was heated at reflux for one hour, filtered, and potassium hydroxide, 2 g., was added. After standing for 12 hours the solution was diluted with water and the product extracted with ether. After removal of the ether there remained 0.45 g. (70% yield) of a solid, m.p. 130–142°. Two crystallizations from pentane gave 0.34 g. (51%) of pure *endo*-norborneol, m.p. and mixed melting point with an authentic sample 149–150°.[3,30] *exo*-Norborneol melts at 127–128°.[3,30]

Hydrolysis of the *endo*-Keto-acetate IIb.—The keto-acetate (100 mg., 0.0006 mole) was dissolved in 1.5 ml. of 1 *N* sodium methoxide in methanol. After 4 minutes at room temperature water was added and the mixture was extracted with ether. The product, about 90 mg., was a neutral amorphous solid which had infrared bands at 5.75 and 6.1 μ. It readily absorbed Br_2 in CCl_4. In a separate experiment 200 mg. of the keto acetate was heated at reflux for 1.5 hours with 5 ml. of 2 *N* aqueous HCl. Extraction with methylene chloride gave a good yield of a colorless oil which had infrared peaks at 5.75 (cyclopentanone) and 3.75 and 5.81 μ (aldehyde). Oxidation with $KMnO_4$ gave an oily keto acid (100 mg.); infrared peaks at 5.75 and 5.83, and a broad peak in -OH region.

Equilibration of Alcohols.—In a typical experiment the alcohol (5 g., 0.03 mole), aluminum isopropoxide (6.8 g., 0.03 mole) and acetone (0.1 ml.) were dissolved in 100 ml. of pure dry isopropyl alcohol. The mixture was heated at reflux for 72 or 120 hours, dilute acid was added and the products extracted with ether. The extracts were washed, dried and the solvent removed. The products were analyzed by g.p.c. Identical results were obtained after 72 and 120 hours of heating.

AMES, IOWA

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(30) H. Toivonen, *Ann. Acad. Sci. Fennicae*, AII, **72**, 1 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

Cyclopentene-3,5-dione. II. Conversion to Cyclopentadienone

BY C. H. DEPUY AND C. E. LYONS

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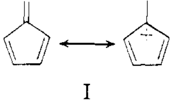
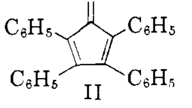
Cyclopentene-3,5-dione has been converted into its anthracene adduct and thence, by methylation and reduction, into the anthracene adduct of cyclopentadienone. On pyrolysis at 350° a reverse Diels–Alder reaction takes place and anthracene and cyclopentadienone (I) are formed. The latter immediately undergoes dimerization followed by decarbonylation to yield 8,9-dihydroindenone (X). An authentic sample of the dimer of cyclopentadienone has also been pyrolyzed and shown to give the same product. An attempted synthesis of β-methoxycyclopentadienone by an analogous method also led, apparently, to dimeric products.

In recent years a number of unsaturated, odd-numbered ring compounds have been prepared whose remarkable stability may be ascribed to the fact that their rings contain $4n + 2\pi$-electrons. Among these compounds may be mentioned cyclopheptatrienone,[1] diphenylcyclopropenone[2] and diazocyclopentadiene.[3] The first two of these owe their stability to the fact that the oxygen of the carbonyl group withdraws electrons, leading to rings with 6- and 2π-electrons, respectively. In the last case the diazo grouping donates electrons, leading again to six electrons in a single cycle. The success of the $4n + 2$ rule is made even more striking when it is recognized that no simple planar molecules which violate it have been prepared in stable form. The numerous attempts to prepare the simplest example, cyclobutadiene, are extremely well known. In many ways cyclopentadienone (I) would be an even more valuable example of such a system to have available for study, since the reactivity of the carbonyl group could readily be correlated with that of more normally situated ones, and studies of the reactivity of cyclopentadienone as a diene and/or dienophile in the Diels–Alder reaction and spectral studies of a variety of types would shed a great deal of light on the electronic interactions in this interesting molecule.



I



II

Until recently,[4] cyclopentadienone itself had never been formed. Nevertheless, a number of substituted cyclopentadienones are known and in general show some remarkable properties.[5,6] Tetraphenylcyclopentadienone (II) which has been studied more extensively perhaps than any other cyclopentadienone,[7] is a black-violet compound whose spectral properties have occasioned interest.[8] With fewer than three phenyl groups attached to the nucleus cyclopentadienones are ordinarily dimers, although sometimes the dimers dissociate to monomers in solution. Allen and Van Allan[6] have summarized the structural requirements for the existance of monomeric and dissociable dimeric cyclopentadienones. Cyclopentadienone oxime may be prepared from cyclopentadiene and ethylnitrite,[9] but exists solely in the dimeric form.

