

1,5,6,7-Tetrahydrocyclohepta[*d,e*]naphthalene (6). 1,2,3,10a-Tetrahydrocyclohepta[*d,e*]naphthalene (750 mg) was dissolved in benzene (5 ml). This solution was sealed in a tube with a nitrogen atmosphere and heated to 150° for 5 days. After this time vpc analysis on a D.E.G.S. column indicated that the initial hydrocarbon was *ca.* two-thirds isomerized. The benzene was evaporated off and the residual oil evaporatively distilled to give 580 mg of a pale yellow oil.

Cyclohexa[*f,g*]benzotropenium Hexachloroantimonate (7). Crude 1,5,6,7-tetrahydrocyclohepta[*d,e*]naphthalene prepared in the above manner (182 mg, 1 mmole) was dissolved in dichloromethane (5 ml) and added to a solution of triphenylcarbonium hexachloroantimonate (400 mg, 0.695 mmole) in dichloromethane (10 ml). The solution immediately turned dark green and deposited yellow crystals of the benzotropenium hexachloroantimonate (7) within 5 min. The crystals were collected on a filter and washed with several portions of dichloromethane to give 149 mg (41%) of the salt.

Anal. Calcd for C₁₄H₁₃SbCl₆: C, 32.60; H, 2.54. Found: C, 32.48; H, 2.59.

The ultraviolet spectrum showed bands [λ_{\max} m μ (ϵ)] at 455 (2790), 362 (3175), 347 (3020), 288 (48,100), and 237 (28,660). Work-up of the resulting solution by extraction with concentrated sulfuric acid, evaporation of the dichloromethane, and chromatography yielded triphenylmethane (160 mg, 95%).

6,7-Dihydrocyclohepta[*d,e*]naphthalene (1). 1,5,6,7-Tetrahydrocyclohepta[*d,e*]naphthalene (182 mg, 1 mmole) as prepared above was dissolved in dichloromethane (5 ml) and added to a solution of triphenylcarbonium fluoroborate (150 mg, 0.45 mmole) in dichloromethane (10 ml). The solution turned dark brown. After 30 min the solution was concentrated under a nitrogen stream to *ca.* 5 ml and 10 ml of carbon tetrachloride was added. This caused separation of a brown oil. The solvent was removed with a dropper and the residue washed with two 10-ml portions of carbon tetrachloride. The oil was then dissolved in dichloromethane (25 ml) and added to a solution of trimethylamine (5 ml) in dichloromethane (25 ml). The brown color immediately faded to a pale yellow. This solution was allowed to stand for 2 hr and then the precipitated salts filtered off. The yellow solution was concentrated under a nitrogen stream to *ca.* 5 ml and diluted with carbon tetrachloride

(10 ml). This solution was reconcentrated under a nitrogen stream to *ca.* 5 ml and chromatographed over alumina. The bright yellow band was collected and concentrated to *ca.* 0.5 ml under a nitrogen stream. The nmr spectrum of such solutions is represented in Figure 1. The solution was diluted to 2 ml with carbon tetrachloride and added dropwise to trifluoroacetic acid (5 ml). The resulting dark brown solution was concentrated on a rotary evaporator to *ca.* 0.05 ml and an nmr spectrum taken. This spectrum was identical with the nmr spectrum of the oil isolated from a similar hydride exchange reaction as described above.

2H-Benz[*c,d*]azulene. 1a,7b-Dihydro-1H-cyclopropal[*e*]acenaphthalene-1-carboxylic acid (1.0 g, 0.0467 mole) was placed in a flask containing ether (25 ml) (not all of the solid dissolved) and cooled in an ice bath while stirring with a magnetic stirrer. To this suspension was added bromine (0.8 g, 0.05 mole) dissolved in ether (25 ml) dropwise over *ca.* 0.5 hr. During this time the suspended solid dissolved. Then a solution of sodium acetate (2.0 g) in water (30 ml) was added and the solution allowed to warm to room temperature while stirring vigorously. After 0.5 hr the ether phase turned bright orange-red and was removed from the aqueous phase and washed with 10% aqueous sodium bicarbonate and water. The ether solution was then concentrated by a nitrogen stream to *ca.* 10 ml and diluted with carbon tetrachloride (15 ml). This solution was concentrated by a nitrogen stream to *ca.* 5 ml and chromatographed over alumina. The bright yellow band was collected and concentrated by a nitrogen stream to *ca.* 0.5 ml. During the concentration, trimethylamine was added periodically to serve as a stabilizer and solutions suitable for nmr spectra contained *ca.* 10% of this amine. A nmr spectrum of this solution of 2H-benz[*c,d*]azulene is shown in Figure 3. It was noted that if the trimethylamine was not added that solutions suitable for nmr spectral analysis could be obtained by nitrogen evaporation but that addition of unpurified tetramethylsilane to such solutions immediately polymerized the hydrocarbon, indicating that there is probably some acidic impurity in undistilled TMS.

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The Synthesis and Bisdecarboxylation of Oxygenated Bicyclo[2.2.*X*]alkanedicarboxylic Anhydrides

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Abstract: Cyclic 1,3-diacetoxy-1,3-dienes, generated *in situ* from cyclic 1,3-diketones and isopropenyl acetate, undergo Diels–Alder reactions with maleic anhydride providing a general route to 1-acetoxybicyclo[2.2.*X*]alkane-dicarboxylic anhydride derivatives. Cyclic 1,2-, 1,4-, and α,β -unsaturated ketones also are converted to adducts of this type in good yield by heating with isopropenyl acetate and maleic anhydride. Bisdecarboxylation of the corresponding diacids with lead tetraacetate, utilizing an oxygen atmosphere, leads to bicycloalkene derivatives in 50–80% yield. For example, dimedone (1) is converted to the adduct 6 in 80.7% yield; bisdecarboxylation of the corresponding keto diacid 31 proceeds to give 1-acetoxy-8,8-dimethylbicyclo[2.2.2]oct-5-en-3-one (32).

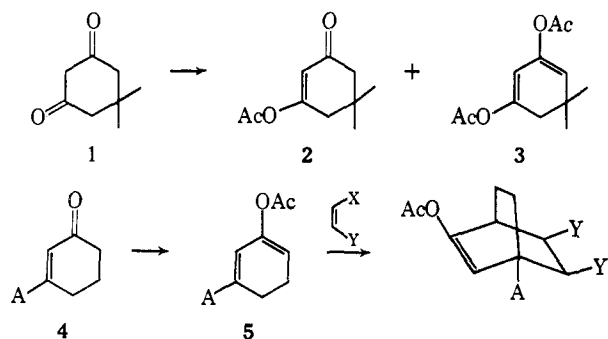
Some 1,3-diketones such as 1,3-cyclohexanedione exist primarily as monoenols and are generally considered as potential dienophiles in the Diels–Alder reaction. In connection with another investigation,¹ the monoenol acetate 2 of dimedone (1) was prepared by acetylation with isopropenyl acetate. Vapor phase chromatographic analysis of the resulting enol acetate 2 demonstrated that it contained 15% of a substance which, on the basis of spectral considerations, was iden-

tified as the dienol acetate 3. This observation suggested that dienophiles of general formula 4 might be readily converted into 1,3-dienes of type 5, which then might serve as the diene participant in a Diels–Alder reaction² to yield oxygenated bicyclic systems. This re-

(2) Conversions of this type involving acyclic α,β -unsaturated carbonyl compounds are well known; *cf.* the conversion of crotonaldehyde to 1-acetoxy-1,3-butadiene (R. K. Hill, A. Joule, and L. J. Loeffler, *J. Am. Chem. Soc.*, **84**, 4951 (1962)). On the other hand, examples involving cyclic α,β -unsaturated ketones are extremely rare; *cf.* A. A. Sayigh, Ph.D. Thesis, Columbia University, 1952; *Disseration Abstr.*, **14**, 1552 (1954).

