometallic reagents or other products which are difficult to separate from the γ-lactone. However, this advantage is

Scheme XXXI SH = solvent

$$SH + (CH_3)_3CO^{\cdot} \longrightarrow S^{\cdot} + (CH_3)_3COH$$



offset by the low yields obtained (35%) due to the thermolysis of the perester at the high reaction temperature used (>130 °C) to initiate the reaction, Equation (21). After the present study, Maillard et al.[81] improved the yields significantly (65-75%) by the use of initiators that thermally decompose at 80 °C. However, the reaction also suffers from the restriction that the substrate (SH) should have only one



(21)

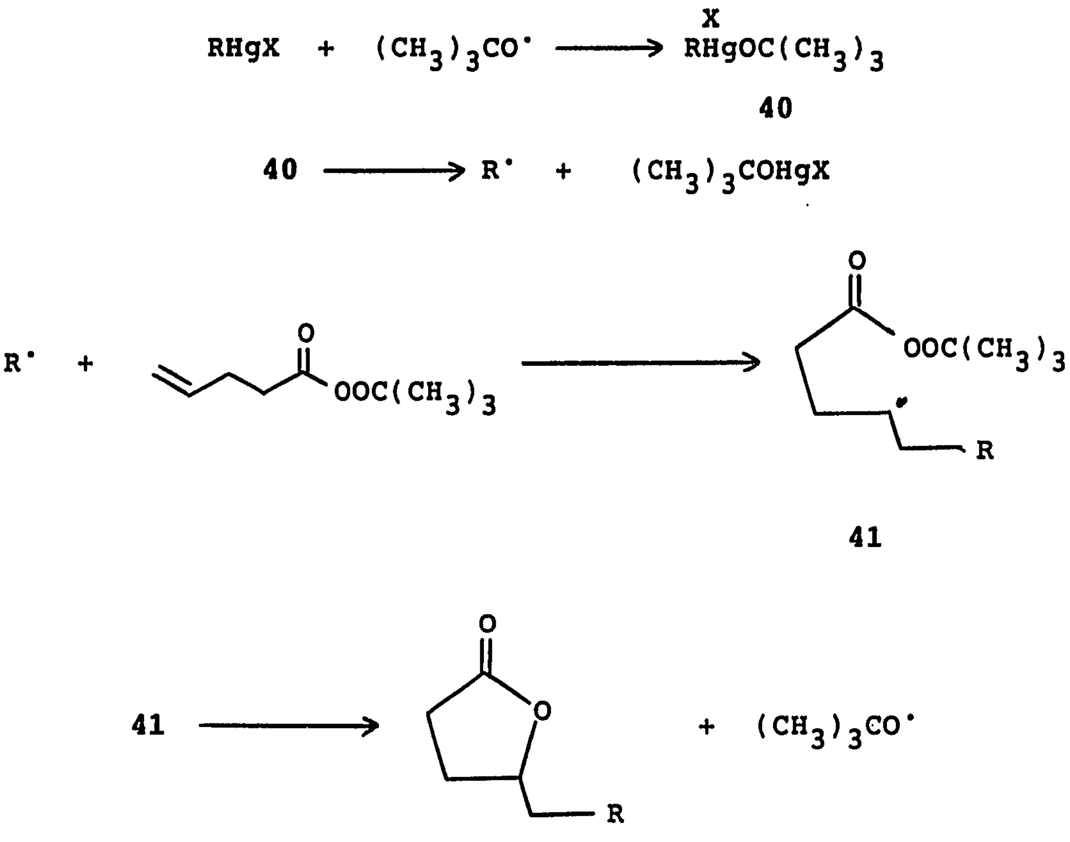
easily abstractable proton and may provide complications in more complex systems due to the reactivity of the tert-butoxy radical.

Statement of Research Problem

Russell and Khanna[82] have made the observation that the tert-butoxy radical will attack alkylmercury halides to release an alkyl radical. In light of Maillard's work, this may be used to generate alkyl radicals and generate the free radical chain sequence depicted in Scheme XXXII. This would eliminate the restriction of the use of substrates with easily abstractable hydrogen atoms and extend the reaction to previously unobtainable alkyl groups. Additionally, dialkylmercurials might be used in a chain sequence in which the tert-butoxy radical abstracts a β-hydrogen atom from the dialkylmercurial to release an alkene, Hg^o and an alkyl radical (reminiscent of Kochi's mechanism for the reaction of carbon tetrachloride with dialkylmercurials). The fact that these synthesis use organometallics is inconsequential since the mercury compounds may be removed by washing with aqueous thiosulphate or as Hg^o.

