result from singlet–singlet sensitization, or sensitization by upper triplet states. At the present time, the multiplicity of the excited state responsible for cyclization should be regarded as uncertain.

The reasons for the low yields in the reactions sensitized by benzophenone, 2-acetonaphthone, and naphthalene are unknown. With the carbonyl sensitizers, some 2 + 2 cycloaddition of the sensitizer to the diene may occur. In the case of naphthalene, we have no hypothesis to explain the diminished yield. This question cannot be answered until the nonvolatile reaction products are investigated.

Registry No.—**4**, 13304-33-1; **5**, 32722-85-3; **6**, 32659-16-8; **7**, 32659-17-9; *cis,anti,cis*-2-methyltricyclo[5.3.0.0^{2,6}]decan-5-one, 32659-18-0; cis,syn,cis isomer, 32659-19-1.

Acknowledgments.—We gratefully acknowledge financial support by the National Science Foundation and the Public Health Service. The senior author (C. H. H.) acknowledges several stimulating discussions on this subject with Professor Kurt Schaffner of the ETH, Zürich, Switzerland. We also thank one of the referees for numerous helpful comments.

Photochemistry of 1,6-Cyclodecadienes. II. Synthesis and Photochemistry of 6-Methyl-1,6-cyclodecadien-3-one[1]

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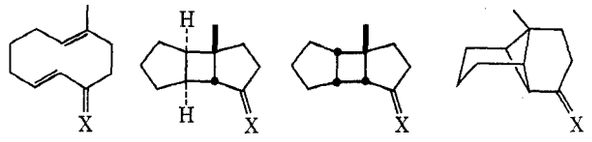
6-Methyl-1,6-cyclodecadien-3-one (**5**) has been synthesized by a multistage route and its photochemical behavior has been examined. Irradiation of dienone **5**, with Pyrex-filtered light in either ether or hexane, gives tricyclic ketones **6**, **7**, and **8**. The interesting tricyclo[4.4.0.0^{2,7}]decanone **8** arises from a triplet intermediate.

In the previous paper in this series, we reported on the photochemical behavior of 1-methyl-(*E,E*)-1,6-cyclodecadiene (**1**).[4] Diene **1** was found to undergo photochemical 2 + 2 cycloaddition, probably in a stepwise fashion, yielding only the tricyclo[5.3.0.0^{2,6}]decanes **2** and **3**. No tricyclo[4.4.0.0^{2,7}]decane (*e.g.*, **4**) was produced. In the present work, we have prepared and photolyzed the analogous ketone, **5**.



1, X = H_2 **2**, X = H_2 **3**, X = H_2 **4**, X = H_2
5, X = O **6**, X = O **7**, X = O **8**, X = O

Preparation of Dienone 5.—The starting point for the preparation of dienone **5**, outlined in Scheme I, was the readily available Wieland–Miescher diketone (**9**),[5] which was transformed by established procedures[6] into the ketal acetate **10**. Oxidation of **10** with *m*-chloroperbenzoic acid in chloroform gave a 1:1 mixture of epoxides **11** and **12**, which could be separated by fractional crystallization. Stereostructures were assigned to compounds **11** and **12** on the basis of their pmr spectra. Williamson has found[7] that angular methyl groups in trans-fused decalins give broader resonance lines ($W_{1/2}$ = 0.80 ± 0.20 Hz) than the corresponding cis-fused isomers ($W_{1/2}$ = 0.25 ± 0.11 Hz). The higher melting isomer, mp 137–139°, was assigned structure **11** since it gave a sharp angular methyl resonance. The lower melting isomer, mp 65.5–66.5°, was assigned the cis structure **12** on the basis of its broad methyl singlet.

Lithium aluminum hydride reduction of **11** and **12** gave corresponding diols **13** (mp 89–90°) and **14** (mp 106–107°), respectively, which were converted, by selective esterification with methanesulfonyl chloride in pyridine, to monomethanesulfonates **15** (mp 104.5–105.5°) and **16** (mp 109–110°). The line widths of the angular methyl resonances in the pmr spectra of compounds **11–14** corroborated the assigned stereostructures.

