was undepressed on admixture with an authentic sample (see below).

2-Bromo-5α-cholest-1-en-3-one (VIII).—A solution of 1.80 g. (3.32 mmoles) of crude 2,2-dibromo-5α-cholestan-3-one[23] in 8 ml. of collidine (freshly distilled) and 15 ml. of dimethylformamide was boiled under reflux for 2.5 hr. under a nitrogen atmosphere. Then the solution was cooled to room temperature and 200 ml. of ether was added, which precipitated 610 mg. of collidine hydrobromide, collected by filtration. The filtrate was washed with three 30-ml. portions of dilute sulphuric acid, then with 20-ml. portions of water until the wash was neutral, dried over anhydrous sodium sulfate, and evaporated to dryness under reduced pressure. The residue was dissolved in 10 ml. of petroleum ether and chromatographed on a column (22 mm. in diameter) of 60 g. of silica gel. Elution with 1:1 petroleum ether–benzene yielded 735 mg. (47.6%) of 2-bromo-5α-cholest-1-en-3-one, which was recrystallized from methanol and then had m.p. 105–107°, $[\alpha]_D$ +44°, $\lambda_{\max}^{\text{EtOH}}$ 256 mμ (ϵ 9400), $\lambda_{\max}^{\text{KBr}}$ 5.92 and 6.28 μ, R_f 0.78; lit.[9a] m.p. 91.5–92.5°, $[\alpha]_D$ +37.4°, $\lambda_{\max}^{\text{EtOH}}$ 256 mμ (ϵ 8500).

Anal. Calcd. for $C_{27}H_{43}BrO$: C, 69.96; H, 9.35. Found: C, 70.16; H, 9.34.

5α-Cholest-1-en-3-one 2,4-Dinitrophenylhydrazone.—Pure bromo ketone I was converted to the 2,4-dinitrophenylhydrazone of 5α-cholest-1-en-3-one in almost quantitative yield by the procedure of Djerassi.[18] Recrystallization from 1:1 benzene–ethanol gave brilliant orange-red scales: m.p. 228–230°, $\lambda_{\max}^{\text{CHCl}_3}$ 384 mμ (ϵ 30,800); lit. m.p. 219–221°,[18] 232–233°,[24] $\lambda_{\max}^{\text{CHCl}_3}$ 384 mμ (ϵ 27,200).[25]

5α-Cholest-1-en-3-one (V). A. By Hydrolysis of the 2,4-Dinitrophenylhydrazone.—The acid-catalyzed hydrolysis of the 2,4-dinitrophenylhydrazone was carried out in acetone according to the procedure of DeMaecker and Martin[24] and gave the the 1-en-3-one V in 75% yield, m.p. 98–101°, homogeneous by t.l.c. and v.p.c. Two recrystallizations from methanol gave an analytical sample: m.p. 100.5–101.5°, $[\alpha]_D$ +62°, $\lambda_{\max}^{\text{KBr}}$ 5.95 and 12.80 μ, $\lambda_{\max}^{\text{EtOH}}$ 230 mμ (ϵ 9650) and 242 mμ (ϵ 7000); lit.[9a] m.p. 98–100°, $\lambda_{\max}$ 231 mμ (ϵ 9950).

Anal. Calcd. for $C_{27}H_{44}O$: C, 84.31; H, 11.53. Found: C, 84.18; H, 11.29.

B. By Debromination of 2-Bromo-5α-cholest-1-en-3-one (VIII).—A mixture of 415 mg. (0.90 mmole) of bromo ketone VIII, 4.0 g. of zinc dust, and 35 ml. of absolute ethanol was boiled under reflux with stirring for 12 hr. The zinc, removed by centrifuging, was washed with hot ethanol, and the combined ethanol solutions were evaporated under reduced pressure to give a bromine-free oil which crystallized from methanol to yield 175 mg. (51%) of the 1-en-3-one V, m.p. 93–97°. Two more recrystallizations from methanol gave m.p. 98.5–99°, $[\alpha]_D$ +68°, $\lambda_{\max}^{\text{KBr}}$ 5.95 and 12.80 μ, $\lambda_{\max}^{\text{EtOH}}$ 230 mμ (ϵ 9400), homogeneous by v.p.c. with T_r 1.15, and t.l.c., R_f 0.69.