Phosphites and phosphines have been documented to react with alkoxy radicals to produce alkyl radicals by Walling

Scheme XXXII



$$RHgX + (CH_3)_3CO^{\cdot} \longrightarrow R\overset{X}{Hg}OC(CH_3)_3$$

40

$$40 \longrightarrow R^{\cdot} + (CH_3)_3COHgX$$

41

41

42

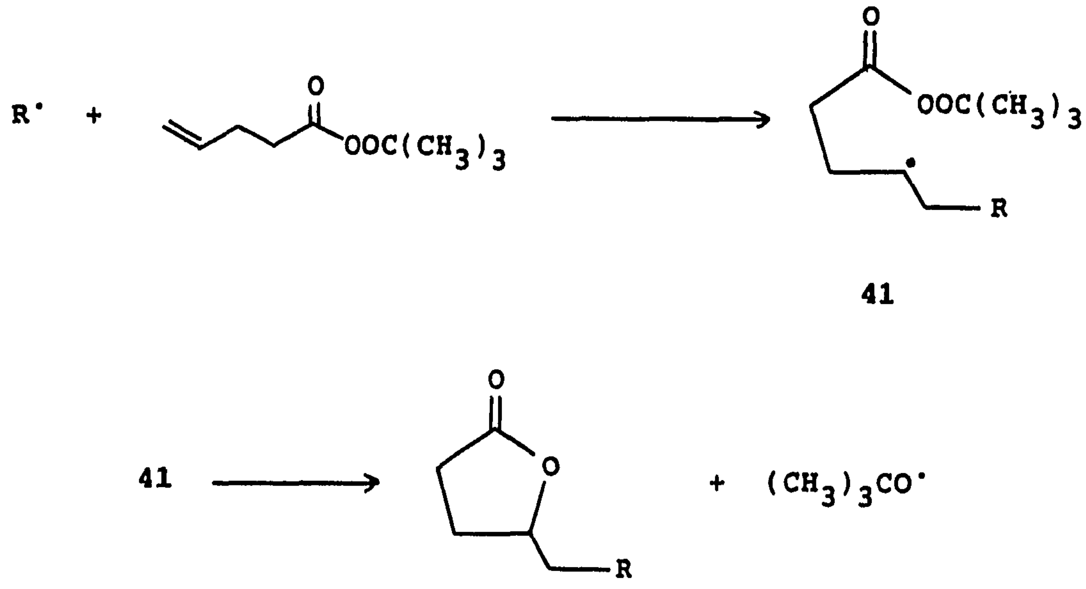
$+ (CH_3)_3CO^{\cdot}$

and Pearson,[83] Buckler,[84] Plumb et al.,[85] Cadogan[86] and Bentrude,[87,88] Equation (22), and may also be able to participate in the free radical chain mechanism, Scheme XXXIII.

$$R_3P + R^1O^{\cdot} \longrightarrow [R_3POR^1] \longrightarrow R_3PO + R^{1\cdot} \qquad (22)$$

With this background, we hoped to synthesize substituted γ-lactones of structure 42 by the reaction of alkyl radicals with tert-butyl peroxy-4-pentenoate in chain mechanisms initiated by the photolytic decomposition of the organomercurial or alkyl peroxides.

Scheme XXXIII $R = (CH_3)_3C$



41

42

$$R_3P + (CH_3)_3CO^{\cdot} \longrightarrow R_3PO + R^{\cdot}$$

RESULTS AND DISCUSSION

Reaction of Alkylmercurials with

tert-butyl peroxy-4-pentenoate

Reaction of alkylmercury chlorides with tert-butyl peroxy-4-pentenoate

Tert-butyl peroxy-4-pentenoate (0.1 M) reacts with 2 equivalents of tert-butylmercury chloride, in benzene or DMSO at 25 °C, under sunlamp photolysis to give 47% and 48% yields of dihydro-5-(2,2-dimethylpropyl)-2(3H)-furanone, 42 (R = tert-butyl), in 15 and 6 hours respectively. The reaction is inhibited by 14 mole % di-tert-butyl nitroxide for about 30 minutes, Figure 6. In the dark, the reaction produces only 1% of 42 (R = tert-butyl) after 24 hours. Isopropylmercury chloride and n-butylmercury chloride react similarly, in DMSO, to give 46% and 43% yields of dihydro-5-(2-methylpropyl)-2(3H)-furanone, 42 (R = isopropyl), and dihydro-5-pentyl-2(3H)-furanone, 42 (R = n-butyl).

