Substituent Effects on the Orientation of Diels–Alder Reactions. I[1,2]

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A novel attempt was initiated to investigate the transition state of the diene synthesis by studying the structures and ratios of adducts formed from 1,4 unsymmetrically disubstituted dienes with 2,6-disubstituted benzoquinones. The competitive *ortho*[3]-directing influence of acetoxy and methyl groups was studied by treating 1-acetoxy-1,3-pentadiene with 2,6-dimethylbenzoquinone in a Diels–Alder reaction. The structures of the two adducts formed (**4** and **5**) were elucidated and their ratio was determined. The acetoxy group was found to be four times more powerful as an *ortho* director than a methyl group. A similar study with methyl sorbate and the same quinone revealed that the relative *ortho*-directing influence of a carbomethoxy group compared with methyl is even more pronounced, since only one of the two possible adducts (**6**) was isolated. The readily available intermediate **10** is a potential precursor for the synthesis of highly oxygenated decanortriterpenes of the quassin type.[4]

Despite intensive efforts devoted to its study, the mechanism of the Diels–Alder reaction warrants further attention. While the concerted nature of the reaction is well established, it is believed that the two σ bonds do not form completely simultaneously.[5-7] The characteristic Diels–Alder orientation rules[8] have been regarded as manifestations of the unequal σ-bond formation in the transition state. The suggested mechanisms postulating the existence of discrete intermediates, however, do not account for all the observations concerning Diels–Alder reactions.[5,6]

The majority of the additions studied involved the reaction of dienes carrying only one substituent at the terminal positions and an α,β-unsaturated carbonyl dienophile.[5,9,10] Owing to the special steric and electronic nature of hydrogen, it would be more informative to study the additions of 1,4 unsymmetrically disubstituted butadienes to 2,6-disubstituted benzoquinones (eq 1, 2).

The determination of the structures and the ratio of the two possible adducts in a number of critically chosen cases should provide a deeper insight into the transition state of Diels–Alder reactions.

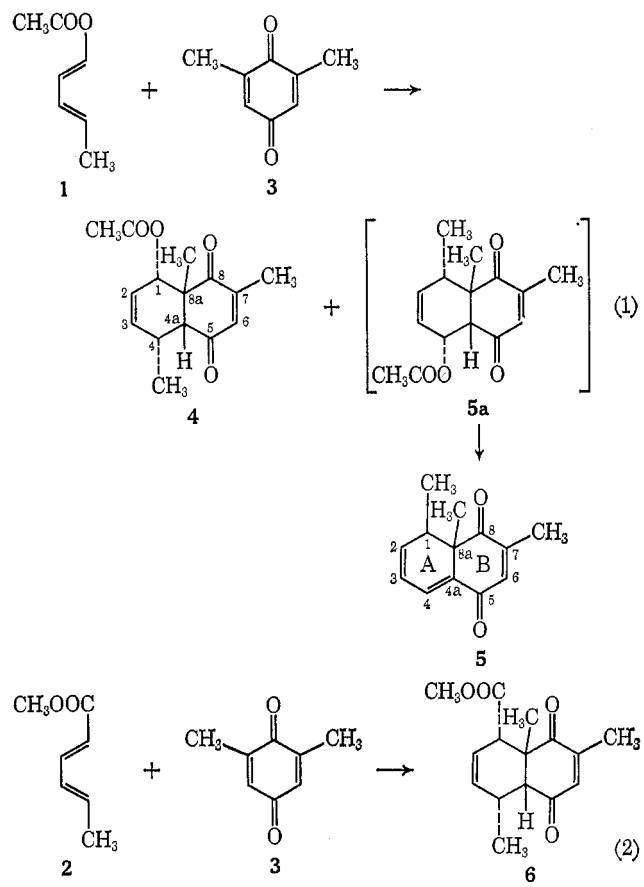
Such an experimental design should have the following advantages compared with the known examples.

(A) The electronic moiety at the four carbon atoms involved in the formation of the two σ bonds can be efficiently varied.

(B) The relative *ortho*-directing influence of the two terminal substituents[11] (other than H) can be studied by allowing competition within the same diene for the *ortho* or *meta*[3] positions in the adduct.

(C) Selecting a 2,6-disubstituted benzoquinone in lieu of an α,β-unsaturated carbonyl compound will allow a more representative study of the role of the substituent itself in the dienophile. The unsymmetrical electric field in the substituted quinone is entirely due to the substituent, whereas in the α,β-unsaturated carbonyl dienophile the presence of only one electron-withdrawing group overwhelms the influence of the substituent.