3,3-(Ethylenedioxy)-2α-bromo-5α-cholestane (X).—To a solution of 3.00 g. (7.00 mmoles) of 3,3-(ethylenedioxy)-5α-cholestane in 20 ml. of tetrahydrofuran (dried over potassium hydroxide and distilled from lithium aluminum hydride) was added 2.45 g. (7.70 mmoles) of pyridinium bromide perbromide.[26] After 30 min. at room temperature, 100 ml. of 5% sodium bicarbonate solution was added and the mixture was extracted with three 30-ml. portions of methylene chloride. The extract was washed with five 20-ml. portions of water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to give a pale yellow solid. This was dissolved in 60 ml. of petroleum ether and chromatographed on a column (25 mm. in diameter) of 75 g. of Florisil. Elution with 280 ml. of petroleum ether gave 2.32 g. (65%) of the bromo ketal X, the infrared spectrum being identical with that of an authentic sample, prepared as reported previously.[27] Recrystallization from methanol gave fluffy needles, m.p. 161–162.5°, which changed to small rods, m.p. 158–160°, if allowed to stand in contact with the mother liquor.

Elution with 60 ml. of benzene gave 775 mg. of a white solid which was recrystallized from methanol and then had m.p. 135–138°; $\lambda_{\max}^{\text{KBr}}$ 7.55, 8.60, 8.93, 10.15, and 10.45–10.60 μ (doublet); positive Beilstein test. When a sample of this material was heated (steam bath) in 80% acetic acid containing a few drops of concentrated sulfuric acid a 75% yield of 2α-bromo-5α-cholestan-3-one was obtained. Another sample was recovered unchanged after boiling under reflux for 3 hr. with collidine. No further attempt was made to identify this material.

Attempted Reaction of 3,3-(Ethylenedioxy)-2α-bromo-5α-Cholestane (X) with Dimethyl Sulfoxide.—A mixture of 595 mg. (7.08 mmoles) of sodium bicarbonate, 595 mg. (1.17 mmoles) of the bromo ketal X, and 15 ml. of dimethyl sulfoxide was stirred and heated at 125° for 60 min., and then cooled to room temperature. The white crystals which formed were collected, washed with water, and dried over calcium chloride to give 595 mg. which had an infrared spectrum identical with that of the starting material. T.l.c. showed only one spot, R_f 0.82, corresponding to starting material.

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The Formation of Cyclopentadienones[1]

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Received June 22, 1964

Cyclopentadienone and 2-chlorocyclopentadienone have been generated in ether solution at room temperature. Once formed, these dienones dimerize extremely readily. The structure of the dimer from chlorocyclopentadienone has been determined by nuclear magnetic double resonance. Cyclopentadienone has been trapped with cyclopentadiene, but all attempts to trap it as a diene, using maleic anhydride and a wide variety of dienophiles, were unsuccessful.

Cyclopentadienone (I) is a potentially interesting but highly elusive molecule whose chemistry is almost completely unknown. Some time ago, we began a study of the chemistry of unsaturated derivatives of cyclopentanone, and a number of the results of the published portion of that study, dealing with cyclopentene-3,5-dione and related compounds, had a direct bearing on the stability and formation of cyclopentadienone.[4] In the following, we deal more directly with the parent dienone and of a simple monochloro derivative.

It has been known for a long time that attempts to generate simply substituted cyclopentadienones lead, invariably, to the formation of dimeric products.

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(1) This work was supported by Grant No. GM-05972, from the Division of General Medical Sciences of the National Institutes of Health. Presented (in part) at the Division of Organic Chemistry, 143rd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962.

(2) Alfred P. Sloan Foundation Fellow, 1960–1964.

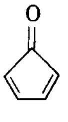
(3) Ohio Oil Co. Fellow, 1961–1962; Procter and Gamble Co. Summer Fellow, 1962.

(4) C. H. DePuy and E. F. Zaweski, *J. Am. Chem. Soc.*, **81**, 4920 (1959).

Japp and Burton,[5] in 1887, generated 3,4-diphenylcyclopentadienone which was isolated as the dimer,[6] and Thiele[7] obtained the dimer of cyclopentadienone oxime by the reaction of cyclopentadiene and ethyl nitrite. Allen and VanAllan[8] have summarized the literature dealing with substituted cyclopentadienones and concluded that in order for the monomeric form to be at all stable, a cyclopentadienone must be at least trisubstituted, and that two of these three substituents must be adjacent to the carbonyl group.

The literature dealing with the unsubstituted ketone is quite meagre. Alder[9] generated it briefly by cracking 1-ketodicyclopentadiene and DePuy and Lyons[10] also postulated its transient existence in the pyrolysis of its anthracene adduct. In both cases, only decarbonylation products of its dimer could be isolated. Other data also point to the fact that cyclopentadienones are reluctant to form. Cyclopentene-3,5-dione (II), for instance, shows no evidence of enolization[4,11] (to give a hydroxycyclopentadienone) despite the fact that its dihydro derivative, cyclopentane-1,3-dione, is completely enolic. The abnormally high reactivity of indenone[12] is also in accord with these observations. It appeared to us that a more critical examination of the formation and reactions of cyclopentadienones was in order. After our work was mainly complete, a publication of Hafner and Goliasch appeared[13] in which many of the same approaches to the problem were attempted. Since in general our conclusions do not agree with theirs, a detailed discussion seems warranted. Some of these results have been reported in preliminary form.[14]