Base-catalyzed fragmentation[8] of either **15** or **16** (or a mixture of the two) with potassium *tert*-butoxide in *tert*-butyl alcohol gave excellent yields (>95%) of the cyclodecenedione monoketal **17**, mp 50.5–51.5°. On the basis of good analogy,[8a] the double bond in **17** can be assigned the *E* configuration. Reduction of **17** with lithium aluminum hydride in ether gave the crystalline hydroxy ketal **18**. The overall yield for the eight stages from enedione **9** to intermediate **18** was 37%.

Compound **18** was hydrolyzed by refluxing with an equal weight of oxalic acid in aqueous acetone. The product, β-hydroxy ketone **19**, showed surprising resistance to dehydration. Attempts to dehydrate the ketol with basic alumina or methanolic potassium hydroxide led only to recovered starting material, as did vacuum distillation from oxalic acid. Treatment of **19** with even trace amounts of mineral acid gave intense violet solutions from which no tractable products could be isolated.[9]

The corresponding acetate, **20**, prepared from **19** by acetylation with acetic anhydride in pyridine, eliminated acetic acid smoothly when warmed to 50° in tri-

(1) This paper was presented in preliminary form at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 8, 1968. See also, C. H. Heathcock and R. A. Badger, *Chem. Commun.*, 1510 (1968).

(2) Fellow of the Alfred P. Sloan Foundation, 1967–1969.

(3) National Institutes of Health Predoctoral Fellow, 1965–1968.

(4) C. H. Heathcock, R. A. Badger, and R. H. Starkey, *J. Org. Chem.*, **37**, 231 (1972).

(5) (a) P. Wieland and K. Miescher, *Helv. Chim. Acta*, **33**, 2215 (1950); (b) S. Ramachandran and M. S. Newman, *Org. Syn.*, **41**, 38 (1961).

(6) C. H. Heathcock and R. Ratcliffe, *J. Amer. Chem. Soc.*, **93**, 1746 (1971).

(7) K. L. Williamson, T. Howell, and T. A. Spencer, *ibid.*, **88**, 325 (1966).

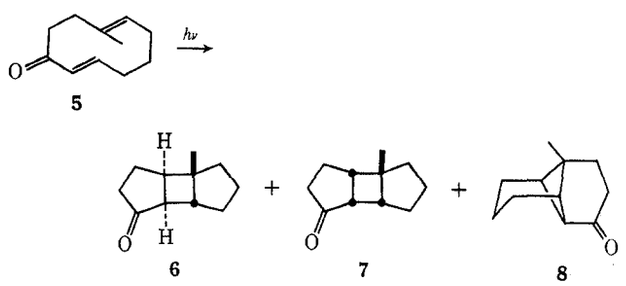
(8) (a) P. S. Wharton and G. A. Hiegel, *J. Org. Chem.*, **30**, 3254 (1965); (b) H. H. Westen, *Helv. Chim. Acta*, **47**, 575 (1964).

(9) Similar behavior was noted with compounds **17**, **18**, **20**, and **5**. The violet color which is produced immediately upon treating a dilute solution of any of these compounds with dilute mineral acid is discharged upon basification.

ethylamine. The product of this reaction was a mixture of the desired α,β-unsaturated ketone **5** (λ_{max} 265 nm; ν_{max} 1665, 1630 cm^{-1}) and its β,γ isomer **21** (ν_{max} 1695 cm^{-1}).

While the trisubstituted double bond in **5** must be assigned the *E* configuration (*vide supra*), the geometry of the conjugated double bond is uncertain. Attempts to separate dienones **5** and **21** by preparative glpc failed, since only thermal rearrangement products were obtained.[10]

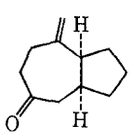
Photochemistry of Dienone 5.—Dienone **5** was irradiated as a 0.1% solution in ether or hexane with Pyrex-filtered light. The irradiation was monitored by observing the diminution of the $\pi \rightarrow \pi^*$ absorption band at 265 nm. The volatile photoproduct was a mixture of compounds containing tricyclic ketones **6**, **7**, and **8**. In ether, products **6**, **7**, and **8** were formed in



relative yields of 32, 3, and 22%, respectively. Several additional products, totaling 43% of the reaction product, were formed and remain unidentified. In hexane, the reaction is much cleaner, yielding **6**, **7**, and **8** in relative yields of 60, 6, and 30%, respectively.

