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The Tricyclo[5.3.0.0^{2,6}]decane System. The Photodimers of Cyclopentenone[1]

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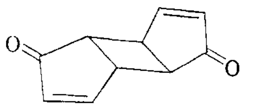
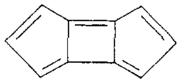
Cyclopentenone is converted by ultraviolet light into two photodimers. These have been assigned structures III and IV. *cis,trans,cis*-Tricyclo[5.3.0.0^{2,6}]deca-4,9-diene-3,8-dione (I) has been prepared.

Light-induced formation of cyclobutanes is a familiar observation.[2] The novelty of such photoproducts has, however, often overshadowed the synthetic utility of the reaction. In particular, photodimerization of α,β-unsaturated ketones, a reaction of remarkable generality,[3] has been used only infrequently in the planned construction of new systems. The applicability of this reaction is illustrated here in the synthesis of the tricyclic diene-dione I,[4] a potential precursor of the non-benzenoid, aromatic hydrocarbon II.[5]

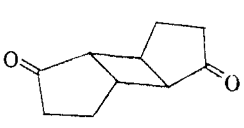


I

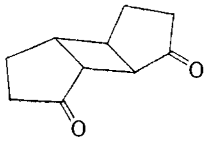


II

Although cyclopentenone is the simplest of stable, alicyclic, α,β-unsaturated ketones, its photochemical behavior has not been previously investigated.[6] On exposure to light of wave lengths above 300 mμ, this ketone, either in solution in a variety of solvents or as the pure liquid, is converted quickly and in high yield to an approximately equal mixture of two dimers, III, m.p. 125–126.5°, and IV, m.p. 66–67°.[7]



III



IV

The infrared spectra of III and IV are free of ethylenic absorption; a strong band at 5.78 μ arises from the five-membered ring ketone stretching vibration. Neither dimer shows any high intensity ultraviolet maximum, nor, in the n.m.r. spectrum, any distinguishing resonances characteristic of vinyl protons.

Wolff–Kishner reduction of III gives a saturated C_{10}-hydrocarbon (V) different from either of the isomeric tetrahydrodicyclopentadienes. The same hydrocarbon is obtained from reduction of IV, hence the photodimers differ only in the relative positions of the oxygen functions.

Baeyer–Villiger oxidation of either photodimer proceeds readily with monoperphthalic acid in ether. The dilactones VI and VII are formed in good yield from dimers III and IV, respectively. Both compounds have an infrared absorption at 5.75 μ in agreement with the standard value for six-membered ring lactones. The n.m.r. spectra (Fig. 1) of the dilactones show two groups of absorptions. The low-field peaks are attributable to the protons on carbon bearing oxygen; the higher-field signals arise from the remaining protons. For both VI and VII these groups are in the ratio of 1:5, a clear demonstration that oxygen insertion has occurred between the carbonyl groups and the cyclobutane ring.

The low-field n.m.r. signals are most revealing. From them, specific structural assignments can be derived. The absorption of the hydrogen nuclei attached to carbon bearing oxygen is divided by spin–spin coupling of those nuclei to adjacent protons. The doublet of doublets in the spectrum of dilactone VI arises from coupling to two protons non-equivalent with respect to the responding nuclei. Among the stereochemical possibilities for the dilactone,[8] this can occur *only* when the cyclobutane hydrogens are in the *cis,trans,cis* configuration and the carbons bearing oxygen are placed diagonally across the cyclobutane ring (structure VI). If the latter condition were met, but the hydrogens were *cis* to one another, the coupling would then be to two protons equivalent with respect to the responding nuclei; a triplet would result. If, on the other hand, the carbons bearing oxygen were adjacent, either orientation of the cyclobutane hydrogens would give rise, in theory, to three pairs of absorption lines, each pair symmetric about a common axis. The outer, most widely separated pair would be extremely weak and not observable. The central pair would be strong. The inner pair, that closest to the common axis, would be weak, though still significant. The shape of the signal actually recorded would depend greatly on the resolution of the spectrometer and the relative positions of the absorption lines. Thus, the broad doublet observed under moderate resolu-

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(1) Presented in part at the 140th Meeting of the American Chemical Society, Chicago, Ill., Sept. 3–8, 1961. It is a pleasure to acknowledge the partial financial support of this work by the General Chemical Division of Allied Chemical Corporation.