Initial rate studies with tert-butylmercury chloride,in DMSO, indicate that 42 (R = tert-butyl) is produced at a rate 6 times the rate of initiation as measured by di-tert-butyl nitroxide product inhibition, Figure 6. Although the chain is not efficient, the reaction appears to proceed by the mechanism depicted in Scheme XXXII. This supports the observation by Russell and Khanna that the tert-butoxy radical will attack alkylmercury halides and release alkyl

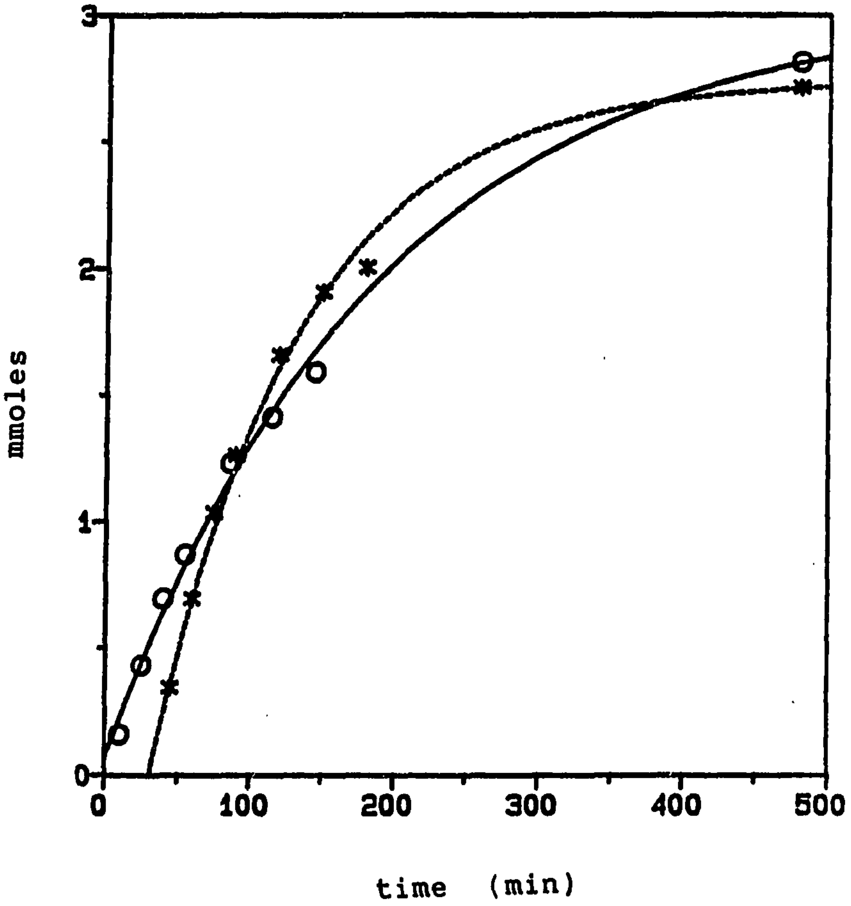


Figure 6. Reaction of tert-butylmercury chloride,0.2 M (10 mmoles) with tert-butyl peroxy-4-pentenoate, 0.1M (5 mmoles), to produce dihydro-5-(2,2-dimethyl propyl)-2(3H)- furanone in the presence (stars) and absence of di-tert-butyl nitroxide 0.014 M (circles)

radical. The inefficiency of the chain may be a result of the reactivity of the *tert*-butoxy radical which can abstract hydrogen atoms from the solvent or from the carbons adjacent to the double bond or carbonyl in the perester. To reduce the possibility of hydrogen atom abstraction from the solvent, benzene was used as a solvent. However, initial rate studies in benzene with *tert*-butylmercury chloride indicated that 42 (R = *tert*-butyl) is produced at a rate only 2 times the rate of initiation as measured by di-*tert*-butyl nitroxide product inhibition. This decrease in the initial chain length probably reflects the inability of benzene to support the highly polar intermediate/transition state 40 (R =*tert*-butyl).