When relatively large amounts of cyclopentenone became available to us, we examined this molecule as a possible precursor of cyclopentadienone. Reaction of the enone with N-bromosuccinimide in CCl_4 solution affords a bromo ketone in yields of up to 75%. This compound, on the basis of its analysis, is clearly a monobromo derivative of cyclopentenone. Hafner and Goliasch[13] assigned this compound the structure III, 5-bromocyclopentenone, on the basis of its reduction and hydrolysis to 2-hydroxycyclopentanone. We reported,[14] on the basis of its nuclear magnetic resonance spectrum, that it is actually IV, 4-bromocyclopentenone. Two vinyl protons, at δ 6.21 and 7.61, are still present, so that the bromine is not attached to the double bond. The other three protons are accounted for in an ABX pattern[15] *in which only the X-proton is coupled to the vinyl protons.* In a wide variety of cyclopentenone derivatives the protons adjacent to the carbonyl group are not coupled to the vinyl protons, while the β-protons invariably are.[16] It seems probable that an allylic rearrangement occurred during reduction.[17]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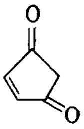
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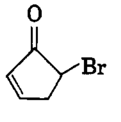
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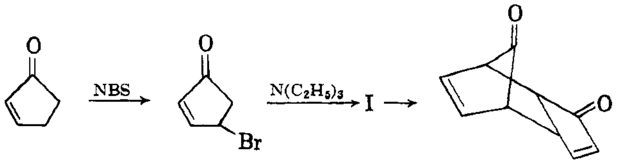
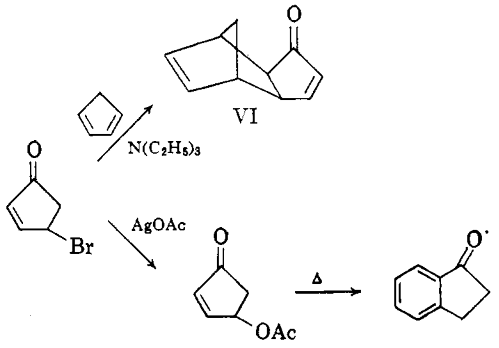


IV

V

When 4-bromocyclopentenone is treated in ether solution with an equimolar amount of triethylamine solution, an immediate reaction occurs, triethylamine hydrobromide precipitates, and, if the ether solution is evaporated after filtration, the dimer of cyclopentadienone (V) is isolated in nearly quantitative yield. The evidence for the intermediacy of cyclopentadienone is as follows. If cyclopentadiene is added to the reaction mixture before the triethylamine, then the major product is 1-ketodicyclopentadiene (VI). In the absence of triethylamine, 4-bromocyclopentenone and cyclopentadiene do not react, even after a long period of time. Apparently, then, cyclopentadiene acts as a trap for cyclopentadienone.



VI

VII

The elimination of HBr from 4-bromocyclopentenone is quite rapid, even at room temperature, but the dimerization of the dienone is a great deal faster. Several attempts were made to examine by ultraviolet spectrometry, at as low a temperature as feasible, solutions of the bromo ketone which were undergoing elimination, in the hopes of recording the spectrum of the dienone. Rapid scanning of the spectrum at about $-30°$ gave no indication of a buildup of monomer. We were able to make an estimate, by ultraviolet analysis, of the relative rate of elimination of 4-bromocyclopentenone and its saturated analog, 3-bromocyclopentanone. In aqueous alcohol using sodium hydroxide as the base, the bromoenone underwent elimination nearly twice as fast as the saturated bromo ketone. In this elimination there appears to be no energy barrier to the formation of cyclopentadienone, but this is reasonable if the rate-

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(15) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 132–138.

(16) C. H. DePuy, C. E. Lyons and L. B. Rodewald, submitted for publication.

(17) That the bromo ketone obtained in the two laboratories is indeed the same compound is shown by the identity of their infrared spectra. We wish to acknowledge the most stimulating and enjoyable correspondence and discussion with Professor Hafner on this and related topics. In other work we have prepared authentic III [C. H. DePuy, E. W. Ponder, and J. D. Fitzpatrick, *J. Org. Chem.*, **29**, 3508 (1964)]. It does not form cyclopentadienone on reaction with base.

determining step in the elimination is the formation of anion,[18] as appears probable.