(1) C. M. Cimarusti and J. Wolinsky, *J. Org. Chem.*, **31**, 4118 (1966).

port describes the successful application of this approach and the bisdecarboxylation of the diacids produced by hydrolysis of the adducts resulting from the use of maleic anhydride as dienophile.



Our investigation began with an attempt to improve upon the 15% yield of dienol acetate **3** obtained initially. However, with the reaction period extended for as long as 192 hr no noticeable improvement in yield of **3** was evident. Rather than resort to more drastic conditions it was decided to generate the diene **5** *in situ* and then trap it by carrying out the Diels-Alder reaction in the acylation mixture. The idea was to avoid the isolation of oxygen, light, and moisture-sensitive dienes **5** by capture with a powerful dienophile such as maleic anhydride.³ Maleic anhydride seemed an excellent choice as a dienophile since it is stable to the action of isopropenyl acetate and it was visualized that bisdecarboxylation of the diacids (X = Y = CO₂H) would provide bicyclic olefins which are formally the adducts of dienes **5** with acetylene.

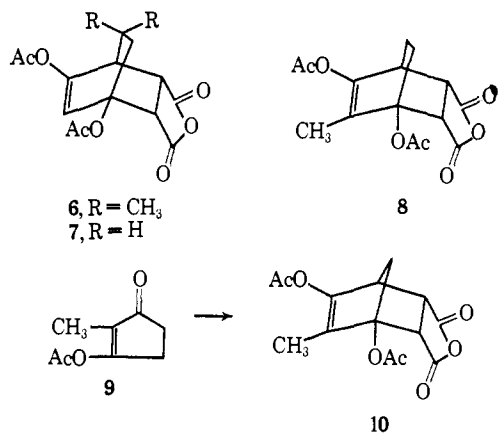
When dimedone (**1**) was heated with 1.2 equiv of maleic anhydride in isopropenyl acetate containing a catalytic amount of *p*-toluenesulfonic acid there was obtained, by direct crystallization, an 80.7% yield of a single product **6**. The infrared spectrum of **6** showed strong peaks at 5.35, 5.5, 5.75, and 6.05 μ indicative of anhydride, enol acetate, and acetate groups and elemental analysis and mass spectroscopy confirmed that this material was a 1:1 adduct of dienol acetate **3** and maleic anhydride.

The nmr spectrum (CDCl₃) of adduct **6** exhibited singlets at 1.07 and 1.20 ppm assigned to the C-8 *gem*-dimethyl group and a singlet at 2.14 ppm attributed to coincidence of the two acetate methyl groups. The C-7 methylene group appeared as an AB type quartet ($J = 13.5$ cps) at 1.52 and 2.27 ppm and the C-5 methine proton as an asymmetric doublet of doublets centered at 3.58 ppm ($J_{5,6} = 10$, $J_{4,5} = 3$ cps) and coupled with the C-6 hydrogen at 4.26 as well as the bridgehead proton (multiplet at 2.63 ppm). The olefinic (C-2) proton at 6.02 ppm was seen as a doublet ($J = 2$ cps) and is coupled through four bonds to the bridgehead proton.

Garbisch⁴ has noted coupling constants of similar magnitude in the bicyclo[2.2.2]oct-2-ene system. Since this allylic coupling occurs between protons constrained to a planar conformation, it has been suggested that its origin involves σ - σ overlap rather than the usual σ - π overlap which characterizes other nonrigid allylic systems.

(3) M. C. Kloetzel, *Org. Reactions*, **4**, 1 (1948).

(4) E. W. Garbisch, *Chem. Ind.* (London), 1715 (1964).



The parent diketone, 1,3-cyclohexanedione, readily gave adduct **7**, while an additional methyl group in the 1,3-diketone system provided no barrier to the condensation since 2-methyl-1,3-cyclohexanedione gave adduct **8** in 65.4% yield.

The general reaction was also extended to derivatives of 1,3-cyclopentanedione and provided an entry into the 1-acetoxycyclo[2.2.1]heptane system. When the enol acetate **9** was treated under the standard experimental conditions a good yield of the adduct **10** resulted.⁵

In view of the success with 1,3-diketones, it seemed reasonable to assume that cyclic 1,2- and 1,4-diketones could also be converted to adducts under these conditions. From 3-methyl-1,2-cyclopentanedione was obtained a mixture of adducts **11** and **12**. The absence of olefinic protons and doublet methyl signals in the nmr spectrum of this mixture showed that other possible adducts such as **13** were not formed in significant amounts. Similar treatment of 1,4-cyclohexanedione, prepared by Jones oxidation of the reduction product of hydroquinone,⁶ gave the adduct **14** which contains two bridgehead acetate groups.

Finally, this reaction was extended to α,β -unsaturated ketones which were converted smoothly to the adducts of their respective enol acetates. Isophorone gave approximately equal amounts of the adducts **15** (5.75 μ ; doublet vinyl methyl signal, 1.82 ppm, $J = 1.5$ cps) and **16** (5.70 and 6.05 μ ; singlet bridgehead methyl signal, 1.47 ppm) which were readily separated by fractional crystallization. The major product from 2-cyclohexenone, on the other hand, was the enol acetate **17**; only minor amounts of bridgehead acetate **18** were obtained. Sayigh² performed an acetoxy-cyclohexadiene mixture from 2-cyclohexenone and observed the formation of *ca.* 20% of adduct **18** and 80% of adduct **17** (47.7% from starting ketone) upon reaction with maleic anhydride.

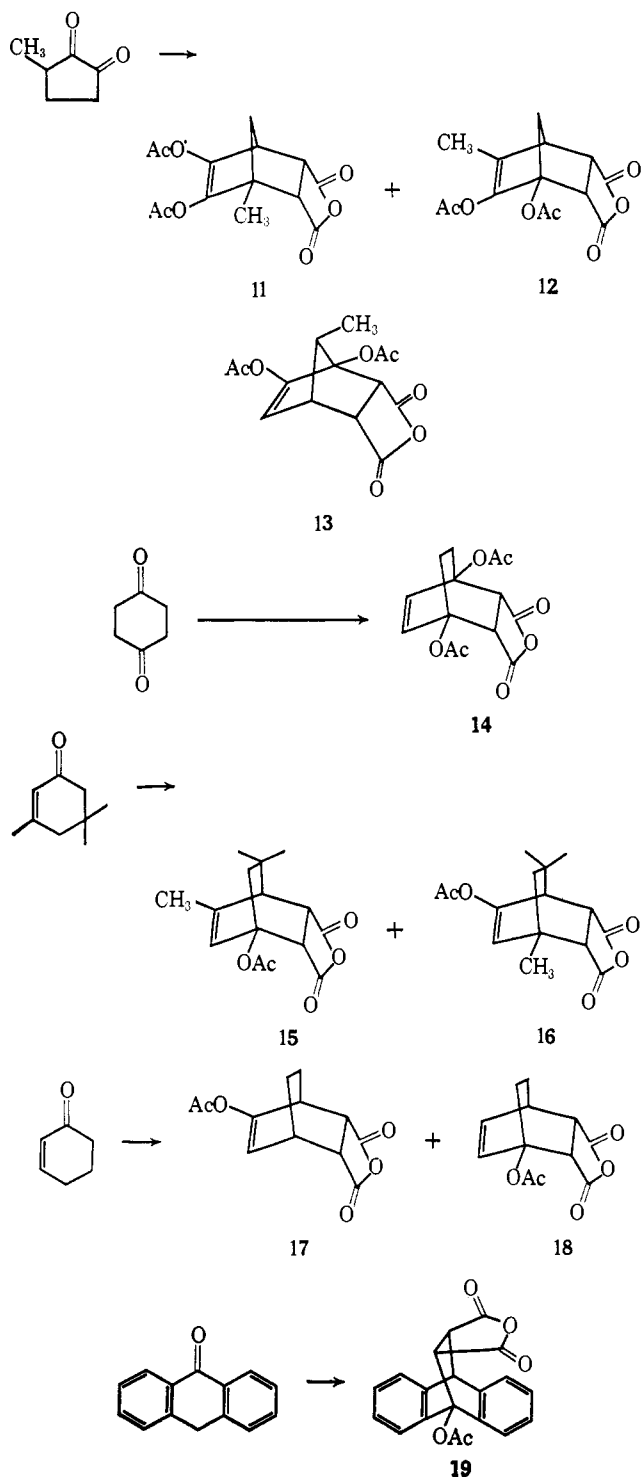
Anthrone gave, in good yield, the adduct **19** which had previously been prepared⁷ by reaction of 9-acetoxyanthracene with maleic anhydride.