(2) See, for example, G. Büchi and I. M. Goldman, *J. Am. Chem. Soc.*, **79**, 4741 (1957); G. Wittig, G. Koenig and K. Claus, *Ann.*, **593**, 127 (1955); W. G. Dauben and R. Cargill, *Tetrahedron*, **15**, 197 (1961).

(3) See, for example, W. Treibs, *J. prakt. Chem.*, **138**, 299 (1933); A. Butenandt and L. Poschmann, *Ber.*, **73**, 893 (1940); R. C. Cookson and J. Hudec, *Proc. Chem. Soc.*, 11 (1959); P. Yates and M. J. Jorgenson, *J. Am. Chem. Soc.*, **80**, 6150 (1958).

(4) Only dibenzo derivatives of this system have been prepared previously. These, the various truxones, are derived from the polymerization of indones; "Elsevier's Encyclopedia of Organic Chemistry," Elsevier Publishing Co., Inc., New York, N. Y., 1940, Vol. 14, pp. 417–419.

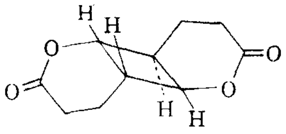
(5) On the assumption that II is planar and strain-free, molecular orbital theory predicts a delocalization energy of 3.42 β; *cf.* naphthalene, 3.68 β; A. Streitweiser, Jr., and J. I. Brauman, "Tables of Molecular Orbital Calculations," Pergamon Press, New York, in press.

(6) Recently, α-eumicolchicine has been shown to be a photodimer of a complex cyclopentenone; O. L. Chapman and H. G. Smith, *J. Am. Chem. Soc.*, **83**, 3915 (1961).

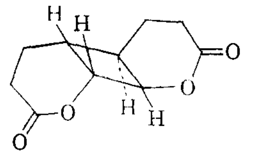
(7) Neither dimer is stable to prolonged ultraviolet excitation; however, no evidence for dimer interconversion could be obtained.

(8) *Trans* fusion of small rings is improbable and is not considered here; *cf.* footnote 17.

tion in the spectrum of dilactone VII results from overlapping of each member of the inner pair of lines with the corresponding member of the central pair.[9]



VI



VII

As Baeyer–Villiger oxidation is known to proceed with retention of configuration,[10] the *cis,trans,cis* geometry of VI must also apply to the precursor, photodimer III. In turn, hydrocarbon V must then be *cis,trans,cis*-tricyclo[5.3.0.0^{2,6}] decane, and, as established by reduction of IV to V, dimer IV and its corresponding dilactone VII must also be in this geometric series. Similarly, the relative positions of the carbonyl groups in the photodimers follow from the dilactone structures.

Dilactones VI and VII are derived, respectively, from 1,3- and 1,2-cyclobutanediols. In the presence of acid, both dilactones are opened by methanol. With even trace amounts of mineral acid, skeletal rearrangement is evident[11]; vinyl and cyclopropyl proton absorptions appear in the n.m.r. spectra of the crude products. With a polystyrylsulfonic acid resin, the unrearranged diester-diols VIII and IX can be obtained.[12] Appropriately, the 1,3-diol VIII is unaffected by lead tetraacetate; the vicinal diol IX undergoes oxidative cleavage.[13]

The introduction of two double bonds into photodimer III is necessary to complete the synthesis of the desired diene-dione I. The classical approach to this conversion by direct bromination and subsequent dehydrohalogenation is troublesome when the transformation must be carried out simultaneously at two identical centers. Indeed, although the bromination of III is quite rapid, no single useful product could be isolated.