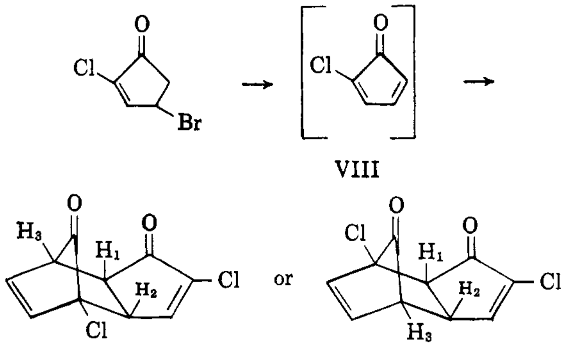
4-Bromocyclopentenone reacts with silver acetate in boiling acetic acid–acetic anhydride solution with the formation of 4-acetoxy cyclopentenone (VII). Its n.m.r. spectrum is completely consistent with its formulation as the 4-isomer and not the 5-isomer as proposed by Hafner and Goliasch.[13] This compound seems to be remarkably stable for a β-acetoxy ketone, and a pure sample can be heated under reflux without decomposition. Acetic acid is readily eliminated on pyrolysis. When dropped through a vertically mounted pyrolysis tube at 450°,[19] 1 molar equiv. of acetic acid is produced and indanone, resulting from dimerization of cyclopentadienone, decarbonylation, and aromatization of the dimer, is formed. In other experiments the acetoxy enone was allowed to evaporate slowly into a furnace held at 500° and 10^{-6} mm. The effluent gases were run directly onto the cold finger of a trap at liquid nitrogen temperature. Again indanone was the major product. No dicyclopentadienone was obtained from any of these pyrolysis runs. This dimer would have been easy to detect because of its characteristic 5.6-μ infrared absorption band due to the bridge carbonyl group.

In the dimerization of cyclopentadienone one molecule serves as a diene, the other as a dienophile. By generating the dienone in the presence of cyclopentadiene we succeeded in trapping it as a dienophile. It seemed also of interest to attempt to trap the dienone as a diene, using a dienophile as a trapping agent. To this end cyclopentadienone was generated slowly in the presence of a large excess of a variety of dienophiles. Initially maleic anhydride and benzoquinone were used.[20] In a typical experiment a mixture of the bromo enone and an excess of benzoquinone was dissolved in ether and a dilute solution of triethylamine in ether was added slowly over a period of up to 24 hr. After the addition, the solvent was evaporated and the excess benzoquinone was removed by sublimation. The residue was chromatographed. From all reactions a good yield of dicyclopentadienone was obtained, *but no adduct between cyclopentadienone and any dienophile.* It was next reasoned that perhaps, since the dienone is very electron deficient, it might react more readily with an electron-rich dienophile.[21] Cyclopentadienone was therefore generated in the presence of a large excess of a variety of olefins and acetylenes, including ethyl vinyl ether, styrene, and tolane. *In each case dimer was the exclusive product, and no mixed adduct could be found.* Finally we considered the possibility that the dienone was such a powerful dienophile that it was able to compete successfully with other dienophiles even at very low relative concentrations. If that were so it should be rather nonselective, reacting with any diene present. When generated in the presence of anthracene, however, again only dimer was obtained.[22]

In summary then, cyclopentadienone may be generated easily at room temperature by elimination of the elements of HBr from 4-bromocyclopentenone. It may also be formed conveniently in the gas phase by pyrolysis of 4-acetoxycyclopentenone. The dimerization of the dienone, once formed, is extremely rapid. This is shown by the fact that no spectroscopic evidence for the existence of a transient monomer could be discovered, even at low temperatures, and also by the fact that in the low-pressure pyrolysis of the acetate only decarbonylated dimers were formed. Since the dimer does not decarbonylate below 100°, if any monomeric cyclopentadienone escaped from the reaction tube and dimerized in the cold trap the bridge carbonyl would have survived. Cyclopentadienone, once formed, must have dimerized immediately.

The very rapid dimerization of cyclopentadienone is an interesting and puzzling reaction since, while the dienone is a good dienophile as shown by its reaction with cyclopentadiene, it does not enter into a normal Diels–Alder reaction as a diene. One would not expect a normal Diels–Alder reaction between two such highly electron-deficient molecules to be as rapid as it appears to be. One attractive hypothesis is that the dienone has a triplet ground state, as appears to be the case with the pentaphenylcyclopentadienyl cation.[23] Two such molecules should dimerize rapidly but might not otherwise show extreme reactivity. No evidence for a triplet ground state has been found, however.

We next turned our attention to a brief examination of the chemistry of 2-chlorocyclopentadienone (VIII), obtained by the action of N-bromosuccinimide (NBS) on chlorocyclopentenone, followed by elimination. It was felt that a substituent of this type might slow down dimerization sufficiently to allow detection of the monomer, or might disturb the ground state symmetry or energy enough to make the molecule a singlet, if the unsubstituted molecule were a triplet. Actually, however, 2-chlorocyclopentadienone behaves exactly



VIII

IX

X

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[18] F. G. Bordwell and E. W. Garbisch, Jr., *J. Org. Chem.*, **28**, 1765 (1963).