The reaction of 2-cyclopentenone proved to be atypical in that the keto anhydride **20**, mp 228.5–230°, rather than the expected enol acetate was isolated in *ca.* 31% yield. Anhydride **20** showed no acetate methyl in its nmr spectrum and a molecular ion at m/e 180.⁸

(5) The insolubility of the parent diketone in refluxing isopropenyl acetate rendered its acetylation extremely slow.

(6) J. C. Sircar and A. I. Meyers, *J. Org. Chem.*, **30**, 3206 (1965).

(7) E. B. Barnett, N. F. Goodway, A. G. Higgins, and C. A. Lawrence, *J. Chem. Soc.*, 1224 (1934).



Hydrolysis to the diacid **21**, mp 163–163.8°, and bis-decarboxylation gave only norbornenone (**22**), thus establishing the gross structure of the adduct. Since **20** was not identical with the *exo*-keto anhydride **25** described by Alder and Stein,⁹ it was concluded that the anhydride **20** had the *endo* configuration.

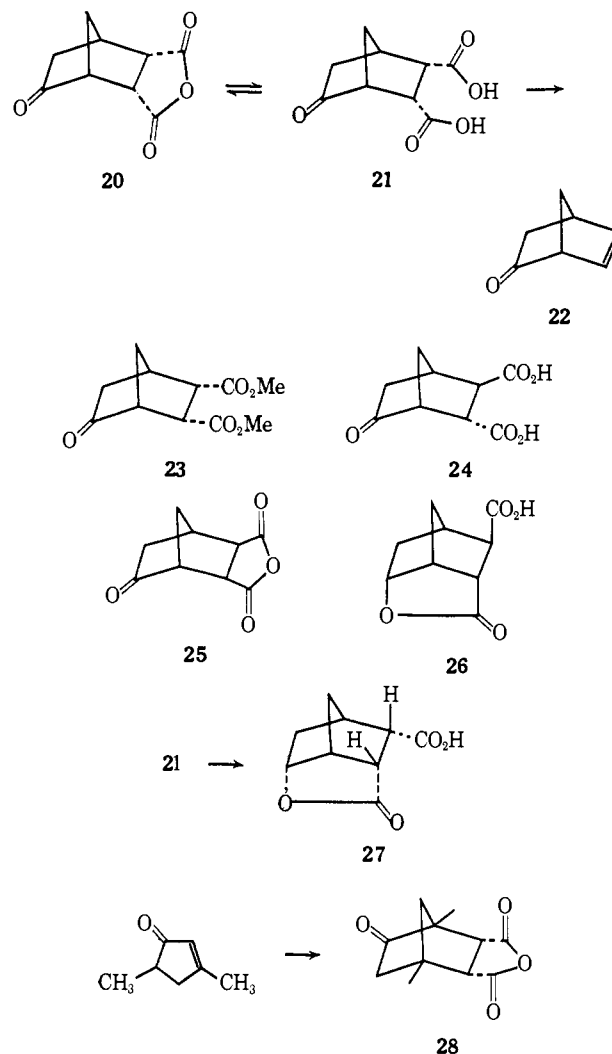
The dimethyl ester **23** (mp 69–70°; semicarbazone, mp 210.5–211.5°) was prepared from diacid **21** by treatment with ethereal diazomethane. This dimethyl ester has been prepared by two routes^{10,11} and was re-

(8) The possibility that this ion results from the loss of ketene with transfer of a hydrogen atom (and thus represents a P – 42 ion) is discounted by the low relative intensity of the *m/e* 43 ion which is usually base peak for adducts of this type.

(9) G. Alder and K. Stein, *Ann.*, **525**, 183 (1936).

ported as an oil (semicarbazone, mp 214–215°¹⁰). Crundwell and Templeton¹¹ reported that saponification of the dimethyl ester gave the *cis*-keto acid **21**, mp 182–184°; however, this melting point coincides with the literature melting point⁹ of 186° for the corresponding *trans*-diacid **24** and suggests that epimerization has accompanied saponification.

Because of these differences we decided to demonstrate the stereochemistry of the anhydride bridge in another manner. Reduction of keto diacid **21** using platinum oxide in acetic acid, conditions which are known to give lactone acid **26** from keto diacid **24**,⁹ gave the lactone **27** which was identical with an authentic sample.¹² This conversion demands that the C-6 carboxyl group be *endo* and since the keto diacid **21** may be reconverted to anhydride **20** by treatment with acetic anhydride, also fixes the *endo* position of the anhydride ring in **20**.



Elizarova¹³ has described the thermal condensation of 3,5-dimethyl-2-cyclopentenone with maleic anhydride which yields the norbornene derivative **28**. With other dieneophiles both thermal and base-catalyzed processes lead to similar products, suggesting that the reaction proceeds by two Michael additions.

(10) I. N. Nazarov, V. F. Kucherov, and V. G. Bukharav, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 192 (1958).

(11) E. Crundwell and W. Templeton, *J. Chem. Soc.*, 1400 (1964).

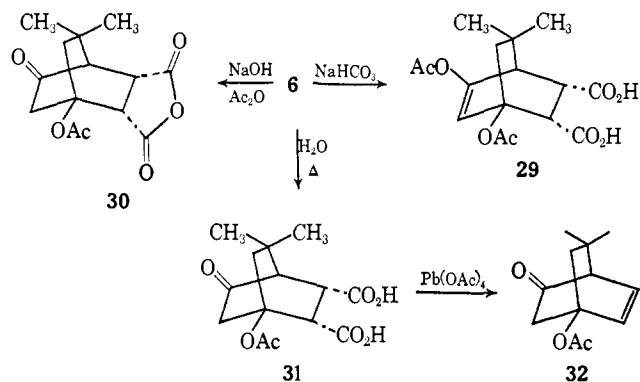
(12) G. Alder and K. Stein, *Ann.*, **514**, 1 (1934).

(13) A. N. Elizarova, *J. Gen. Chem. USSR*, **34**, 3251 (1964).

In our hands, condensation between isophorone and maleic anhydride does not occur in the absence of isopropenyl acetate and *p*-toluenesulfonic acid, suggesting that conversion of **4** to **5** followed by a Diels-Alder condensation is involved in the adduct formation.

With a procedure for the preparation of oxygenated bicyclic compounds in hand we next turned our attention to the hydrolysis of the adducts and bisdecarboxylation of the resulting diacids. When adduct **6** was stirred with excess sodium bicarbonate solution for 48 hr, the diacid **29** was the major product as evidenced by its conversion to starting material by brief heating. Treatment with sodium hydroxide solution led to only partial hydrolysis of the enol acetate function as shown by conversion of the diacid which resulted to a mixture of anhydrides **6** and **30** by heating with acetic anhydride. The apparent stability of the enol acetate function to base is probably related to the proximity of the two negatively charged carboxylate anions.

Fortunately adducts such as **6**, **7**, and **16** were hydrolyzed smoothly to the corresponding keto diacids when refluxed (4-5 hr) with water. Enol acetates **8** and **10** which had methyl groups on the enol acetate double bond, underwent only partial hydrolysis under these conditions. It is apparent that under these conditions the dibasic acids are formed and promote acid-catalyzed hydrolysis of the enol acetate function. Perhaps because of their extreme insolubility, anhydrides **15** and **19** were not hydrolyzed to an appreciable extent by boiling water. These anhydrides were converted to their corresponding diacids by treatment with hot sodium bicarbonate solution.