In the present study the electron-donating properties of an acetoxy group in diene **1** are exposed to the



(1) Presented in part at the 52nd C.I.C. Conference, Montreal, Canada, May 28, 1969.

(2) This work was carried out entirely on the premises of St. Dunstan's University, Charlottetown, Prince Edward Island, Canada.

(3) The terms *ortho* and *meta* refer to the relative positions of the angular methyl group to the two substituents contained in the cyclohexene ring of the Diels–Alder adduct (see eq 1).

(4) Z. Valenta, A. H. Gray, D. E. Orr, S. Papadopoulos, and C. Podešva, *Tetrahedron*, **18**, 1433 (1962).

(5) A. S. Onishchenko, "Diene Synthesis," Israel Program for Scientific Translations, Jerusalem, 1964.

(6) J. Sauer, *Angew. Chem. Int. Ed. Engl.*, **6**, 16 (1967).

(7) A. Wassermann, "Diels–Alder Reactions," Elsevier Publishing Corp., New York, N. Y., 1965.

(8) (a) Addition of a 1-substituted butadiene to an unsymmetric dienophile results in a high *ortho/meta* isomer ratio. (b) Addition of a 2-substituted butadiene to the same dienophile leads to a high *para/meta* isomer ratio. (c) The structure of the predominant adduct of 1,2- or 1,3-disubstituted dienes corresponds to that predicted for a 1-substituted diene (see ref 5, 6).

(9) A. A. Petrov and N. P. Sopov, *Zh. Obshch. Khim.*, **27**, 1795 (1957).

(10) A. A. Petrov and V. Lyndvig, *ibid.*, **25**, 739 (1955).

(11) The directing influence of a terminal group outweighs that of any other substituent in the diene (ref 8c). It is therefore advisable to concentrate on 1,4-disubstituted butadienes.

mechanistic challenge of the nearly neutral methyl group, which is endowed only with hyperconjugative electron donation (eq 1).

The second diene **2** allows comparison of the electron-withdrawing carbomethoxy group with a methyl group in the same manner (eq 2).

Diels–Alder reactions of these two dienes are studied with the same dienophile—2,6 dimethylbenzoquinone (**3**).

The steric requirements of the three groups involved are as close to each other as such a selection permits.

Results

Diels–Alder Reaction of 1-Acetoxy-1,3-pentadiene (1) with 2,6-Dimethylbenzoquinone (3).—The novel 1-acetoxy-1,3-pentadiene was readily prepared from 2-penten-1-al using acetic anhydride and potassium acetate in 89% yield.[12] Since the homogeneous product reacts with the quinone without any difficulty, diene **1** is assumed to possess the *trans,trans* configuration.

The reaction of the acetoxydiene **1** and xyloquinone **3** in benzene at 150° led to an 85% yield of **4** and **5** in a ratio of 4:1. An attempt to convert **4** into **5** under the same reaction conditions proved to be unsuccessful, indicating a difference in orientation[13] of the two products.

The structure of the minor product **5** follows from its manner of formation. The molecular weight of the product at *m/e* 202 represents the loss of acetic acid from the primary Diels–Alder product **5a** (mol wt, 262), which, however, could not be observed. The elimination of acetic acid at this relatively low temperature can be explained by the 1,3 positions of the acetoxy and keto group.

The uv spectrum of the bright yellow product indicates a novel conjugated system. The low intensity of the highest peak at 342 mμ (ϵ 7000) might be explained by the nonlinear conjugation of the butadiene system in ring A with the enedione system of ring B. The nmr and ir of product **5** are in agreement with the assigned structure.

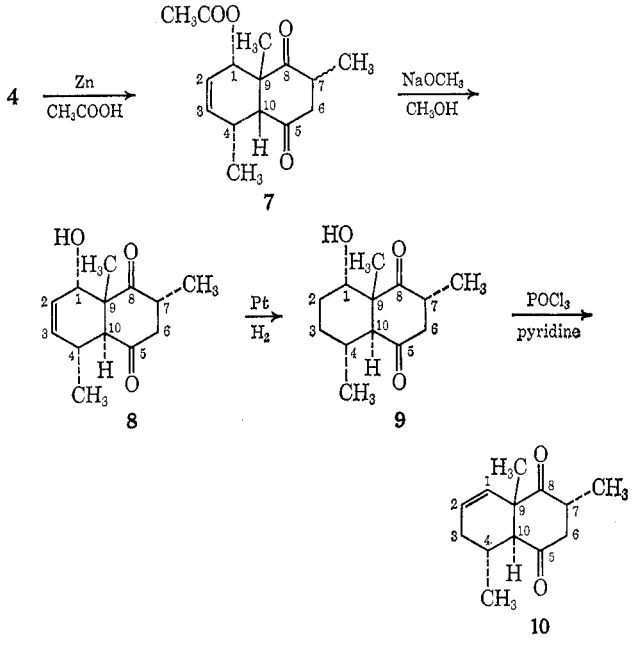
Since position 1 in compound **5** is vinylogously α to the 5-keto group, it can be assumed that the 1-methyl group is in the more stable quasiequatorial position.