The yields with all three alkylmercury chlorides are suspiciously close to 50% and cannot be increased by an increase in the alkylmercurial concentration. This suggests that there are other non-productive reactions which consume *tert*-butyl peroxy-4-pentenoate. There are two possibilities that could account for this. First, the primary source of initiation may be the photolytic cleavage of the oxygen-oxygen bond in the perester. But, the observed kinetic chain length indicates that 6 molecules of 42 are produced for every *tert*-butoxy radical produced by any source of initiation and thus would not be expected to limit the reaction to a 50% yield.

The second possibility is that the tert-butoxymercury chloride (produced by the attack of tert-butoxy radicals on the alkylmercury chloride), containing a very electrophilic mercury atom, may add across the double bond of tert-butyl peroxy-4-pentenoate, effectively halving the amount of perester leading to 42. Attempts to verify this possibility by NMR have not been successful and still leave this as a matter for conjecture.

Reaction of di-tert-butylmercury with tert-butyl peroxy-4-pentenoate

Tert-butyl peroxy-4-pentenoate (0.1 M) reacts with 2 equivalents of di-tert-butylmercury, in DMSO at 25 °C, under sunlamp photolysis to produce 42 (R = tert-butyl) in a 67% yield in 2.5 hours. The reaction is inhibited by 10 mole % di-tert-butyl nitroxide for approximately 20 minutes and in the dark produces only 2% of 42 after 24 hours.

Though a kinetic analysis of the system has not been performed, the reaction appears to be best described by the chain mechanism in which the tert-butoxy radical abstracts a β-hydrogen from the di-tert-butylmercury. The fact that the reaction proceeds faster, with only a slight increase in the initiation rate, with di-tert-butylmercury than with tert-butylmercury chloride, qualitatively supports this conclusion. Although a mechanism in which the tert-butoxy radical attacks di-tert-butylmercury at the mercury atom, Equation 23 and 24,

$$((CH_3)_3C)_2HgOC(CH_3)_3 \longrightarrow \underset{\textbf{43}}{((CH_3)_3C)_2HgOC(CH_3)_3} \qquad (23)$$

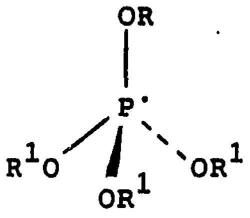
$$\textbf{43} \longrightarrow (CH_3)_3C^{\cdot} + (CH_3)_3CHgOC(CH_3)_3 \qquad (24)$$

cannot be rigorously ruled out, Nugent and Kochi's data and my observations on the β-hydrogen atom abstraction from dialkylmercurials by the trichloromethyl radical indicate that this is an unlikely possibility.

Photolysis of Tert-butyl peroxy-4-pentenoate with Trialkylphosphites

Tert-butyl peroxy-4-pentenoate (0.1 M) reacts with 2 equivalents of tri-tert-butyl phosphite, in benzene at 25 °C, in the presence of 7 mole % of tert-butyl peroxide (as initiator) under 14 hours of sunlamp photolysis to give a 75% yield of 42 (R = tert-butyl). The reaction is inhibited by 9 mole % of di-tert-butyl nitroxide and, in the dark, produces only 3% of 42 after 24 hours. Tri-methyl phosphite reacts with tert-butyl ester of 4-penteneperoxoic acid under similar conditions to give a 76% yield of 42.

The only mechanism that supports these results is the free radical mechanism depicted in Scheme XXXIII. At first glance, it would seem that this is a useless reaction because the structure of R in structure 42 is restricted to tert-butyl. However, Bentrude[87] has shown that the attack of alkoxy radical on trialkyl phosphites produces an intermediate of structure 44. This phosphoranyl radical then decomposes to give alkyl radicals in statistical proportions determined by the alkyl radicals relative stabilities and number in the phosphoranyl radical. This suggests that if a 4-perpentenoate that will release an alkoxy radical with an alkyl fragment that leads to an unstable radical is used in the system, variation of the R group of the γ-lactone 42 may be achieved by varying the structure of the trialkyl phosphite used. Unfortunately, peresters with primary and secondary alkyl groups are unstable and not readily available.



