[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Reactions of 2,6,6-Trimethyl-2,4-cyclohexadienone with Olefins[1]

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2,6,6-Trimethyl-2,4-cyclohexadienone (I) or its dimer II reacts with butadiene to give, at 150°, a mixture of 1,1,3-trimethylbicyclo[4.4.0]-3,7-decadiene-2-one (V) and 1,3,3-trimethyl-7- or 8-vinylbicyclo[2.2.2]-5-octene-2-one (IVa) or (IVb) in a ratio of 1:4. The dienone I with cyclopentadiene gives 1,8,8-trimethyltricyclo[2.2.2.$3^{2,6}$]-3,10-undecadiene-9-one (VIa) or its Δ^4-isomer VIb, either at room temperature or 150°. The dienone I when treated with excess butadiene at room temperature reacts only with itself to form dimer II. It follows that in the reaction of butadiene and cyclopentadiene with I, these simple dienes behave as dienophiles in the major reaction in each case; with cyclopentadiene being considerably more reactive than butadiene in this respect. The dienone I or its dimer II reacts with vinyl acetate at 150° to give 7-acetoxy-1,3,3-trimethylbicyclo-[2.2.2]-5-octene-2-one (X) and 8-acetoxy-1,3,3-trimethylbicyclo[2.2.2]-5-octene-2-one (IX) in nearly equal amounts. The acetates have been reduced, hydrolyzed and oxidized to a mixture of 1,3,3-trimethylbicyclo-[2.2.2]octane-2,5-dione (XVI) and 1,3,3-trimethylbicyclo[2.2.2]octane-2,6-dione (XV). The diketone XVI has been isolated by selective basic hydrolysis of XV to an acid which is easily separated; XV and XVI were identified further by the differences in their infrared and n.m.r. spectra. The infrared spectrum of XV is of interest since the carbonyls show splitting apparently due to vibrational coupling. Catalytic hydrogenation of the dimer II has been shown to lead to 1,4,6,6,9,9-hexamethyltricyclo[2.2.2.$4^{2,7}$]-3-dodecane-5,10-dione (XX) and osmium tetroxide attacks the conjugated double bond of II to give 3,4-dihydroxy-1,4,6,6,9,9-hexamethyltricyclo[2.2.2.$4^{2,7}$]-11-dodecane-5,10 dione (XXII).

The ready availability of 2,6,6-trimethyl-2,4-cyclohexadienone (I) by the alkylation of lithium 2,6-dimethylphenoxide with methyl iodide[2] has led to an examination of certain of its reactions and also those of its dimer, *endo*-1,4,6,6,9,9-hexamethyltricyclo-[2.2.2.$4^{2,7}$]-3,11-dodecadiene-5,10-dione (II).[2a]

Because of the tendency of the dienone to dimerize on standing, the possibility of carrying out reactions of the Diels–Alder type by treating the dimer II with the appropriate reagent and taking advantage of the fact that the dimer is in equilibrium with dienone at elevated temperatures[2a] was attractive. It was found that the dimer II reacts with maleic anhydride at 150° in 1 hour to give the maleic anhydride–dienone adduct III in 67% yield. The structure III was confirmed by infrared absorption of a chloroform solution at 1785 and 1865 cm.$^{-1}$ attributed to the anhydride carbonyl groups and at 1730 cm.$^{-1}$ due to the unconjugated carbonyl group.[3]

The reaction of the dienone I with butadiene was next investigated. When the freshly prepared dienone was allowed to stand in a sealed tube at room temperature with a threefold excess of butadiene, only the dienone dimer II was obtained. It may be concluded then that in the reaction with butadiene the dienone I reacts considerably faster as both dienone and dienophile than butadiene. However, when the dimer II was heated with an equimolar amount of butadiene at 150° for 24 hours, a mixture of 1-1 dienone–butadiene adducts was formed in about 80% yield. The infrared spectrum showed carbonyl absorption both at 1665 and at 1715 cm.$^{-1}$ in a ratio of 1:3 as well as at 915 cm.$^{-1}$ and thus suggested that both adducts IV and V were present.[6] Vapor chromatography and the ultraviolet spectrum also indicated that two products were present in a ratio of 4 to 1. Distillation made possible the separation of IV (still contaminated with about 3% of the isomer V). It was not possible, however, to determine whether this substance has structure IVa or IVb or is a mixture of the two. On catalytic hydrogenation IV rapidly reacted with one mole of hydrogen to give a product no longer having terminal methylene absorption at 915 cm.$^{-1}$. A similar change in the spectrum was observed on osmium tetroxide oxidation. These reactions thus occur selectively at the vinyl side chain. The comparison of the behavior of butadiene with that of cyclopentadiene is of interest. When the dienone I was allowed to stand at room temperature mixed with a fourfold excess of cyclopentadiene, there was obtained after 3 days a 94% yield of the adduct VI and no evidence for the presence of the dimer II was found. In the assignment of a structure to this product two other possibilities must be considered. Since structure VII contains an α,β-unsaturated ketone function it is excluded by the observation that the carbonyl absorption occurred at 1719 cm.$^{-1}$ and by the absence of ultraviolet absorption in the 230-mμ region. Structure VIII cannot be rigorously excluded but is most unlikely since in other reactions in which the dienone I behaves as a dienophile it reacts at the γ,δ-double bond rather than at the α,β. The position of the double bond in the five-membered ring of VI is not established by the present evidence.