The structure of **4** was elucidated by chemical means (Scheme I). The spectroscopic properties, mass spectroscopic molecular weights, and elemental analyses of the crystalline compounds **4–10** were in agreement with the proposed structures.

The diketo alcohol **9** was recovered unchanged when its methanol solution was heated in the presence of dilute sulfuric acid. The only other possible structure, **11**, possessing the alternative orientation, is therefore excluded. A β-hydroxy ketone under these conditions should have led to an α,β-unsaturated ketone. This elimination was inhibited by the presence of the angular methyl group in **9** at C-9.

The fact that **9** was recovered after the above-mentioned treatment allows the tentative assignment of its stereochemistry as portrayed. The ring junction is assumed to be *trans*, and the 7-methyl group is regarded to be equatorial in order to avoid 1,3-diaxial interaction with the angular methyl group. The 4-methyl and 1-hydroxy groups can be assigned *trans* to the angular methyl group as a consequence of the *endo,-cis*-addition principle of Diels–Alder reactions.

SCHEME I



It is possible that during the acidic treatment of **9**, a retro aldol reaction took place; this however, must have been reversible, regenerating the original compound.

In order to obtain more positive proof, the diketo alcohol was converted into the unsaturated ketone **10** by treatment with phosphorus oxychloride in pyridine. Compound **10** was recovered unchanged after refluxing its methanol solution in the presence of sodium methylate. The fact that the β,γ-unsaturated ketone did not isomerize to the α,β isomer confirms the position of the angular methyl group. The lack of change allows the stereochemical assignment in **10** as drawn. The additional bonus of structure **10** is that it could serve as a precursor for the synthesis of quassin and other decanortriterpenes,[4] representing rings A and B with the correct stereochemistry and manageable functionality.

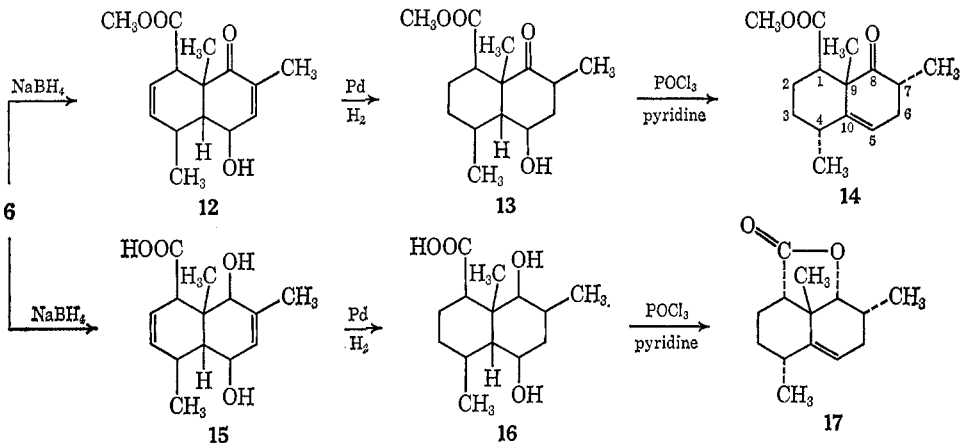
Diels–Alder Reaction of Methyl Sorbate (2) with 2,6-Dimethylbenzoquinone (3).—The reaction of 2,6-dimethylbenzoquinone with methyl sorbate was carried out by heating the benzene solution of the two compounds in a sealed tube for 35 hr at 150°. Only one product, **6**, was isolated from the reaction mixture corresponding to an 80% yield based on the amount of reacted quinone. Attempts were unsuccessful to detect the adduct with the alternative orientation. Adduct **6** had the correct mass, elemental analysis, and spectroscopic properties in agreement with the proposed structure, elucidated by chemical means as outlined in Scheme II.

Reduction with sodium borohydride led to a mixture of **12** and **15**, which was hydrogenated without separation in the presence of palladium on charcoal, giving **13** and **16**. The latter two components were then subjected to phosphorous oxychloride and pyridine, leading to **14** and **17**, which could be readily separated by

(12) A similar procedure was used for the preparation of 1-acetoxybutadiene: B. Y. Blanc, *Helv. Chim. Acta*, **44**, 1 (1961).