44

CONCLUSION

Alkyl radicals will attack the double bond of _tert_-butyl peroxy-4-pentenoate to give an adduct radical which will cyclize to form γ-lactones in moderate to good yields. The _tert_-butoxy radical released by the cyclization will propagate the chain reaction by attacking alkylmercury halides or dialkylmercurials to release an alkyl radical. In the reaction of alkylmercury chlorides with _tert_-butyl peroxy-4-pentenoate, there appears to be a consumption of two equivalents of perester per equivalent of the γ-lactone produced. The reason for this apparent consumption is still a matter of conjecture but, may be a result of an electrophilic attack of _tert_-butoxymercury chloride upon a second mole of the perester.

Phosphites have been shown to participate in a chain reaction with _tert_-butyl peroxy-4-pentenoate to produce dihydro-5-(2,2-dimethylpropyl)-2(3H)-furanone. With _tert_-butyl esters, this reaction is restricted by the propagation steps to the production of only _tert_-butyl radicals. However, variation of the alkoxy fragment of the peroxy-4-pentenoate may provide a synthesis of γ-lactones produced by the attack by other radicals.

EXPERIMENTAL

General Considerations

Instrumentation

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^1H NMR spectra (300 MHz) were recorded on a Nicolet Magnetics Corp. NMC-1280 spectrometer in $CDCl_3$ with the residual nondeuterated solvent peak as the internal chemical shift standard. Infrared spectra (IR) were recorded on a Beckman 4250 spectrophotometer. GC analyses were carried out on a Varian 3700 equipped with a thermal conductivity detector and a Hewlett-Packard 3390A integrator. GC mass spectra were recorded on a Finnegan 4000.

Equipment

Irradiations were carried out 6 inches in front of a 275 W Sylvania sunlamp.

All glassware and syringes were dried at 150 °C for at least 24 hours and then allowed to cool in a desiccator. Disposable syringe needles were used for all solution transfers of less that 5 mL.

Materials

Purified Davidson 4A molecular sieves purchased from Fisher Scientific were activated by drying, in vacuo, at 230 °C for 16 hours.

Benzene purchased from Fisher Scientific was dried by refluxing with sodium for 14 hours. The dry benzene was then distilled, stored over activated 4A molecular sieves and purged of oxygen by passing argon through the solvent for one hour.

Dimethyl sulfoxide (DMSO), purchased form Fisher Scientific, was purified by refluxing for 16 hours, at 0.5 torr, over calcium hydride. Sodium amide was added just before vacumm distillation (<50 ^{o}C). The DMSO was stored over activated 4A molecular sieves and purged of oxygen by passing argon through the solvent for one hour.

Tetrahydrofuran (THF), purchased from Fisher Scientific, was distilled from litium aluminum hydride. The dry THF was stored over activated 4A molecular sieves and purged of oxygen by passing argon through the solvent for one hour.

Tert-butyl alcohol, purchased from Fisher Scientific, was dried by refluxing over cacium hydride for 16 hours. The solvent was then distilled, stored over activated 4A molecular sieves and purged of oxygen by passing argon through the solvent for one hour.

Unpurified Trimethylposphite, 4-pentenoic acid, *tert*-butyl hydroperoxide, di-*tert*-butyl nitroxide, and chloroform-d was purchased from Aldrich Chemical Company. Thionyl chloride, sodium chloride, sodium thiosufate, mercuric chloride and pyridine were purchased from Fisher Scientific.

Phosphorus trichloride and phenyl ether was purchased from Mallinkrodt and Eastman Kodak respectively.

Preparation of Starting Materials

Alkylmercury chlorides

Isopropylmercury, *tert*-butylmercury and *n*-butylmercury chloride were prepared as described in Part I.