While this work was in progress, Alder, Flock and Lessenich[8] reported that 6,6-dimethyl-2,4-cyclohexadienone reacted with cyclopentadiene to form an adduct analogous to VI. (The position of the double bond in the five-membered ring was not established.)

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(1) Abstracted from the Ph.D. Thesis submitted to the University of Illinois by Robert R. Fraser, June, 1958.

(1a) Texas Company Fellow, 1957–1958.

(2) (a) T. L. Brown, D. Y. Curtin and R. R. Fraser, THIS JOURNAL, **80**, 4339 (1958); (b) D. Y. Curtin and R. R. Fraser, *ibid.*, **80**, 6016 (1958).

(3) These values differ slightly from those obtained previously[4,5] for a related structure, probably largely because the latter spectra were obtained in Nujol mull.

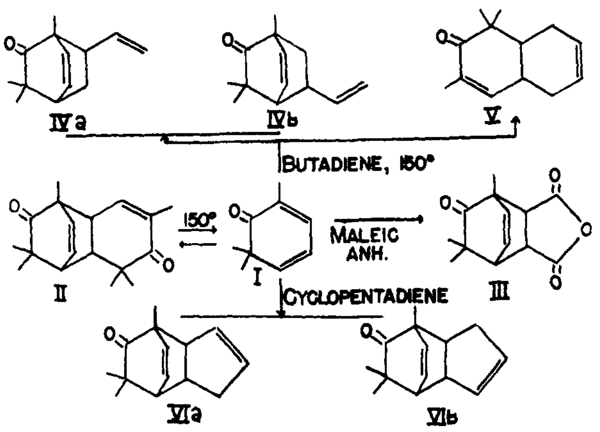
(4) H. Conroy and R. A. Firestone, THIS JOURNAL, **78**, 2290 (1956).

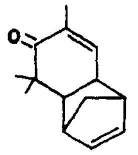
(5) D. Y. Curtin and R. J. Crawford, *ibid.*, **79**, 3156 (1957).

(6) The relative carbonyl intensities are not significant since the integrated absorption intensity is a function of the environment of the carbonyl. It is interesting that if relative carbonyl intensities for the saturated and α,β-unsaturated carbonyls are estimated[7] as 2.55 and 3.65, calculation of the product composition gives 80% of IV and 20% of V, in agreement with the vapor chromatography and ultraviolet results.

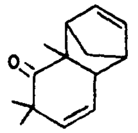
(7) R. N. Jones and C. Sandorfy, "Chemical Applications of Spectroscopy," edited by A. Weissberger, Interscience Publishers, Inc., New York, N. Y., 1956, p. 465.

(8) K. Alder, F. H. Flock and H. L. Lessenich, *Chem. Ber.*, **90**, 1709 (1957).





VII



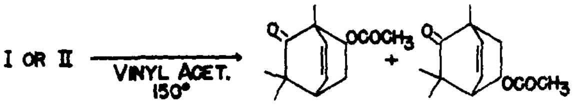
VIII

The question arises whether the ratio of products from the reaction of butadiene with dienone I at 150° was kinetically controlled or whether the products were equilibrated under the conditions employed. To settle this point a mixture of IV and V shown by ultraviolet analysis to contain 29% of V and 71% of IV was heated for 24 hours at 150° after which a spectrophotometric analysis indicated that the amount of V had increased to 38%. It follows that the two isomers are being slowly equilibrated but also that the kinetically controlled reaction gives predominately IV (with not more than 20% of V and possibly much less).

It is of some interest that both butadiene and cyclopentadiene in their reaction with the dienone I react preferentially as dienophiles. It is also noteworthy that cyclopentadiene is more reactive *as a dienophile* than is butadiene. This is probably explained by the fact that in order to have maximum overlap in the transition state butadiene must be twisted to the *cis* conformation which introduces additional strain amounting to some 2.3 kcal.[9] Cyclopentadiene, on the other hand, is already properly oriented in the initial state for maximum overlap.[10]

Either the dienone I or the dimer II reacted readily with vinyl acetate at 150° to form a mixture of bicyclic acetates IX and X in nearly equal amounts. Although on vapor chromatography the product gave a single (broad) peak it was shown to be a mixture by hydrolysis with methanolic sodium hydroxide which converted X to the hydroxy ketone XII which was stable to sodium hydroxide whereas the hydroxy ketone XI presumed to be formed from IX was a β-hydroxyketone and was apparently cleaved to acidic products which were not, however, identified. The structure of the hydroxy ketone XII was established by reduction of the carbon–carbon double bond and oxidation of the resulting hydroxy ketone XIV to the diketone XVI. The infrared spectrum of XVI showed the stretching absorption of the two slightly dissimilar carbonyl functions as a broad band at 1722–1735 cm.$^{-1}$, with only a suggestion of resolution of the two components.