[19] C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

[20] Tetracyanoethylene was not stable in the presence of the base necessary for the elimination.

[21] J. Sauer and H. Wiest, *Angew. Chem.*, **74**, 353 (1962).

[22] Hafner and Goliasch[13] report two examples of adducts in which cyclopentadienone had apparently acted as a diene in Diels–Alder reactions. In one case it is reported that when generated in the presence of cyclopentadiene a minor product is 8-ketodicyclopentadiene, the product to be expected if cyclopentadiene acts as a dienophile and the dienone as a diene. In the other case it is stated that 2-phenyl-7-ketonorbornadiene is formed in small yield when 4-bromocyclopentenone is treated with base in the presence of phenylacetylene. Careful examination of the experimental section of this paper fails to convince us that either of these proposals are on very firm grounds. Evidence for the first reaction consists of the fact that a 1790-cm.$^{-1}$ infrared band appears in the spectrum of the residue from the reaction. This band could arise, however, from some dicyclopentadienone which would undoubtedly also be formed in this reaction. The physical and chemical properties ascribed to 2-phenyl-7-ketonorbornadiene are not those which we would anticipate for a compound of this unique structure. The reported carbonyl absorption at 1730 cm.$^{-1}$ seems much too high for such a strained carbonyl group, and the conversion to biphenyl in only 7% yield on heating at 200° also appears incompatible with the assigned structure. There is good reason to think that a molecule with this structure would decarbonylate at or below room temperature.

[23] R. Breslow, H. W. Chang, and W. A. Yager, *J. Am. Chem. Soc.*, **85**, 2033 (1963).

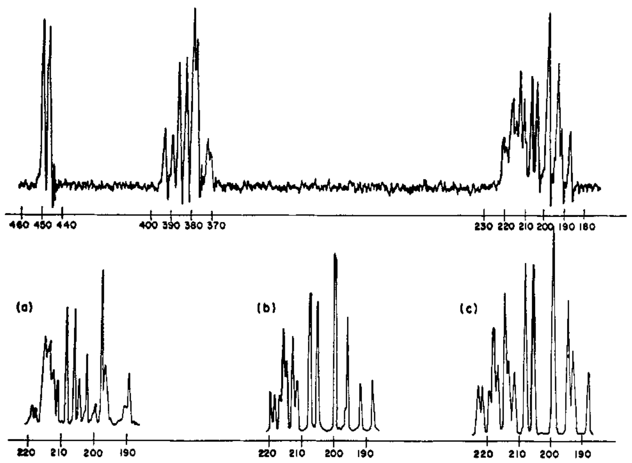


Fig. 1.—(Top) N.m.r. spectrum of 2-chlorocyclopentadienone dimer in deuteriochloroform solution (60 Mc./sec.). Peak positions are listed in cycles per second downfield from internal tetramethylsilane (chloroform resonance deleted). (Bottom) Calculated spectra for aliphatic region of 2-chlorocyclopentadienone dimer: (a) structure X, theoretical parameters; (b) structure IX, theoretical parameters; and (c) structure IX, corrected parameters.

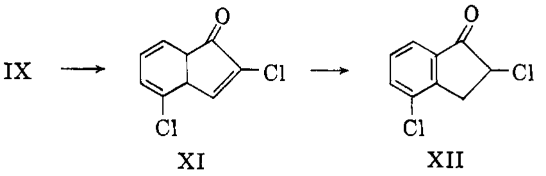
like its unsubstituted parent, dimerizing extremely rapidly and not entering into Diels–Alder reactions as a diene.

The structure of the 2-chlorocyclopentadienone dimer was rigorously established by interpretation of the following spectral data. (1) The typical bridged ketone band at 5.54 μ in the infrared spectrum shows that a Diels–Alder type dimer was formed. (2) Of the eight possible Diels–Alder dimers, four were eliminated by inspection of the ultraviolet spectrum, $\lambda_{max}^{C_2H_5OH}$ 2338 Å. (ϵ 9200), characteristic of the 2-chlorocyclopent-2-enone chromophore [$\lambda_{max}^{C_2H_5OH}$ 2340 Å. (ϵ 9300)]. (3) The ring fusion should be *endo* as in the equivalent dimer of cyclopentadienone (this point has been verified by subsequent ring closure to a cage structure[24]). (4) The n.m.r. spectrum of the compound is shown in Fig. 1. Consideration of the foregoing data limits the structure to IX and X, and a choice between these structures was made by superficial analysis of the n.m.r. spectrum. Although considerable support for structure IX may be gained from this analysis of the closely coupled ABC (high-field multiplet) pattern, the complex nature of the spectrum does not permit an unequivocal assignment. Additional support for structure IX was obtained in two ways.