Two recent reports indicate that cyclopentadienones may be prepared, at least transiently, by pyrolysis of their Diels–Alder adducts. Pavolini[10] pyrolyzed what was claimed to be the anthracene adduct of 3-methylcyclopentadienone (III). When heated beyond its melting point of 231°, the adduct regenerated anthracene and a second compound which gave a correct analysis for 3-methylcyclopentadienone, although its boiling point (218–220°) was surprisingly high. This compound readily polymerized, but was not otherwise characterized.

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(1) (a) W. von E. Doering and L. H. Knox, THIS JOURNAL, **74**, 5683 (1952); (b) H. J. Dauben and H. J. Ringold, *ibid.*, **73**, 876 (1951).

(2) R. Breslow, R. Haynie and J. Mirra, *ibid.*, **81**, 247 (1959).

(3) W. von E. Doering and C. H. DePuy, *ibid.*, **75**, 5955 (1953).

(4) K. Alder and F. H. Flock, *Chem. Ber.*, **87**, 1916 (1954).

(5) For leading references see C. F. H. Allen, *Chem. Revs.*, **37**, 209 (1945).

(6) C. F. H. Allen and J. Van Allan, THIS JOURNAL, **72**, 5165 (1950).

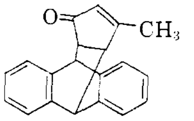
(7) (a) A. Lowenbein and G. Ulich, *Ber.*, **58**, 2662 (1925); (b) K. Zeigler and B. Schnell, *Ann.*, **445**, 266 (1925).

(8) W. Dilthey, O. Trasken, K. Plum and W. Schommoer, *J. prakt. Chem.*, **141**, 331 (1934).

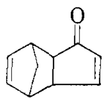
(9) J. Thiele, *Ber.*, **33**, 669 (1900).

(10) T. Pavolini, F. Gambarin and L. Verza, *Ann. chim.*, **42**, 158 (1952).

Alder and co-workers[4] recently reported on the pyrolysis of 1-ketodicyclopentadiene (IV). At 350° this molecule apparently underwent a reverse Diels–Alder reaction. The products obtained from this reaction were those to be expected in the resultant mixture of monomers redimerized in all possible ways (*vide infra*).



III

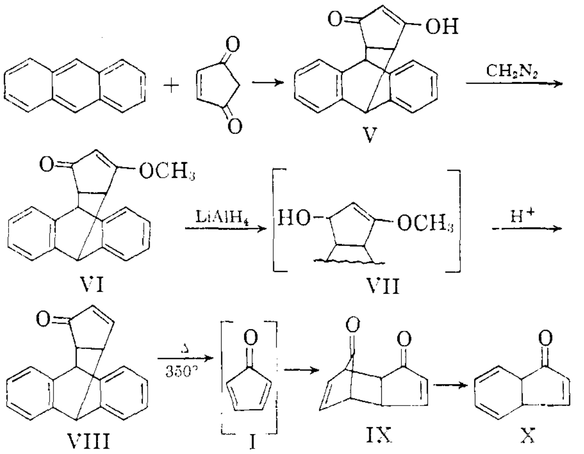


IV

The availability of cyclopentene-3,5-dione[11] led us to a further investigation of the formation of cyclopentadienones by the reversal of the Diels–Alder reaction. The formation of molecules by this route has the advantage that they can be generated without the use of acids, bases and solvents, and hence in the absence of the most common reactants and contaminants. The main difficulties involved are the high temperatures usually required to bring about the reaction and the separation of the desired product from the other component of the adduct. It was hoped that both of these difficulties could be minimized by use of an anthracene adduct, since the regeneration of the anthracene aromatic system might provide a driving force for the reversal and the high melting and boiling point of anthracene might make its separation from the dienone easy. As will presently be seen, only the latter of these two advantages was actually realized.

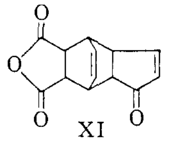
The sequence of reactions by which cyclopentene-3,5-dione was converted, *via* its anthracene adduct, into cyclopentadienone is given in Chart I. The endione is a very good dienophile[11] and the completely enolic anthracene adduct was formed in excellent yield after four days heating in refluxing benzene. Because of its insolubility, the adduct could not be completely purified, but upon treatment with ethereal diazomethane it was smoothly converted into its enol ether VI. Reduction of this ketone with lithium aluminum hydride followed by acid hydrolysis of the presumed intermediate hydroxy enol ether VII led to the anthracene adduct of cyclopentadienone (VIII). The yield in the reduction step was low and the desired product was contaminated by material in which reduction beyond the enone stage had occurred. Careful chromatography through alumina was necessary for purification.