Although the diketone XV was not isolated the mixture of XV with XVI was of some interest since it provided the opportunity to obtain information about XV by comparison of the mixture with the pure diketone XVI just described. For this reason the mixture of the unsaturated keto acetates IX and X obtained from the vinyl acetate addition was reduced to the pair of saturated keto acetates XVII and XVIII and these were hydrolyzed in 88% yield with 5% aqueous sodium hydroxide to the hydroxy ketones XIII and XIV. Although the hydroxy ketone XIII has the hydroxyl group β- to the carbonyl function it did not undergo a reversal of the aldol condensation under these conditions to any appreciable extent. The hydroxy ketone mixture XIII and XIV was readily oxidized in 95% yield with chromic acid to a mixture of ketones XV and XVI. Treatment of the diketone mixture with dilute aqueous methanolic sodium hydroxide left 36% of the diketone mixture as the 2,5-isomer but converted 48% to a liquid acid product which was not characterized but which had the correct infrared spectrum (broad carbonyl absorption at 1708 cm.$^{-1}$ and broad absorption above 2500 cm.$^{-1}$ typical of carboxylic hydroxyl absorption) for the expected cleavage product XIX. These data suggest that the relative amounts of ketones XV and XVI are about 60:40. The contribution expected on this basis of XVI to the infrared spectrum of the mixture of ketones was subtracted in the region 1700–1750 cm.$^{-1}$ to obtain the spectrum of the diketone XV in the carbonyl region. The resultant spectrum showed two strong bands at 1712 and 1749 cm.$^{-1}$. Although the two carbonyl groups are in slightly different environments and could therefore be expected to give rise to absorption at somewhat different frequencies, comparison of the absorption of this ketone with that of its isomer XVI (two unresolved maxima at 1722–1735 cm.$^{-1}$) suggests that vibrational coupling between the two carbonyl groups, similar to that which occurs in anhydrides and diacyl peroxides,[11] is present here. It has been reported[12] that α-diketones show such coupling when the carbonyl groups are oriented *cis* to one another but not when they are *trans*. Corey and Proskow[13] have observed such coupling with certain cyclic β-diketones with no enolizable hydrogen. It seems likely, then, that the infrared spectrum provides a generally useful method of determining the orientation of the carbonyl groups in diketones such as XV and XVI.



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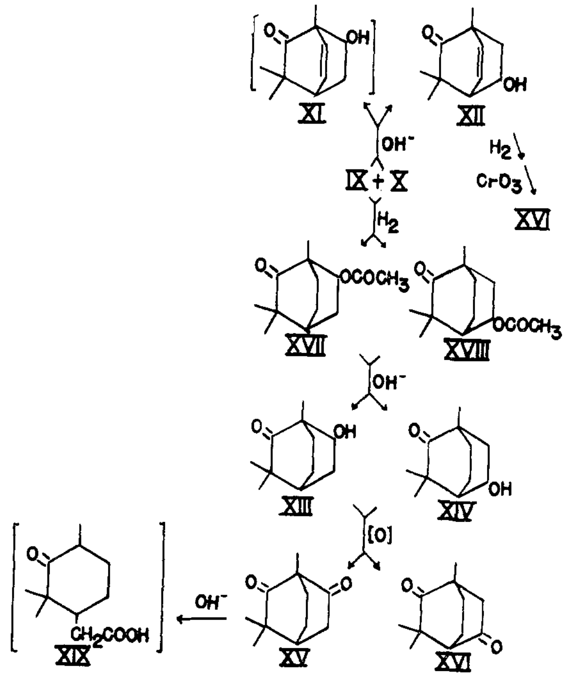
[9] J. G. Aston, G. Szasz, H. W. Woolley and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946).

[10] See M. C. Kloetzel, "Organic Reactions," Vol. IV, edited by R. Adams, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 10 ff.

[11] R. N. Jones and C. Sandorfy, ref. 7, pp. 495 ff.

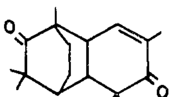
[12] K. Alder, H. K. Shaefer, H. Esser, H. Krieger and R. Reubke, *Ann.*, **593**, 23 (1955).

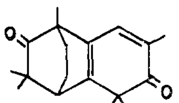
[13] E. J. Corey and S. Proskow, private communication. For example, 2,2,5,5-tetramethylcyclohexane-1,3-dione in carbon disulfide has absorption at 1696 and 1729 cm.$^{-1}$.