The two structures bear an interesting relationship to one another, IX has a linear six-spin system and X a branched six-spin system. Accordingly, the magnitude of the coupling constants should be nearly identical, whichever structure is chosen. Although splittings are readily obtained from the spectrum, it was decided to use coupling constants from model systems to compute theoretical spectra for IX and X.[25] In these computations, identical values for the chemical shifts and coupling constants were used. The resultant computed spectra are shown in Fig. 1 (a for X and b for IX). The parameters used were ν_1 195.0, ν_2 209.0, ν_3 215.0, ν_4 376.0, ν_5 386.0, ν_6 452.0; $J_{1,2}$ = 8.0 c.p.s., $J_{1,3}$ (for b only) = 4.0 c.p.s., $J_{2,3}$ (for a only) = 4.0 c.p.s., $J_{2,6}$ = 2.6 c.p.s., $J_{3,4}$ = 1.0, $J_{3,5}$ = 3.1 c.p.s., and $J_{4,5}$ = 6.0 c.p.s. The correspondence between b (a linear six-spin system) and the observed spectrum (ABC pattern) for the dimer is clearly seen in Fig. 1. A small correction of the parameters gave computed spectrum c which matches the observed spectrum both in frequency and intensity. The parameters used for c were ν_1 194.7, ν_2 209.1, ν_3 217.5, ν_4 374.7, ν_5 385.1, ν_6 449.0; $J_{1,2}$ = 6.25 c.p.s., $J_{1,3}$ = 4.85 c.p.s., $J_{2,6}$ = 2.80 c.p.s., $J_{3,4}$ = 1.78 c.p.s., $J_{3,5}$ = 3.98 c.p.s., and $J_{4,5}$ = 7.10 c.p.s.

More definite n.m.r. evidence in favor of structure IX was obtained by the use of nuclear magnetic double resonance.[26] When the two vinyl protons in the norbornene ring were irradiated, the low-field proton of the ABC multiplet collapsed into a doublet, thus identifying the bridgehead proton. Irradiation of the vinyl proton in the cyclopentenone ring caused the center of the ABC multiplet to collapse into a doublet. Since H_2 was then identified as a doublet after removal of coupling with the vinyl proton, structure IX was again favored. Although we do not consider this evidence as conclusive "proof" of structure, taken together it provides strong presumptive support for the assignment of structure.

When the dimer IX was heated briefly at 180°, it lost carbon monoxide and formed 2,4-dichloro-3a,7a-dihydroinden-1-one (XI). An n.m.r. spectrum taken immediately on the product was completely consistent with this structure (see Experimental). On standing in CCl_4 for 24 hr., the compound aromatized to 2,4-dichloroindanone (XII). The ABX pattern for the aliphatic protons was analyzed and the lack of coupling between an *ortho* proton and the benzylic position (AB of the ABX spectrum) serves as further support for structure X.



Experimental

Cyclopentenone.—This ketone was prepared from the cyclopentenediols by the method of DePuy and Eilers.[27]

4-Bromocyclopent-2-enone (IV).—A mixture of 10.1 g. (0.213 mole) of cyclopent-2-enone (b.p. 55° at 21 mm.), 22 g. (0.124 mole) of N-bromosuccinimide, and *ca.* 0.5 g. of α,α'-azodiisobutyronitrile in 150 ml. of carbon tetrachloride was heated on a steam bath for 1 hr. After cooling in an ice–water bath, the mixture was filtered and the filter cake was washed with cold carbon tetrachloride. The filtrate was washed successively with two 100-ml. portions of ice–water and dilute sodium thiosulfate solution, dried over anhydrous magnesium sulfate, and the carbon tetrachloride was removed under reduced pressure (40°). The residual oil was distilled through a short Vigreux column to yield 14.4 g. (72%) of IV, b.p. 36–37° at 0.1 mm. All samples of IV were stored in a freezer at 0° until use. Samples stored under these conditions decomposed within 2 weeks. Ultraviolet showed λ_{max} 2150 Å. (log ϵ 4.01).

4-Acetoxycyclopent-2-enone (VII).—The acetoxy compound was prepared following the method of Crombie.[28] Silver acetate was freshly prepared by precipitation from an aqueous solution containing 34 g. (0.2 mole) of silver nitrate by the addition of

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[24] *Cf.* P. E. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.*, **86**, 692 (1964).

[25] We are indebted to Dr. A. A. Bothner-By of the Mellon Institute for a copy of his program for the computation.

[26] J. D. Baldeschweiler and E. W. Randall, *Chem. Rev.*, **63**, 81 (1963).

[27] C. H. DePuy and K. L. Eilers, *J. Org. Chem.*, **24**, 1380 (1959).

[28] L. S. Crombie, M. Elliot, and S. H. Harper, *J. Chem. Soc.*, 971 (1950).

