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New five membered ring chemistry

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NEW FIVE MEMBERED RING CHEMISTRY

by

Edward Felix Zaweski

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1959

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INTRODUCTION

Over the past decade a vast amount of work has appeared on the synthesis and reactions of highly unsaturated seven-membered ring compounds. This work has led to a completely new type of chemistry, and to new aromatic and pseudoaromatic ring systems. Although similarly interesting and unusual unsaturated five-membered ring compounds might be imagined, little synthetic work has so far appeared. The purpose of this work is to describe the synthesis and reactions of cyclo-pentene-3,5-dione I. This molecule has, for theoretical reasons, a great deal of interest in its own right and also might serve as a suitable starting material for the prepara-tion of other molecules of theoretical and practical impor-tance.

Cyclopentene-3,5-dione can be considered a potentially useful compound for a number of reasons. First, the only stable, completely unsaturated cyclopentane compounds known are those which are substituted with electron-donating groups (i.e., diazo-cyclopentadiene II,[1] and triphenylphosphonium cyclopentadienylide III[2]). These compounds have so far not proven amenable to further synthetic utilization. Secondly,
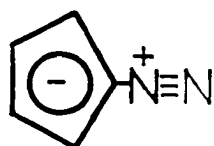

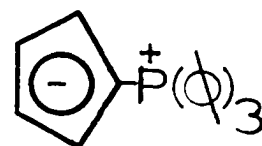[1]W. von E. Doering and C. H. DePuy, J. Am. Chem. Soc., 75, 5955 (1953)

[2]F. Ramirez and S. Levy, J. Am. Chem. Soc., 79, 67 (1957)

$$\text{I} \qquad\qquad \text{II} \qquad\qquad \text{III}$$

monosubstituted cyclopentadienes are susceptible to dimerization and thirdly, the mobility of the protons in a cyclopentadiene ring makes the isolation of the pure isomer difficult.[3,4] These considerations led us to the synthesis of the dione, which contains neither an intact cyclopentadiene ring, nor a completely unsaturated ring but which, because it contains three different kinds of functional groups, and because all of its carbon atoms are potentially reactive, should prove to be an ideal starting material for syntheses in this field.

In addition to cyclopentene-3,5-dione's interest as a synthetic intermediate, it presents the opportunity for investigation of certain problems of theoretical interest. These problems arise primarily because of the relationship it bears to cyclopentadienone IV. In its enol form, cyclopentene-3,5-dione would be a hydroxy-cyclopentadienone V.

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[3] M. Rosenblum, J. Am. Chem. Soc., 79, 3179 (1957)

[4] R. J. Day, Dissertation Abst., 19, 39 (1950)
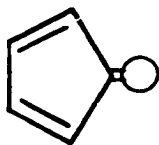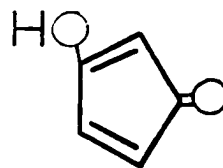
$$\underline{IV} \qquad \underline{I} \qquad \underline{V}$$

Cyclopentadienone itself has never been isolated. The electron-withdrawing effect of the carbonyl oxygen reduces the number of electrons to fewer than the 6π electrons necessary for aromatic character. This matter will be discussed in more detail in the sequel.

HISTORICAL

For the past seventy years very little work has been done on the preparation and reactions of cyclopentendiones. A literature survey reveals that what little has been done has been on halogen, alkyl, and aryl substituted enediones. More information is available on the formally similar indandiones, but the presence of the aromatic ring obscures the picture a great deal.

Wolff,[5] in 1896, claimed the isolation of 4,4-dibromo VII, and 1,4-dibromocyclopentene-3,5-diones VIII. The former was claimed from the treatment of 3,5-dibromolevulinic acid VI with fuming sulfuric acid and the latter by treatment of this same compound with concentrated sulfuric acid. However, work performed in this laboratory[6] has shown that although the elemental analysis is satisfactory, a more favorable structure can be formulated. Infrared analysis shows that both compounds are probably unsaturated lactones instead of ketonic structures.

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[5]L. Wolff and F. Rudel, Ann. Chem., Liebigs, 294, 183 (1896)

[6]C. H. DePuy, P. R. Wells and R. Thurn, Ames, Iowa. Bromination of cyclopentene-3,5-dione. Private communication. 1959
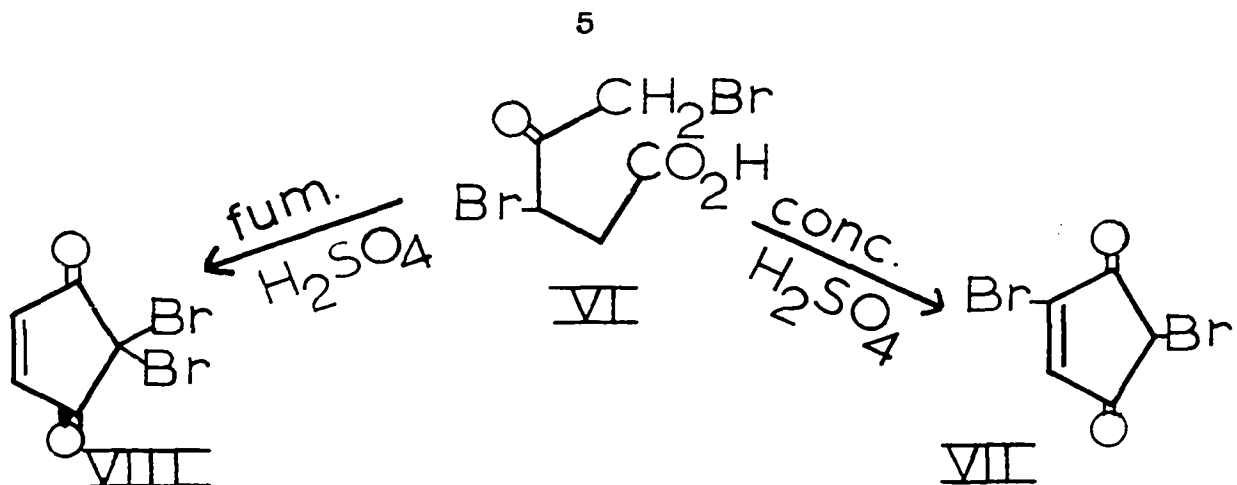
In 1898, Zincke[7] synthesized 1,2-dichlorocyclopentene-
3,5-dione X by the tin-hydrochloric acid reduction of amines
obtained from the reaction of ammonia with hexachloro-2-
cyclopentenone. McBee[8] prepared the same compound by another
method (vide infra).

Henle,[9] in 1907, prepared tetrabromocyclopentene-3,5-
dione XII by treating 3,3,5-tribromocyclopentantrione with
phosphorous pentabromide in benzene. The tetrabromodione
was obtained as yellow prisms (m.p. 142-143°). The same
tetrabromo compound XII was prepared by others.[10,11]

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[7]Th. Zincke and A. Rohde, Ann. Chem., Liebigs, 299, 1317
(1898)

[8]E. T. McBee, C. W. Roberts and K. Dinsbergs, J. Am.
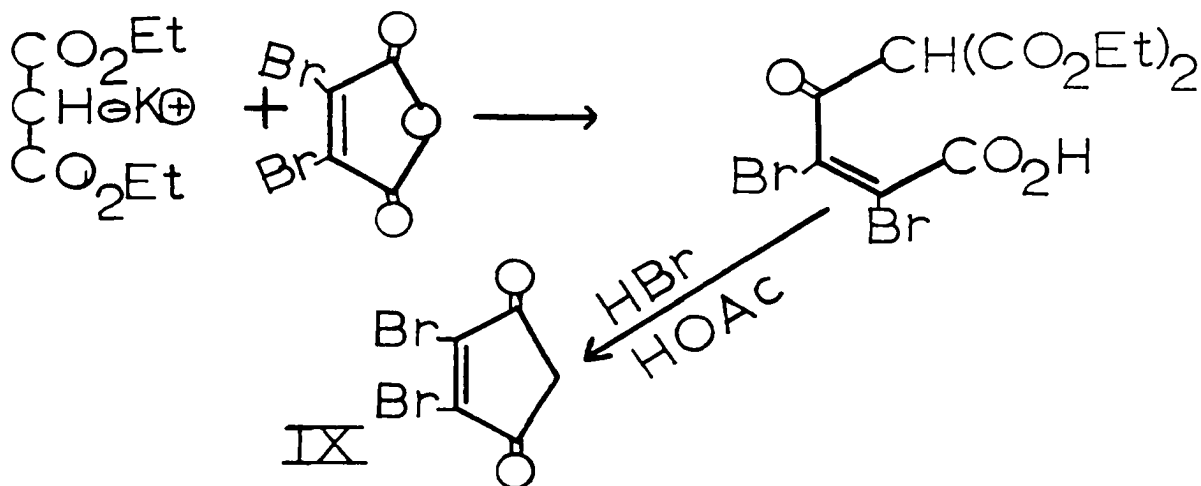Chem. Soc., 78, 489 (1956)

[9]Franz Henle, Ann. Chem., Liebigs, 352, 45 (1907)

[10]C. L. Jackson and H. A. Flint, Am. Chem. J., 43, 135
(1910)

[11]Th. Zincke and Emmy Weishaupt, Ann. Chem., Liebigs,
437, 86 (1924)

Otto Diels[12] obtained 1,2-dibromocyclopentene-3,5-dione

product with bromine in chloroform; he converted it into the known tetrabromo derivative XII, thus supporting the structure of this compound.

The most reliable work on halocyclopentene-3,5-diones appears to be that published by McBee[13] wherein 1,2-dichloro X, 1,2,4,4-tetrachloro XI, 1,2,4,4-tetrabromo XII, and 1-chloro-2-bromocyclopentene-3,5-diones XIII were formed by the following series of reactions. The starting material, 1,2,3,3,5,5-hexachloro-4-(dichloromethylene)-cyclopentene[14] was prepared by heating a mixture of hexachloropropene and hexachlorocyclopentadiene at a pot temperature of 218° C

[12]Otto Diels and Martin Reinbeck, Chem. Ber., 43, 129 (1910)

[13]E. T. McBee, C. W. Roberts and K. Dinsbergs, J. Am. Chem. Soc., 78, 489 (1956)

[14]E. T. McBee, H. E. Ungnade, H. Rakoff and K. Dinsbergs, J. Am. Chem. Soc., 77, 4379 (1955)

CCl₂

Structures and labels in the reaction scheme:

Top center structure: CCl_2 (exocyclic), ring with Cl_2, Cl_2, Cl, Cl

Left arrow: $AlBr_3$ / CBr_4

Right arrow: $f\ HNO_3$ / Se

Left structure: CBr_2 (exocyclic), Br_2, Br_2, Cl, Br

Down arrow left: $f\ HNO_3$ / Se

Right structure: CCl_2 (exocyclic), Cl, Cl

Down arrow right: 95% aq. EtOH

Lower-left structure: CBr_2 (exocyclic), Cl, Br

Arrow: 95% aq. EtOH

Structure XIII: Cl, Br — **XIII**

Structure X: Cl, Cl — **X**

Arrows from X: Cl_2 / HOAc and Br_2 / HOAc

Structure XI: Cl_2, Cl, Cl — **XI**

Structure XII: Br_2, Br, Br — **XII**

and distilling the formed tetrachlorethylene to drive the reaction toward completion.

Most of the other reported work has been accomplished on phenylated cyclopentene-3,5-diones. Lampe,[15] in 1913, by reacting cinnamoyl chloride with diethylmalonate in the presence of an ethereal solution of metallic sodium produced compound XIV as the major product and compound XV as a by-product.