On attempted pyrolysis of VIII, it was clear that the presence of the anthracene moiety had not conferred any special lability on the system. In early experiments the adduct was sublimed unchanged at atmospheric pressure when heated with a free flame. However, when a flask containing a small amount of the compound was immersed in a bath at 350°, pyrolysis gradually took place and the most volatile products were swept into a Dry Ice-cooled receiver. Under these conditions the reaction was complete in about 50 minutes. A large amount of anthracene was formed, and most of it condensed on the upper part of the pyrolysis flask. During the reaction a yellow liquid slowly collected in the receiver. The yield of this distillate was about 40%.



It was immediately obvious from an examination of the infrared spectrum of the distillate that the product did not contain dicyclopentadienone, for the 5.6 μ band characteristic of the bridge carbonyl group[11] was missing. It did, however, exhibit a strong band at 5.85 μ, characteristic of cyclopentenones.[12] The compound was freed from traces of anthracene by evaporative distillation and converted into a red 2,4-dinitrophenylhydrazone, m.p. 266.5–268° dec. Microanalysis indicated that it was derived from a ketone C_9H_8O. It appeared then that, as in the pyrolysis of 1-keto dicyclopentadiene,[4] the product might be dihydroindenone (X) arising from loss of the bridge carbonyl group of the initially formed dicyclopentadienone (IX).

To determine if the product were indeed that formed by pyrolysis of the dienone dimer, an authentic sample of IX[13] was subjected to the pyrolysis conditions. When placed in a flask at 350° dicyclopentadienone was rapidly converted to an oil which was collected in the receiver. The product no longer exhibited the 5.6 μ infrared band, and its spectrum was practically identical with that of the product obtained on pyrolysis of the anthracene adduct. A portion of the product was converted to its 2,4-dinitrophenylhydrazone which had a melting and mixture melting point identical to that above. The rest of the distillate was dissolved in benzene and treated with maleic anhydride. An adduct XI formed readily, and its melting point (243–244°) and analysis were the same as that reported earlier by Alder[4] for the maleic anhydride adduct of the product from the pyrolysis of 1-ketodicyclopentadiene.



XI

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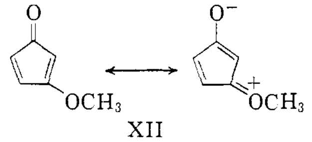
(11) C. H. DePuy and E. F. Zaweski, This Journal, **81**, 4920 (1959).

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., p. 148.

(13) C. H. DePuy and B. W. Ponder, This Journal, **81**, 4629 (1959).

It appears then that cyclopentadienone can be formed by pyrolysis of its anthracene adduct, but that high temperatures are required and the dienone immediately dimerizes. This is in contrast to the results of Pavolini,[10] but agrees well with the findings of Alder.[4] The subsequent loss of the bridge carbonyl group from dicyclopentadienone on heating has ample analogy.[5] It is interesting that the temperature necessary to bring about the reversal of the Diels–Alder reaction in the case of the anthracene adduct is about the same as reported by Alder for the cyclopentadiene adduct. Apparently little of the additional resonance energy being gained in the former case is felt in the transition state. It must also be true that the dimerization and decarbonylation reactions of the monomer take place very rapidly, since no evidence for dimer could be found even on the relatively cool walls of the distilling head. Had any monomer escaped from the flask and dimerized later, either in the receiver or in the head, it would have been easily detectable by its characteristic infrared spectrum.

One possible advantage that this synthetic scheme has is that it would allow the introduction of substituents into the adduct before pyrolysis. On heating, substituted cyclopentadienones would be formed, and if the substituents were correctly chosen the resultant product might be monomeric. Although this possibility was not extensively investigated, some studies were made of the pyrolysis of the enol ether VI. This compound is the anthracene adduct of 3-methoxycyclopentadienone (XII) and it seemed possible that the methoxyl group could at least partially overcome the electron deficiency of the ring (see resonance structures). Pyrolysis of VI did not proceed at any lower temperature than did the unsubstituted case, and no evidence for either monomer or dimer could be found. The product, too, seemed analogous to that found for the unmethoxylated compound, and, since several isomeric adducts might have been formed, no extensive investigation of its structure was made.