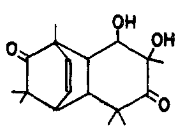


The n.m.r. spectrum of the ketone mixture is also of interest since in addition to the absorption at +260 mentioned earlier as being characteristic of XVI there is a poorly resolved doublet at +238 parts/10^8 due probably to the two hydrogen atoms alpha to a carbonyl group and adjacent to the bridge-head hydrogen atom.

Some exploratory attempts to confirm the structure of the dimer II are of possible interest. The substance readily absorbs one mole of hydrogen to give a compound assigned structure XX since the carbonyl absorption in the infrared still shows the presence of an α,β-unsaturated carbonyl group. Bromination of the dimer II with N-bromosuccinimide was unsuccessful. The dihydro dimer XX with N-bromosuccinimide gave a mixture, which was estimated from the analytical data and the ultraviolet spectrum to consist of about 40% of an allylic bromide together with 60% of a dienone, presumably XXI. Performic acid treatment of the dimer II gave only starting material. Treatment with osmium tetroxide gave a glycol, which although not obtained analytically pure was shown by its infrared spectrum to be mostly the glycol XXII formed from II by oxidation of the α,β-double bond.


XX


XXI



XXII

Experimental[14]

Reaction of Dienone Dimer II with Maleic Anhydride.—A mixture of 0.45 g. (3.3 mmoles) of 2,6,6-trimethyl-2,4-cyclohexadienone dimer (II) and 0.325 g. (3.3 mmoles) of freshly sublimed maleic anhydride was heated for 1 hr. at 150° in an oil-bath. The oily product, after extraction with ether and removal of the ether, crystallized from a mixture of hexane and ethyl acetate. The white crystals, m.p. 89–90.5°, weighed 0.45 g. (67%). The infrared spectrum of this adduct contained bands at 1730, 1785, and 1865 cm.$^{-1}$. Recrystallization of a portion of solid from hexane–ethyl acetate gave a white solid, m.p. 90.5–91.5°.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.7; H, 6.0. Found: C, 66.6; H, 6.2.

Reaction of Dienone I with Butadiene at Room Temperature.—A mixture of 0.60 g. (4.4 mmoles) of I produced by distillation of dimer II into a flask immersed in Dry Ice and 0.65 g. (12.0 mmoles) of butadiene was sealed in two tubes; n.m.r. spectra were measured periodically. When there was no further change in the spectrum (2 days) the tubes were opened and the excess butadiene allowed to evaporate. Starting material (II) as a white solid, m.p. 109–111°, weighing 0.39 g. remained. Its infrared spectrum contained all the bands present in a spectrum of pure dimer and a few additional ones at 1650, 1365 and 1225 cm.$^{-1}$. Recrystallization from hexane gave 0.35 g. of II, m.p. 109.5–110.5°.

Reaction of Dimer II with Butadiene at 150°.—A mixture of 0.50 g. (3.7 mmoles) of dimer II and 0.20 g. (3.7 mmoles) of butadiene was heated in a sealed tube at 150° for 24 hr. The adduct mixture, 550 mg. (79%), the infrared spectrum of which contained bands at 1715 and 1665 cm.$^{-1}$, was purified by chromatography over alumina. The infrared spectrum of the eluted material showed that no separation of adducts had occurred since the ratio of intensities of the bands at 1715 and 1665 cm.$^{-1}$ remained unchanged in the eluted fractions (ratio was 3:1). Other prominant bands in the infrared occurred at 915 and 1645 cm.$^{-1}$. The ultraviolet spectrum in cyclohexane had a maximum at 230 mμ.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.5. Found: C, 81.9; H, 9.6.

A more careful chromatography of the product over alumina gave a partial separation of the mixture. The material eluted in hexane was shown by vapor phase chromatography over polyethylene glycol at 220° to contain two components, the minor one making up 17% of the mixture. The last eluted fractions gave two peaks whose areas were in the ratio 53:47 the initially lesser component now being present in a larger amount. The proportion of the lesser component (V) in the total eluted product was 19%. Attempts at fractional sublimation failed.

Following the procedure of Shriner, Fuson and Curtin,[15] 0.225 g. (1.2 mmoles) of the butadiene adduct mixture was heated with a solution of 0.4 g. (2.0 mmoles) of 2,4-dinitrophenylhydrazine in 10 ml. of ethanol containing 3 ml. of water and 2 ml. of concentrated sulfuric acid. No crystals precipitated and evaporation of the solution gave only starting materials. Following Vogel's procedure,[16] 0.10 g. (0.52 mmole) of adduct was added to a solution of 0.2 g. (1.0 mmole) of 2,4-dinitrophenylhydrazine in 4 ml. of methanol containing 0.4 ml. of concentrated hydrochloric acid. After two days no crystals had formed. Prolonged heating failed to give any product.