(13) Orientation is defined as the influence of a substituent in the diene or dienophile on the relative positions of substituents in the Diels–Alder adduct.

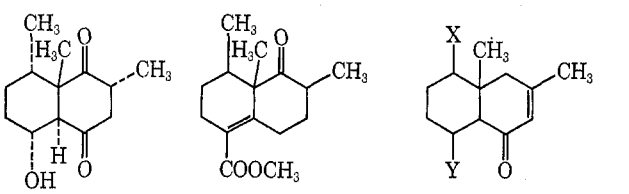
SCHEME II



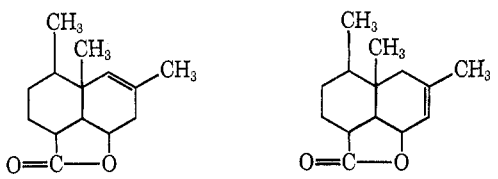
preparative thick layer chromatography. The total yield of the latter two compounds corresponded to 70% based on **6**. The ratio of **14** to **17** was 2:1.

The unsaturated keto ester **14** had the correct mass and spectroscopic properties. Compound **14** was recovered unchanged after treatment with sodium methylate in methyl alcohol or after similar acidic treatment at 60° for 6 hr.

The fact that **14** remained unchanged and did not isomerize to a uv-active compound proves that the structure of the adduct is **6**, since a similar series of reactions with the alternatively oriented compound should have produced **18** instead of **14**.



11 **18** **19**, X, Y = CH_3, $COOCH_3$



20 **21**

It is also clear that in **6** the less hindered 5-keto group was reduced to a hydroxyl group, giving **12**, since the reduction of the more hindered keto group followed by hydrogenation and elimination should have produced **19**, contrary to the chemical and spectroscopic data.

An examination of the spectroscopic properties of the crystalline **17** adduces evidence for the assignment of the orientation in **6**. The lactone (mol wt, 220) shows only end absorption in the uv. The nmr of **17** contained a singlet for the angular methyl group and two doublets for the other two methyl groups.

These data prove that the orientation of adduct **16** was as represented. Had it been the opposite, the structure of the lactone could have been only **20** or **21**, contrary to the fact that the nmr spectrum of compound **17** does not indicate a methyl group situated on a double bond. It is therefore concluded that **6** has the structure shown.

The stereochemistry of **14** was assigned as follows. The angular methyl group should be *trans* to the 4-methyl group as a consequence of the *endo,cis*-addition principle. The carbomethoxy and 7-methyl groups are assumed to be in the equatorial position, since the compound was recovered unchanged after attempts of isomerization.

The γ-lactone **17** should have the angular methyl group *trans* to the 4-methyl group for the same reasons as in **14**. Inspection of a Dreiding model shows that the γ-lactone must be *trans* to the angular methyl group. The 7-methyl group is assumed to be in the more stable equatorial position.

Discussion

The present orientation study demonstrates for the first time that the *ortho*-directive influence of either an electron-donating group (acetoxy) or an electron-withdrawing group (carbomethoxy) is more powerful than that of a methyl group as defined in the present experimental design.

This indicates that polarity considerations should not be given high priority in the investigation of the transition state of the diene synthesis.

The results cannot be attributed to steric reasons, since the three groups are of similar sizes at least in the vicinity of the reaction sites—the terminal positions of dienes.

The internal electronic competition of a carbomethoxy group against a methyl led only to the *ortho* isomer, whereas the directive influence of an acetoxy group against its methyl counterpart led to a 4:1 *ortho–meta* mixture. From this it appears that the carbomethoxy group is a more powerful *ortho*-orienting group than the acetoxy group.

The results therefore indicate the following order of *ortho*-orienting influence, as defined by eq 1 and 2.

$$COOCH_3 > OCOCH_3 > CH_3$$

The recently published[14–17] perturbational MO calculations concerning the orientation problem of Diels–Alder reactions could be applied to the examples of the present paper.

(14) J. Feuer, W. C. Herndon, and L. H. Hall, *Tetrahedron*, **24**, 2575 (1968).
(15) L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968).
(16) W. C. Herndon and L. H. Hall, *Theor. Chim. Acta*, **7**, 4 (1967).
(17) J. Klopman, *J. Amer. Chem. Soc.*, **90**, 223 (1968).

It is hoped that accumulation of further orientation studies will lead to a better understanding of the mechanism and extend the synthetic utility of the reaction.