In contrast to the situation obtaining in the case of diene **1**,[4] dienone **5** yields a significant amount of a product with the tricyclo[4.4.0.$0^{2,7}$]decane skeleton. In order to test the multiplicity of the reactive state in this case, we carried out the irradiation of **5** in the presence of piperylene, a well-known triplet quencher.[13] Somewhat to our surprise, the relative rate of formation of product **8** was greatly reduced. The ratio of **6** to **8** in this experiment (0.1% solution of **5** in a 20:1 mixture of hexane–piperylene, Pyrex-filtered light) changed from 2:1 to 9:1. Thus, 1-methyltricyclo-[4.4.0.$0^{2,7}$]decan-8-one (**8**) must arise from a triplet state. The tricyclo[5.3.0.$0^{2,6}$]decanones **6** and **7** either

(10) The thermochemistry of dienone **5** is interesting, although we have not made a rigorous study of it. When the crude mixture of **5** and **21** was injected into any of several glpc columns at 150–200°, several products were formed from thermal rearrangement. The two major products were isolated and examined spectrally. The major product with smaller retention time was identified as the cis,anti,cis tricyclic ketone **6**, *uncontaminated with any of its cis,syn,cis isomer* **7**. The other major product, tentatively assigned structure **22** on spectral grounds, is identical spectrally and chromatographically with the minor product isolated from the pyrolysis at 375°



22

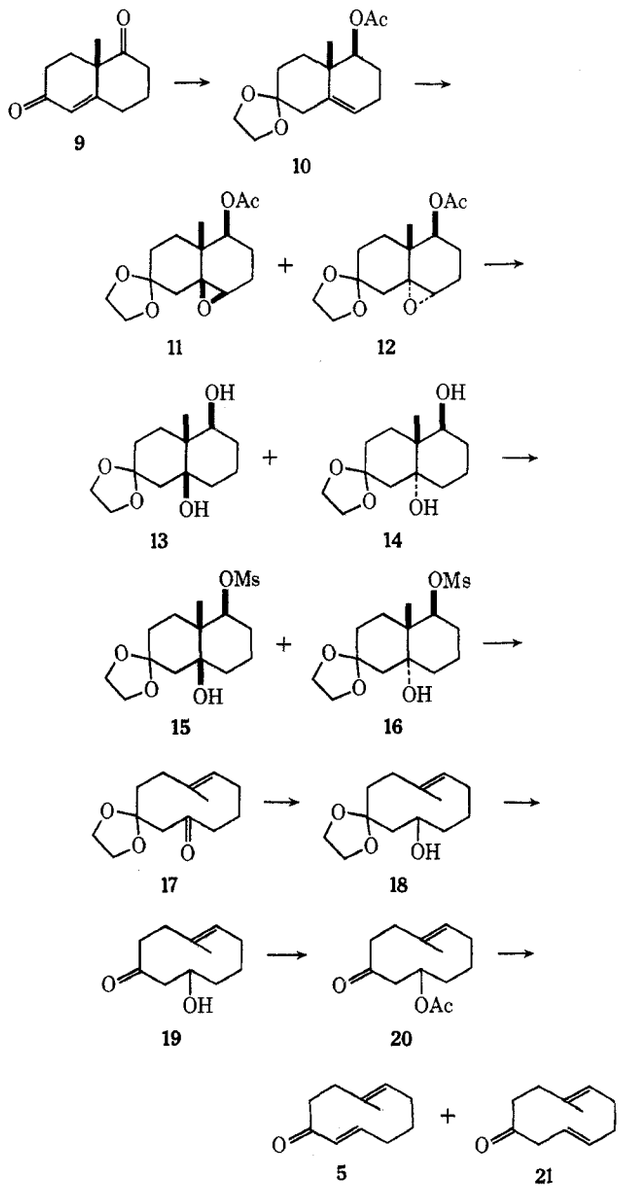
of tricyclic ketone **8**.[11] When the mixture of **5** and **21** was pyrolyzed in a sealed Pyrex tube at 200°, the only product formed was compound **22**. The thermal lability of **5** is remarkable, in light of the fact that diene **1** is completely stable when heated in a sealed Pyrex tube at 220–240°.[12]