Di-tert-butylmercury

Di-*tert*-butylmercury was prepared by a method adapted from Markarova and Nesmeyanov.[40] A 250 mL flask, equipped with a magnetic stirrer, addition funnel and an argon inlet, was charged with 100 mL of dry THF and 21 g (77 mmole) of mercuric chloride and cooled to -78 °C. The addition funnel was charged with 100 ml (0.17 mole) of 2.1 M *tert*-butyllithium. The *tert*-butyllithium was dropped into the reaction flask, with stirring, over a period of one hour, while maintaining the temperature of the solution at -78 °C. After the addition was complete the reaction was allowed to warm to room temperature. Methanol (25 mL) was added to destroy any excess *tert*-butyllithium. The reaction mixture was then poured into 200 mL of cold water and extracted twice with 200 mL portions of water. The ether fractions were combined, dried over sodium sulphate, filtered and the solvent evaporated under reduced pressure. The crude di-*tert*-butylmercury was then recrystallized from pentane to yield 17 g (68%) of white needles with a m.p. in good agreement with literature values; m.p. 37 °C.

Tert-butyl peroxy-4-pentenoate

Tert-butyl peroxy-4-pentenoate was prepared by a method adapted from Maillard et al.[79] A 100 mL flask, equipped with a magnetic stirrer, distillation head and an argon inlet, was charged with 17 g (0.17 mole) of 4-pentenoic acid, 53 g (0.422 mole) of thionyl chloride and three drops of DMF. The mixture was refluxed under an argon atmosphere for one hour and then distilled to yield 14.4 g (71%) of 4-pentenoyl chloride as a colorless liquid, b.p. 115 °C.

A three necked flask, equipped with a magnetic stirrer, an addition funnel and an argon line, was charged with 100 mL of dry THF, 12.6 g (0.140 moles, corrected) of 90% tert-butylhydroperoxide and 12.8 g (0.162 moles) of pyridine and cooled to -10 °C. The addition funnel was then charged with 14 g of the previously prepared 4-pentenoyl chloride. The 4-pentenoyl chloride was added dropwise, with stirring, over a period of 30 minutes while maintaining the temperature of the reaction at -10 °C. The reaction was allowed to warm to room temperature for one hour and was then cooled to -20 °C and added to 100 mL of cold ether. The ether was extracted once with cold 10% aqueous sulfuric acid, once with cold saturated aqueous sodium bicarbonate and once with cold aqueous saturated sodium chloride. The organic layer was then dried over powdered calcium sulfate, filtered and the solvent removed under reduced pressure. The crude tert-butyl ester of 4-penteneperoxoic acid was distilled under vacuum to give 14.2 g (70%) of the pure tert-butyl peroxy-4-pentenoate with a b.p. and ^{1}H NMR spectra in good agreement with literature values.

b.p. 45 °C (1.5 torr).

^{1}H NMR δ 5.88-5.71 (m, 1H), 5.11-4.96 (m, 2H), 2.47-2.35 (m, 4H), 1.29 (s, 9H).

Tri-tert-butyl phosphite

Tri-tert-butyl phosphite was prepared by the method of Mark and Van Wazer.[89] A two-necked 1000 mL flask, equipped with a mechanical strirrer, dropping funnel and an argon line, was charged with 400 mL of anhydrous ether, 95 mL (1.0 mole) of tert-butyl alcohol and 155 mL (1.1 mole) of triethylamine. After the solution had been cooled to -78 °C, a solution of 29 mL (0.33 mole) phosphorus trichloride was added, with stirring, to the reaction flask over a period of one hour. The solution was then allowed to warm to room temperature and stirred for an additional 16 hours. The reaction mixture was then filtered to remove the triethylamine hydrochloride. The mother liquor was evaporated under reduced pressure (at 5 - 15 °C) to yield a light yellow, sweet smelling liquid. The liquid was placed into 200 mL of hexane and cooled to -78 °C to produce white feather-like crystals. The crystals were filtered rapidly and then rapidly removed to a cold flask purged with argon. The crystals then melted at approximately 5 - 6 °C. ^1H NMR showed a mixture consisting of 93% tri-*tert*-butyl phosphite (δ = 1.359) and 7% of tri-*tert*-butyl phosphate (δ = 1.466, m.p = 72 - 73 °C). The corrected yield of tri-*tert*-butyl phosphite was 87%.

Photolysis Reactions of *tert*-butyl peroxy-4-pentenoate

GC analysis

The GC analyses were carried out on a 1/8 in x 10 ft 7% OV-3 on Chromsorb W. A temperature program of 3 min at 120 °C, 120 to 310 °C at 15 °C/min was used for all product analyses. The product yields were determined by use of internal standards and are corrected for molar response of the γ-lactones produced.