Experimental Section[18]

1-Acetoxy-1,3-pentadiene (1).—A 60-g sample of 2-penten-1-al prepared according to the procedure of Grunager and Greco[19] was refluxed with 180 ml of acetic anhydride in the presence of 60 g of anhydrous potassium acetate for 6 hr. An efficient mechanical stirrer was used to agitate the rather viscous solution. The mixture was then cooled to 50° and poured on ice. The solution was extracted three times with benzene. The combined benzene extracts were stirred mechanically with a 10% solution of sodium bicarbonate while cooling with ice water. Some solid sodium bicarbonate was also added every 10 min to maintain the solution alkaline. After 2 hr the pH of the water solution remained permanently alkaline. This treatment completely removed the excessive acetic anhydride and acetic acid from the solution. The benzene phase was then separated, washed with saline solution in the presence of ice, and dried with magnesium sulfate. Most of the benzene was removed by atmospheric distillation. The residue was then fractionated at 100 mm. After the collection of 1–3 ml of forefraction, the product was distilled at 100–105° (100 mm), yielding 79 g (89%) of diene acetate. The product appeared to be homogeneous when analyzed using vpc on several columns: mass spectrum (70 eV) *m/e* (rel intensity) 126 (76, parent peak), 98 (9.5), and 83 (100); ir (CCl_4) 2900, 1770, 1670, 1620, and 1200 cm^{-1}; uv max (95% C_2H_5OH) 242 mμ (ϵ 19,000); nmr ($CDCl_3$) τ 8.28 (d, 3, J = 8.2 Hz, $=CHCH_3$), 7.94 (s, 3, $OCOCH_3$), and 4.21 (m, 4, olefinic protons).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.60; H, 7.98. Found: C, 66.20; H, 7.91.

1,5,8,8a-Tetrahydro-1β,7,8aβ-trimethyl-5,8-dioxonaphthalene (5) **and** ***cis*-1,4,4a,5,8,8a-Hexahydro-1α-acetoxy-4α,7,8,8aβ-trimethyl-5,8-dioxonaphthalene** (4).—A solution of 10 g of 2,6-dimethylbenzoquinone and 20 g of 1-acetoxy-1,3-pentadiene in 50 ml of benzene was heated for 18 hr at 150° in a sealed tube. The brown reaction mixture was distilled at 100 mm. After the removal of benzene, 12 g of unreacted diene was collected, distilling at 100–105° (100 mm). The residue was then distilled at 0.2 mm.

A 2-g sample of unreacted 2,6-dimethylbenzoquinone was recovered by sublimation. Using tlc it was established that the residue contained two products along with a small amount of quinone. A quantitative glpc determination revealed that the molar ratio of **4** to **5** was 4:1. The two compounds were separated by chromatographing on a 75-fold amount of neutral alumina, eluting with ether–benzene (1:5). The small amount of residual quinone was destroyed on the surface of alumina.

From the first fractions, 2.06 g of bright yellow **5** was isolated, corresponding to a 16% yield based on the amount of quinone reacted. It was recrystallized from pentane: mp 36°; mass spectrum (70 eV) *m/e* (rel intensity) 202 (100, parent peak), 187 (43), 159 (93), etc.; ir (CCl_4) 2900, 1690, 1665, 1620, 1450, and 1300 cm^{-1}; uv max (95% C_2H_5OH) 342 mμ (ϵ 7000), 248 (12,650), and 217 (8650); nmr (CCl_4) τ 9.11, (d, 3, J = 7.3 Hz, CH_3-1), 8.67 (s, 3, CH_3-8a), 7.96 (s, 3, CH_3-7), 7.16 (q, 1, proton on Cl), 3.93 (m, 2, olefinic protons), 3.33 (m, 1, olefinic proton), and 3.14 (m, 1, olefinic proton).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.30; H, 6.99. Found: C, 77.10; H, 6.91.

The more polar product **4** was isolated from the subsequent chromatographic fractions; 10.45 g of crystalline **4** was isolated, corresponding to a 69% yield based on the amount of converted quinone. It was recrystallized from methanol: mp 136°; ir (CCl_4) 2950, 1750, 1690, 1370, and 1240 cm^{-1}; uv max (95% C_2H_5OH) 242 mμ (ϵ 10,200); mass spectrum (70 eV) *m/e* (rel intensity) 262 (53, parent peak), 220 (48), 202 (100), etc.; nmr ($CDCl_3$) τ 8.93 (s, 3, CH_3-8a), 8.80 (d, 3, J = 3.1 Hz, CH_3-4), 7.30 (m, 1, proton at C-4), 6.90 (d, 1, J = 6.7 Hz, proton at C-4a), 4.65 (d, 1, J = 4.5 Hz, proton at C-1), 4.20 (m, 2, olefinic protons at C-2 and -3), and 3.36 (m, 1, proton at C-6).