(11) C. H. Heathcock and B. E. Ratcliffe, *J. Org. Chem.*, **33**, 3650 (1968).

(12) C. H. Heathcock, unpublished results.

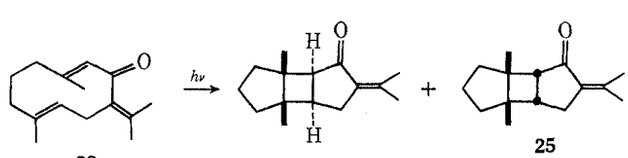
(13) G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Amer. Chem. Soc.*, **83**, 2396 (1961).

SCHEME I



arise from a singlet state or an unquenchable triplet. A tempting hypothesis is that 1,6-cyclodecadienes always give tricyclo[4.4.0.$0^{2,7}$]decane products from a triplet manifold.[14]

The observation that dienone **5** yields a significant amount of the tricyclo[4.4.0.$0^{2,7}$]decane product **8** is in striking contrast to the finding by Scheffer and Boire[15] that isogermacrone (**23**) yields only photoproducts **24** and **25** upon irradiation. The multiplicity of the reacting state in this case has not been reported.



23 **24** **25**

(14) This postulate would require that the observed conversion of diene **1** to products **2** and **3** in the presence of benzophenone, naphthalene, and 2-acetonaphthone[4] be ascribed to singlet–singlet sensitization. Because of concentrations used in that work, this may just be possible. We thank Professor Kurt Schaffner for suggesting this possibility.

(15) J. R. Scheffer and B. A. Boire, *Tetrahedron Lett.*, 4005 (1969).

Experimental Section

Melting points (Pyrex capillary) are uncorrected. Infrared spectra (ir) were recorded on a Perkin-Elmer 237 spectrophotometer. Proton magnetic resonance spectra were taken on Varian A-60 and T-60 spectrometers. Chemical shifts are relative to internal tetramethylsilane and are given on the Tiers τ scale; the multiplicity, peak areas, coupling constant, and proton assignments are given in parentheses. Elemental analyses were performed by the Microanalytical Laboratory, operated by the Department of Chemistry, University of California, Berkeley, Calif.

4aβ-Methyl-5β-acetoxy-8β,8aβ-oxido-3,4,4a,5,6,7,8,8a-octahydronaphthalen-2(1*H*)-one Ethylene Ketal (11).—A chilled solution of 73.7 g (0.276 mol) of ketal acetate **10**[6] in 100 ml of chloroform was treated dropwise with a solution of 55 g (0.320 mol) of 85% *m*-chloroperbenzoic acid in 500 ml of chloroform. The addition required 42 min. The resulting solution was stirred at 0° for an additional 2 hr and then at room temperature overnight, during which time solid *m*-chlorobenzoic acid precipitated out. Filtration through sintered glass removed the acid, and the excess peracid was destroyed by stirring the filtrate for 30 min with 300 ml of 30% sodium sulfite solution. The organic layer was separated, washed with 10% sodium hydroxide (two 250-ml portions) and salt solutions (one 300-ml portion), dried, and evaporated to yield 81 g of white, semisolid material, the pmr ($CHCl_3$) of which showed two angular methyl peaks at τ 8.90 and 8.86, in an approximate ratio of 53:47. The slurry was triturated with 50 ml of ether and filtered, giving 39.3 g of white solid, mp 135–138°. Recrystallization from ethyl acetate–ether gave an analytical sample: mp 137–139°; pmr (CCl_4) τ 8.86 (s, 3, angular Me), 8.06 (s, 3, acetoxy Me), 6.08 (m, 4, ketal Hs), and 5.04 (m, 1, C-8 H); ir (CCl_4) 1730, 1370, 1250, and 1120 cm^{-1}.