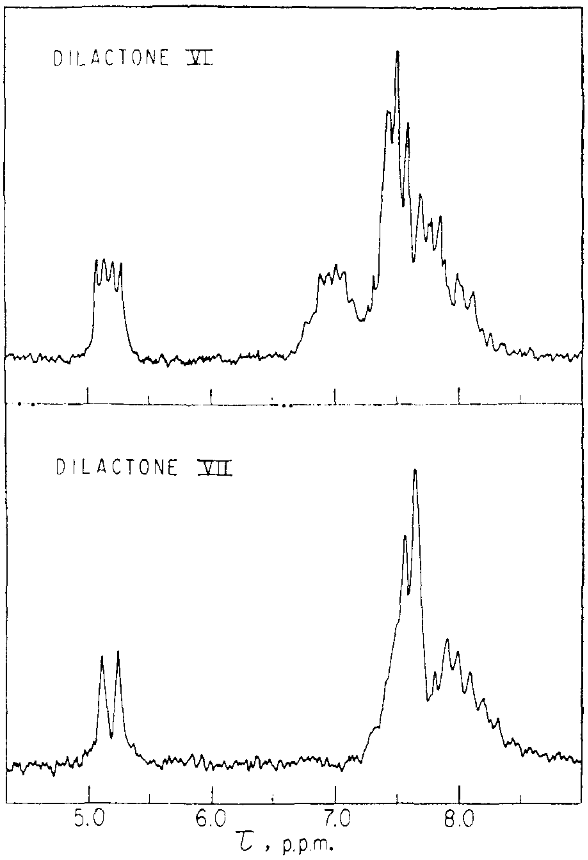
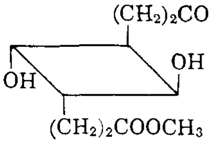
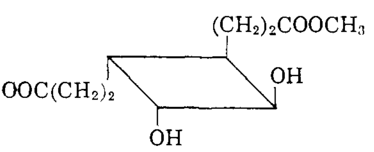


Fig. 1.—The 60 megacycle n.m.r. spectra of dilactones VI and VII in deuteriochloroform.



VIII



IX

Acid-catalyzed acetate exchange of III with isopropenyl acetate gives the dienol acetate X in fair yield. Mild base hydrolysis of X regenerates the photodimer; this precludes skeletal rearrangement coincidental with enol acetylation. Vinyl proton absorption in the n.m.r. spectrum of X at $\tau = 4.50$ p.p.m. establishes the direction of enolization. Enolization toward the cyclobutane ring would give rise to tetrasubstituted double bonds.

Bromination of X at −65° in methylene chloride with two molar equivalents of bromine is rapid and presumably[14] leads to the tetrabromide

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[9] The theoretical, low field spectrum for each of the possible stereoisomeric dilactones is readily calculated. Negligible 1,3-proton coupling constants are assumed. The simple splitting rules are applicable, as given in the text, to the dilactones in which the carbons bearing oxygen are located diagonally across the cyclobutane ring. For the remaining stereoisomers, the A_2X_2 approach outlined by 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. 140–142] is utilized. All *cis*-cyclobutane 1,2-proton coupling constants can be taken as 4 c.p.s., the *trans* as 8 c.p.s. These are consistent with the values obtained from the spectrum of dilactone VI, 4.1 and 8.3 c.p.s. The 1:2 ratio of constants agrees well with that observed in the spectrum of diene-dione I. The calculated positions in cycles per second relative to the common axis (and the relative intensities) of the three pairs of low-field lines in the theoretical spectra of the dilactones in which the carbons bearing oxygen are adjacent are: for the *cis,trans,cis* configuration (dilactone VII), ±9.6 (0.15), ±4 (3), ±1.6 (0.85); for the all *cis* configuration, ±17 (0.05), ±4 (3), ±1 (0.95). Although high-resolution spectroscopy should allow separation of these lines, this was considered unnecessary as the spectrum of dilactone VI established the stereochemical identities essential to the subsequent arguments. The spectrum of dilactone VII is utilized only as a confirmation of the general structure pattern. Professors C. H. DePuy, D. S. Noyce and C. H. Sederholm offered many suggestions useful in this analysis. Their assistance is gratefully acknowledged.

[10] See, for example, J. A. Berson and S. Suzuki, *J. Am. Chem. Soc.*, **81**, 4088 (1959).

[11] Carbonium ion rearrangements of cyclobutyl systems are familiar; see, for example, R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959).

[12] The n.m.r. and infrared spectra are completely consistent with these formulations (see Experimental section).

[13] It is a pleasure to thank Professor George Büchi for making available his unpublished data on the lead tetraacetate cleavage of a similar *trans*-cyclobutanediol.