General work-up procedure

The following work-up procedure was used for all the reactions in this section. The reaction mixture was poured into 30 mL of distilled water. Diphenyl ether (0.020 mL, 0.126 mmole) was added as an internal standard. The distilled water was then extracted three times with 30 mL of ethyl ether. The ether extracts were combined and washed once with distilled water and once with saturated sodium chloride solution. The ether layer was then dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was then dissolved in chloroform and analyzed by GC as described above.

Typical procedure for the photolysis of tert-butyl peroxy-4-pentenoate in the presence of alkylmercurials

This procedure was followed for *tert*-butylmercury chloride, isopropylmercury chloride, *n*-butylmercury chloride and di-*tert*-butylmercury. An 18 x 150 mm test tube was charged with 1 mmole of *tert*-butyl peroxy-4-pentenoate and 2 mmole of the alkylmercurial and fitted with a septum. The test tube was purged with argon and 10 mL of benzene of DMSO was syringed into the test tube. The test tube was then inverted a few times to mix its components and placed 6 inches in front of a 275 W sunlamp for 24 hours. After photolysis the reaction was worked-up and analyzed as previously described.

Typical procedure for the photolysis of tert-butyl peroxy-4-pentenoate in the presence of trialkylphosphites

This procedure was followed for tri-*tert*-butyl phosphite and trimethyl phosphite. An 18 x 150 mm test tube was charged with 1 mmole of *tert*-butyl peroxy-4-pentenoate, 4 mmole of of the phosphite and 0.1 mmole of di-*tert*-butyl peroxide and fitted with a septum. The test tube was purged with argon and 10 mL of benzene of DMSO was syringed into the test tube. The test tube was then inverted a few times to mix its components and placed 6 inches in front of a 275 W sunlamp for 24 hours. After photolysis the reaction was worked-up and analyzed as previously described.

Kinetic chain length study of the photolysis of tert-butyl peroxy-4-pentenoate in the presence of tert-butylmercury chloride

This procedure was followed with DMSO or benzene as the solvent. A 50 mL volumetric flask, wrapped in aluminum foil, was charged with 10 mmoles of *tert*-butylmercury chloride and 5 mmoles of *tert*-butyl peroxy-4-pentenoate and fitted with a septum. The volumetric flask was purged with argon and 40 mL of the solvent was syinged into the volumetric flask. The volumetric flask was swirled to dissolve its contents and diluted to bring the total volume to 50 mL.

A 50 mL flask was fitted with a septum purged with argon and charged with 23 mL of the previously prepared solution of *tert*-butylmercury chloride and *tert*-butyl ester of 4-pentene-peroxoic acid. The flask was then photolyzed 6 inches in front of a 275 W sunlamp. Aliquots (2 mL) were removed by syringe at predetermined times and added to 10 ml of distilled water containing 0.010 mL of diphenyl ether and the mixture extracted extracted three times with 10 mL of ether. The ether extracts were combined, extracted once with distilled water and once with saturated sodium chloride. The ether layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was dissolved in chloroform and analyzed by GC.

A second 50 mL flask was charged with 0.0198 g (0.137 mmole) of di-*tert*-butyl nitroxide and fitted with a septum. The flask was purged with argon and charged with 23 mL of the previously prepared solution of *tert*-butylmercury chloride and *tert*-butyl ester of 4-penteneperoxoic acid. The flask was then photolyzed 6 inches in front of a 275 W sunlamp. Aliquots (2 mL) were removed by syringe at predetermined time and worked-up and analysed as described in the previous paragragh.

Isolation and Assignment of the Products

The products of the reactions were isolated from reaction employing 25-50 mmole of the perester and isolated on an alumina column using a solvent system of hexane (90%) - ethyl acetate (10%). All lactones were assigned structures based on the ^{1}H NMR and GCMS in Table 16. Dihydro-5-pentyl-2(3H)-furanone and dihydro-5-(2-methylpropyl)-2(3H)-furanone have been sythesized before. The most recent stereospecific preparations have been by Cardellach et al.[90] and Snider and Johnston[91] respectively. As there has been no previous report of dihydro-5-(2,2-dimethylpropyl-2(3H)-furanone in the literature, it was also characterized by G.C. exact mass spectrometry; calculated mass = 156.11503, measured mass =

156.11517, error = +0.9ppm.