Anal. Calcd for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 63.76; H, 8.02.

4aβ-Methyl-5β-acetoxy-8α,8aα-oxido-3,4,4a,5,6,7,8,8a-octahydronaphthalen-2(1*H*)-one Ethylene Ketal (12).—The pmr spectrum of the filtrate above showed that about 90% of the isomer with the lower field angular methyl signal had been removed. Triturating the mother liquors with pentane and ether caused the other isomer to crystallize. Filtration afforded 36.4 g of white solid, mp 63–67°. A small portion was recrystallized from ether: mp 65.5–66.5°; pmr ($CHCl_3$) τ 8.89 (s, 3, angular Me), 8.00 (s, 3, acetoxy Me), 6.17 (s, 4, ketal Hs), and 5.44 (s, 1, C-8 H); ir ($CHCl_3$) 1740, 1355, 1230, 1100, and 835 cm^{-1}.

Anal. Calcd for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 63.62; H, 7.69.

For a subsequent preparative-scale reaction, 140.0 g of crystalline ketal acetate in 600 ml of chloroform was chilled to 0°, treated with 105 g of 85% *m*-chloroperbenzoic acid in 1000 ml of warm chloroform, and allowed to stir at room temperature overnight. After a work-up similar to that described above, 153 g of semisolid was obtained, the pmr spectrum of which showed the two angular methyl peaks in a ratio of 58:42, with the upfield signal again predominating. The crude product was utilized directly in the subsequent reaction.

4aβ-Methyl-5β,8aβ-dihydroxy-3,4,4a,5,6,7,8,8a-octahydronaphthalen-2(1*H*)-one Ethylene Ketal (13).—A solution of 20.76 g (74.5 mmol) of crystalline *cis*-epoxy acetate **11**, mp 137–139°, in 200 ml of dry tetrahydrofuran was added to a stirring slurry of 12.0 g (316 mmol) of lithium aluminum hydride in 300 ml of tetrahydrofuran. The mixture was heated at reflux under a drying tube for 19 hr. The excess hydride was destroyed with ethyl acetate and the grey slurry was refluxed with 36 ml of 5% potassium hydroxide solution for 30 min. The organic solution was separated from the white slurry by vacuum filtration through sintered glass, dried over magnesium sulfate, refiltered, and evaporated to yield 17.0 g (95.0%) of colorless oil that solidified upon standing. A portion was recrystallized from ether to give a white solid: mp 90–92°; pmr (CCl_4) τ 8.90 (s, 3, $W_{1/2}$ = 0.4 Hz, angular Me), 8.34 (broad s, 2), and 6.11 (m, 4, ketal Hs); ir 3650, 3500, 1080 cm^{-1}.

Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.17; H, 9.42.

4aβ-Methyl-5α,8aα-dihydroxy-3,4,4a,5,6,7,8,8a-octahydronaphthalen-2(1*H*)-one Ketal (14).—To a stirring slurry of 18.0 g (474 mmol) of lithium aluminum hydride in 250 ml of tetrahydrofuran was added a solution of 33.7 g (119 mmol) of crystalline *trans*-epoxy acetate (**12**) in 200 ml of dry tetrahydrofuran. Reaction time and work-up procedure were similar to reaction of the cis compound above. The yield of crude trans ketal diol was 25.5 g (88.5%) of colorless oil that crystallized from ether: mp 104–105°; pmr ($CHCl_3$) τ 9.07 (s, 3, $W_{1/2}$ = 0.8 Hz, angular Me) and 6.06 (s, 4, ketal Hs); ir ($CHCl_3$) 3630, 3500, 1090, 1015, and 845 cm^{-1}.

Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.38; H, 9.10.