COCH=CHφ
CO₂Et

XIV

CO₂Et

XV
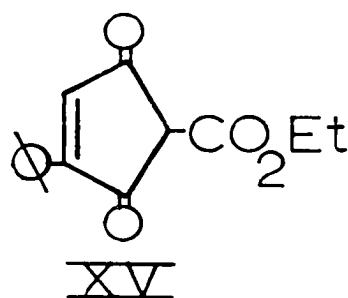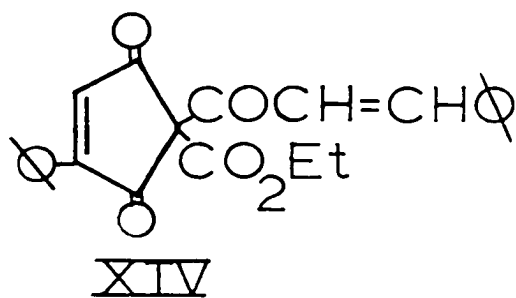
Paul Ruggli[16] obtained 1,4-diphenylcyclopentene-3,5-dione by the hydration of 2,4-diphenyl-5-hydroxy-cyclopentane-1,3-dione, which was obtained by the reduction of 3,5-diphenyl-cyclopentantrione over Rainey Ni in alcohol.

Allen[17] synthesized 1,2,4-triphenylcyclopentene-3,5-dione as yellow plates (m.p. 166°) in a 32% yield by the

[15]V. Lampe and J. Milobedzka, Chem. Ber., 46, 2235 (1913)

[16]Paul Ruggli and Julius Schmidlin, Helv. Chim. Acta, 27, 499 (1924)

[17]C. F. H. Allen, E. E. Massey and R. V. V. Nichols, J. Am. Chem. Soc., 59, 679 (1937)

following series of reactions. Koelsch[18] investigated the enolization and properties of this compound. He observed no
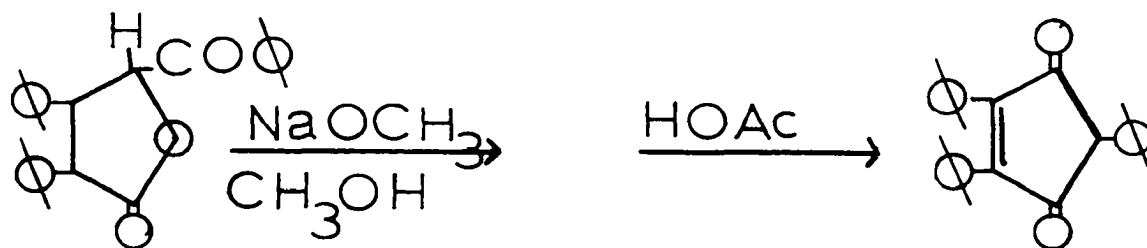
reaction with bromine in chloroform and also reported that the compound dissolved in aqueous base, indicating that the dione was an acid. Acidification regenerated the dione. From these and other observations, Koelsch concluded that compounds containing this nucleus appear to be close to 100% ketonic.

Calythrone XVI was first isolated from Calythrix tetragona by Penfold[19] in 1940. Its structure was elucidated by Birch[20] in 1951 as being a β-triketone of structure XVI, containing a cyclopentene-3,5-dione nucleus.

---

[18]C. F. Koelsch and Stanley Wawzonek, J. Org. Chem., 6, 684 (1941)

[19]A. R. Penfold and J. L. Simonsen, J. Chem. Soc., 412 (1940)

[20]Arthur J. Birch, J. Chem. Soc., 3026 (1951)

$$CH_3\text{-}C=C\text{-}CH_3\ \text{ring with two C=O, }\text{-COCH}_2\text{CH(CH}_3)_2$$
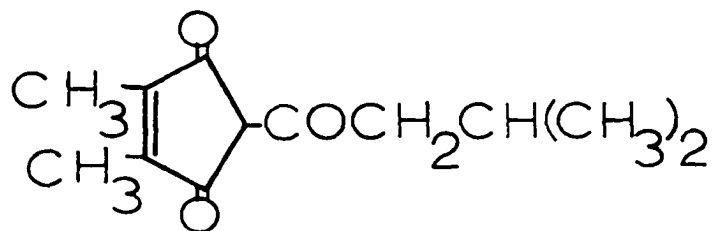
__XVI__

Due to the formal similarity that exists between indane-1,3-dione and cyclopentene-3,5-dione, some of the reactions of the former deserve mention. Wislicenus,[21] in 1888, found that indane-1,3-dione on bromination in acetic acid medium produced 2,2-dibromoindane-1,3-dione. He also synthesized the 2-oximino compound by nitrosation with sodium nitrite and sulfuric acid. On heating the dione with benzaldehyde at 120°, Wislicenus[22] isolated 2-benzylidene-indane-1,3-dione. On treatment with phenylhydrazine a retroaldol was observed, the phenylhydrazones of indane-1,3-dione and benzaldehyde being the major products. Similar products were obtained with other aldehydes, but no apparent reaction was observed with ketones.

Even less work has been carried out with cyclopentene-3,4-diones. Wenzlick[23] reported the synthesis of the parent

[21] W. Wislicenus, Ann. Chem., Liebigs, 246, 347 (1888)

[22] W. Wislicenus, Ann. Chem., Liebigs, 252, 7? (1889)

[23] H. W. Wenzlick and W. Sucrow, Chem. Ber., 91, 2727 (1958)

compound in very poor yields (1.1%) by a selenium dioxide oxidation of cyclopent-2-enone. Dane,[24] in 1937, synthesized 2-methylcyclopentene-3,4-dione by the oxidation of 2-methyl-cylopentene-3-one with selenium dioxide. The yields were very much higher than with the unsubstituted cyclopentenone. Almost no work on the properties or reactions of these compounds has so far been published.

[24]Elisabeth Dane, Joseph Schmitt and Curt Rautenstreuch, Ann. Chem., Liebigs, 532, 29 (1937)

DISCUSSION

Because we envisioned cyclopentene-3,5-dione as a useful synthetic intermediate, it was especially desirable that the scheme for its preparation involve readily-available starting materials so that the preparation could be carried out on a moderately large scale. Starting materials available for the synthesis of any cyclopentane derivative are very limited in number, especially those containing more than a single functional group. Cyclopentadiene XVII, readily obtainable in the form of its easily cracked dimer was, at the time of our initial experiments, the only difunctional cyclopentane derivative commercially available. Its availability and inexpensiveness made it a logical starting material.
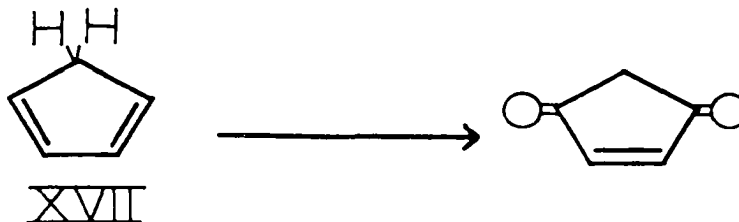
It had recently been shown that low temperature bromination of cyclopentadiene led to the formation, in 20% yield, of crystalline cis-3,5-dibromocyclopentene.[25] The cis isomer was selected so that later experiments would not be complicat-

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[25]W. G. Young, H. K. Hall and S. W. Winstein, J. Am. Chem. Soc., 78, 4338 (1956)

ed by the presence of a mixture of diasteriomers. Later work
(vide infra) shows that the synthesis would have been success-
ful with a mixture of cis and trans isomers. The dibromo
compound was treated with a very reactive nucleophile,
pyridine-N-oxide, to give the O-alkylpyridinium salt XVIII
as shown in Eq. 1. The decomposition of O-alkylpyridinium
salts to carbonyl compounds is a well known reaction[26,27]
which has not found appreciable synthetic utility. Rolih[27]

Eq. 1
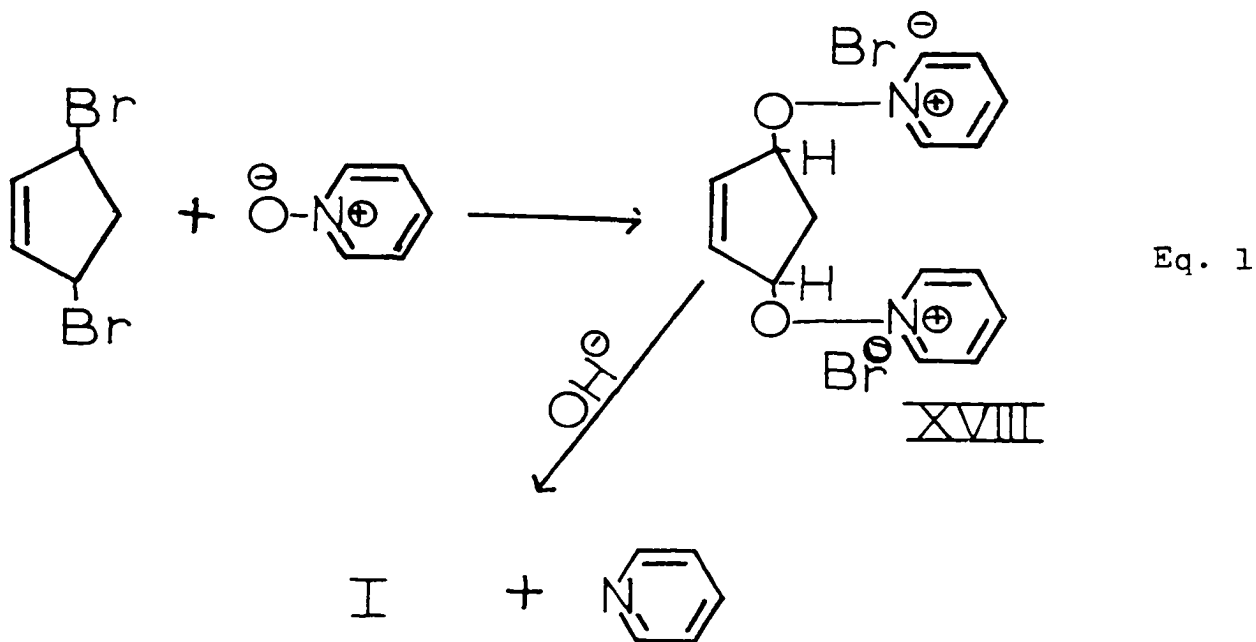
obtained p-nitrobenzaldehyde in 53% yield by heating a 2 to 1

---

[26]E. Ochiai, M. Kotada and T. Naito, J. Pharm. Soc.,
Japan, 64A, 210 (1944)

[27]R. Rolih, Amine Oxides as Oxidizing Agents, Unpublished
Ph.D. Thesis, Ames, Iowa, Library, Iowa State University of
Science and Technology, 1956

mixture of pyridine-N-oxide and p-nitrobenzylbromide at 135°

for 9 hours. A mechanistically similar reaction, which has
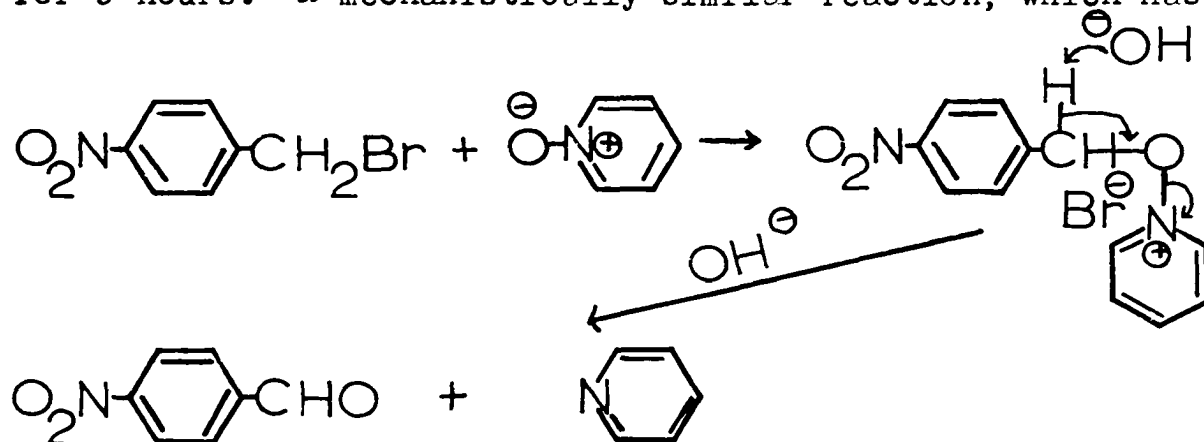
found synthetic use, is that of dimethyl sulfoxide[28] with

halides to form aldehydes.