[14] E. Filachione, *J. Am. Chem. Soc.*, **61**, 1705 (1939); P. Bedoukian, *ibid.*, **66**, 651 (1944).

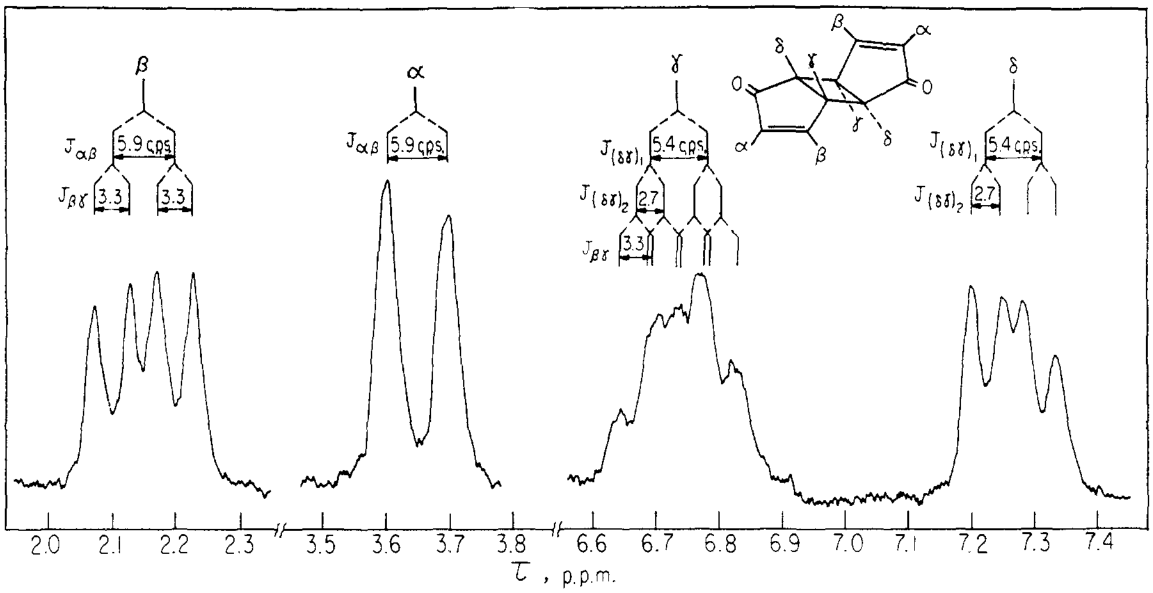
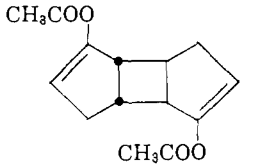
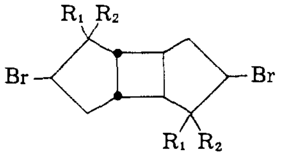


Fig. 2.—The high resolution n.m.r. spectrum of diene-dione I at 60 megacycles in deuteriochloroform.

XI. This was not isolated but was converted by methanolysis to XII, a dibromo-diketal. Dehydrobromination of XII with potassium *t*-butoxide in *t*-butyl alcohol and subsequent acid hydrolysis of the ketal functions gives I, *cis,trans,cis*-tricyclo[5.3.0.0^{2,6}]deca-4,9-diene-3,8-dione.



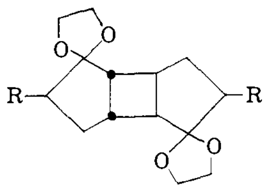
X



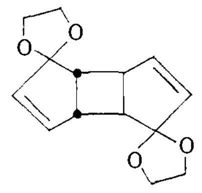
XI, $R_1 = -OOCCH_3$, $R_2 = -Br$
XII, $R_1 = R_2 = -OCH_3$

Experimentally, this transformation of III into I is difficult and tedious; further, the over-all yield is low, approximately 10%. The scope of the proposed investigation of the diene-dione did not permit acceptance of this early synthetic scheme.