We next turned our attention to the bisdecarboxylation of the diacids with the hope of obtaining bicyclic olefins of more general synthetic utility. Doering¹⁴ introduced the bisdecarboxylation of succinic acid derivatives with lead dioxide and utilized this procedure in a synthesis of bicyclo[2.2.2]octan-1-ol.² Grob¹⁵ later substituted lead tetraacetate for the specially prepared lead dioxide and was able to achieve bisdecarboxylation of 1,2-diacids in acceptable yields under much less drastic conditions. Applications of this latter procedure have recently been reviewed by Criegee.¹⁶

Our initial attempts to bisdecarboxylate crude preparations of keto diacid **31** were unpromising. It was

(14) W. von E. Doering, M. Farber, and A. Sayigh, *J. Am. Chem. Soc.*, **74**, 4370 (1952).

(15) C. A. Grob, M. Ohta, and A. Weiss, *Angew. Chem.*, **70**, 343 (1958).

(16) R. Criegee in "Oxidation in Organic Chemistry," Part A, K. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, pp 297-301.

noted, however, that exclusion of oxygen (by purging the reaction mixture with prepurified nitrogen¹⁷) had no noticeable effect on the yield of olefin **32**. In order to gauge the effect of oxygen on the yield of olefin several reactions were carried out in which the only variable was the gas purging the mixture (entries 2-4, Table I).

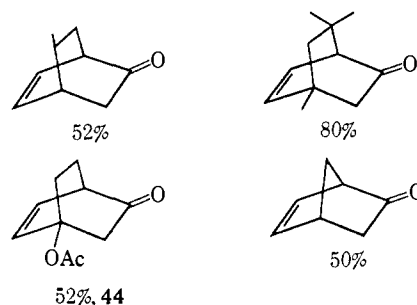
Table I

Time	<i>m</i> (Pb(OAc) ₄)		Yield ^b of 32 , %
	<i>m</i> 31	Gas ^a	
3.5 hr	1.0	...	35.6
2.5 hr	1.1	N ₂	38.4
2.5 hr	1.1	Air	43
2.5 hr	1.1	O ₂	52
10 min	1.55	O ₂	61.5
8 min	2.0	O ₂	69

^a The gas was bubbled vigorously through a magnetically stirred solution for at least 15 min prior to and during the reaction. ^b The yield is based on material isolated after recrystallization from pentane.

Qualitatively at least, it is evident that oxygen does not retard bisdecarboxylation of diacids as it does in the case of monoacids¹⁸ and actually provides a substantial increase in the yield of olefin. When the amount of lead tetraacetate was increased and the reaction time shortened an even more dramatic increase in yield of **32** was effected. This procedure has been applied to the diacids described in the foregoing section and in most cases has afforded a good yield of the corresponding olefin as shown in Table II.

Table II. Per Cent Yield of Olefins by Bisdecarboxylations of Corresponding Diacids



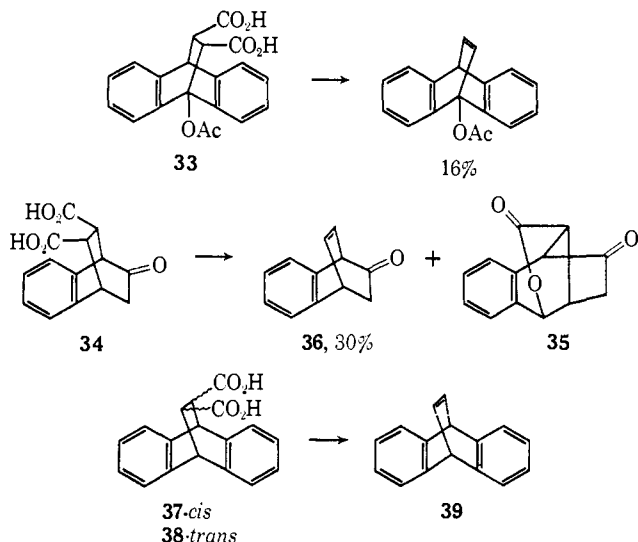
In contrast to the results with other diacids, bisdecarboxylation of the diacid **33** derived from anthrone proceeded in reduced yield and gave substantial amounts of unidentified oils which exhibited carbonyl absorption in the infrared. Examination of the literature revealed that the related keto diacid **34** gave rise to lactone **35** and saturated diacetates in addition to the expected olefin **36**.¹⁹ Under the standard conditions employed in this work a 30% yield of olefin **36** was obtained in addition to 7.8% of lactone **35**. The *cis,trans* pair of diacids **37** and **38** gave rise to 18 and 29% yields of olefin **39**, respectively. The crude product in each case exhibited infrared absorption at 5.55 μ indicative of lactone for-

(17) L. F. Fieser, *J. Am. Chem. Soc.*, **46**, 2639 (1924).

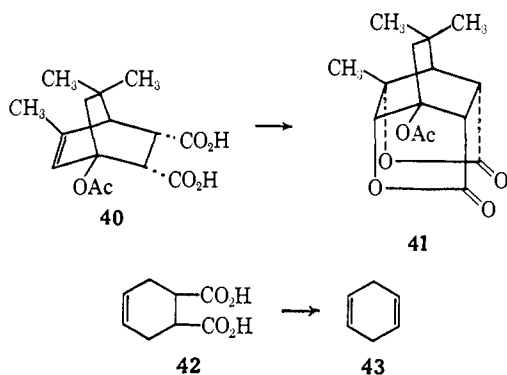
(18) J. K. Kochi, *ibid.*, **87**, 1811 (1965).

(19) K. Kitahonoki and Y. Takano, *Tetrahedron Letters*, 1597 (1963).

mation. Column chromatography of these mixtures gave the olefin **39** and significant amounts of unidentified oils.



Bisdecarboxylation of the olefinic diacid **40** was unsuccessful. In this case participation of the double bond led to the dilactone **41** in small yield. The necessity of the close proximity of the double bond to the acid groups in order for lactonization to occur is shown by the fact that diacid **42** is converted to dihydrobenzene **43** in 76% yield using our modification of the bisdecarboxylation procedure.



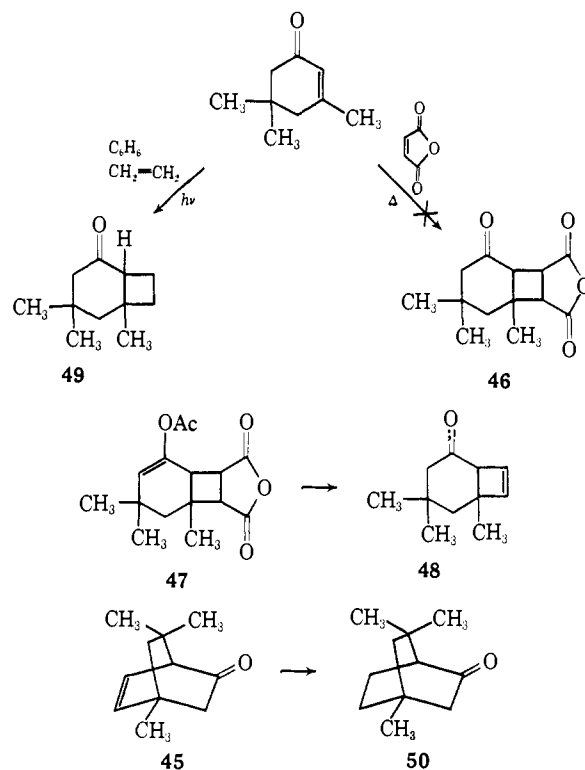
The structures of the olefins described in the foregoing discussion were confirmed by their spectral properties. Keto olefins **32** and **44** exhibited infrared bands at 5.75, 6.2, and 14.5 μ . Their nmr spectra were virtually identical in the olefinic region. In keto olefin **44** the C-3 olefinic proton appeared as an asymmetric quartet (6.08 ppm) with $J_{2,3} = 8.8$ cps and $J_{3,4} = 6.4$ cps. The C-2 proton appeared as a broadened doublet (6.54 ppm) with $J_{2,3} = 8.8$ cps. The C-4 proton in olefin **32** appears as a doublet of doublets with $J_{3,4} = 6.4$ cps and $J_{2,4}$ slightly less than 1 cps; however this coupling is not resolved in the C-2 doublet and leads only to broadening. Interestingly, the allylic coupling constant ($J_{2,4}$) is of much smaller magnitude in these unsubstituted olefins than in the enol acetates **6** and **7**.