Decomposition of XVIII with aqueous base led mainly to

a red, presumably polymeric material from which, by continuous

ether extraction, a small amount of white crystalline com-

pound, m.p. 96-98° C, could be isolated. Infrared analysis

(Figure 1 on page 31) showed absorption maxima at 5.60μ and

5.85μ , and analytical and molecular weight determinations

suggested a formula $C_{10}H_8O_2$. The compound was identified as

the dimer of cyclopentadienone XIX by comparison with an

authentic sample[29] prepared by the hydrolysis of the corre-

[28]N. Kornblum, J. W. Powers, J. G. Anderson, W. J. Jones, H. O. Larson, O. Levand and W. M. Weaver, J. Am. Chem. Soc., 79, 6562 (1957)

[29]C. H. DePuy and B. W. Ponder, J. Am. Chem. Soc., 81, 4629 (1959)

sponding dioxime.[30]

The yields of dimeric ketone varied from zero to 13% in a number of runs. One path for its formation is given in Eq. 2. An alternative path which might seem reasonable for

Eq. 2
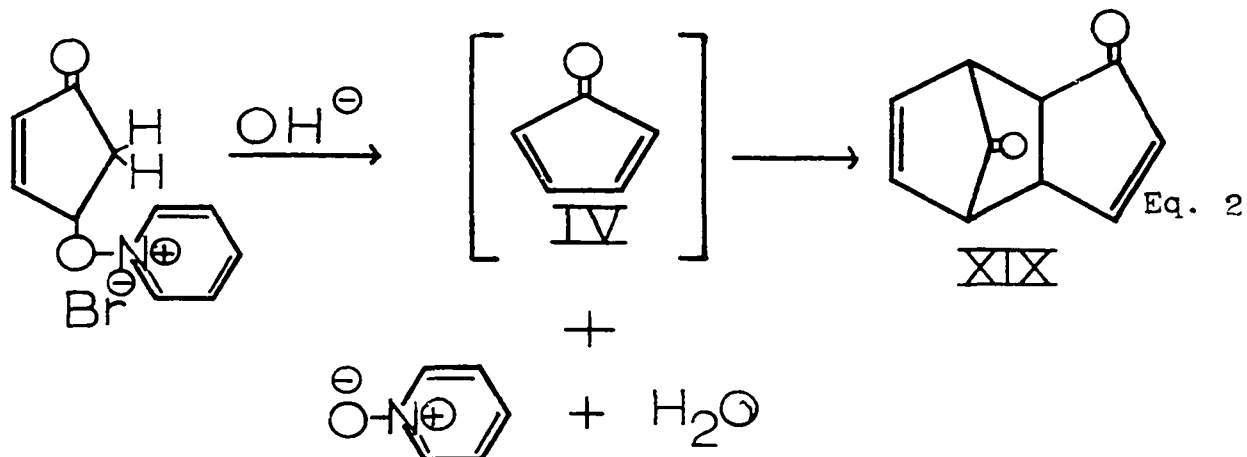
the formation of XIX is given in Eq. 3. This explanation was made unlikely by the observation that no dimeric ketone could be isolated when the product from equimolar quantities of dibromide and pyridine-N-oxide was reacted with base.

Eq. 3

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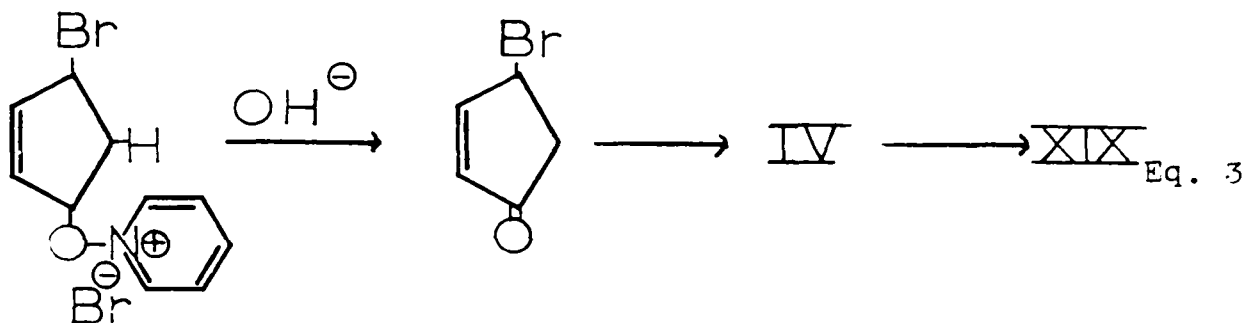
[30] J. Thiele, Chem. Ber., 33, 669 (1900)

We then turned to more conventional means of synthesizing
I. The 3,5-dibromide was converted to the 3,5-diacetate with
tetraethylammonium acetate in dry acetone,[31] conditions which
minimize rearrangement of the dibromide, and the diacetate
was hydrolyzed to cyclopentene-3,5-diol.[32] Chromic acid
oxidation of alcohols to carbonyl compounds is a well known
reaction,[33],[34] and when the 3,5-diol was oxidized with CrO_3
in acetic acid, or acetone-sulfuric acid, cyclopentene-3,5-
dione was obtained in yields of about 50%. After we had
developed this method of preparation of the 3,5-dione,[35] a
synthetic mixture of cyclopentendiols became available commer-
cially.[36] The commercial product was a mixture of all pos-
sible isomers of cyclopentene-3,5 and 3,4-diols. Vacuum dis-
tillation of the mixture of diols through a spinning brush
column of approximately twenty theoretical plates cleanly
separated the 3,4- and 3,5-cyclopentendiols into two frac-
tions, I, b.p. 70-90°/0.5 mm ($n_D^{25°}$ = 1.494), and II, b.p.

---

[31]L. N. Owen and P. N. Smith, J. Chem. Soc., 4043 (1952)

[32]G. O. Schenck and D. E. Dunlap, Angew. Chem., 68, 248
(1956)

[33]F. H. Westheimer, Chem. Ber., 45, 419 (1949)

[34]W. A. Waters, Quart. Rev., 12, 277 (1958)

[35]C. H. DePuy and E. F. Zaweski, J. Am. Chem. Soc., 79,
3923 (1957)

[36]Columbia-Southern Chemical Co., One Gateway Center,
Pittsburg, Pa.

90-95°/0.5 mm ($n_D^{25°}$ = 1.501). Fraction I was shown to con-
tain greater than 95% of the 3,4-diol by a quantitative
periodate titration. By a similar titration fraction II was
shown to contain less than 5% of the 3,4-diol. Oxidation of
the 3,5-diol (presumably a mixture of cis and trans isomers)
gave the dione in yields comparable to those obtained by the
oxidation of the pure cis diol. Thus, cyclopentene-3,5-dione
is available in 40-50% yields from commercially available
material.

Cyclopentene-3,5-dione is an interesting and unique com-
pound. It is of obvious synthetic utility as will be dis-
cussed later. It is also of theoretical interest because of
its relationship to the hitherto unknown molecule cyclopenta-
dienone IV. This dienone is presumably unstable for elec-
tronic reasons. Cyclopentadienone is a completely-conjugated
planar monocyclic polyolefin and its unstability is due to
the fact that it does not obey the $(4n+2)\pi$-electron rule
because the highly electronegative oxygen atom of the carbonyl
group will have the tendency to withdraw electrons from the
ring. This will then lead to a positively charged, completely
unsaturated five-membered ring without the necessary 6π-
electrons needed for aromatic stability. In its enol form,
cyclopentene-3,5-dione would be a hydroxycyclopentadienone
and hence would be of theoretical interest.
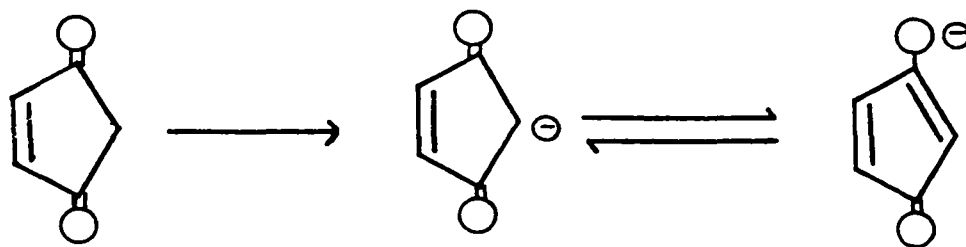
Cyclopentene-3,5-dione is a yellow, volatile solid melting at 37-38° C and soluble in water and most organic solvents except hydrocarbons. The yellow color is due to two low intensity bands at 312mμ (log ε 1.30) and 367mμ (log ε 1.30). The 3,5-dione also exhibits a strong absorption maximum at 222mμ (log ε 4.16). The ultraviolet spectrum of the 3,5-dione is shown in curve A on page 33. The infrared spectrum (Figure 1) on page 31 shows two peaks in the carbonyl region in chloroform solution, a strong absorption at 5.83μ and a slight one at 5.73μ.[37] In the vapor phase there is a single peak at 5.82μ.

A physical property of the dione of interest is the dissociation constant. An accurate determination of this constant has not been possible because of the rapid self-condensation of the 3,5-dione in base.[38] Nevertheless,

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[37](a) R. N. Jones, "Techniques of Organic Chemistry", Vol. IX, New York, N.Y., Interscience Publishers, Inc.; (b) H. K. Hall, Jr. and R. Zbinden, J. Am. Chem. Soc., 80, 6428 (1958)

[38]C. H. DePuy and P. R. Wells, J. Am. Chem. Soc., [to be published in 82, ca 1960].

studies of the acidity of the 3,5-dione in 0.1 $\underline{N}$ aqueous
solution suggest an approximate pKa value of 6. This value
represents the acidity constant of the 3,5-dione in its
ketonic form, because no detectable enol content appeared in
the infrared or nuclei magnetic resonance spectra ($\underline{vide}$
$\underline{infra}$). A comparison of the pKa value of the 3,5-dione with
that of its dihydroderivative, cyclopentane-1,3-dione, is
indeed of interest. The 1,3-dione is completely enolic and
in its enolic form has a pKa of 4.5.[39] If we assume 1% of
diketone at equilibrium, cyclopentane-1,3-dione would have a
pKa of 2.5. Hence, we see that the reduction of the double
bond in I increases the Ka by three or four powers of ten.
The lesser acidity of cyclopentendione may be due in part at
least to the fact that structures with the negative charge
on oxygen (XXb,c) also contain a cyclopentadienone ring. The
instability of this ring may decrease the importance of these
structures and hence decrease the resonance stabilization of
the dione.