The mixture of adducts IV and V was then distilled through a micro spinning band column. After a small fore-run, 1.2 g. of colorless adduct IV, b.p. 105–109° (11 mm.), was collected using a reflux ratio of 5:1. The infrared spectrum of this liquid contained a strong band at 1720 cm.$^{-1}$ and a weak band at 1672 cm.$^{-1}$ The ultraviolet absorption spectrum showed very weak absorption in the 230 mμ region. The liquid was also subjected to vapor phase chromatography over polyethylene glycol at 195°. The percentage of higher boiling adduct V present in the distillate was calculated to be 10, 3 and 0% from the infrared, ultraviolet and v.p.c. curves, respectively, The infrared spectrum of the pot residue contained a strong band at 1720 and a medium one at 1672 cm.$^{-1}$ from which 28% of the higher boiling adduct was calculated to be present.

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[14] All melting points are corrected. Microanalyses were performed by Mr. J. Nemeth, Miss C. Higham, Mrs. M. Stingl and Mrs. F. Ju. Infrared spectra were measured by Mr. P. McMahon, Mr. J. Brader, Mr. B. Cloonan and Miss M. DeMott using 0.1 mm. cells with a model 21 Perkin–Elmer spectrophotometer. Ultraviolet spectra were determined by Mr. M. Chao and Mr. J. Chiu in 1-cm. cells with a Cary model 14M spectrophotometer. Photographs of the original spectra are available in the Ph.D. Thesis of R.R.F.,[1] available on microfilm from Univ. Microfilms, Ann Arbor, Mich.

[15] R. L. Shriner, R. C. Fuson and D. Y. Curtin, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., p. 219.

[16] A. I. Vogel, "Practical Organic Chemistry," Longmans Green and Co., New York, N. Y., 1956, p. 344.

A solution of 108 mg. (0.56 mmole) of adduct IV in 10 ml. of ethyl acetate was stirred under hydrogen with 2 mg. of previously hydrogenated platinum oxide. At the end of 8 min. the reaction was stopped at which point 14.4 ml. (0.58 mmole) of hydrogen had been absorbed. The solution was filtered and the solvent removed by distillation. The residue was 90 mg. (82%) of an oil of which the infrared spectrum contained a strong band at 1717 cm.$^{-1}$ but no absorption in the 915 cm.$^{-1}$ region.

A solution of 100 mg. (0.526 mmole) of adduct IV, b.p. 105–109° (11 mm.), in 3 ml. of ether was added to 135 mg. (0.53 mmole) of osmium tetroxide in 7 ml. of ether containing 0.15 ml. of pyridine.[17] At the end of 5 hr. the dark brown precipitate which had formed was filtered off, wt. 185 mg., dissolved in 15 ml. of tetrahydrofuran and heated under reflux for 2 hr. with 15 ml. of water containing 4 g. of sodium sulfite. The mixture was then continuously extracted with ether for 14 hr. and the ether extracts dried over magnesium sulfate. Removal of solvent left 115 mg. of an oil whose infrared spectrum possessed bands at 3400, 1718 and 690 cm.$^{-1}$.

A mixture (0.40 g.) of IV and V, estimated from its ultraviolet and corrected[6] infrared spectrum to contain 29 and 28%, respectively, of the higher boiling adduct V, was heated in a sealed tube at 150° for 24 hr. and its composition again determined spectrophotometrically. The mixture was estimated after heating to contain 38 and 31% (corrected)[6] of V from the ultraviolet and infrared spectra, respectively.

Reaction of Cyclopentadiene with Dimer II. 1,8,8-Trimethyltricyclo[2.2.2.3^{2,6}]-3,10- or 4,10-undecadiene-9-one (VI).—A solution of 1.34 g. (4.5 mmoles) of dimer II, m.p. 107–110°, and 0.80 g. (12.0 mmoles) of cyclopentadiene, b.p. 42°, in 50 ml. of xylene was heated under reflux for 18 hr. The solvent was removed by distillation and the residual liquid purified by chromatography over alumina. In all 1.87 g. (93%) of liquid was collected in 12 fractions. These fractions were shown to be identical by examination by vapor phase chromatography. A small amount (less than 10%) of a very volatile component was detected in all the v.p.c. graphs. A portion of the eluted material, 540 mg., was distilled under reduced pressure giving colorless adduct VI, b.p. 110° (2 mm.), whose infrared spectrum contained a strong band at 1719 cm.$^{-1}$. The ultraviolet absorption spectrum in cyclohexane had no absorption at 230 mμ characteristic of the dimer II but did have a maximum in the 300 mμ region which could be accounted for by 5% of dienone I formed during the distillation of adduct VI.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.1; H, 9.0. Found: C, 83.0; H, 9.1.