Photodimer III is ketalized with remarkable ease. The bis-ethyleneketal XIII is formed in 90% yield directly from III and ethylene glycol in the presence of trace quantities of hydrochloric acid. Bromination of this ketal with pyridinium bromide perbromide in tetrahydrofuran gives XIV, a high melting dibromide completely resistant to further bromination under these conditions.[15] Although XIV cannot be readily dehydrohalogenated with potassium *t*-butoxide in *t*-butyl alcohol (compare the bis-dimethylketal analog XII), this base in dimethyl sulfoxide[16] readily effects conversion to the unsaturated ketal XV. Aqueous acid hydrolysis of XV gives I. This synthesis is most convenient and proceeds in 40% yield from the photodimer.



XIII, R = –H
XIV, R = –Br



XV

The infrared absorptions at 5.87 and 6.33 μ, and the ultraviolet spectrum, λ_{max}^{EtOH} 225 mμ (ε 15,600), are in accord with predicted values for the diene-dione. The high resolution n.m.r. spectrum (Fig. 2) agrees, in detail, with this structure. The four major signals appear in the ratio of 1:1:1:1. The α- and β-vinyl protons are coupled to one another. The β-proton absorption is resplit by the γ-proton. The saturated δ-proton signal is divided into a doublet of doublets by the two γ-hydrogens (compare the n.m.r. spectrum of dilactone VI). Finally, the γ-protons are coupled both to the δ- and β-protons; line fusion collapses the octet expected for this coupling into a quintet.

Catalytic hydrogenation of the diene-dione regenerates photodimer II.[17] Extended ozonolysis in aqueous acetic acid at room temperature, followed by oxidative decomposition with hydrogen peroxide and subsequent esterification with diazomethane, gives *cis,trans,cis*-tetracarbomethoxycyclobutane (XVI),[18] identical with that prepared by the photodimerization of solid dimethyl fumarate.[19] These interrelations ascertain the *cis,trans,cis* geometric order of the photodimers.

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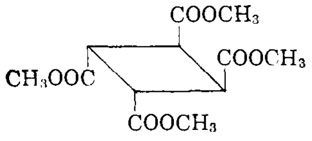
[15] This resistance is presumably a reflection of the marked stability of XIV in aqueous acid; *cf.* the reaction mechanism proposed by A. Marquet, H. B. Kagan, M. Dvolaitzky, L. Mamlok, C. Weidmann and J. Jacques, *Compt. rend.*, **248**, 984 (1959).

[16] It has been estimated that potassium *t*-butoxide in dimethyl sulfoxide is many powers of ten more basic than in *t*-butyl alcohol; D. J. Cram, B. Rickborn, C. A. Kingsbury and P. Haberfield, *J. Am. Chem. Soc.*, **83**, 3678 (1961).

[17] Had a *trans* ring fusion been present in photodimer III, base-catalyzed epimerization would have occurred in the transformation XIV to XV. The reduction of I would then have led to an isomer of III.

[18] The possibility of an acid-catalyzed epimerization during the oxidation has been eliminated in prior work; G. Griffin and D. Veber, *J. Am. Chem. Soc.*, **82**, 6417 (1960).



XVI

The determination of the complete structures of the cyclopentenone dimers prompts a consideration of the mechanism of photodimerization. This and the chemistry of the tricyclic diene-dione I will be subjects of future communications.

Experimental[20]

Photodimerization of Cyclopentenone.—Cyclopentenone[21] (82 g.) was placed in a water-cooled Pyrex chamber and exposed, through two thicknesses of Pyrex glass, to the output of a Hanovia, 450 watt, mercury arc lamp. The sample remained at, or slightly below, room temperature. The irradiation was continued for 24 hr. The products were dissolved in methylene chloride, and the solution was concentrated to 100 ml. and then diluted with 300 ml. of carbon tetrachloride. Further concentration removed most of the residual methylene chloride, in which the photodimers are remarkably soluble. On cooling, the concentrate deposited nearly white crystals of III. These were washed free of adhering mother liquor with cold carbon tetrachloride, recrystallized from that solvent, and dried *in vacuo* overnight. Sublimation at 115° (0.5 mm.) gave a good grade of material. In various runs, the yield ranged from 35–40 g. (43–49%).