Cyclopentene-3,5-dione I is completely ketonic as men-
tioned above. It does not give a color with ferric chloride.
Nuclear magnetic resonance studies with D_2O and with D_2O and
DCl (0.6 $\underline{N}$) on the 3,5-dione showed that the rate of exchange
was about the same in both cases. The absence of an O-H band

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[39]J. H. Boothe, R. G. Wilkinson, S. Kushner and J. H. Williams, $\underline{J}$. $\underline{Am}$. $\underline{Chem}$. $\underline{Soc}$., $\underline{75}$, 1732 (1953)
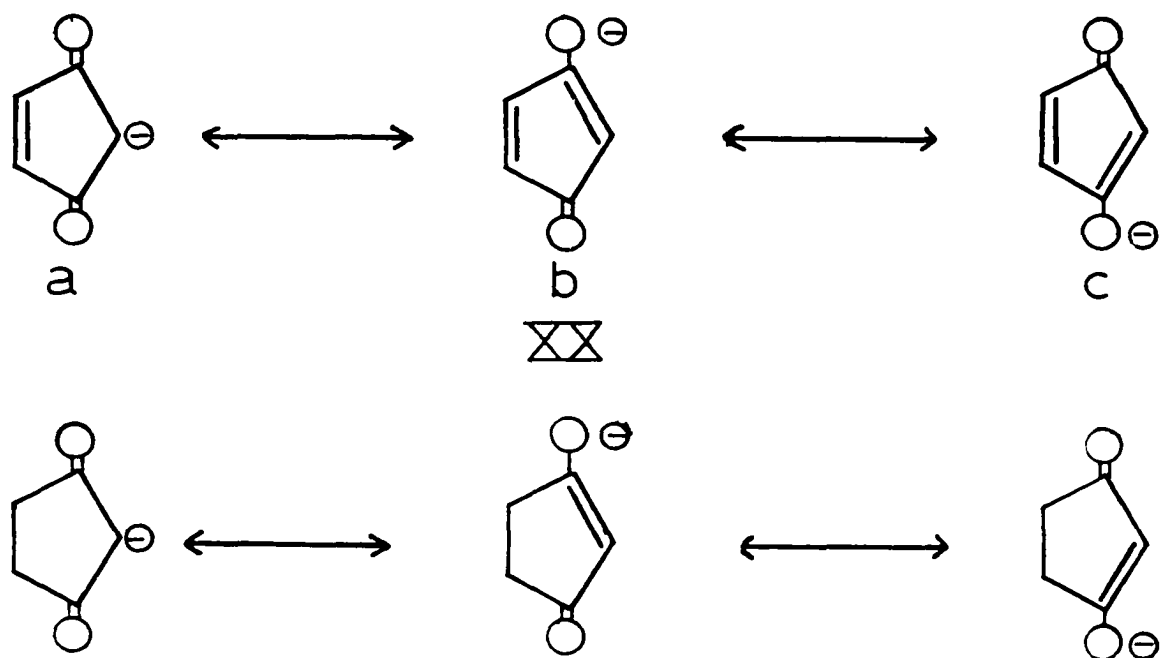
on the isomer shows that very little or no enol is present at
equilibrium. The deuterium exchange rate fails to increase
in acid solution. Usually, the rate of deuteration is faster
when enolization can occur. This does not necessarily pre-
clude that under higher acid concentrations enolization might
occur, for acid catalyzed condensations (vide infra) can be
performed. This is tantamount to saying that there is an
energy barrier that must be overcome in order for enolization
to occur. Further work on deuterium exchange in various
deutero acid concentrations should give an approximate value
of the energy needed to form the enol structure V. An esti-

mate of the half-life of the deuterium exchange reaction (7 minutes) can be obtained from the nmr spectrum.

Chemically, cyclopentene-3,5-dione is extremely reactive under most conditions. Reactions at the methylene group are complicated by the fact that even in the presence of small amounts of base the 3,5-dione is more reactive with itself than with other substances. In an attempt to alkylate the 3,5-dione with methyl iodide and potassium tertiary butoxide, an uncharacterizable residue was obtained which was insoluble in organic solvents and which melted above 300°. Thus, in order to substantiate the course of reaction, the 3,5-dione was allowed to react with various bases. In a dilute solution of aqueous sodium hydroxide, a water soluble, enolic, tan product is formed which analyzes correctly for $C_5H_4O_2 \cdot$ 2/3 H_2O. The compound, however, is insoluble in organic solvents. Addition of a drop of piperidine to a benzene solution of the 3,5-dione results in the rapid precipitation of an enolic, water soluble product. From the observations, one might conclude that the 3,5-dione is undergoing a Michael addition to give what is probably a polymeric material. It is possible to conceive of two paths by which condensation might take place. One reasonable path A would be represented by the formation of anion XXI and the rapid Michael addition of this anion across the double bond leading to a polymer containing the cyclopentane-1,3-dione nucleus. Infrared data
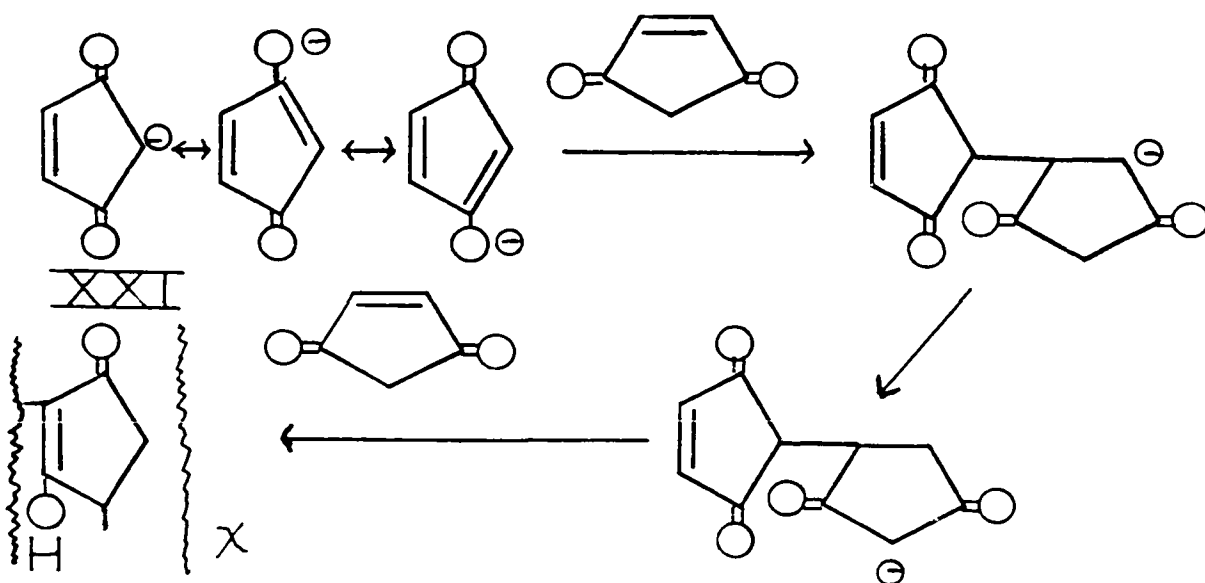
Path A

XXI
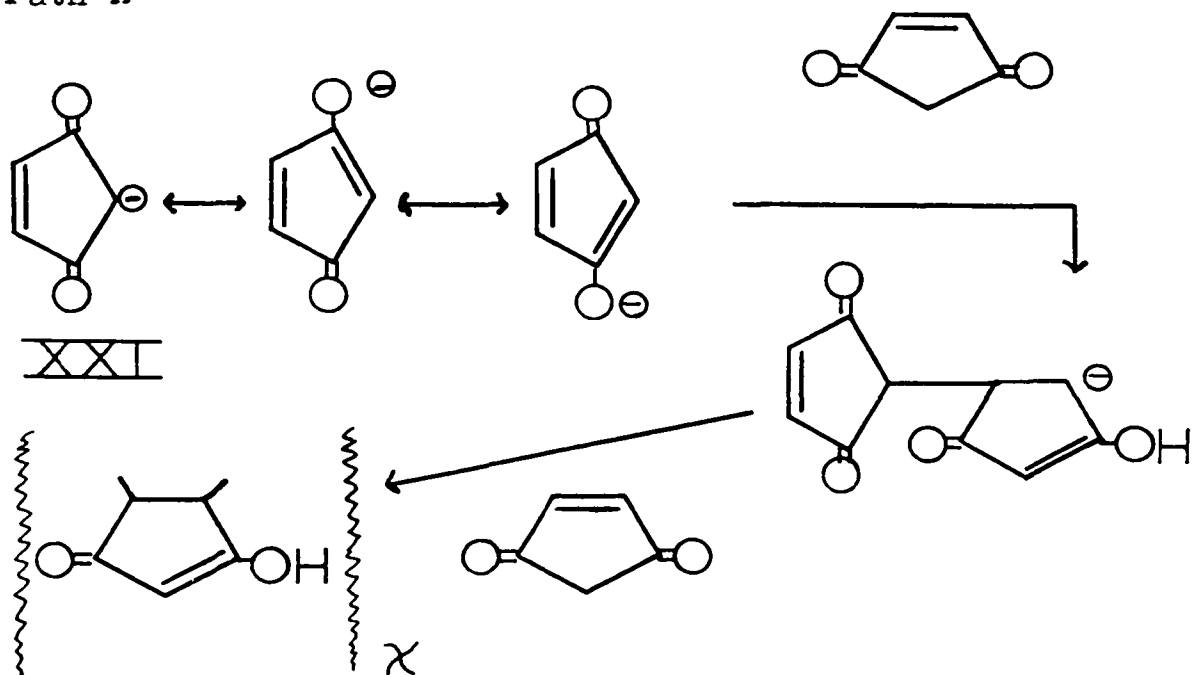
seems to support this mechanism. Another possible path B
would be the formation of anion XXI, addition to the double
and then hydrogen transfer. Ultraviolet analysis seems to

Path B

XXI

support this path. The correct path of condensation has not been ascertained and may be a combination of paths. A more detailed discussion of this condensation, including possible kinetics, is given in a paper by C. H. DePuy.[40]

In aqueous acidic solutions, cyclopentene-3,5-dione is a stable molecule and a Claisen condensation has been observed with benzaldehyde in glacial acetic catalyzed by a few drops of concentrated sulfuric acid.[41] The formation of the benzylidene derivative XXII presumably goes through an enol intermediate, β-hydroxycyclopentadienone V, under these conditions. This is tantamount to saying that under highly acidic conditions an equilibrium exists between the enol and ketone. The benzylidene compound was prepared in 22% yield by reacting cyclopentene-3,5-dione with the preformed benzyl-idene-bis-piperidene.[42] However, when reactions were performed in which base was added to a mixture of benzaldehyde on the 3,5-dione, only a negligible amount (5%) of the benzylidene compound was obtained. Its infrared spectrum is given on page 31 (Figure 1). Infrared data, as given in Table 1, show a similarity between indane-1,3-dione and its

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[40]C. H. DePuy and P. R. Wells, J. Am. Chem. Soc. [To be published in 82, ca 1960].

[41]Vernon L. Bell and Norman H. Cromwell, J. Org. Chem., 23, 789 (1958)

[42]Nelson J. Leonard, John C. Little and A. Jerry Kresge, J. Am. Chem. Soc., 79, 6436 (1957)
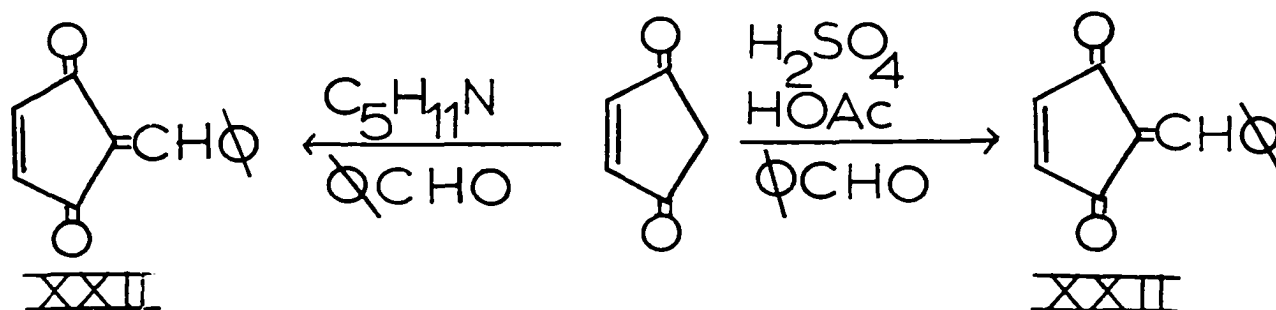
Table 1. Carbonyl frequencies of cyclopentene-3,5- and indane-1,3-diones

Compound	(μ)
Indane-1,3-dione	5.71, 5.85
2-Benzylidene-indane-1,3-dione	5.76, 5.89
Cyclopentene-3,5-dione	5.73, 5.83
4-Benzylidene-cyclopentene-3,5-dione	5.73, 5.93

2-benzylidene derivative and cyclopentene-3,5-dione and its 4-benzylidene compound. Its ultreviolet spectrum (curve B) on page 33 shows a similarity to that of the 3,5-dione.