The crude mixture of **13** and **14** from the large-scale epoxidation (152 g, 538 mmol) was dissolved in 600 ml of dry tetrahydrofuran and added to 40.0 g (1.05 mol) of lithium aluminum hydride in 500 ml of tetrahydrofuran over a period of 50 min. The mixture was stirred at room temperature for 17 hr and then carefully quenched with ethyl acetate until the solvent no longer boiled. Then the mixture was treated with 130 ml of 10% potassium hydroxide solution and heated at reflux for 45 min. Suction filtration removed the white salts which were washed with ether (two 300-ml portions). The organic solution was dried and evaporated to give 107.1 g (82.3%) of pale yellow oil, shown by pmr to be a 58:42 mixture of diols **13** and **14**.

4aβ-Methyl-5β,8aβ-dihydroxy-3,4,4a,5,6,7,8,8a-octahydronaphthalen-2(1*H*)-one Ethylene Ketal 5-Methanesulfonate (15).—A solution of 16.0 g (66 mmol) of *cis*-ketal diol (**13**) in 250 ml of dry pyridine was treated with 6.00 ml (9.00 g, 78.5 mmol, 19% excess) of methanesulfonyl chloride. The pale yellow solution was allowed to stand at room temperature for 48 hr before being poured into 400 ml of ice water and extracted with chloroform (three 200-ml portions) and ether (one 200-ml portion). The combined organic layers were washed with water (one 200-ml portion), dried, and evaporated to 17.1 g of pale red oil that partially solidified. The crude product was dissolved in ethyl acetate, decolorized with Norit carbon, and chilled to give 7.49 g of white crystals: mp 104.5–105.5°; pmr ($CHCl_3$) τ 9.00 (s, 3, angular Me), 7.12 (s, 3, mesylate Me), and 6.06 (m, 4, ketal Hs); ir ($CHCl_3$) 3580, 1340, 1175, 1100, 1060, 950, and 870 cm^{-1}.

Anal. Calcd for $C_{14}H_{24}O_6S$: C, 52.45; H, 7.54; S, 9.98. Found: C, 52.52; H, 7.67; S, 9.79.

The mother liquors were concentrated to give 9.5 g of red gum, the pmr spectrum of which displayed two mesyl peaks at τ 7.05 and 7.00 in an approximate ratio of 2:1. After standing at room temperature for several days, a sample of *cis*-mesylate **15** spontaneously decomposed to a red-brown oily solid.

4aβ-Methyl-5β,8aα-dihydroxy-3,4,4a,5,6,7,8,8a-octahydronaphthalen-2(1*H*)-one Ethylene Ketal 5-Methanesulfonate (16).—In a similar reaction, 20.0 g (82.7 mmol) of crystalline trans diol **14** was allowed to react with 7.0 ml (10.5 g, 92 mmol, 11% excess) of methanesulfonyl chloride in 250 ml of pyridine over a period of 45 hr. After a similar extraction sequence, 26.03 g of pale red oil was obtained. After decolorizing, an ethyl acetate solution afforded 9.52 g of white crystals: mp 98–103°; recrystallization from ethyl acetate–pentane sharpened the melting point range to 109–110°; pmr (CCl_4) τ 9.04 (s, 3, angular Me), 7.06 (s, 3, mesylate Me), 6.10 (s, 4, ketal Hs), and 5.20 (m, 1, C-5 H); ir (CCl_4) 3500, 3050, 1360, 1220, 1175, 930, and 870 cm^{-1}.

Anal. Calcd for $C_{14}H_{24}O_6S$: C, 52.45; H, 7.54; S, 9.98. Found: C, 52.34; H, 7.53; S, 9.72.

The crude mixture of ketal diols (**13** and **14**) (104 g, 440 mmol) was dissolved in 500 ml of pyridine and treated with 35 ml (52.5 g, 460 mmol) of methanesulfonyl chloride. After standing overnight at room temperature, the mixture was poured into 500 ml of ice water and extracted with methylene chloride (three 600-ml portions). The extracts were washed with two 300-ml portions of water, dried over magnesium sulfate, and evaporated under vacuum to give 128 g (94.2%) of red oil that cooled to a glass. The pmr spectrum showed that the product was a mixture of **15** and **16** in a ratio of 54:46.