Analytical material was prepared by recrystallization from methylene chloride–hexane followed by resublimation; m.p. 125–126.5°, λ_{max} 5.78 μ.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.31; mol. wt., 164.2. Found: C, 72.89; H, 7.26; mol. wt. (Rast), 184.

The mother liquors from the crystallization of III were concentrated under vacuum and then distilled quickly at 125° (1 mm.). The distillate, now free of the colored polymeric products of the photoreaction, solidified easily. After several recrystallizations from hexane, pure IV (30–37 g., 37–45%) was obtained, m.p. 66–67°, λ_{max} 5.78 μ.[22]

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.31; mol. wt., 164.2. Found: C, 72.99; H, 7.26; mol. wt. (Rast), 182.

Wolff-Kishner Reduction of the Photodimers: *cis,trans,cis*-Tricyclo$[5.3.0.0^{2,6}]$decane (V).—Dimer III (2 g.) was dissolved in a mixture of 85% hydrazine hydrate (15 ml.) and diethylene glycol (15 ml.). A spontaneous exothermic reaction took place. The solution was warmed to its boiling point and allowed to reflux for 15 min. The heating bath was removed, and, after the solution had cooled slightly, potassium hydroxide pellets (5 g.) were added. The temperature of the mixture was raised to 190°; the hydrocarbon V steam-distilled rapidly. The aqueous distillate was extracted three times with pentane. These extracts were combined, dried over sodium sulfate, and concentrated. A sample of the residual crude hydrocarbon (total crude, 1.1 g.) was passed through a vapor phase chromatograph column of diethylene glycol succinate at 80°. Except for traces of pentane, the material was essentially homogeneous. Sufficient pure hydrocarbon V for characterization could be obtained conveniently by vapor phase chromatography. This material did not decolorize bromine in carbon tetrachloride. The n.m.r. spectrum of V was free of vinyl proton absorptions.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.95. Found: C, 87.92; H, 11.95.

By an equivalent procedure, dimer IV was converted to the same hydrocarbon. This identification was made by a comparison of the behavior of the two samples on vapor phase chromatography. The detailed fingerprint regions of the infrared spectra were superimposable.[23]

Baeyer-Villiger Oxidation of the Photodimers: Dilactones VI and VII.—A solution of photodimer III (5.00 g., 0.0305 mole) in absolute ether (100 ml.) was cooled in an ice-bath. Monoperphthalic acid (11.8 g., 0.0648 mole) in ether (145 ml.) was added in one portion. The solution came rapidly to a boil and was allowed to reflux gently. Titration indicated that all but the last trace of peracid was consumed within 45 min. The precipitate of phthalic acid was removed and washed with chloroform. The washings were combined with the main body of solution, and the solvents evaporated under vacuum. The residual solids were triturated with chloroform. These extracts were concentrated. Addition of carbon tetrachloride precipitated impure dilactone VI. After six recrystallizations, three times each from benzene and carbon tetrachloride, the dilactone (3.6 g., 60%) melted at 156–157°. Further recrystallization did not improve this melting point.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.22; H, 6.17. Found: C, 61.03; H, 6.09.

In similar fashion, the dilactone VII was prepared in 55% yield from dimer IV; m.p. 103–105°. The spectral data for both compounds are recorded within the text.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.22; H, 6.17. Found: C, 61.10; H, 6.11.

Preparation of the Diester-diols VIII and IX.—A solution of dilactone VI (1.0 g.) in methanol (25 ml.) was refluxed over a polystyrylsulfonic acid resin[24] (10 mg.) for 15 hr. The resin was removed on a fine sintered glass funnel, and the solution concentrated overnight at room temperature under high vacuum. The crude oil could not be further purified; spontaneous closure to the starting lactone occurred at the elevated temperatures necessary for molecular distillation. The infrared absorptions of the crude material are consistent with simple methanolysis; 2.87 μ (hydroxyl), 5.77 μ (ester carbonyl). Two low-field absorptions appeared in the n.m.r. spectrum, τ 6.3 p.p.m. (methyl ester) and τ 5.7 p.p.m. (proton on carbon bound to hydroxyl). In addition, a mobile absorption characteristic of a hydroxyl proton was observed in the region of τ 6–7 p.p.m. The many absorptions of the remaining protons appeared at higher fields. The ratio of the intensities of the three concentration independent absorptions was approximately 1:3:5.