Reaction of Dienone I with Cyclopentadiene at Room Temperature.—A mixture of 0.38 g. (2.8 mmoles) of freshly distilled dienone I and 0.8 g. (12 mmoles) of cyclopentadiene, b.p. 42°, was allowed to stand at room temperature for 3 days. The low boiling material was removed by distillation under vacuum. The residue, 0.9 g., possessed an infrared spectrum which contained strong bands at 1678 and 1720 cm.$^{-1}$. This material was dissolved in hexane containing 25% of benzene and passed through a column of alumina using hexane as eluent. The first five fractions were discarded and the next fraction contained 270 mg. of colorless liquid of which the infrared spectrum was identical to that of pure adduct VI prepared as described above. Another 270 mg. of eluted product was shown to be the same as the previous fraction by its retention time on the graph obtained by vapor phase chromatography over polyethylene glycol. The total yield of adduct VI was 94%.

Reaction of Dienone I with Vinyl Acetate. 7- and 8-Acetoxy-1,3,3-trimethylbicyclo[2.2.2]-5-octene-2-one (IX and X).—A mixture of 0.67 g. (4.9 mmoles) of dienone I obtained by distillation of the dimer and 3.0 g. (35 mmoles) of vinyl acetate together with 0.05 g. of hydroquinone was heated in a sealed tube at 150° for 24 hr. After removal of the excess vinyl acetate by distillation, the residue, wt. 600 mg., was purified by chromatography over alumina. A fraction of adduct, 300 mg., was eluted in hexane–ether mixture. Its infrared spectrum contained bands at 1725, 1740 and 715 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{18}O_3$: C, 70.2; H, 8.2. Found: C, 70.5; H, 8.4.

Further preparations of the mixture of adducts IX and X using dimer as starting material gave, before purification, yields of over 93%. The graph obtained by vapor phase chromatography of the mixture through a polyethylene glycol column at 190° contained only a single peak.

Hydrolysis of Mixture of IX and X. 8-Hydroxy-1,3,3-trimethylbicyclo[2.2.2]-5-octene-2-one (XII).—A solution of 1.05 g. (5.3 mmoles) of adduct IX and X in 10 ml. of methanol and 8 ml. of 10% sodium hydroxide was heated under reflux for 2 hr. The mixture was cooled, diluted with 50 ml. of water and extracted twice with 50-ml. portions of ether. The extracts were acidified with concentrated hydrochloric acid and extracted with ether. These extracts were washed with water and dried over magnesium sulfate (acid fraction). The neutral fraction, 210 mg., after removal of solvent was an oil which on distillation gave 180 mg. (21%) of XII, b.p. 100° (1 mm.). The yield of keto alcohol XII based on the percentage of X in starting material is 50%. The distillate crystallized on standing. A portion was recrystallized from a mixture of hexane and ethyl acetate giving XII as a white solid, m.p. 79–80°. The infrared spectrum of this compound showed strong absorption at 1715, 3450 and 3560 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.3; H, 9.0. Found: C, 73.3; H, 9.0.

In an identical hydrolysis of the mixture of IX and X the neutral product, 100 mg., was again heated under reflux for 2 hr. in alcoholic alkali and worked up as before. The neutral fraction weighed 100 mg. and had essentially the same infrared spectrum as that of pure XII. The acid fraction from the first hydrolysis after removal of solvent weighed 620 mg. The infrared spectrum of a smear of the liquid contained strong bands at 3420 and 1700 cm.$^{-1}$. The liquid slowly crystallized to a sticky solid a portion of which was recrystallized from a large volume of hexane giving white solid, m.p. 135–152°. Further recrystallization and sublimation under reduced pressure raised the m.p. to 152–153°. The infrared spectrum of this solid showed strong absorption at 3620, 3450 and 1725 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{30}O_5$: C, 66.2; H, 9.3. Found: C, 66.3; H, 9.4.

Acetylation of Hydroxy Ketone XII. 8-Acetoxy-1,3,3-trimethylbicyclo[2.2.2]-5-octene-2-one.—A solution of 54 mg. (0.30 mmole) of alcohol XII, m.p. 79–80°, in 1 ml. of pyridine was heated on a steam-bath with 44 mg. (0.56 mmole) of acetyl chloride for 1 min. The mixture was then thrown into 20 ml. of water and extracted with ether. Removal of the solvent left 45 mg. of an oil of which the infrared spectrum still contained a band of medium intensity at 3460 cm.$^{-1}$, which suggested that the reaction was incomplete. The oil was then re-acetylated, this time continuing the heating for 5 min. The product after the same work-up amounted to 34 mg. (51%) of colorless liquid of which the infrared spectrum differed from that of the original vinyl acetate adduct mixture only in that it had no band at 1050 cm.$^{-1}$ whereas the original adduct had strong absorption at this position.

Hydrogenation of XII Over Platinum. 5-Hydroxy-1,3,3-trimethylbicyclo[2.2.2]octane-2-one (XIV).—A solution of 50 mg. (0.28 mmole) of keto alcohol XII in 10 ml. of ethyl acetate containing 1 mg. of previously hydrogenated platinum oxide was stirred under an atmosphere of hydrogen. The theoretical uptake of hydrogen, 7.0 ml., occurred in 5 min. at the end of which time the rate of uptake had almost become zero. The solution was filtered and the solvent removed by distillation leaving 40 mg. (80%) of liquid of which the infrared spectrum had strong bands at 1714 and 3480 cm.$^{-1}$ but no absorption at 655 or 3050 cm.$^{-1}$ where the starting material absorbs. Distillation gave 30 mg. (49%) of keto alcohol XIV as a liquid. The n.m.r. spectrum had no absorption below a frequency of 0 c.p.s. (40 Mc. rel. to water).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.5; H, 10.0. Found: C, 71.8, 71.8; H, 10.0, 10.0.