The coupling pattern is consistent only with the orientation represented by **4**; the opposite assumption is irreconcilable with the present nmr data.

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.70; H, 6.92. Found: C, 68.81; H, 6.95.

The combined yield for **4** and **5** corresponds to 85% based on the amount of quinone consumed.

***cis*-1α-Acetoxy-4α,7,9β-trimethyl-2-octal-5,8-dione** (7).—A solution of 1.268 g of the crystalline adduct **4** in 30 ml of glacial acetic acid was stirred and heated at 60° for 1 hr in the presence of 3 g of zinc dust. After cooling, acetone was added to the reaction mixture. The excessive zinc and zinc acetate was filtered using a Büchner funnel and the precipitate was washed with acetone. The filtrate was evaporated to incipient dryness using a rotary evaporator. The residue was dissolved in 50 ml of chloroform. The residual acetic acid was removed by washing the chloroform solution in succession with 10% sodium bicarbonate solution and water; it was dried with magnesium sulfate; and the chloroform was evaporated, yielding 1.218 g (96.2%) of crystalline diketone **7**. An analytical sample was prepared by recrystallization from methyl alcohol: mp 147.5°; ir (CCl_4) 2950, 1750, 1718, and 1250 cm^{-1}; uv end absorption; nmr ($CDCl_3$) τ 9.06 (s, 3, CH_3-9β), 8.92 (two coinciding doublets, J = 6.2 Hz, CH_3-6,4 and -7), 6.71–7.63 (m, 5, protons at C-4, -4α, -6, -7), 4.80 (t, 1, proton at C-1), and 4.56 (m, 2, olefinic protons), mass spectrum (70 eV) *m/e* (rel intensity) 264 (15, parent peak), 221 (40), and 190 (100).

Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.60; H, 7.62. Found: C, 68.81; H, 7.68.

***trans*-1α-Hydroxy-4α,7α,9β-trimethyl-2-octal-5,8-decaldione** (8).—A 1.10-g sample of **7** was dissolved in 10 ml of methyl alcohol containing 0.32 g of sodium methylate. The solution was allowed to stand for 1 hr at room temperature, 15 ml of water was added, and the solution was extracted with four 35-ml portions of ether. The combined ether extracts were washed with saline solution and dried with magnesium sulfate and the ether was evaporated. A crystalline material, yield 0.9 g (97%), was isolated. Tlc analysis of the product revealed the presence of one compound. It was recrystallized from methyl alcohol: mp 129°; mass spectrum (70 eV) *m/e* (rel intensity) 222 (15), 207 (25), and 133 (100); ir ($CHCl_3$) 3500, 2950, 1710, 1460, and 1000 cm^{-1}; uv end absorption; nmr ($CDCl_3$–D_2O) τ 9.18 (s, 3, CH_3-9), 8.88 (d, 6 H, J = 6.3 cps, CH_3-4 and -7), 8.16–6.77 (m, 5, protons at C-4, -6, -7, and -10), 5.82 (d, 1, CHOH), and 4.33 (m, 2, olefinic protons at C-2 and -3).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.30; H, 8.17. Found: C, 70.34; H, 8.15.

***trans*-1α-Hydroxy-4α,7α,9β-trimethyl-5,8-decaldione** (9).—A solution of 0.90 g of **8** in 50 ml of methanol was hydrogenated overnight in the presence of 20 mg of Adams catalyst. After the catalyst had been filtered, the methanol was evaporated, yielding 0.85 g (95%) of a chromatographically homogeneous crystalline product. An analytical sample was obtained by recrystallization from benzene: mp 127°; mass spectrum (70 eV) *m/e* (rel intensity) 224 (80), 177 (50), and 167 (100); ir ($CHCl_3$) 3500, 2900, 1710, and 1470 cm^{-1}; uv end absorption; nmr ($CDCl_3$) τ 9.17 (s, 3, CH_3-9), 8.98 (d, 3, J = 6 cps, CH_3-4), 8.92 (d, 3, J = 6 cps, CH_3-7), and 8.67–6.73 (m, 10).

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.60; H, 8.98. Found: C, 69.52; H, 8.90.

A solution of 20 mg of **9** in 5 ml of methanol–water (2:1) was refluxed for 5 hr in the presence of 1 ml of 10% sulfuric acid. After cooling, the solution was extracted with four 10-ml portions of ether. The combined ether extracts were washed with saline solution and dried with magnesium sulfate. After the evaporation of ether, the tlc and ir of the product were found to be identical with those of **9**.