19.6 g. (0.2 mole) of potassium acetate. The filtered precipitate was washed by heating the suspension twice in glacial acetic acid and once in a mixture of glacial acetic acid and acetic anhydride. The solution was washed with ether and dried.

To a solution of 22.7 g. (0.14 mole) of bromoenone (IV) in 200 ml. of glacial acetic acid was added 24.9 g. (0.5 mole) of silver acetate. The resulting suspension was stirred at reflux for 24 hr. Silver bromide (26.8 g.) was removed by filtration, and the acetic acid was removed by distillation at aspirator pressure. Vacuum distillation of the residue gave 13.9 g. (71%) of 4-acetoxycyclopent-2-enone, b.p. 57–58° (2 mm.).

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

Dicyclopentadienone (V).—The bromoenone (IV, 2 g. 0.012 mole) was dissolved in 20 ml. of ether, and triethylamine (1.25 g., 0.012 mole) dissolved in 15 ml. of ether was added. A white precipitate formed immediately. After standing for 4 hr., the solution was filtered, the precipitate was washed with ether, and the ether was removed from the filtrate. The solid residue, after removal of the ether, was sublimed to give 0.92 g. (92%) of dicyclopentadienone, m.p. 99–99.5°, identical with an authentic sample.[29]

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

Dicyclopentadien-1-one (VI).—Freshly distilled cyclopentadiene (24.2 g., 0.366 mole) and triethylamine (5.05 g., 0.05 mole) were dissolved in 50 ml. of ether and to this solution was added, dropwise with vigorous stirring, a solution of 4-bromocyclopent-2-enone (4 g., 0.025 mole) in 50 ml. of ether. After the addition was complete (2 hr.), the mixture was allowed to stand for an additional 4 hr. and washed with two 50-ml. portions of water; the solvent was removed at room temperature under vacuum. The resulting oil was taken up in pentane and, upon cooling in Dry Ice, a solid precipitate which was recrystallized from pentane and sublimed to give 2.25 g. (62%) of 1-ketodicyclopentadiene, m.p. 58–60° (lit.[30] m.p. 59–59.5°).

A 2,4-dinitrophenylhydrazone was prepared in the usual manner, m.p. 196–197° (lit.[31] m.p. 199.2–199.5°). The ketone was reduced by lithium aluminum hydride to β-1-hydroxydicyclopentadiene, m.p. 85.0–85.5° (lit.[31] m.p. 85.0–85.8°).

2-Chlorocyclopent-2-enone.—This compound was obtained as a by-product in the chlorination of cyclopentanone to form 2-chlorocyclopentanone by the procedure of Wanzlick and Gollmer.[32] 2-Chloro-2-cyclopentenone obtained in this manner was contaminated with a small amount of 5-chloro-2-cyclopentenone from which it could not be separated by distillation (b.p. 96–100° at 16 mm.). The presence of two components was shown in its n.m.r. spectrum and by g.l.p.c. with a 1-ml. Carbowax 20M on regular Chromosorb W column at 82°.

4-Bromo-2-chlorocyclopent-2-enone (V).—A mixture of 11.6 g. (0.1 mole) of 2-chlorocyclopent-2-enone (contaminated with 5-chlorocyclopent-2-enone), 17.8 g. (0.1 mole) of N-bromosuccinimide, and *ca.* 0.5 g. of α,α′-azodiisobutyronitrile (AIBN) in 200 ml. of anhydrous carbon tetrachloride was heated at reflux for 2 hr. The major portion of the solid N-bromosuccinimide was consumed as evidenced by the succinimide floating to the surface of the solution. The mixture was cooled in an ice bath and filtered; the filter cake was washed with cold carbon tetrachloride. The filtrate was washed successively with ice–water, sodium thiosulfate solution, and ice–water, dried over anhydrous magnesium sulfate, and distilled under reduced pressure to yield 12.1 g. (62%) of 4-bromo-2-chlorocyclopent-2-enone, b.p. 65–66° (0.1 mm.). The distillate solidified and after recrystallization from ether melted at 55–56°.

Anal. Calcd. for C_5H_4BrClO: C, 30.72; H, 2.06; Br, 40.88; Cl, 18.15. Found: C, 30.84; H, 2.08; Br, 41.00; Cl, 18.01.

Spectra were infrared (KBr), C=O (5.84 μ), C=C (6.29 μ), plus other bands at 7.79, 10.33, 10.75, 10.91, 11.4, 13.26, and 14.45 μ; ultraviolet, $\lambda_{\mathrm{mau}}^{\mathrm{C_2H_5OH}}$ 2340 Å. (ε 9300); n.m.r., AB of ABX 2.98 (multiplet), X of ABX 5.2 (multiplet), vinyl proton 7.56 (doublet) downfield from tetramethylsilane (TMS) in CCl_4 solution.