XII

Experimental[14]

Cyclopentene-3,5-dione.—The enedione was prepared by oxidation of commercially available cyclopentendiol with chromic acid in acetone solution by the method of DePuy and Zaweski.[11]

Anthracene Adduct.—Cyclopentene-3,5-dione (3.42 g., 0.036 mole) and anthracene (6.25 g., 0.036 mole) were dissolved in 50 ml. of benzene and heated at reflux for four days. The precipitated adduct was filtered and freed from anthracene by dissolution in dilute sodium hydroxide, filtration and reprecipitation with dilute hydrochloric acid. The white solid product weighed 8.68 g. (88.8 % yield). The adduct melted at 302–305° dec. and could not be recrystallized.

9,10-Dihydroanthracene-9,10-α,β-3-methoxycyclopentenone (VI).—Two molar equivalents of an ethereal solution of diazomethane were added in several portions over a 2-hour period to a stirred ether slurry of 8.68 g. (0.030 mole) of the anthracene adduct V. The reaction mixture was maintained at 0° by external cooling. After four hours at 0° the mixture was stirred an additional 4 hours at room temperature. The solvent was removed by gentle warming and the white crystalline product was recrystallized from absolute methanol to yield enol ether, 6.16 g. (67% yield), m.p. 211–211.5°.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.3; H, 5.6. Found: C, 83.6; H, 5.9.

9,10-Dihydroanthracene-9,10-α,β-cyclopentenone (VIII).—To a solution of 8.01 g. (0.028 mole) of the enol ether VI dissolved in 125 ml. of tetrahydrofuran was added dropwise with stirring 0.94 g. (0.028 mole) of lithium aluminum hydride. After the vigorous initial reaction had subsided the mixture was stirred at room temperature for two hours, poured into water and acidified with dilute sulfuric acid. The layers were separated, the water layer was extracted several times with methylene chloride and the extracts were combined, washed and dried over anhydrous sodium sulfate. Removal of the solvent left a white solid product which melted over a wide range and exhibited peaks of nearly equal intensity at 5.80 and 5.90 μ in the infrared.

The solid was chromatographed on a 7-ft. column filled with alumina. Elution with hexane effected virtually complete separation of the two carbonyl compounds. The first compound collected had the 5.80 μ infrared peak and melted at 200–205°, yield 1.50 g. (20.9%). Further elution with hexane gave the desired adduct, 1.34 g. (18.7% yield), infrared max. 5.90 μ, ultraviolet max. 223 (shoulder). After recrystallization from methanol it had m.p. 218–219.5°.

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.3; H, 5.5. Found: C, 88.0; H, 5.2.

Pyrolysis of Anthracene-cyclopentadienone Adduct.—The adduct (1.97 g., 0.004 mole) was placed in a 50-ml. distilling flask equipped with a short side-arm and a receiving flask immersed in a Dry Ice–acetone-bath. The distilling flask was equipped with an inlet through which a slow stream of nitrogen was passed, and then immersed in a bath that had previously been heated to 350°. Vigorous refluxing took place, a clear liquid gradually appeared in the receiver and a fluorescent white solid (anthracene) collected in the distilling head. The liquid distillate weighed 0.1 g. (40% yield) and was separated from a small amount of anthracene by evaporative distillation. It was converted in high yield to a 2,4-dinitrophenylhydrazone, m.p. 266.5–268° dec.

Anal. Calcd. for $C_{15}H_{12}O_4N_4$: C, 57.7; H, 3.9; N, 17.9. Found: C, 57.7; H, 3.4; N, 18.1.

Pyrolysis of Cyclopentadienone Dimer.—A sample of the dimer of cyclopentadienone (0.44 g., 0.0027 mole) obtained by the hydrolysis of the dioxime with levulinic acid,[13] was heated at 350° under nitrogen in the same apparatus used for the pyrolysis of the anthracene adduct. The product, 0.20 g. (55.5% yield), was a pale yellow liquid which was purified by evaporative distillation. The 2,4-dinitrophenylhydrazone, prepared in the usual manner, melted at 268–268.5° and did not depress the melting point of that formed above.

The maleic anhydride adduct of the product was prepared by dissolving equimolar amounts of the yellow liquid and maleic anhydride in benzene. After standing for two hours at room temperature the white, crystalline adduct was filtered. It had a m.p. 243–244° (reported[4] 241°).

Anal. Calcd. for $C_{13}H_{10}O_4$: C, 67.8; H, 4.4. Found: C, 67.9; H, 4.6.

A sample of the liquid product was reduced with hydrogen and platinum. Absorption of hydrogen stopped after the uptake of 3.0 molar equivalents of H_2.

Ames, Iowa

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(14) Melting points are uncorrected.