***trans*-4α,7α,9β-Trimethyl-1-octal-5,8-dione** (10).—A solution of 1.50 g of **9** in 30 ml of methylene chloride and 5 ml of dry pyridine was cooled with ice water, 1.5 ml of phosphorus oxychloride was added, and the mixture was allowed to stand overnight. Next morning the reaction mixture was poured on ice. The solution was extracted four times with 20 ml of chloroform. The com-

(18) All melting points were taken on a Fisher–Johns melting point apparatus and are uncorrected. The elemental analyses were carried out by Pascher Mikroanalytical Laboratorium, Bonn, West Germany, and Schwarzhopf Mikroanalytical Laboratory, Woodside, N. Y. The ir spectra were recorded on a Perkin–Elmer Model 137 B infracord spectrophotometer. The uv spectrograms were taken on a Coleman–Hitachi Model 124 double-beam grating spectrophotometer. The nmr spectra were recorded on a Varian Associates 56.4-MHz spectrophotometer. The mass spectra were obtained with a Hitachi Perkin–Elmer Model RMS-4 spectrometer.

(19) R. Grunanger and D. Greco, *Gazz. Chim. Ital.*, **88**, 296 (1958).

bined chloroform extracts were washed in succession with water, dilute sulfuric acid (in the presence of ice), water, 5% sodium bicarbonate, solution and water. The chloroform solution was then dried with magnesium sulfate and evaporated to dryness, yielding 1.150 (85%) of a crystalline, tlc-homogeneous product. An analytical sample was prepared by recrystallization from benzene: mp 98°; mass spectrum (70 ev) *m/e* (rel intensity) 206 (20, parent peak), 191 (15), and 107 (100); ir ($CHCl_3$) 2900, 1720, and 1460 cm^{-1}; uv end absorption; nmr ($CDCl_3$) τ 9.00 (s, 3, CH_3-9), 8.81 (d, 6, J = 7 Hz, CH_3-4 and -7), 8.38–6.89 (m, 7), 4.37 (m, 1, olefinic protons), and 4.06 (m, 1, olefinic protons).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.70; H, 8.78. Found: C, 75.63; H, 8.74.

***cis*-1,4,4a,5,8,8a-Hexahydro-1α-carbomethoxy-4α-7,8aβ-trimethyl-5,8-dioxonaphthalene (6).**—The methyl sorbate was prepared according to Wheeler[20] by the esterification of sorbic acid with methyl alcohol.

A solution of 37.8 g of methyl sorbate and 13.6 g of 2,6-dimethylbenzoquinone in 30 ml of benzene was heated at 150° for 36 hr in a sealed tube. After the tube had been opened, the reaction mixture was distilled under vacuum. A 15-g sample of diene was recovered from the fraction distilling at 50–65° (20 mm). A 1.5-g sample of the unreacted quinone was collected by sublimation at 100° (0.2–0.6 mm), corresponding to an 89% conversion of quinone. The brown residue was then chromatographed on 600 g of neutral alumina, eluting with benzene. The first fraction contained some unreacted sorbate. From the subsequent fractions, 18.6 of chromatographically homogeneous **6** was collected corresponding to an 80% yield based on the quinone consumed. An analytical sample was obtained by recrystallization from methyl alcohol: mp 109–110°; mass spectrum (70 eV) *m/e* (rel intensity) 262 (50, parent peak), 247 (40), 230 (45), and 188 (100); ir (CCl_4) 2900, 1745, 1690, and 1610 cm^{-1}; uv max (96% C_2H_5OH) 242 mμ (ε 10,500); nmr ($CDCl_3$) τ 8.98 (s, 3, CH_3-8a), 8.80 (d, 3, J = 7.2 Hz, CH_3-4), 8.02 (s, 3, CH_3-7), 7.43 (m, 1, proton at C-4), 6.69 (m, 2, protons at C-10 and -1), 6.34 (s, 3, carbomethoxy), 4.42 (m, 2, protons at C-2 and -3), and 3.49 (m, 1, proton at C-6).

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.70; H, 6.92. Found: C, 68.78; H, 6.93.