Keto olefin **45** showed infrared absorption at 5.70, 6.2, and 14.2 μ . The ABX system which includes the C-2, -3, and -4 hydrogens gave rise to an apparent five-signal pattern in deuteriochloroform. The dissimilarity of this spectrum with those of olefins **32** and

44 led us to carefully examine the structures assigned to **45** and its precursors.

A patent²⁰ claims that the thermal condensation of isophorone with maleic anhydride affords the cyclobutane derivative **46**.²¹ We therefore considered the possibility of a 1,2-cycloaddition under our reaction conditions leading to **46** which was acetylated to give the enol acetate **47**. Hydrolysis and bisdecarboxylation would then give the cyclobutene **48** rather than olefin **45**.

This possibility was eliminated on the basis of the following evidence. Photolysis of a benzene solution of isophorone saturated with ethylene gave 4,4,6-trimethylbicyclo[4.2.0]octan-2-one (**49**).²² The nmr spectrum of this material showed three singlet methyl resonances indicating that it is a single compound. By analogy to results obtained with 3-methylcyclohexenone²² we assign a *cis* ring juncture to **49**.



Now, catalytic hydrogenation of olefin **45** afforded a saturated ketone which was clearly not identical with the cyclobutane **49**, which suggests by a process of elimination that it is the epihomocamphor **50**.

Returning to the unexpected nmr spectrum of **45**, analysis²³ leads to the conclusion that in deuteriochloroform the chemical shift difference between the protons at C-2 and C-3 ($\nu_a - \nu_b$ in the terminology of ref 23) is equal to 0 ± 0.2 cps. Calculations utilizing $J_{2,3} = 7.9 \pm 0.1$, $J_{2,4} = 0.8 \pm 0.1$, and $J_{3,4} = 6.4 \pm 0.1$

(20) O. Huppert, U. S. Patent 2,385,281 (1945); *Chem. Abstr.*, **40**, 1887 (1946).

(21) Repetition of this reaction gave no condensation product. The reaction mixture exhibited identical infrared spectra before and after heating. After long standing crystals of maleic acid were produced, but only isophorone was identified in the volatile material. The residue appeared to be maleic acid.

(22) This is essentially the procedure successfully applied to 3-methylcyclohexenone; cf. Y. Yamada, H. Uda, and K. Nakanishi, *Chem. Commun.*, 423 (1966).

(23) 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.

reproduce the high-resolution spectrum to within ± 0.2 cps. In solvent benzene the spectrum is more complex and rough calculations indicate that here $\nu'_a - \nu'_b$ is 4 ± 0.4 cps. Significantly the value of $(J_{2,4} + J_{3,4})$ obtained from the X part of the spectra both in deuteriochloroform and benzene is 7.35 ± 0.1 cps. Since the calculations cited above indicate that $J_{3,4} = 6.4 \pm 0.1$ cps (and numerous examples exhibit $J_{3,4} = 6.0 \pm 0.5$ cps), it is evident that the relative signs of $J_{2,4}$ and $J_{3,4}$ are the same. Since the vicinal coupling constant is taken as positive, the allylic coupling constant $J_{2,4}$ must be positive. This conclusion has been reached by several groups for the bicyclo[2.2.1]heptene system^{24, 25} as well as for the bicyclo[2.2.2]octene system.²⁶

Nmr Spectra

The nmr spectra of a large number of bicyclo[2.2.2]octene derivatives have been cataloged and discussed.²⁷ The values of $J_{2,3}$ (7.9–9.0 cps) and $J_{3,4}$ (6.0–6.9 cps) we have observed for the compounds described earlier compare favorably with those reported. Nevertheless several features deserve further comment.

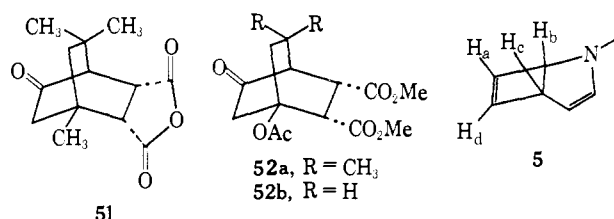
Geminal Coupling. In those cases amenable to a first-order analysis the geminal coupling constant is ca. 12.5 cps, essentially the value found for methane.²⁸ The keto olefin **36** exhibits $J_{gem} = 17$ cps. The calculated²⁸ π contribution of the adjacent carbonyl group is 4.3 cps, giving $J_{gem} = 12.4 + 4.3 = 16.7$ cps.

Vicinal Coupling. In the bicyclo[2.2.2]octene system three distinct coupling constants are encountered, each of which occurs through a dihedral angle of 0° : $J_{2,3}$, $J_{3,4}$, and $J_{5,6}$.

The value of $J_{5,6}$ is sensitive to changes in the geometry of the rest of the molecule. Anhydrides with a 2,3 double bond show $J_{5,6}$ of approximately 9.0 cps while the keto anhydrides **30** and **51** exhibit coupling constants of 9.5 and 10.0 cps, respectively. The dimethyl esters **52a** and **52b** show $J_{5,6} = 12.0$ cps as does the diacid **40**. This variation in $J_{5,6}$ probably reflects the changes in internal dihedral angle as well as changes in the electronegativity of the substituents (anhydride carbonyl vs. ester carbonyl), factors which are known to affect vicinal coupling constants.^{29, 30}

Allylic Coupling. The allylic coupling constants encountered in this work range from ca. 0.8–2.1 cps. The largest values of $J_{2,4}$ are exhibited by enol acetates such as **7** which have an acetate group on the double bond. The methyl substituted olefin **15** exhibits $J_{2,4} = 1.5$ cps while unsubstituted olefins show a coupling constant of slightly less than 1 cps. Paquette³¹ has noted a somewhat similar dependence of the allylic coupling constant on electronegative substituents. In the olefin **53**, the value of $J_{b,d}$ is 2.6 cps while the corresponding value for $J_{a,c}$ is less than 0.4 cps. It is not clear whether this involves the same type of effect since significant π contributions to the coupling constant are expected in this case. Furthermore, the coupling con-

stant is probably negative³² in olefin **53**, in contrast to the bicyclo[2.2.2]octene system in which only σ contributions should be important and where the sign of the allylic coupling constant is positive (*vide supra*).



As pointed out by Paquette³¹ structural arguments based on the dihedral angle relationships indicated by the magnitude of long-range coupling constants must be made with caution.

Experimental Section³³

Acetylation of Dimedone (1). A mixture of 5.0 g (0.036 mole) of dimedone (**1**), 15 ml of isopropenyl acetate and 10 mg of *p*-toluenesulfonic acid was refluxed for 192 hr. Distillation, first at atmospheric pressure and then *in vacuo*, gave 5.48 g of product, bp $62-71^\circ$ (0.04 mm). Glpc analysis showed the presence of two components in all fractions. The first component showed λ_{max} 5.7, 6.0, and 6.2 μ and nmr absorptions at 1.13 (s, *gem*-dimethyl), 2.07 (s, two acetate methyls), 4.98 (d, $J = 1.5$ cps), and a multiplet at 5.46 ppm and was assigned structure **3**. The second component had λ_{max} 5.6, 5.8, and 6.0 and nmr signals at 1.06 (s, *gem*-dimethyl), 2.16 (s, acetate methyl), and 5.68 ppm (t, $J = 1.5$ cps, olefinic proton) and is therefore the mono-enol acetate **2**.