Cyclopentene-3,5-dione may be reduced to the known[43] cyclopentane-1,3-dione in 45% yield by zinc dust in acetic

[43]J. H. Boothe, R. G. Wilkinson, S. Kushner and J. H. Williams, J. Am. Chem. Soc., 75, 1732 (1953)

acid. In order for this reaction to proceed, the 3,5-dione must be added to a hot mixture of zinc and acid; inverse addition gives exclusively a compound having the characteristics of that resulting from the reaction of the 3,5-dione and base. Catalytic reduction of the 3,5-dione with Adams catalyst results in the uptake of approximately 2.7 molar equivalents of hydrogen without an appreciable break in the rate of hydrogen uptake. Less than 2% of cyclopentane-1,3-dione is formed, as measured by base titration of the product. Gas chromatography and infrared spectra indicate that cyclopentanone and β-hydroxycyclopentanone are formed in roughly equal amounts. This was confirmed by the preparation and chromatography on alumina of the 2,4-dinitrophenylhydrazones (2,4 DNP) of the product. Cyclopentanone 2,4 DNP and cyclopentenone 2,4 DNP (formed by dehydration of the β-hydroxycyclopentanone under experimental conditions) were isolated in about equal amounts. The apparent course of the hydrogenation is shown in Eq. 4.

As would be expected, cyclopentene-3,5-dione I is a very reactive dienophile. It reacts immediately and quantitatively with cyclopentadiene to form an adduct XXIII. Like cyclopentane-1,3-dione, the adduct is completely enolic. With anthracene the reaction is slower. An adduct is formed in 90% yield when equimolar amounts of the dione and anthracene are heated at reflux in benzene for four days. The

Eq. 4
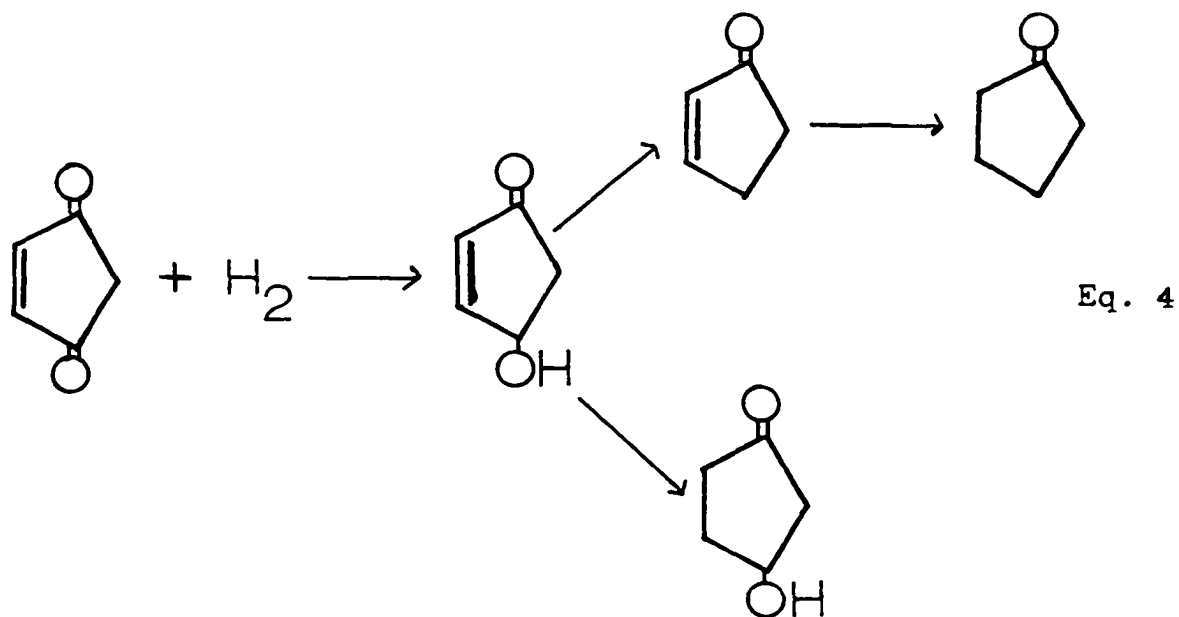
Diels-Alder reaction, thus, provides an excellent method for preparing a variety of substituted cyclopentane-1,3-diones, which are otherwise difficult to obtain.
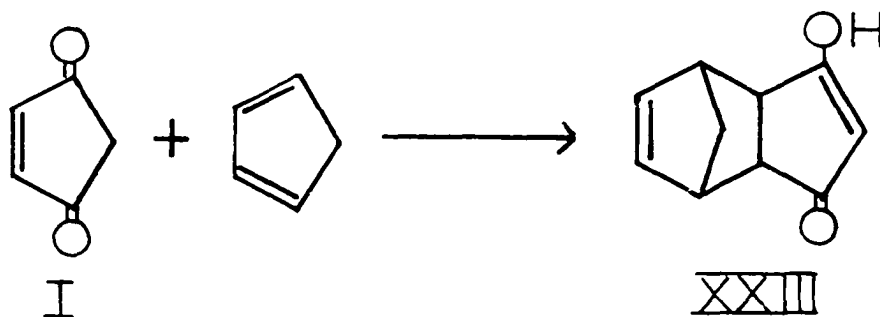
The carbonyl groups of cyclopentene-3,5-dione are extremely reactive, and mono- and dicarbonyl derivatives are formed immediately. The following mono- and/or diderivatives

have been prepared: oximes, phenylhydrazones, O-methyl-oximes, and p-toluenesulfonylhydrazones. In each case infrared spectral data, and analysis, showed that addition had taken place to the carbonyl group and not to the double bond.

We took advantage of the carbonyl reactivity and tried various base condensations with mono- and di-O-methyloximes. In the attempted oximation of the monoderivative with n-butyl nitrite and sodium ethoxide, the only product obtained was a brown solid, m.p. $>230^{\circ}$, which could not be purified. Presumably, some sort of self-condensation had occurred as with the original 3,5-dione. To support this suggestion, the monoxime was allowed to react with base. Upon acidification, a polymeric residue similar to that obtained with butyl nitrite was obtained. The di-O-methyloxime when treated with base and isoamyl nitrite could be recovered quantitatively.

One final reaction, or rather lack of reaction, needs to be considered. As mentioned previously, we prepared the monotosylhydrazone of the 3,5-dione and attempted to prepare from it the vinylogous diazoketone XXV by treatment with base, following the method of Cava et al.[44] This diazoketone was of interest because of the possibility of its enolizing to a derivative of diazocyclopentadiene XXVI. Compound XXIV a salt with sodium hydroxide but was recovered unchanged even

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[44]M. P. Cava, R. L. Little and D. R. Napier, J. Am. Chem. Soc., 80, 2257 (1958)
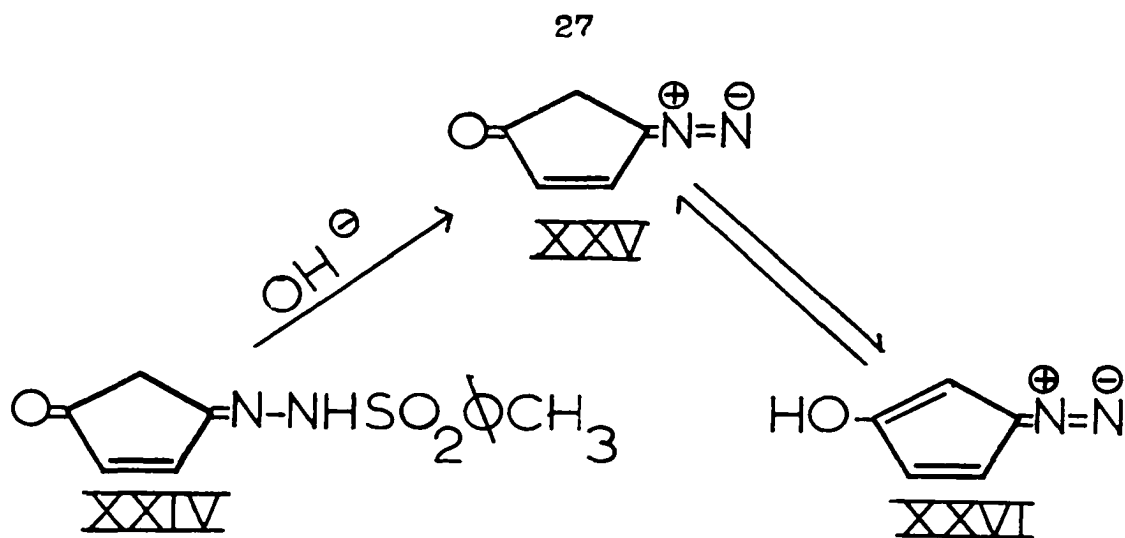
after prolonged boiling with aqueous sodium hydroxide. It appears probable that the added stability of the anion imparted by the increased conjugation may make the reaction too slow.

With the easy preparation of cyclopent-2-enone,[45] we decided to attempt the synthesis of the 3,5-dione by a different method. Bromination of the 2-enone with N-bromosuccinimide in carbon tetrachloride gave the 4-bromocyclopent-2-enone in 78.4% yield. This bromoderivative is very unstable[46] and must be stored over Dry Ice to avoid decomposition. Nevertheless, the bromoderivative could be converted to an acetoxycyclopentenone in good yields by treatment with silver acetate in refluxing glacial acetic acid.[47]

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[45]C. H. DePuy and K. L. Eilers, J. Org. Chem. [To be published in 27, ca 1959].

[46]C. H. DePuy and M. Isaks, Ames, Iowa. Dehydrobromination of 4-bromocyclopentenone. Private communication. 1959

[47]L. S. Crombie, Michael Elliot and Stanley H. Harper, J. Chem. Soc., 971 (1950)

Hydrolysis of the acetoxycompound and oxidation of the corresponding alcohol should yield the known cyclopentene-3,5-dione I. However, no effective means of hydrolysis could
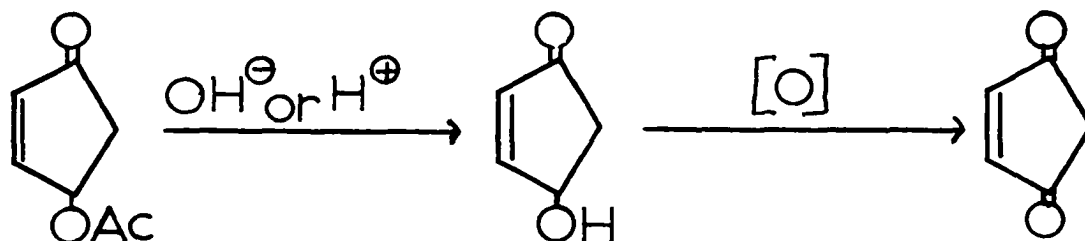
be found. It appears that isomeric acetoxycyclopentenones were formed. Analysis by Gas Chromatography showed that three compounds were present with two being minor constituents of less than 5%. Elemental analysis was correct for $C_7H_8O_3$; hence, one can assume that isomeric acetoxy compounds were present. The conversion of the bromoderivative to the ace-toxyderivative with silver acetate has been shown by others[47] to proceed without rearrangement. Thus, from this we can assume that the major component of the mixture is probably the 4-acetoxy-cyclopent-2-enone. Ultraviolet spectrum and infrared spectrum indicate the possibility of an α-acetoxy-cyclopentenone. The compound displays a maximum at 207mμ in the ultraviolet as compared to 218mμ for the unsubstituted enone. Infrared spectrum shows a carbonyl band at 5.90μ. This is a shift of about 0.05μ which is normal for α-substituted ketones. Further work on this compound and nmr studies definitely will solve its structure.

SPECTRA

Ultraviolet absorption spectra were measured with Cary Model 14 recording spectrophotomer and the infrared spectra with Perkin-Elmer Infracord and Perkin-Elmer Model 21 instruments using sodium chloride prisms.