1,3,3-Trimethylbicyclo[2.2.2]octan-2,5-dione (XVI).—The alcohol XIV (140 mg., 0.77 mmole) in 3 ml. of glacial acetic acid containing 156 mg. (1.56 mmoles) of chromic anhydride was heated for 10 min. on a steam-bath and then allowed to stand for 12 hr. Removal of acids by extraction of an ether solution of the product with 10% sodium carbonate solution and evaporation of the ether left 120 mg. (87%) of neutral liquid which on distillation gave 70 mg. of dike-

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(17) R. Criegee, B. Marchand and H. Wannowius, *Ann.*, **550**, 99 (1942).

tone XVI, b.p. 90° (1 mm.) which gradually crystallized to a white solid, m.p. 51–52°, with strong infrared absorption at 1720 cm.$^{-1}$ (shoulder 1733 cm.$^{-1}$) and a singlet at +104 c.p.s. in the n.m.r. spectrum of an 18% carbon tetrachloride solution.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.3; H, 9.0. Found: C, 73.1; H, 9.3.

Hydrogenation, Hydrolysis and Oxidation of the Adduct Mixture IX and X. Mixture of 1,3,3-Trimethylbicyclo[2.2.2]octane-2,5- and 2,6-dione (XV) and (XVI).—A solution of 0.996 g. (0.0045 mmole) of vinyl acetate adduct (IX and X) in 15 ml. of ethyl acetate containing 5 mg. of Adams catalyst was stirred under an atmosphere of hydrogen at room temperature. At the end of 45 min. the uptake of hydrogen had ceased. The volume absorbed was 112 ml. (0.0045 mmole). The solution was then filtered and the ethyl acetate removed by distillation under reduced pressure. A 210-mg. portion of the residue, wt. 990 mg. (93%), was distilled giving a mixture of XVII and XVIII as a colorless liquid, b.p. 140° (3 mm.), of which the infrared spectrum was similar to that of starting material with the notable exception that the bands at 715 and 3050 cm.$^{-1}$ were absent.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.6; H, 9.0. Found: C, 69.9; H, 9.0.

The hydrogenated adduct XVII and XVIII (870 mg., 3.9 mmoles) was heated under reflux in 5 ml. of 5% sodium hydroxide solution for 2 hr. After cooling, the mixture was extracted twice with ether, the ether extracts washed with water and dried over magnesium sulfate. Removal of the ether under reduced pressure left 610 mg. (88%) of the mixture of XIII and XIV of which the infrared spectrum contained all the bands present in the spectrum of the keto alcohol XIV. Several additional bands including a strong band at 1125 cm.$^{-1}$ were present. A portion of this liquid (245 mg., 1.39 mmoles) was dissolved in 1.5 ml. of glacial acetic acid and added to a solution of 290 mg. (2.9 mmoles) of chromic anhydride in 5.8 ml. of glacial acetic acid. The mixture was heated on a steam-bath for 30 min. and allowed to stand overnight. The mixture was then made alkaline with an excess of 5% sodium bicarbonate solution and extracted twice with ether. The residue after removal of ether weighed 230 mg. (95%). The infrared spectrum of this diketone mixture exhibited strong absorption at 1710, 1720 and 1731 cm.$^{-1}$. Distillation of this liquid gave 130 mg. of a mixture of diketones XV and XVI of which the n.m.r. spectrum (27% in carbon tetrachloride) showed a singlet at +260 p.p. 10^8 (relative to the water) and also a doublet at +237. The yield of distillate was decreased by the adherence of the viscous product to the sides of the condenser.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.3; H, 9.0. Found: C, 73.7; H, 8.8.

Basic Cleavage of the Diketones XV and XVI.—The oxidation of the mixture of XIII and XVI was repeated and the product obtained (180 mg., 1.0 mmole) was heated under reflux for 3 hr. in a solution of 10 ml. of absolute methanol and 10 ml. of 10% sodium hydroxide. The solution after cooling was diluted with 10 ml. of water and extracted twice with ether. The ethereal extracts were washed with water and dried over magnesium sulfate. Removal of the ether left 65 mg. (36%) of diketone XVI. Distillation of this material gave 15 mg. of liquid of which the infrared spectrum was identical to that of XVI described above. The acid fraction obtained by acidification and extraction of the aqueous extracts weighed 95 mg. (48%). The total yield of product is thus 84%. The infrared spectrum of the acidic product contained a strong band at 1708 cm.$^{-1}$ and a broad band of medium intensity in the region 2700–2500 cm.$^{-1}$.