General Procedure for Adduct Formation. A weighed amount of diketone (0.022–0.25 mole), maleic anhydride (25% excess), and 50–100 mg of *p*-toluenesulfonic acid was refluxed for 72 hr with 15–150 ml of isopropenyl acetate. The acetone was largely removed on a rotary evaporator at room temperature and the resulting solution was cooled to 0° and then -20° . The crude product was filtered and recrystallized (Norit) from mixtures of hexane–ethyl acetate. If crystallization did not occur, the reaction mixture was filtered through a column of alumina with the aid of ethyl acetate, and the eluates were reduced in volume, diluted with hexane, and cooled. Solvent A refers to hexane–ethyl acetate mixtures.

endo-1,3-Diacetoxy-8,8-dimethylbicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Anhydride (6). From 25 g (0.178 mole) of dimedone (**1**) there was obtained 46 g (80%) of crude **6**. Recrystallization from solvent A gave colorless crystals, mp $164-166^\circ$, λ_{max} 5.35, 5.5, 5.75, and 6.05 μ . Two sublimations (110° (0.1 mm)) gave the analytical sample, mp $165.5-167^\circ$.

Anal. Calcd for $C_{16}H_{18}O_7$: C, 59.62; H, 5.63. Found: C, 59.66; H, 5.55.

The diacid **31** (mp $146.5-148.5^\circ$ dec) was prepared by heating **6** with water for 4–5 hr followed by ether extraction. The dimethyl ester prepared by reaction of the diacid **31** with diazomethane showed mp $116.5-117.5^\circ$ and singlet resonances in the nmr at 1.02, 1.18, 1.97, 3.59, and 3.63 ppm.

Anal. Calcd for $C_{16}H_{22}O_7$: C, 58.89; H, 6.79. Found: C, 58.90; H, 6.80.

Treatment of the diacid with acetic anhydride gave the keto anhydride **30**, mp $225-227^\circ$, λ_{max} 5.35, 5.6, and 5.75 μ and nmr absorptions at 0.98 and 1.09 (s's, C-8 *gem*-dimethyl) and 1.97 ppm (s, acetate methyl). Sublimation at 140° (1 mm) gave the analytical sample, mp $226-228^\circ$.

Anal. Calcd for $C_{14}H_{16}O_6$: C, 59.99; H, 5.75. Found: C, 59.71; H, 5.50.

endo-1,3-Diacetoxybicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Anhydride (7). The reaction of 12.0 g (0.106 mole) of 1,3-cyclohexanedione with maleic anhydride gave 23 g (73%) of recrystallized **7**,

(32) Cf. E. W. Garbisch, *Chem. Ind.* (London), 1715 (1964), and references cited therein.

(33) All boiling and melting points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer, Model 137-B. Nuclear magnetic resonance spectra were determined at 60 Mc on a Varian Associates A-60 spectrometer. Chemical shifts are recorded in ppm with reference to tetramethylsilane as an internal standard. Microanalyses were performed by Dr. C. S. Yeh and associates.

(24) E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964).

(25) P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964).

(26) Cf. footnote 71 in ref 25 as well as R. G. Miller and M. Stiles, *ibid.*, **85**, 1798 (1963).

(27) K. Tori, Y. Takano, and K. Kitahonoki, *Ber.*, **97**, 2798 (1964).

(28) M. Bartfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963).

(29) K. L. Williamson, *ibid.*, **85**, 516 (1963).

(30) O. L. Chapman, *ibid.*, **85**, 2016 (1963).

(31) L. A. Paquette and J. H. Barrett, *ibid.*, **88**, 1718 (1966).

mp 156–159°, λ_{\max} 5.4, 5.5, 5.75, and 6.05 μ , and prominent nmr signals (CDCl₃) at 2.15 (two acetate methyls) and 5.88 ppm (d, $J = 2$ cps, C-2 olefinic proton). Two sublimations (110° (0.5 mm)) gave the analytical sample, mp 158–160°.

Anal. Calcd for C₁₄H₁₄O₇: C, 57.14; H, 4.79. Found: C, 57.01; H, 4.84.

The keto diacid (mp 148–151° dec) was obtained by refluxing 7 with water (5 hr) and cooling the resulting solution. The dimethyl ester had mp 94.5–96° and singlets in its nmr spectrum at 1.98, 3.59, and 3.64 ppm.

Anal. Calcd for C₁₄H₁₈O₇: C, 56.37; H, 6.08. Found: C, 56.63; H, 6.31.

endo-1,3-Diacetoxy-2-methylbicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Anhydride (8). The reaction of 7.5 g (0.029 mole) of 2-methyl-1,3-cyclohexanedione with maleic anhydride gave, upon cooling, 17.5 g of crude product. Recrystallization afforded 13.5 g (65.4%) of **8**, mp 155.5–156.5°, λ_{\max} 5.4, 5.6, 5.75, and 5.95 μ , and prominent nmr signals at 1.68 (s, vinyl methyl) and 2.15 and 2.17 ppm (acetate methyls). Several further recrystallizations gave the analytical sample, mp 155.5–156.5°.

Anal. Calcd for C₁₅H₁₆O₇: C, 58.44; H, 5.23. Found: C, 58.53; H, 5.32.

endo-1,3-Diacetoxy-2-methylbicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic Anhydride (10). The reaction of 7.8 g (0.05 mole) of enol acetate **9** with maleic anhydride gave 11.7 g (80%) of crude **10**. Recrystallization from solvent A gave 9.37 g (63.6%) of **10**, mp 137.5–139°, λ_{\max} 5.35, 5.6, 5.7, and 5.95 μ , and prominent nmr signals at 1.61 (s, C-2 methyl) and 2.14 and 2.16 ppm (s's, two acetate methyls). An analytical sample had mp 138.5–139.5°.

Anal. Calcd for C₁₄H₁₄O₇: C, 57.14; H, 4.80. Found: C, 57.23; H, 5.11.

endo-1,4-Diacetoxybicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Anhydride (14). The reaction mixture from 2.5 g (0.022 mole) of 1,4-cyclohexanedione and maleic anhydride was filtered through a short column of alumina with the aid of ethyl acetate. The eluates were partially evaporated, diluted with hexane, and cooled. The semicrystalline material so obtained was recrystallized (Norit) several times from solvent A to give 840 mg (13%) of **14**, λ_{\max} 5.4, 5.6, 5.75, 6.15, and 14.3 μ and prominent nmr signals at 2.10 (s, acetate methyls) and 6.53 (s, olefinic protons). The analytical sample was crystallized from solvent A and showed mp 209–210.5°.

Anal. Calcd for C₁₄H₁₄O₇: C, 57.14; H, 4.80. Found: C, 57.33; H, 4.94.