Figure 1. Infrared spectra
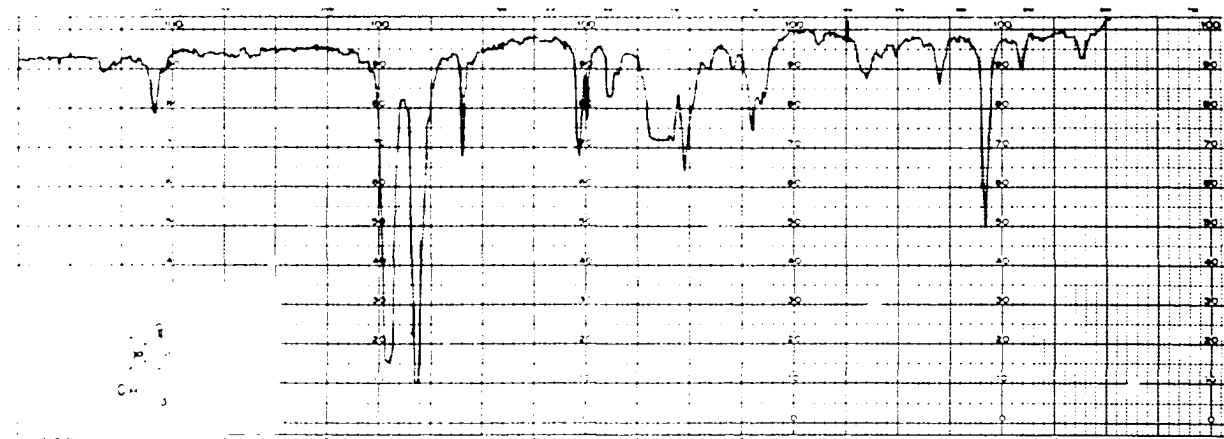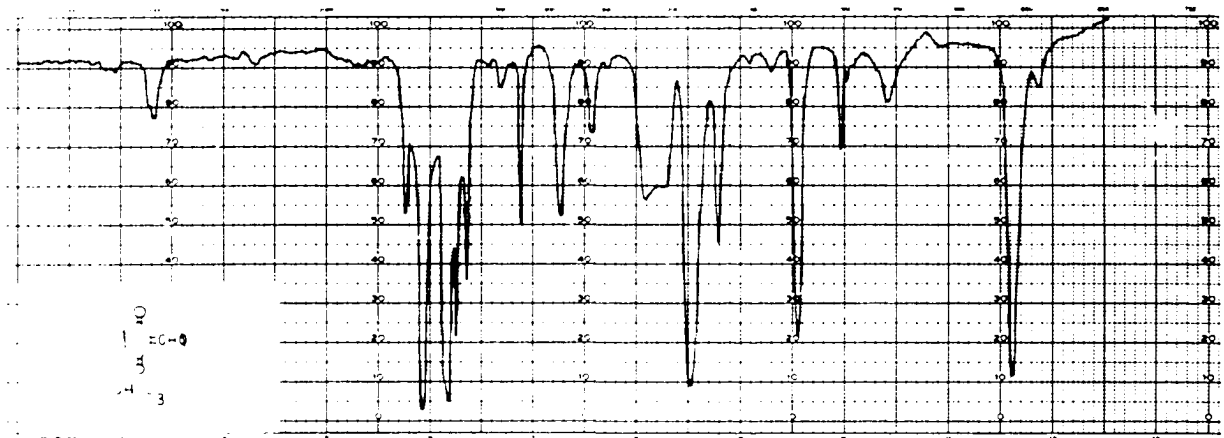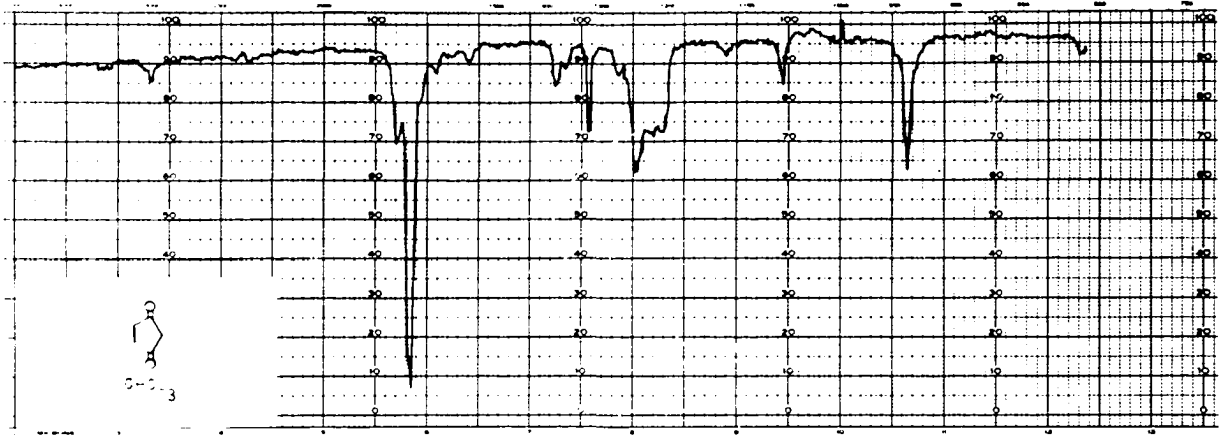
Figure 2. Ultraviolet spectra

Curve A. Cyclopentene-3,5-dione
Curve B. 4-Benzylidene-cyclopentene-3,5-dione
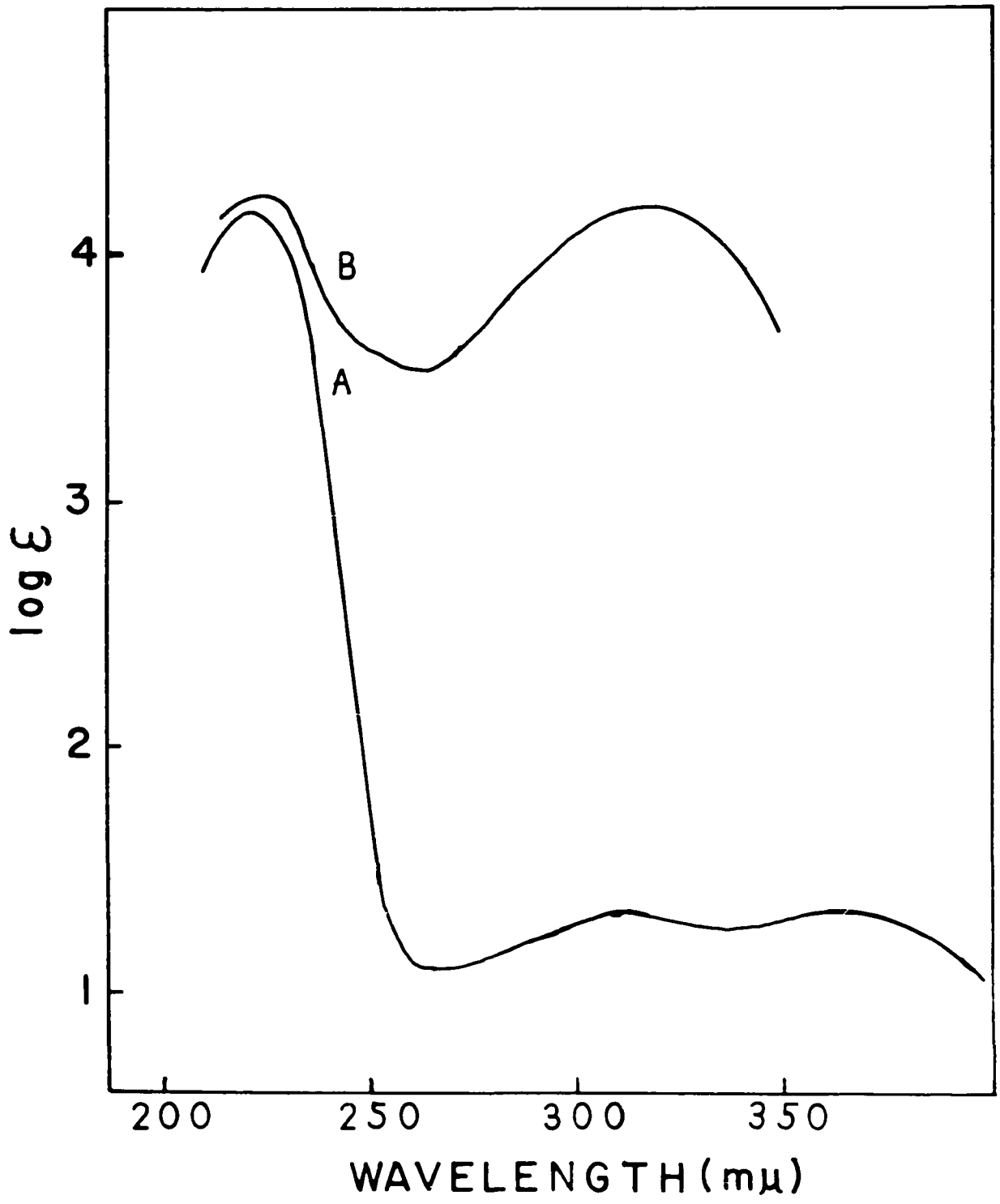
EXPERIMENTAL[*]

Cyclopentadiene

The commercially available dicyclopentadiene (Eastman Technical Grade) was cracked by heating at 150-170°, and the monomer (b.p. 40°) distilled through a column packed with glass helices into a receiver placed in an ice bath. The monomer was stored at 0° over anhydrous calcium chloride until ready for use. Polymerization of monomer occurs fairly rapidly at room temperature, but it could be kept at 0° for at least two weeks.[48]

Cis-3,5-dibromocyclopentene

This dibromide was prepared by bromination of cyclopentadiene following the procedure of Young et al.[49] A solution of 564 g. (3.52 moles) of bromine in 400 ml. of petroleum ether (b.p. 35-40°) was added with stirring to a solution of 232 g. (3.52 moles) of freshly distilled cyclopentadiene in

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[*]All melting points and boiling points are uncorrected. Ultraviolet absorption spectra were measured with Cary Model 14 recording spectrophotomer and the infrared spectra with Perkin-Elmer Infracord and Perkin-Elmer Model 21 instruments using sodium chloride prisms. Analyses were done by Weiler and Strauss, Microanalytical Laboratory, Oxford, England.

[48]P. Unger, Analyst, 80, 820 (1955)

[49]W. G. Young, H. K. Hall and S. Winstein, J. Am. Chem. Soc., 78, 4338 (1956)

176 ml. of petroleum ether (b.p. 35-40°). During the addition
the temperature was maintained at -25° to -35° by external
cooling with a Dry-Ice acetone bath. A white precipitate
appeared as the addition proceeded. After the addition was
complete, pyridine (24 ml.) was added and the mixture brought
to 0°. After the addition of a solution of 24 ml. of glacial
acetic acid, 30 g. of calcium chloride, and 180 ml. of water,
two liquid phases resulted. The organic layer was separated
and chilled overnight in Dry Ice, during which time the
crystalline cis-3,5-dibromocyclopentene precipitated.

The solid white mass was quickly filtered in a previously
chilled Buchner funnel and recrystallized from petroleum
ether (b.p. 60-70°) to give 165 g. (21%) of pure white
crystals of 3.5 dibromocyclopentene. The product must be
stored over Dry Ice to avoid decomposition.

Pyridine-N-Oxide

In a liter flask equipped with a reflux condenser, a
solution of 79 g. (1 mole) of pyridine, 600 ml. of glacial
acetic acid, and 100 ml. of 30% hydrogen peroxide was heated
for three hours on a steam bath. An additional 70 ml. of 30%
hydrogen peroxide were added and the reaction mixture heated
for twelve hours as above. The mixture was then concentrated
to 200 ml., 200 ml. of water added, and the mixture concen-
trated as far as possible. The residue was made strongly

alkaline with anhydrous sodium carbonate, shaken with 250
ml. of chloroform, and allowed to stand. The resulting sodium
acetate and sodium carbonate crystals were filtered and the
filtrate was dried over anhydrous sodium sulfate. The solvent
was removed and the residue distilled to give 60.9 g. (64.3%)
of pyridine-N-oxide, b.p. 138-140° (15 mm.).