(*E*)-6-Methyl-Δ^6-1,3-cyclodecenedione 3-Ethylene Ketal (17). A.—A lump of potassium metal weighing 897 mg (22.9 mmol) was washed with benzene to remove the protective mineral oil and added to 300 ml of dry distilled *tert*-butyl alcohol (distilled from CaH_2). The mixture was heated at reflux under dry nitrogen until the metal completely dissolved. Then the solution was cooled and maintained at 40–42° while a solution of 7.31 g (22.8 mmol) of hydroxy mesylate **15** in 200 ml of *tert*-butyl alcohol was added dropwise over a period of 20 min. A pale yellow color and a fine white precipitate (potassium methanesulfonate) formed at once. The mixture was stirred under nitrogen at 42–52° over a period of 2 hr. Then 400 ml of ice water was added, and the mixture was saturated with salt and extracted with ether (three

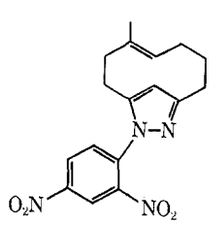
400-ml portions). The extracts were washed with saturated salt solution (two 100-ml portions) and then with water (one 100-ml portion), dried, and evaporated to yield 4.54 g (88.8%) of yellow oil. Distillation from an oil-jacketed still at 35–55° (0.2 mm) gave 3.98 g of colorless oil.

B.—The trans-fused isomer **16** (9.13 g, 28.4 mmol), in 200 ml of *tert*-butyl alcohol was added over a period of 12 min to a solution of potassium *tert*-butoxide prepared from 1.11 g (28.4 mmol) of potassium metal dissolved in 250 ml of *tert*-butyl alcohol. The resulting yellow mixture was stirred at 38–44° for 6 hr and then allowed to stand at room temperature overnight. After work-up, 5.75 g (90.5%) of white oil was obtained that solidified when chilled. Recrystallization from petroleum ether (bp 30–60°) gave white crystals with a melting point range of 50.5–51.5°: pmr (CCl_4) τ 9.04 (d, 3, J = 1 Hz, C-6 Me), 7.33 (s, 2, C-2 Hs), 6.02 (s, 4, ketal Hs), and 4.88 (m, 1, vinyl H); ir 1715, 1430, 1355, 1075, and 940 cm^{-1}.

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.50; H, 8.73.

C.—A solution of potassium *tert*-butoxide was prepared under nitrogen by dissolving 15.45 g (396 mmol) of potassium in 1500 ml of dry *tert*-butyl alcohol at reflux. Ten hours was required to completely dissolve the metal. The solution was cooled to 30°, and a solution of 127 g of crude hydroxy mesylate (**15** and **16**) in 800 ml of warm *tert*-butyl alcohol was added dropwise over a period of 1.5 hr. The temperature of the dark brown solution was maintained at 44° for 12 hr. Ice water (1000 ml) was added, the mixture was saturated with salt and extracted with ether (three 500-ml portions), and the extracts were washed (three 200-ml portions of saturated NaCl and three 200-ml portions of water) until no longer basic to pH paper, dried, and evaporated to give 83.59 g of brown oil (94.0%), the nmr spectrum of which was that of the desired keto ketal. The crude product was dissolved in ether and eluted through 320 g of activity I neutral alumina. Early fractions gave 43.1 g of water-white oil from which 17.6 g of crystals precipitated. Later fractions were distilled at reduced pressure to give 11.35 g of oil that displayed a slightly different nmr spectrum from the pure ketal ketone. Partial cracking to the dione may have occurred, as a small amount of ether-insoluble liquid was produced during the distillation.