Mixture of Adducts 11 and 12. The reaction mixture from 26 g (0.2 mole) of 3-methyl-1,2-cyclopentanedione and maleic anhydride was filtered through 200 g of alumina with the aid of 1 l. of ethyl acetate, and the eluate was reduced in volume, diluted with hexane, and cooled. The oily solid which resulted was recrystallized to give a colorless solid, λ_{\max} 5.4, 5.6, 5.75, and 6.1 μ . The nmr spectra of several different fractions of this material showed two singlet methyl groups (1.37 and 1.49 ppm) and four acetate methyls (2.1–2.2 ppm). The ratio of the absorptions at 3.30–3.90 ppm to the rest of the spectrum was 3:11 in all fractions.

endo-1-Acetoxy-3,8,8-trimethylbicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Anhydride (15). After removal of acetone, the reaction mixture from 138 g (1.0 mole) of isophorone and maleic anhydride was seeded with adduct **15**.³⁴ Cooling to 0° gave 100 g (36%) of material whose infrared showed little enol acetate absorption. One recrystallization from solvent A gave, in two crops, 87 g (31.8%) of **15**, mp 140–142°, λ_{\max} 5.4, 5.6, 5.78, and 6.2 μ , and nmr signals at 0.97 and 1.16 (s, C-8 gem-dimethyl), 1.87 (d, $J = 1.5$ cps, C-3 vinyl methyl), 2.15 (s, acetate methyl), 1.44 and 2.20 (d's, $J = 12$ cps, C-7 methylene group), 2.65 (m, C-4 methine), 3.60 (q, $J_1 = 9$, $J_2 = 3$ cps, C-5 methine), and 4.21 (d, $J = 9$ cps, C-6 methine) and 5.88 ppm (m, C-2 olefinic proton). An analytical sample showed mp 141.5–142.5°.

Anal. Calcd for C₁₅H₁₈O₅: C, 64.74; H, 6.52. Found: C, 64.96; H, 6.31.

The corresponding diacid **40**, mp 141–142° dec, was prepared by heating a suspension of **15** with 5% aqueous sodium bicarbonate until solution occurred. The dimethyl ester was prepared in the usual manner and exhibited mp 82.5–84° and singlets in the nmr spectrum at 0.92 and 1.10 (C-8 gem-dimethyl), 1.97 (acetate methyl), and 3.53 and 3.58 ppm (two methoxy methyls).

Anal. Calcd for C₁₇H₂₄O₆: C, 62.95; H, 7.46. Found: C, 63.23; H, 7.32.

endo-3-Acetoxy-1,8,8-trimethylbicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Anhydride (16). The mother liquor obtained from crystallization of **15** was seeded with **16** to give after one recrystallization from solvent A, 76 g (27.4%) of **16**, mp 102–104°, λ_{\max} 5.4, 5.6, 5.65, and 6.05 μ , and nmr signals at 1.00 and 1.13 (s's, C-8 gem-dimethyl) 1.22 (s, C-7 methylene), 2.63 (m, C-4 methine), 2.88 (d, $J = 9$ cps, C-6 methine), 3.53 (d of d, $J_1 = 9$, $J_2 = 3$ cps, C-5 methine) and 5.65 ppm (d, $J = 2$ cps, C-2 olefinic proton). The analytical sample was crystallized from solvent A and showed mp 104–105.5°.

Anal. Calcd for C₁₅H₁₈O₅: C, 64.74; H, 6.52. Found: C, 64.96; H, 6.69.

16 was refluxed with water for 5 hr, cooled, and dried *in vacuo* to give the corresponding diacid, mp 143–147° dec. The dimethyl ester, prepared in the usual manner, showed mp 80.5–81° and nmr singlets at 0.96, 1.02, and 1.11 (three quaternary methyls), and 3.58 and 3.62 ppm (two methoxy methyls).

Anal. Calcd for C₁₅H₂₂O₅: C, 63.88; H, 7.85. Found: C, 63.99; H, 7.86.

Treatment of the diacid with acetic anhydride gave the keto anhydride **51**, λ_{\max} (Nujol) 5.35, 5.6, and 5.75 μ , and nmr singlets at 1.02, 1.17, 1.29 (three quaternary methyls). The analytical sample was crystallized from solvent A and displayed mp 160.5–161.5°.

Anal. Calcd for C₁₃H₁₆O₄: C, 66.09; H, 6.83. Found: C, 65.48, 65.34; H, 7.06, 7.08.

endo-2-Acetoxybicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Anhydride (17). From the reaction of 10.0 g (0.104 mole) of 2-cyclohexen-1-one employing the general conditions described earlier there was obtained 17 g of tan solid upon cooling. Further cooling after volume reduction gave an additional 2.6 g (total 19.6 g, 79%). The infrared spectrum showed strong enol acetate peaks (5.6 and 6.0 μ) and no saturated acetate absorption (5.75 μ). Fractional recrystallization gave a total of 13.8 g of colorless **17**, mp 138.5–140.5° (lit.² 137–138°), λ_{\max} 5.4, 5.5, 5.6, and 6.0 μ , and prominent nmr signals at 2.17 (s, acetate methyl) and 5.88 (d of d's, $J_1 = 7$, $J_2 = 2$ cps, C-3 olefinic proton).

The mother liquors yielded several hundred milligrams of a mixture of **17** and **18** (ca. 1:1 by nmr), with signals at 2.14 (s, acetate methyl) and 6.2–6.3 ppm (m, C-2 olefinic protons).

9-Acetoxy-9,10-ethanoanthracene-11,12-dicarboxylic Anhydride (19). The reaction of 10 g (0.05 mole) of anthrone with maleic anhydride gave 11.5 g (68%) of adduct **19** contaminated with a small amount of anthrone. Recrystallization from solvent A gave colorless **19**, mp 237–239°, λ_{\max} 5.35, 5.5, and 5.75 μ . An analytical sample had mp 239.5–240° (lit.⁷ mp 240°).

Anal. Calcd for C₂₀H₁₄O₅: C, 71.85; H, 4.22. Found: C, 71.68; H, 4.33.

The corresponding diacid was prepared by heating an aqueous suspension of **19** in dilute sodium bicarbonate until solution occurred; this was followed by filtration, acidification, and ether extraction. The dimethyl ester showed mp 163.5–164° after several recrystallizations from solvent A.

Anal. Calcd for C₂₂H₂₀O₆: C, 69.46; H, 5.30. Found: C, 69.64; H, 5.33.

endo-Bicyclo[2.2.1]heptan-2-one-5,6-dicarboxylic Anhydride (20). The reaction of 15.0 g (0.182 mole) of cyclopentenone with maleic anhydride gave 10.9 g (31.4%) of crude **20**. Recrystallization from ethyl acetate afforded a colorless solid, mp 228.5–230°, λ_{\max} 5.35, 5.6, and 5.7 μ . The nmr spectrum (pyridine) showed multiplet absorptions centered at 1.95, 2.25, 3.1, and 4.1 ppm of approximately equal intensity.

Recrystallization from ethyl acetate gave the analytical sample, mp 229–230.5°.

Anal. Calcd for C₇H₈O₄: C, 59.94; H, 4.44. Found: C, 59.99; H, 4.49.

Characterization of Adduct 20. Adduct **20** could be hydrolyzed to diacid **21**, mp 163–163.8°, by crystallization from a small amount of water. This diacid could be transformed back to anhydride **20** by heating with acetic anhydride. The dimethyl ester, mp 69–70° (lit.^{10,11} liquid), prepared by reaction with diazomethane gave a semicarbazone mp 210.5–211.5° (lit.¹⁰ mp 214–215°).

Reduction of 250 mg (0.00125 mole) of diacid **21** with PtO₂ in acetic acid after the procedure of Alder and Stein⁹ gave, in two crops, 60.5 mg of solid (λ_{\max} 5.65 and 5.9 μ) whose infrared spectrum was identical with an authentic sample of lactone **27**.¹² Recrystallization from water gave crystals, mp 198–199°, which did not depress the melting point of an authentic sample of **27**. The mother liquors afforded 130 mg of unreacted diacid **21**.

(34) A mixture of adducts **15** and **16** may easily be separated by virtue of the greater insolubility of adduct **15** in ethyl acetate–hexane mixtures

General Procedure for Bisdecarboxylation. Oxygen was bubbled through a stirred amount (*ca.* 10 ml/g of diacid) of pyridine (distilled from barium oxide) for *ca.* 15 min. A sample of weighed diacid (0.003–0.02 mole) and lead tetraacetate (50% excess, recrystallized from acetic acid and dried over potassium hydroxide *in vacuo*) were added, and the flask was immersed in an oil bath at $67 \pm 2^\circ$. After several minutes carbon dioxide evolution began. After 8–10 min the reaction mixture was cooled, poured into excess dilute nitric acid, and extracted with ether. The ether was washed with aqueous bicarbonate, saturated salt solution, and dried. Removal of solvent usually gave the olefin in substantially pure form, except as noted in the Discussion.