Akylation of Pyridine-N-Oxide

In a one liter, three-necked flask equipped with a
stirrer, reflux condenser, and addition funnel were placed
30 g. (0.32 mole) of pyridine-N-oxide in 50 ml. of dry ben-
zene. A solution of 35.8 g. (0.16 mole) of cis-3,5-dibromo-
cyclopentene in 50 ml. of dry benzene was added dropwise with
stirring. After addition was complete, the mixture was
stirred for four hours at room temperature and the product
removed by filtration. The white solid was washed well with
benzene and dried in a vacuum desicator. The resultant O-akyl
pyridinium salt (XVII) weighed 56 g. (84% yield), and could
not be purified by recrystallization. It melted with dec.
at 110°.

Anal. Calcd. for $C_{15}H_{16}N_2O_2Br$: C, 43.27; H, 3.85;
N, 6.73; Br, 38.5. Found: C, 42.04; H, 3.85; N, 6.67;
Br, 38.3.

Base Cleavage of the O-akyl Pyridinium Salt

To 100 g. (0.24 mole) of solid O-akyl pyridinium salt
was added, dropwise with stirring, a solution of 27 g. (0.48
mole) of potassium hydroxide in 300 ml. of water. The reac-
tion flask was immersed in an ice bath. The addition took
one hour and the resultant red substance was stirred an addi-
tional half-hour, and then continuously extracted for two
days with ether. The ether extract was washed with 2 N
hydrochloric acid to remove the pyridine and then success-
ively with 5% sodium carbonate, water and saturated sodium
chloride. The resultant solution was dried over anhydrous
sodium sulfate and the ether carefully removed to give a
light brown oil. Sublimation at 1 mm. gave 2.6 g. (13%) of
white crystalline solid (m.p. 98-99°) which did not depress
the melting point of an authentic sample of 1,8-diketo-4,7-
methano-3a,4,7,7a-tetrahydroindene (XIX).

Anal. Calcd. for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found:
C, 74.96; H, 5.23. Infrared: 5.6 μ and 5.85 μ.

Tetraethylammonium Acetate

To a solution of 395 g. (1.86 moles) of tetraethyl-
ammonium bromide in a liter of water was added slowly with
stirring 250 g. (1.08 moles) of silver oxide and the reac-
tion mixture was allowed to stir overnight. The precipitated
silver bromide was filtered and the solution neutralized with

glacial acetic acid. After concentration at reduced pressure, tetraethylammonium acetate was obtained as a solid. It was recrystallized from dry acetone at -80° to give 258 g. (73.5%) of product.

Cis-3,5-diacetoxycyclopentene

This compound was obtained from the dibromide by the reaction with tetraethylammonium acetate in dry acetone according to the directions of Owen and Smith.[50] Cis-3,5-dibromo-cyclopentene, 99.2 g. (0.44 mole), was dissolved in 150 ml. of dried acetone and added to a stirred solution of tetraethylammonium acetate, 283 g. (1.5 moles), in 500 ml. of dried acetone. As the addition proceeded tetraethylammonium bromide began to separate and the solution became dark. After the addition was complete (1 hour), the mixture was kept at 0° for 16 hours, filtered, and the precipitate washed with anhydrous acetone. The combined filtrate and washings were concentrated under reduced pressure, 400 ml. of water was added and the aqueous mixture was extracted with ether (3 X 100 ml.). After removal of the ether, the residue was distilled to give 59.5 g. (74%) of cis-3,5-diacetoxycyclopentene, b.p. 86° (2 mm.).

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[50]L. N. Owen and P. N. Smith, J. Chem. Soc., 4043 (1952)

Cis-3,5-cyclopentenediol

Cis-3,5-diacetoxycyclopentene, 38 g. (0.2 mole), was hydrolyzed by heating in an alcoholic solution under reflux for 24 hours with barium hydroxide, 128 g. (0.75 mole). The precipitated barium salts were removed by filtration and carbon dioxide was passed into the solution until no more barium carbonate precipitated. Evaporation of the solvent and vacuum distillation gave 14.6 g. (73%) of the diol, b.p. 120° (2 mm.). It formed a __bis__ phenylurethan, m.p. $195-196^\circ$, lit.[51] m.p. $195-196^\circ$.

Cyclopentene-3,5-diols

A mixture of cyclopentenediols, kindly furnished by Columbia-Southern Chemical Company, was subjected to a careful fractionation through a spinning brush column of approximately 20 theoretical plates. The 3,4-diol distilled below 90° (0.5 mm.) and the 3,5-diol could be obtained in 50-60% yield, b.p. $90-95^\circ$ (0.5 mm.) $n_D^{25^\circ}$ 1.501. Periodic acid titration of the latter showed it to contain less than 5% of the 3,4-diol. The early fractions contained greater than 95% 3,4-diol as determined similarly.

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[51] G. O. Schenck and D. E. Dunlap, __Angew. Chem.__, __68__, 248 (1956)

Cyclopentene-3,5-dione

Procedure one

To a cold solution of the 3,5-diol 8.7 g. (0.087 mole) in 15 ml. of 80% acetic acid was added, dropwise with stirring, 232 ml. of 3 $\underline{N}$ chromic acid in glacial acetic acid. The rate of addition was regulated so that the temperature of the reaction mixture remained below 0°. After addition was complete, the mixture was allowed to stir overnight at room temperature. Most of the acetic acid was removed at room temperature under vacuum. The residue was diluted with 400 ml. of water and extracted with methylene chloride (3 X 100 ml.). After drying over anhydrous sodium sulfate, the solvent was removed and the resulting oil placed in a sublimator. The crystalline dione sublimed at 50° and 3 mm. Recrystallization from ether-petroleum ether (b.p. $60\text{-}70^{\circ}$) gave 4.6 g. (55%) of the diketone as a yellow solid with an irritating odor. The melting point was $37\text{-}38^{\circ}$.

$\underline{\text{Anal}}$. Calcd. for $C_5H_4O_2$: C, 62.5; H, 4.17. Found: C, 62.3; H, 4.0. Mol. wgt.: Calcd.: 96. Found: 96. Ultraviolet: λ max. 222mμ(log$\mathcal{E}$4.16), 312mμ(log$\mathcal{E}$1.30), 367mμ(log$\mathcal{E}$1.30). Infrared: 5.73μ, 5.83μ(CHCl$_3$). Active hydrogen: 1.19.

Procedure two

To a cold stirred solution of the diol, 20 g. (0.20 mole), in 200 ml. of acetone was added, dropwise with stirring, a solution of chromic acid, 30 g. (0.3 mole), 60 ml. of concentrated sulfuric acid and 142 ml. of water. The reaction flask was surrounded by an ice bath, and the addition so regulated that the temperature in the flask did not rise above 0°. After the addition was complete, the reaction mixture was stirred an additional two hours at 0°, allowed to warm to room temperature, diluted with 400 ml. of water and extracted with methylene chloride (3 X 300 ml.). The combined extracts were washed with 100 ml. of water, dried over anhydrous sodium sulfate, and the dione isolated as above. Yields are generally about 8 g. (42%), but despite the lower yields this procedure is more convenient than the oxidation in acetic acid.

Cyclopentane-1,3-dione

A solution of 0.50 g. (0.0052 mole) of cyclopentene-3,5-dione in 25 ml. of glacial acetic acid was added dropwise to a vigorously stirred mixture of 5 g. of zinc dust in 25 ml. of glacial acetic acid. The addition took 45 minutes, during which time the flask was immersed in an oil bath at 85°. The reaction was cooled, filtered and the acetic acid removed

at room temperature under vacuum. The residue was extracted
in a Soxhlet apparatus with chloroform. The chloroform was
evaporated and cyclopentane-1,3-dione sublimed at 120° and
4 mm. to yield 0.23 g. (45%), m.p. 149-150°; lit.[52] 150-151°.

Catalytic Hydrogenation of Cyclopentene-3,5-dione

The dione (1.0 g.) in 25 ml. of ethyl acetate was hydro-
genated at room temperature and atmospheric pressure using
Adams catalyst.[53] Absorption stopped after 2.7 molar equiva-
lents of hydrogen had been taken up. The solution was fil-
tered and the solvent removed. Titration of an aliquot of
the oily product showed that not more than 2% of acidic
material was present. The infrared spectrum showed a single
carbonyl peak at 5.75μ and an intense hydroxyl band. Gas
chromatography showed the presence of two compounds in about
equal amounts, one of which had the same retention time as
did cyclopentanone. The 2,4-dinitrophenylhydrazone of the
mixture was prepared and chromatographed on alumina. Roughly
equal amounts of the 2,4-DNP of cyclopentanone (m.p. 142-
143°) and of cyclopentenone (m.p. 166-167°) were isolated.

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[52]J. H. Boothe, R. G. Wilkinson, S. Kushner and J. H.
Williams, J. Am. Chem. Soc., 75, 1732 (1953)

[53]An apparatus which is especially convenient for this
hydrogenation, and for others in which a relatively large
amount of hydrogen is absorbed (in this case 620 ml.), is
described by P. R. Story and C. H. DePuy, J. Chem. Ed.,
 in press

Monotosylhydrazone of Cyclopentene-3,5-dione

To 500 mg. (0.0052 mole) of the dione in 10 ml. of hot methanol were added 915 mg. (0.0049 mole) of tosylhydrazine. The mixture was allowed to stand and then cooled to 0° and filtered. Recrystallization from 95% ethanol gave 1.15 g. (90%) of the monotosylhydrazone, m.p. 185–186° (decomp.).

Anal. Calcd. for $C_{12}H_{12}O_3N_2S$: c, 54.54; H, 4.58; N, 10.60. Found: C, 54.45; H, 4.68; N, 10.9.

This tosylhydrazone was readily soluble in dilute sodium hydroxide. It could be recovered in 90% yield by acidification after heating at 100° with base. Although some coloring of the solution took place, no evidence for the presence of a diazo grouping could be found.

Cyclopentadiene Adduct

The adduct could be prepared in quantitative yield by mixing equimolar amounts of the dione and cyclopentadiene in four times their volume of benzene and allowing the mixture to stand at room temperature. The adduct began to precipitate in a very short time. After a few hours the solution was filtered and the precipitate was recrystallized from a mixture of chloroform-carbontetrachloride. Sublimation at 120–130° (1 mm.) gave the adduct (m.p. 169.5–170.5°) which appeared to be 100% enolic.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.1; H, 6.2 Found: C, 73.9; H, 6.05.

Reaction of Cyclopentene-3,5-dione with Aqueous Base

To 500 mg. of the dione in 5 ml. of water was added 53 ml. of 0.1 $\underline{N}$ sodium hydroxide. After stirring at room temperature for twenty minutes, the brownish-red solution was passed through an Amberlite I.R. 120 ion-exchange column to remove sodium ions. The aqueous solution of the polymer was then evaporated to dryness leaving a tan, highly enolic powder which was insoluble in organic solvents.

Anal. Calcd. for $C_5H_4O_2 \cdot 2/3 H_2O$: C, 55.55; H, 4.97. Found: C, 55.44; H, 4.87.

Attempted Selenium Dioxide Oxidation of Dione

To a solution of 0.2 g. (0.002 mole) of cyclopentene-3,5-dione in 20 ml. of dioxan was added 0.24 g. (0.002 mole) of selenium dioxide. The mixture was heated at reflux for 24 hours. Selenium was filtered and lead acetate added to reduce any unreacted selenium dioxide. After removal of dioxan, a brown polymeric substance (m.p. $>$ 300°) resulted which was insoluble in organic solvents. When the above reaction was performed in toluene, acetic acid, and acetic anhydride, similar results were obtained.