Methanolysis of VII under the same conditions gave the diester-diol IX, characterized only as the crude oil. The spectral data were comparable to that of VIII.

Titration indicated no consumption of reagent after 48 hr. (as compared to a standard) when VIII was treated with lead tetraacetate in damp acetic acid at room temperature. Reaction of IX with lead tetraacetate was rapid and nearly quantitative.

Preparation of the Dienol Acetate X.—A mixture of III (40 g.), *p*-toluenesulfonic acid (100 mg.) and isopropenyl acetate (200 ml.) was heated at 90° for 24 hr. The liberated acetone and 50 ml. of excess reagent were then boiled off from the solution. On cooling, the residue deposited 42 g. of yellow, waxy crystals. These could be purified by repeated crystallization from hexane or, more conveniently, but with a large decrease in yield, by chromatography over Woelm grade I neutral alumina. By the former method, 35 g. of colorless material was obtained; the latter procedure gave 16 g. of identical material. These correspond to yields of 58 and 26%, respectively. The purified material had m.p. 95–96°; λ_{max} 5.69, 6.05 μ; τ 4.50 (vinyl protons), 7.85 p.p.m. (methyl protons) in a ratio of 1:3.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.72; H, 6.49. Found: C, 67.77; H, 6.50.

Hydrolysis of X. Regeneration of III.—The dienol acetate (100 mg.) was treated with sodium carbonate (100 mg.) in 50% aqueous methanol. After 24 hr., the solution was

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[19] G. Griffin, J. Basinski and A. Vellturo, *Tetrahedron Letters*, **3**, 13 (1960).

[20] Melting points are uncorrected. Carbon tetrachloride was used as solvent for infrared spectral determinations. The n.m.r. spectra were recorded on a Varian Associates 60 megacycle spectrometer. Deuteriochloroform containing tetramethylsilane as an internal standard was used as solvent for these determinations.

[21] K. Alder and F. Flock, *Ber.*, **89**, 1732 (1956).

[22] Dr. Margaret Jorgenson of these laboratories isolated the first pure sample of IV.

[23] Wolff-Kishner reduction of the mixture obtained directly from the irradiation of cyclopentenone gives V contaminated with a few per cent. of a similar hydrocarbon, tentatively identified as the all-*cis* isomer of V. This implies a low yield photochemical conversion of cyclopentenone to stereoisomers of III and IV.

[24] Bio-Rad cation exchange resin AG 50W-X8, 50-100 mesh, hydrogen form.

extracted twice with methylene chloride. The extracts were combined, washed with water, and evaporated to dryness. The residue was crystallized from methylene chloride–hexane and gave 54 mg. of III, identified by melting point, infrared spectrum, and mixture melting point.

Bromination of the Dienol Acetate: Formation of XI.—A solution of X (16.00 g.) in methylene chloride (500 ml.) was cooled to −65° in a Dry Ice–acetone-bath. The solution was stirred as bromine (20.65 g.), diluted with methylene chloride (25 ml.), was added dropwise at a rate commensurate with the disappearance of its color. Methanol (200 ml.) was added and the mixture allowed to warm to room temperature. The solution was distilled slowly until the boiling point rose to that of methanol. During the distillation it was necessary to add two additional 100-ml. portions of methanol. The methanolic solution was boiled under reflux for 12 hr. The precipitated solids (13.4 g.) were filtered from the cooled solution. No carbonyl group absorption appeared in the infrared spectrum of this material. Insolubility in the common solvents prohibited further characterization or analytical sampling.

Dehydrobromination of XI: Formation of *cis,trans,cis*-Tricyclo[5.3.0.0^{2,6}]deca-4,9-diene-3,8-dione (I).—Compound XI (13 g.) was suspended with an equal weight of commercial potassium *t*-butoxide in *t*-butyl alcohol (125 ml.), and the mixture refluxed overnight. The cooled suspension was poured into water containing chipped ice. The white precipitate was collected and washed repeatedly with 0.01 *N* sodium hydroxide solution. The crude material was treated with 3% aqueous hydrochloric acid at 45°. The diene-dione I formed almost immediately; it was collected, washed with water, and purified by repeated crystallization from methylene chloride–carbon tetrachloride. White microcrystallites (3.7 g., *ca.* 36% from X) were obtained; m.p. 231–233° with a prior phase change at 100–125°. The spectral data are given within the text.