To a solution of 1.3 g. (6.7 moles) of 4-bromo-2-chlorocyclopent-2-enone in 30 ml. of anhydrous ether cooled in an ice bath was added slowly *ca.* 5 ml. of anhydrous trimethylamine. A precipitate formed immediately on contact of the amine with the solution. After standing overnight, at room temperature, the mixture was filtered, and the ether was evaporated. The filter cake was washed with water to remove salts and the remaining solid was combined with that from ether evaporation. The combined solids were dissolved in carbon tetrachloride and recrystallized to yield 0.5 g. (65%) of a 2-chlorocyclopentadienone dimer, m.p. 155–156° (with evolution of a gas). The melt would not crystallize. 2-Chlorocyclopentadienone dimer was characterized by the following analysis and spectral features.

Anal. Calcd. for $C_{10}H_6Cl_2O_2$: C, 52.42; H, 2.64; Cl, 30.97. Found: C, 52.41; H, 2.57; Cl, 31.05.

Spectra were infrared (KBr), C=O (5.54, bridged C=O, and 5.83 μ), C=C (6.29 μ); ultraviolet, $\lambda_{\max}^{\mathrm{C_2H_5OH}}$ 2338 Å. (ε 9200); n.m.r. ($CDCl_3$), complex multiplet for three protons centered at δ 3.42, eight-line multiplet for two vinyl protons at δ 6.34 (AB of ABX), doublet at δ 7.50 for one vinyl proton β to carbonyl group.

2,4-Dichloro-3a,7a-dihydroinden-1-one (**XI**).—A sample (*ca.* 0.5 g.) of 2-chlorocyclopentadienone dimer (IX) was placed in an evacuated Pyrex tube, sealed, and heated to 180° in a preheated oil bath. The sample melted and decomposition (gas evolution) was evident. After heating for 15 min., the tube was cooled and opened (caution—pressure). The oil was taken up in carbon tetrachloride containing 1% TMS and filtered, and its n.m.r. spectrum, determined immediately, gave the following pattern: two-proton multiplet with centers at δ 3.62 and 3.85, three vinyl proton multiplet with centers at δ 5.41 and 5.66, and a single proton (doublet) at δ 7.63. From the chemical shifts and splittings of the multiplets the following was ascertained: proton on C-3 is located at δ 7.63 split by proton on C-3a (splitting 2.5 c.p.s.), proton on C-3a is located at δ 3.62 (splitting 2.5 and 10 c.p.s.), proton on C-7a is located at δ 3.85 (splittings 10, 2.8, and 1.4 c.p.s.). The vinyl protons could not be distinguished from one another on the basis of splittings within the multiplet.

2,4-Dichloroindanone (**XII**).—The sample containing 2,4-dichloro-3a,7a-dihydroinden-1-one (XI) was concentrated to about one-half volume and allowed to stand for 24 hr. with deposition of white crystals, m.p. 78–79°. The n.m.r. spectrum of this substance was as follows: AB of ABX centered at δ 3.74, X of ABX at δ 4.45, and a three-proton aromatic multiplet (ABC) at δ 7.49.

Analysis of the ABX portion of this spectrum gave the following parameters: ν_A = 191.0 c.p.s., ν_B = 225.3 c.p.s., ν_C = 267.0 c.p.s.; J_{AB} = 18.20 c.p.s., J_{AX} = 3.58 c.p.s., J_{BX} = 7.64 c.p.s. (chemical shifts in c.p.s. at 60 Mc./sec. downfield from TMS). These parameters were used to compute a spectrum. The computed spectrum agreed with the actual spectrum with an average deviation in the line positions (frequencies) of ±0.4 c.p.s. The intensity pattern was entirely consistent with the observed spectrum.

Pyrolysis of 4-Acetoxycyclopent-2-enone (**VII**).—Small amounts [0.5–1.5 g.] of 4-acetoxycyclopent-2-enone were passed through a 100-mm. glass helices packed column in a nitrogen stream at temperatures from 369–500°. On several runs only the liberated acetic acid was titrated. On one run (455°) the pyrolysis product was freed of acetic acid and its ultraviolet spectrum determined. The spectrum was identical with that of 1-indanone. In another run (426°) the pyrolysis products were analyzed by g.l.p.c. on a 1-m. Ucon LB550X column. Four peaks were found and one of these was identical in retention time with that for 1-indanone. The outlet port of the g.l.p.c. was attached to a tube containing 5 ml. of a 2,4-dinitrophenylhydrazine solution in diglyme and the peak corresponding in retention time to 1-indanone was allowed to pass into this solution. The precipitate was shown to be 1-indanone 2,4-dinitrophenylhydrazone by m.p. 258–259°, mixture melting point with authentic sample not depressed.

Acknowledgment.—We are indebted to the National Science Foundation through Grant G-14916 for the purchase of the ultraviolet spectrophotometer used in this work.

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