Hydrogenation of Dimer II. 1,4,6,6,9,9-Hexamethyltricyclo[2.2.2.4^{2,7}]-3-dodecene-5,10-dione (XX).—A solution of 1.0 g. (3.7 mmoles) of dimer, m.p. 110–110.5°, in 20 ml. of ethyl acetate containing 5 mg. of previously hydrogenated platinum oxide was stirred under a hydrogen atmosphere at room temperature for 6 hr. At the end of this time 87 ml. (3.5 mmoles) of hydrogen had been absorbed and the uptake had ceased. The solution was filtered, the solvent removed and the residual solid, 1.0 g. (98%), was recrystallized from hexane giving 0.69 g. (68%) of XI as white crystals, m.p. 107.5–108.5°. The infrared spectrum of this solid was very similar to that of dimer II except for the absence of bands at 915 and 3030 cm.$^{-1}$, indicative of the disappearance of the Δ^{11}-double bond.

Anal. Calcd. for $C_{18}H_{26}O_2$: C, 78.8; H, 9.6. Found: C, 78.9; H, 9.8.

Bromination of Dihydro Dimer XX.—A solution of 0.66 g. (2.4 mmoles) of the hydrogenation product XI, m.p. 107.5–108.5°, was heated under reflux in 30 ml. of carbon tetrachloride for 16 hr. with 0.43 g. (2.4 mmoles) of N-bromosuccinimide. The solution was then filtered, washed with water and dried over magnesium sulfate. The carbon tetrachloride was distilled off and the residual yellow oil crystallized from hexane. The first crop of yellow crystals 0.25 g., m.p. 145–150°, was recrystallized again from hexane giving 55 mg. of yellow solid, m.p. 153.5–155°. The infrared spectrum of this dienone XII contained strong bands at 1722, 1656 and 1635 cm.$^{-1}$. The ultraviolet absorption spectrum possessed $\lambda_{\max}^{\text{cyclohexane}}$ 332 mμ (ϵ 6250). On basis of mixture of 61% olefin and 39% bromide, ϵ 9058.

Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.4; H, 8.9. Found: C, 72.3; H, 8.1. Calcd. for $C_{18}H_{25}O_2Br$: C, 61.19; H, 7.13. Calcd. for mixture 61% olefin and 39% bromide: C, 72.3; H, 8.2.

Reaction of Dimer II with Osmium Tetroxide. 3,4-Dihydroxy-1,4,6,6,9,9-hexamethyltricyclo[2.2.2.4^{2,7}]-11-dodecane-5,10-dione (XXII).—A solution of (0.735 mmole) of dimer II in 2 ml. of ether was added to 100 mg. (0.74 mmole) of osmium tetroxide in 10 ml. of ether containing 0.2 ml. of pyridine. After 1 hr. the mixture had turned brown and a precipitate had formed. This was filtered off and weighed. Since only 100 mg. was obtained, the filtrate was set aside for 8 hr. then filtered again. The total precipitate, 0.35 g., was then dissolved in 30 ml. of tetrahydrofuran to which 40 ml. of a saturated solution of sodium sulfite was added and the mixture heated under reflux for 2 hr. The reaction mixture was continuously extracted with ether for 24 hr. and the extracts were separated and dried over magnesium sulfate. Removal of the ether gave 160 mg. (70%) of glycol which was recrystallized from hexane giving 75 mg. (33%) of XXII, m.p. 147.5–149°. The infrared spectrum of this solid had a strong band at 1715 and a weak band at 3560 but only a shoulder at 1682 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{26}O_4$: C, 70.6; H, 8.6. Found: C, 69.3; H, 8.4.

Attempted Oxidation of Dimer II with Performic Acid.[18]—To a solution of 0.25 g. (0.90 mmole) of dimer II in 3 ml. of 90% formic acid was added 0.95 ml. (9.5 mmoles) of 30% hydrogen peroxide. During the addition the temperature was kept below 40°. The mixture was then heated at 40° for 30 min. and allowed to stand overnight. The excess hydrogen peroxide was decomposed by the addition of 20 ml. of a 5% ferrous sulfate solution. The white solid which precipitated during the addition amounted to 0.22 g., m.p. 101–103°, and its infrared spectrum was identical to that of starting material.

Attempted Bromination of Dimer II.—A mixture of 340 mg. (1.25 mmoles) of dimer II, m.p. 107–110°, and 240 mg. (1.35 mmoles) of freshly recrystallized N-bromosuccinimide, m.p. 169–170° (softens 145), was heated under reflux in carbon tetrachloride for 16 hr. The residual yellow oil after removal of solvent weighed 375 mg. After recrystallization from hexane the white needles melted 110–111°. A mixture of this solid with starting material had m.p. 108–110°.

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(18) A. Roebuck and H. Adkins, *Org. Syntheses*, **28**, 35 (1948).