Table 16. ^1H NMR and GCMS data for the assignment of the dihydro-5-substituted-2(3H)-furanones

substituent	GCMS m/e (relative intensity)	^1H NMR[a] (δ ppm)
$CH_2C(CH_3)_3$	156 (M^+, 0.14), 141 (6), 100 (46), 85 (100), 57 (3), 56 (20)	4.65-4.51 (m, 1H), 2.57-2.45 (m, 2H), 2.38-2.24 (m, 1H), 1.90-1.42 (m, 3H), 0.98 (s, 9H)
$CH_2CH(CH_3)_2$	142 (M^+, 0.33), 127 (1), 100 (2), 85 (100), 57 (10), 56 (13)	4.61-4.49 (m, 1H), 2.55-2.45 (m. 2H), 2.37-2.24 (m, 1H), 1.89-1.60 (m, 3H), 1.44-1.32 (m, 1H), 0.97-0.87 (m, 6H)
$CH_2(CH_2)_3CH_3$	156 (M^+, 0.33), 138 (2), 128 (4), 114 (4), 100 (5), 85 (100), 57 (7), 56 (10), 55 (10)	4.53-4.38 (m, 1H), 2.56-2.44 (m, 2H), 2.36-2.23 (m, 1H), 1.91-1.19 (m, 9H), 0.91-0.83 (t, 3H, *J* = 6.3 Hz)

[a] $CDCl_3$ solutions.

GENERAL SUMMARY

Part I of this dissertation presents data on the formation of isopropyldichloro and isopropyldiiodomercurates and the subsequent reaction of the isopropyldiiodomercurate with bromotrichloromethane. A solution composed of approximately 55% mercurate (the rest being uncomplexed isopropylmercury iodide) reacts in a two stage process. The first stage is a fast dark reaction believed to be a long free radical chain (initial kinetic chain length > 38,000) in which the trichloromethyl radical (produced by the abstraction of a bromine atom from bromotrichlormethane) is reduced by the mercurate to produce a tricoordinate mercury species which decomposes to give an isopropyl radical and mercuric iodide. The second stage of the reaction is less clear and may be the photolytic decomposition of isopropylmercury iodide that remains in solution after the fast dark reaction or, the reaction of the mercurate as the equilibrium between isopropylmercury iodide and isopropyldiiodomercurate tries to reestablish itself.

Part II of this dissertation presents the reaction of free radicals generated from the thermolysis of AIBN or PAT with vinyl ethers in the presence or absence of added electron acceptors. In the absence of added electron acceptors, the 1-cyano-1-methylethyl radical reacts with vinyl ethers to produce an intermediate radical whose fate is dependent upon the alkyl substituent (R^3) attached to the oxygen atom. In DMSO, THF or tert-butyl alcohol and when R^3 is trimethylsilyl, the intermediate radical appears to be oxidized by another 1-cyano-1-methylethyl radical. In benzene solution the reaction either occurs via a radical-radical coupling or by an oxidation forming a tight ion pair. When R^3 is methyl, in DMSO, THF, benzene or tert-butyl alcohol solvent, the 1-cyano-1-methylethyl radical can no longer oxidize the intermediate radical and the reaction proceeds by a radical-radical coupling.

In the presence of para-dinitrobenzene, the reaction appears to proceed by the formation of an inner sphere electron transfer complex. This complex then disassociates and appears to form a bond with the leaving group of the intermediate radical.

PAT reacts with vinyl ether to give moderate yields of substituted products. The reaction appears to proceed by the oxidation of the intermediate radical (produced from the attack of the phenyl radical on the vinyl ether) by the persistent triphenylmethyl radical. The presence of para-dinitrobenzene did not significantly change the products of the reaction.

Part III of this dissertation present the reaction of free radicals with tert-butyl peroxy-4-pentenoate. Alkylmercury halides react with the perester to form moderate yields (43-48%) of 5-substituted dihydro-2(3H)-furanones. The reaction appears to be complicated by a second reaction that also consumes the perester. Di-*tert*-butylmercury and trialkyl phosphites react with the perester to give better yields (75-86%) of dihydro-5-(2,2-dimethylpropyl)-2(3H)-furanone. All of the reactions are believed to proceed in a free radical chain mechanism.

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