Attempted Oximation of Dione with N-butyl Nitrite

To a solution of 0.5 g. (0.005 mole) of dione in 5 ml. of absolute ethanol was added 0.8 ml. of n-butyl nitrite. The reaction flask was immersed in an ice bath. To this solution was added 1.5 ml. of hydrochloric acid. This mixture was allowed to stir for 2 hours and then placed in a refrigerator overnight. Evaporation of ethanol led to a semisolid which was dissolved in methylene chloride. The methylene chloride extract was washed with water and dried over anhydrous sodium sulfate. Distillation of solvent gave a semisolid substance appearing reddish brown in color and infrared analysis showed indications of an oxime being present. The ferric chloride test was positive. However, no effective means of purification were found.

Attempted Oximation of Cyclopentene-3,5-dione with Phenyl Lithium

Phenyl lithium was prepared according to the method of Gilman.[54] A solution of 0.5 g. (0.0052 mole) of dione in 20 ml. of anhydrous ether was added dropwise to a stirred solution of 10 ml. of 0.518 $\underline{N}$ phenyl lithium in ether. A reddish tan precipitate was formed. This mixture was allowed to stir for 10 minutes and 0.5 ml. of ethyl nitrite was

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[53]A. H. Blatt, "Organic Synthesis", Collective Volume II, New York, N.Y., John Wiley and Sons, Inc., 1943, p. 517.

added. The entire system was then stoppered and allowed to stir for 24 hours. This mixture was poured into 100 ml. of water and extracted with methylene chloride. The methylene chloride extracts were dried over anhydrous magnesium sulfate and then distilled to give the same results as those reported from the previous oximation.

Attempted Akylation of Cyclopentene-3,5-dione with Potassium Tertiary Butoxide

A solution of 0.1 g. (0.001 mole) of dione in tertiary butanol was cautiously added to a stirred solution of 20 ml. of 0.1 $\underline{N}$ butoxide and 0.25 ml. of methyl iodide. The solution turned brown with turbidity appearing. The above reaction mixture was allowed to stir overnight at room temperature and then extracted with methylene chloride and worked up in the usual manner. The only product was polymer.

Preparation of Mono-O-methyl Oxime of Cyclopentene-3,5-dione

To a stirred solution of 2 g. (0.02 mole) of dione in 5 ml. of water was added 43 ml. of 0.583 molar methoxyamine hydrochloride solution. The reaction mixture was allowed to stir for five hours and the resulting crystals were removed by filtration. Ether extraction of the filtrate and removal of ether produced a second crop of crystals. Sublimation at 50° (1 mm.) of the combined product gave 1.4 g.

(56%) of mono-O-methyl oxime of the dione (m.p. 87-89°).

Anal. Calcd. for $C_6H_7O_2N$: C, 57.6; H, 5.60; N, 11.20. Found: C, 57.33; H, 5.79; N, 11.05. Ultraviolet: λ max. 281mμ(logε 4.61) in 0.1 $\underline{N}$ OH . Infrared: 5.84μ(CHCl$_3$).

Preparation of Di-O-methyl Oxime of Cyclopentene-3,5-dione

To a stirred solution of 2 g. (0.02 mole) of dione in 5 ml. of water was added 86 ml. of 0.583 molar methoxyamine hydrochloride. This reaction mixture was allowed to stir for 24 hours. The resulting crystals were filtered and the filtrate extracted with ether and worked up as in the case of the mono derivative. Purification of product by recrystallization from 95% ethanol gave 2.86 g. (93%) of di-O-methyl oxime of dione (m.p. 116-117°).

Anal. Calcd. for $C_7H_{10}O_2N_2$: C, 54.53; H, 6.54; N, 18.17. Found: C, 54.60; H, 6.23; N, 18.35. Ultraviolet: λ max 284mμ(logε 4.28).

Attempted Oximation of Mono-O-methyl Oxime of Dione with N-butyl Nitrite

To a stirred solution of 1.08 g. (0.008 mole) of mono derivative in 5 ml. of anhydrous ethanol was added 87 ml. of 0.1 $\underline{N}$ sodium ethoxide. The solution was allowed to stir for five minutes and 1 ml. of n-butyl nitrite was added. The reaction mixture was stirred for twelve hours and then made

neutral with hydrochloric acid. Extraction with methylene chloride and evaporation of solvent produced a brown solid (m.p. $>$ 230°). Presumably some sort of polymerization had taken place as with the dione and base.

Attempted Oximation of Di-O-methyl Oxime of Dione with Isoamyl Nitrite

To a stirred solution of 1.46 g. (0.009 mole) of di derivative in 95 ml. of 0.1 N sodium hydroxide was added 1.27 ml. of isoamyl nitrite. This was stirred overnight and then extracted with methylene chloride. After drying over anhydrous sodium sulfate, the solvent was removed to give unreacted starting material.

Preparation of 4-Benzylidene Derivative of Cyclopentene-3,5-dione

Procedure one

The derivative was prepared following the procedure of Leonard et al.[55] A solution of 1.7 g. of benzaldehyde and five drops of piperidine in 10 ml. of anhydrous ether was allowed to stir for five minutes. To this solution was added 0.5 g. (0.005 mole) of dione and the mixture was stirred overnight. A small amount of tan precipitate was filtered and

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[55]Nelson J. Leonard, John C. Little and A. Jerry Kresge, J. Am. Chem. Soc., 79, 6438 (1957)

not characterized. Petroleum ether (b.p. 60-70°) was added
to the ethereal solution and the solution cooled at 0° for
12 hours. The resulting crystals were filtered and recrystal-
lized from 50% aqueous acetone to give 0.2 g. (21.8%) of a
pale yellow solid (m.p. 145-146°).

Procedure two

To a solution of 0.2 g. (0.002 mole) of dione and 0.4
ml. of benzaldehyde in 10 ml. of glacial acetic acid was
added three drops of concentrated sulfuric acid. This solu-
tion was heated at reflux for two hours, cooled and then ex-
tracted with methylene chloride. The methylene chloride ex-
tracts were washed with water, 5% sodium bicarbonate, and
saturated sodium chloride solution. Evaporation of solvent
and recrystallization from 50% aqueous acetone gave 0.155 g.
(42%) of 4-benzylidene-cyclopentene-3,5-dione (XXII), m.p.
145-146°.

Anal. Calcd. for $C_{12}H_8O_2$: C, 78.25; H, 4.38. Found:
C, 78.19; H, 4.29. Ultraviolet: λ max. 225mμ(log.ϵ 4.30),
318mμ(log.ϵ 4.22).

Preparation of Cyclopent-2-enone

This enone was prepared by the method of DePuy and
Eilers.[56] To 256 g. (2.56 moles) of a mixture of cyclo-

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[56]C. H. DePuy and K. L. Eilers, J. Org. Chem. [To be
published in 27, ca 1959].

pentenediols, kindly furnished by Columbia-Southern Chemical Company, was added 0.7 g. of p-toluenesulphonic acid. The solution was heated at a pressure of 10 mm. and a pot temperature of 185-190°. Under these conditions cyclopentenone gradually distilled at 40° to 60° and was collected in an ice-cooled receiver. When no more distillate was collected (1-1 1/2 hours), the reaction was stopped. The residue weighed 24 g. The product was extracted with methylene chloride. After removal of solvent, the product was distilled to give 141 g. (67%) of cyclopenten-2-enone, b.p. 150-151°.

$\underline{Anal}$. Calcd. for C_5H_6O: C, 73.14; H, 7.37. Found: C, 72.86; H, 7.63. Ultraviolet: λ max. 218 mμ(log.$\mathcal{E}$ 4.84).

Preparation of 4-Bromocyclopent-2-enone

To 20 g. (0.23 mole) of cyclopent-2-enone in 100 ml. of carbon tetrachloride was added 44 g. (0.24 mole) of N-bromosuccinimide. The reaction mixture was heated at reflux temperature for 12 hours. After cooling, the resulting succinimide was removed by filtration. Evaporation of the carbon tetrachloride and distillation of the residue gave 30.2 g. (78.4%) of 4-bromocyclopent-2-enone, b.p. 47° (2 mm.). The product was stored over Dry Ice to avoid decomposition.

$\underline{Anal}$. Ultraviolet: λ max. 215mμ(log.$\mathcal{E}$ 3.87).

Preparation of 4-Acetoxycyclopent-2-enone

The acetoxy compound was prepared from the bromo deriva-
tive following the method of Crombie et al.[57] Silver acetate
was freshly prepared by precipitation from an aqueous solution
containing 34 g. (0.2 mole) of silver nitrate by the addition
of 19.6 g. (0.2 mole) of potassium acetate. The filtered
precipitate was washed twice by heating the suspension in
glacial acetic acid and once in glacial acetic acid and acetic
anhydride mixture. The adsorbed acetic acid was removed
during the last filtration by thoroughly washing with ether.
The dried silver acetate weighed 25 g.

To a solution of 22.7 g. (0.14 mole) of bromoketone in
200 ml. of glacial acetic acid was added 24.9 g. (0.15 mole)
of silver acetate. The resulting suspension was stirred at
reflux temperature for 24 hours. Silver bromide (26.8 g.)
was filtered and the acetic acid distilled at aspirator pres-
sure. Vacuum distillation of the residue gave 13.9 g. (71%)
of 4-acetoxycyclopent-2-enone, b.p. 57° (2 mm.).

Anal. Calcd. for $C_7H_8O_3$: C, 59.99; H, 5.75. Found:
C, 60.01; H, 5.97.

In an attempt to eliminate acetic acid from the acetoxy
ketone, a small quantity of 4-acetoxycyclopent-2-enone was

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[57]L. S. Crombie, Michael Elliot and Stanley H. Harper,
J. Chem. Soc., 971 (1950)

distilled at 190° and atmospheric pressure from a trace of p-toluenesulphonic acid. No evidence of decomposition was observed and the acetoxy compound was recovered quantitatively.

Attempted Preparation of Cyclopentene-3,4-dione

To a solution of 10 g. (0.12 mole) of cyclopent-2-enone in 15 ml. of glacial acetic acid was added 15 g. (0.13 mole) of selenium dioxide. The mixture was warmed on a steam bath for three minutes and then the reaction was allowed to proceed by itself until no further evidence of reaction was observed. Then the mixture was heated on a steam bath for an additional 1 1/2 hours. Removal of acetic acid under vacuum produced a tarry mass. Sublimation at 200° (2 mm.) gave a small amount of yellow crystals. Infrared analysis showed indications of cyclopentene-3,4-dione.

SUMMARY

Cyclopentene-3,5-dione was synthesized by chromic acid oxidation of cyclopentene-3,5-diols. The 3,5-dione is a yellow, volatile solid melting at 37-38° C and soluble in water and most organic solvents except hydrocarbons.

Cyclopentene-3,5-dione is an interesting compound for theoretical reasons, because in its enol form, the 3,5-dione would be a β-hydroxyderivative of the hitherto unknown molecule cyclopentadienone.

The 3,5-dione is unstable in basic solutions and rapidly condenses with itself to form a polymeric species. Attempted base catalyzed condensations at the methylene position proved to be fruitless.

In aqueous acid solutions, cyclopentene-3,5-dione is a stable molecule. In moderately acidic solutions an equilibrium exists between the enol and keto form of the 3,5-dione. Advantage was taken of this fact to form the 4-benzylidene-cyclopentene-3,5-dione.

Reduction of the 3,5-dione by zinc dust in acetic acid yielded cyclopentane-1,3-dione, while catalytic reduction with hydrogen and platinum gave roughly equal amounts of cyclopentanone and β-hydroxycyclopentanone and less than 2% of cyclopentane-1,3-dione.

Cyclopentene-3,5-dione is a very reactive dienophile and undergoes Diels-Alder reactions quite readily with cyclo-

pentadiene and anthracene. Its carbonyl groups are extremely reactive, and mono- and/or diderivatives are formed immediately. The monotosylhydrazone of the 3,5-dione was prepared and an attempt to form β-hydroxydiazocyclopentadiene from it is discussed.

The synthesis of an acetoxycyclopentenone is also discussed.

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