Anal. Calcd. for $C_{10}H_8O_2$: C, 74.99; H, 4.97. Found: C, 74.81; H, 4.93.

Preparation of the Bis-ethyleneketal XIV.—Dimer III (40 g.) was dissolved in ethylene glycol (250 ml.) at 100°. Anhydrous hydrogen chloride was passed over the solution surface for a few seconds. Formation of the ketal was exothermic and virtually instantaneous. Within a few moments, the solution gelled. It was cooled to room temperature and filtered. The solid product was washed thoroughly with 5% aqueous sodium carbonate and taken up in methylene chloride. The solution was separated from adhering water and dried over sodium sulfate. After dilution with hexane, the solution was concentrated. Two crops of glistening white platelets of XIV were taken (56 g., 91%), m.p. 143–143.5°.

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.53; H, 8.06.

Bromination of XIV: Formation of XV.—The bis-ethyleneketal XIV (54.5 g., 0.216 mole) was dissolved in anhydrous tetrahydrofuran (500 ml.). Pyridinium bromide perbromide (174 g., 0.545 mole) was added. Precipitation of pyridinium hydrobromide occurred almost immediately. The mixture was refluxed for 1 hr., then poured into water. The white precipitate was washed thoroughly with water followed by methanol. The air-dried residue XV (45.1 g., 54%), was sufficiently pure for analysis; m.p. 200° decomp.

Anal. Calcd. for $C_{14}H_{18}O_4Br_2$: C, 41.00; H, 4.42. Found: C, 41.36; H, 4.67.

Dehydrobromination of XV: Formation of XVI.—A solution of XV (45 g.) in dimethyl sulfoxide (250 ml.) was warmed on the steam-bath for 1 hr. with potassium *t*-butoxide (50 g.). The mixture was subsequently diluted with water, and the precipitate collected, washed with distilled water, and crystallized twice from hexane. Stout prisms (23 g., 84%) of XVI were obtained, m.p. 177–178°, λ_{max} 6.19 μ.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.52; H, 6.46.

Hydrolysis of XVI to the Diene-dione I.—The unsaturated ketal XVI (10 g.) was dissolved in warm tetrahydrofuran (100 ml.) and an equal volume of 0.1 *N* hydrochloric acid was added. The solution was cooled in the refrigerator. The diene-dione crystallized slowly. After recrystallization from carbon tetrachloride, this material (5.9 g., 91%) was identical in all respects to that prepared through the dienol acetate X.

Reduction of I: Regeneration of III.—A solution of I (100 mg.) in glacial acetic acid (25 ml.) containing palladium-on-charcoal (10 mg.) was exposed to hydrogen gas at atmospheric pressure. Two molar equivalents of hydrogen were absorbed rapidly. The solution was filtered, diluted with an equal volume of water, and extracted with methylene chloride. Evaporation of the extract and crystallization of the residue from methylene chloride–hexane gave 57 mg. of III, identified by melting point and mixture melting point determinations.

Oxidation of I: Formation of *cis,trans,cis*-Tetracarbomethoxycyclobutane (XVII).—Ozone (0.05 mmole/min.) was passed into a solution of I (500 mg.) in 90% aqueous acetic acid (50 ml.) for 2 hr. at room temperature. At the end of this time, water (10 ml.) and 30% hydrogen peroxide (3 ml.) were added. After standing at room temperature for 1.5 hr., the mixture was taken to dryness at ambient temperature under high vacuum. The residue was taken up in methanol; diazomethane in ether was added until the color of diazomethane persisted for at least 5 min. The solution was filtered and evaporated to dryness. The residue was purified by repeated crystallizations, first from methanol and then from methylene chloride–petroleum ether (b.p. 30–60°). The infrared spectrum of the colorless product (250 mg., 28%), was identical to that of an authentic sample, m.p. 143–144° (lit.[19] 144–145°), produced by irradiation of solid dimethyl fumarate. Admixture of the two samples gave no melting point depression.