Conversion of 6 into 1-Carbomethoxy-4α,7α,9β-trimethyl-$\Delta^{5,10}$-octal-8-one (14) and 8α-Hydroxy-4α,7α,9β-trimethyl-$\Delta^{5,10}$-octalin-1α-carboxylic Acid α-Lactone (17). A. Reduction with Sodium Borohydride.—To a solution of 2.097 g of **6** in 20 ml of methanol, cooled by ice water, 0.896 of sodium borohydride was added in 1 hr. The reaction was allowed to proceed at room temperature for 18 hr. The mixture was then poured onto ice and dilute hydrochloric acid and extracted three times with 40 ml of ether. The combined extracts were washed with saline solution, dried with magnesium sulfate, and evaporated to dryness. An oily product (2.27 g, 91%) was obtained. The material appeared to be homogeneous according to tlc. However, the spectral properties and chemical behavior described below revealed the presence of **12** and **15** in the ratio of 2:1: ir (CCl_4) 3500, 2950, 1745, 1710, 1690, and 1473 cm^{-1}; uv max (EtOH) 238 mμ (ε 7000). The mass spectrum of the mixture showed a prominent molecular peak for **12** at *m/e* 264. The nmr spectrum of the mixture indicated olefinic protons and signals corresponding to structures **12** and **15**. The two components were used without separation.

B. Hydrogenation.—The mixture of **12** and **15** (2.27 g) was hydrogenated in the presence of 200 mg of 10% palladium on charcoal in 30 ml of methyl alcohol for 18 hr at room temperature, at 10 psi. After the catalyst had been filtered, the methyl alcohol was evaporated, giving 2.00 g (90%) of an oily material, nmr of which revealed the complete absence of olefinic protons; ir (CCl_4) 3500, 3300, 2950, 1740, 1710, and 1475 cm^{-1}; uv end absorption. The mixture of **13** and **16** was used without isolation.

(20) J. Wheeler, *J. Amer. Chem. Soc.*, **70**, 3468 (1948).

C. Elimination.—To a dry solution of 1.128 g of **13** and **16** in 20 ml of methylene chloride, 10 ml of dry pyridine was added. Then 2 ml of phosphorus oxychloride dissolved in 10 ml of methylene chloride was dripped in while the solution was stirred and cooled with ice–water during 15 min. The solution was then allowed to stand for 18 hr at room temperature. The reaction mixture was then poured on ice and extrasted with four 50-ml portions of ether. The combined ether extracts were washed in succession, in the presence of crushed ice, with saline solution, twice with diluted sulfuric acid, saline solution, 10% sodium bicarbonate, and saline solution. The ether solution was then dried with magnesium sulfate and evaporated to dryness. The residue weighed 1.01 g. The product consisted of two well-defined components, which were separated by thick layer chromatography on silica gel plates using chloroform for the development. The bands were detected with the iodine spraying method. The more polar oily product amounted to 0.60 g, corresponding to a 50% yield based on **6**. The unsaturated keto ester **14** had the appropriate spectroscopic properties: mass spectrum (70 eV) *m/e* (rel intensity) 250 (20, parent peak), 218 (40), and 135 (100); ir (CCl_4) 2950, 1745, and 1710 cm^{-1}; uv max (96% C_2H_5OH) end absorption; nmr ($CDCl_3$) τ 8.95 (d, 6, J = 6.4 Hz, CH_3-4 and -7), 8, 76 (s, 3, CH_3-9), 6.45 (s, 3, CH_3COO), and 4.50 (t, 1, proton on C-5). An analytical sample was obtained by distilling the sample at 100–105° (0.2 mm).

Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.90; H, 8.79. Found: C, 72.05; H, 8.72.

A 20-mg sample of **14** was refluxed in 10 ml of methanol–water (1:1) in the presence of 10% sulfuric acid for 6 hr. The sample was recovered unchanged according to ir and tlc. An attempt at isomerization in the presence of sodium methylate in methanol under nitrogen led to similar results.

The less polar compound **17** (330 mg) was isolated in crystalline form, corresponding to a 31.5% yield based on **6**. The chromatographically homogeneous lactone was recrystallized from benzene–pentane: mp 83–84°; mass spectrum (70 eV) *m/e* (rel intensity) 220 (60, parent peak), 205 (20), 175 (20), and 159 (100); ir ($CHCl_3$) 2950, 1790, 1470, and 1100 cm^{-1}; uv end absorption; nmr ($CDCl_3$) τ 9.04 (d, 3, J = 7.7 Hz, CH_3-4), 8.86 (d, 3, CH_3-7), 8.75 (s, 3, CH_3-9), 6.1 (d, 1, J = 2.0 Hz, proton on C-8), and 4.6 (m, 1, proton on C-5).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.30; H, 9.13. Found: C, 76.37; H, 9.08.

Registry No.—**1**, 17616-45-4; **4**, 23804-07-1; **5**, 23804-08-2; **6**, 23804-09-3; **7**, 23804-10-6; **8**, 23804-11-7; **9**, 23804-12-8; **10**, 23804-13-9; **14**, 23804-14-0; **17**, 23804-15-1.

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