Bicyclo[2.2.2]oct-2-en-5-one. From 601 mg (2.83 mmoles) of bicyclo[2.2.2]octan-5-one-2,3-dicarboxylic acid was obtained 215 mg (84%) of crude bisdecarboxylation product. Sublimation (1 mm) gave 130 mg (51.8%) of bicyclo[2.2.2]oct-2-en-5-one, λ_{max} 5.78, 6.2, and 14.3μ . The 2,4-dinitrophenylhydrazone derivative showed mp $148.5\text{--}149.5^\circ$ after one recrystallization from ethanol (lit.³⁵ 150.5°).

1,8,8-Trimethylbicyclo[2.2.2]oct-2-en-5-one (45). From 2.54 g of 1,8,8-trimethylbicyclo[2.2.2]octan-5-one-2,3-dicarboxylic acid was obtained 1.5 g (90%) of a light brown oil. Examination by vpc showed it to be essentially pure 45 with a little ether remaining. Olefin 45 showed λ_{max} (cap film) 5.70, 6.2, and 14.2μ and prominent nmr signals at 0.92, 1.03, and 1.21 (s's, three quaternary methyl groups), an apparent triplet (separation of 3.5 cps) at 2.68, and an apparent doublet (separation of 3.5 cps) at 6.10 ppm. In benzene solution the nmr spectrum showed singlets at 0.73 (s, quaternary methyl) and 0.88 (s, two quaternary methyls), an apparent quartet (2.47, 2.55, and 2.59 ppm), and a five-signal multiplet at *ca.* 5.80 ppm. Vpc collection gave the analytical sample.

Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}$: C, 80.44; H, 9.82. Found: C, 80.25; H, 10.03.

9-Acetoxy-9,10-dihydro-9,10-ethenoanthracene. From 1.69 g (0.005 mole) of diacid 33 was obtained 0.850 g of material. The ether (10 ml) soluble portion (550 mg) was applied to a column of 30 g of neutral alumina. Elution with 10% ether in pentane gave 186 mg of 9-acetoxy-9,10-dihydro-9,10-ethenoanthracene, mp $143.5\text{--}145^\circ$, λ_{max} (CCl_4) 5.70 and 14.8μ , and nmr signals at 2.41 (s, acetate methyl), 5.06 (d of d's, $J_1 = 6$, $J_2 = 2$ cps, C-10 methine proton), and 6.8–7.5 ppm (m's, two olefinic and eight aromatic protons). The analytical sample had mp $145.5\text{--}147^\circ$ after crystallization from solvent A.

Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{O}_2$: C, 82.42; H, 5.38. Found: C, 82.58; H, 5.36.

Bicyclo[2.2.1]hept-2-en-5-one (22). From 1.80 g (0.009 mole) of diacid 21 was obtained 450 mg of a yellow oil. Vpc showed essentially one component besides some solvent. The nmr spectrum and vpc retention time were identical with those of an authentic sample of 22. The 2,4-dinitrophenylhydrazone derivative of 22 showed mp $165\text{--}170^\circ$ and did not depress the melting point of an authentic sample.

1-Acetoxy-8,8-dimethylbicyclo[2.2.2]oct-2-en-5-one (32). From 1.51 g (0.005 mole) of diacid 31 was obtained 718 mg (69%) of

olefin 32 (*cf.* Table I, entry 6), λ_{max} 5.75, 6.2, and 14.5μ and prominent nmr signals at 1.00 and 1.09 (s's, C-8 *gem*-dimethyl), 2.06 (s, acetate methyl), 2.72 (q, $J_{3,4} = 6$, $J_{2,4} \cong 1$ cps, C-4 methine), 6.07 (q, $J_{2,3} = 9$ cps, C-3 olefinic proton), and 6.54 ppm (d, $J_{2,3} = 9$ cps, C-2 olefinic proton).

Sublimation at 45° ($<1 \text{ mm}$) gave the analytical sample, mp $59.5\text{--}60^\circ$.

Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_2$: C, 69.21; H, 7.74. Found: C, 69.24; H, 7.99.

1-Acetoxybicyclo[2.2.2]oct-2-en-5-one (44). From 2.70 g (0.01 mole) of 1-acetoxybicyclo[2.2.2]octan-5-one-2,3-dicarboxylic acid was obtained 932 mg (51.6%) of olefin 44, after recrystallization from pentane. Olefin 44 showed λ_{max} 5.75, 6.2, and 14.55μ and prominent nmr signals at 2.09 (s, acetate methyl), 6.08 (q, $J_{2,3} = 9$, $J_{3,4} = 5.5$ cps, C-3 olefinic proton), and 6.58 ppm (d, $J_{2,3} = 9$ cps, C-2 olefinic proton).

The analytical sample, prepared by sublimation, had mp $49.5\text{--}50.0^\circ$.

Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{O}_2$: C, 66.65; H, 6.71. Found: C, 66.85; H, 6.86.

Dilactone 41. The ether extract from the reaction of 4.4 g (0.015 mole) of diacid 40 with lead tetraacetate was concentrated to 50 ml whereupon 0.4 g of crystalline 41 was obtained, λ_{max} 5.55 and 5.7μ and nmr signals (pyridine) at 1.13 and 1.22 (s's, *gem*-dimethyl), 1.72 (s, C-3 methyl), 2.01 (s, acetate methyl), 2.10 (m, C-4 methine proton), 2.03 and 2.32 (d's, $J = 13.5$ cps, C-7 methylene), 3.18 (m's, C-5 and C-6 methine protons), and 4.75 ppm (broadened s, C-3 methine proton). Recrystallization from solvent A gave the analytical sample mp $155.5\text{--}157^\circ$.

Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_6$: C, 61.22; H, 6.16. Found: C, 61.03; H, 6.12.

The remainder of the ether was removed and the residue crystallized from solvent A to give 1.0 g of anhydride 15.

1,3,3-Trimethylbicyclo[4.2.0]octan-5-one (49). A solution of 7.0 g (0.056 mole) of isophorone in 60 ml of benzene was irradiated (450-w Hanovia immersion lamp, Corex filter) for 15 hr with ethylene bubbling gently through the solution. The benzene was removed *in vacuo* to give 7.2 g of an orange oil. Distillation of 5.0 g of this oil gave 2.59 g of colorless liquid, bp $42\text{--}55^\circ$ (0.6 mm) and a semi-crystalline residue. Vpc examination of the distillate showed two major components (3 m 20% Carbowax on Chromosorb at 170°). The first of these was shown to be isophorone by infrared, nmr, and vpc peak enhancement techniques. The second component showed a carbonyl peak at 5.75μ and nmr signals at 0.92, 1.07, and 1.28 ppm. Vpc collection gave the analytical sample.

Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.46; H, 10.91. Found: C, 79.81, 79.81; H, 11.00, 10.95.

1,8,8-Trimethylbicyclo[2.2.2]octan-3-one (50). A solution of 250 mg of crude 45 (1.52 mmoles) was stirred with 80 mg of pre-reduced platinum oxide in 25 ml of ethyl acetate under 1 atm of hydrogen until hydrogen uptake ceased (36 ml, 1.60 mmoles, 105%). The catalyst was removed by filtration and the filtrate evaporated to give 253 mg (101%) of light yellow oil which showed, in addition to some solvent, one peak by vpc. Ketone 50 displayed λ_{max} (cap film) 5.75μ and singlets at 0.89, 0.92, and 1.07 ppm (three quaternary methyls) in the nmr spectrum. The analytical sample was obtained by vpc collection.

Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.46; H, 10.91. Found: C, 79.34; H, 10.85.

(35) W. C. Wildman and D. R. Saunders, *J. Org. Chem.*, **19**, 381 (1954).