A small sample of crystalline **17** (200 mg) in ethanol (2 ml) was treated with 8 ml of 2,4-dinitrophenylhydrazine reagent (0.134 mmol/ml).[16] After 15 min, the initially yellow precipitate darkened to deep red. Filtration and recrystallization afforded 165 mg of brick-red solid, mp 136–138°. On the basis of its empirical formula and its spectra, this derivative has been assigned the pyrazole structure **26**. The pmr spectrum (in $CDCl_3$)



26

had bands at τ 8.10 (broad s, 3, vinyl Me), 6.41 (m, 1, vinyl H), 3.68 (s, 1, pyrazole ring H), and 2.10 (m, 3, benzene ring Hs); ir ($CHCl_3$) 3200, 3030, 1625, 1600, 1525, 1430, 1350, 1330, 930, and 835 cm^{-1}.

Anal. Calcd for $C_{17}H_{18}N_4O_4$: C, 59.64; H, 5.30; N, 16.37. Found: C, 59.64; H, 5.37; M, 16.40.

8-Methyl-3-hydroxy-Δ^7-cyclodecenone Ethylene Ketal (18).—To a stirring slurry of 2.39 g of lithium aluminum hydride in 100 ml of dry ether was added over a period of 25 min 5.16 g of crystalline ketal ketone **17** in 50 ml of ether. The mixture was stirred for 20 hr at room temperature and then treated carefully with ethyl acetate. When the excess hydride had been destroyed, 10 ml of 10% potassium hydroxide solution was added and the mixture was refluxed for 30 min to precipitate the lithium and aluminum salts. After filtration, drying, and evaporation a pale yellow oil was obtained that crystallized when triturated with petroleum ether. The white solid, which weighed 4.45 g, mp 43.5–45.5°, was recrystallized from ether–pentane to give the analytical sample: mp 46–46.5°; pmr (CCl_4) τ 8.33 (d, 3, J = 1 Hz, vinyl Me), 6.10 (s, 4, ketal Hs), and 4.75 (m, 1, C-3 H); ir (CCl_4) 3580, 1120, 1060, and 955 cm^{-1}.

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.69; H, 9.89.

8-Methyl-3-hydroxy-Δ^7-cyclodecenone (19).—A solution of 2.711 g of crystalline hydroxy ketal **18** in 150 ml of reagent grade acetone was treated with 2.70 g of oxalic acid dihydrate. The resulting mixture was heated at reflux for 15 hr. The solution was concentrated to 50 ml on a rotary evaporator, neutralized with 35 ml of saturated sodium bicarbonate solution, diluted with ether, and separated. The aqueous layer was extracted with ether (two 80-ml portions) and the organic layers were combined, washed with salt water (two 50-ml portions), and dried over magnesium sulfate. Removal of solvent at reduced pressure yielded 2.109 g (96.3%) of yellow oil. A portion was distilled through a Hickman still, pot temperature 150–180° (0.2 mm), head temperature 100–110°. An ir spectrum of the distillate showed no dehydration. The rest of the crude material was triturated with ether–pentane, chilled on Dry Ice, and scratched to induce crystallization. The collected solid melted at 41.5–43°: pmr (CCl_4) τ 8.28 (s, 3, vinyl Me), 6.06 (m, 1, C-3 H), and 4.75 (m, 1, vinyl H); ir (CCl_4) 3500, 1700, 1120, 1065, and 1050 cm^{-1}.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.58; H, 10.19.

8-Methyl-3-acetoxy-Δ^7-cyclodecenone (20).—A solution of 5.01 g of crystalline hydroxy ketone **19** in 50 ml of acetic anhydride was treated with 2.0 ml of pyridine and allowed to react at room temperature for 22.5 hr. The solvent was removed by rotary evaporation at 60°, and the residue was diluted with 3 ml of pentane. Chilling induced crystallization, and 3.39 g (55.1%) of colorless crystals were collected in two crops. Recrystallization from pentane gave the analytical specimen: mp 42–43°; pmr (CCl_4) τ 8.28 (d, 3, J = 1 Hz, vinyl Me), 8.09 (s, 3, acetoxy Me), 4.87 (m, 1, C-3 H) and 5.98 (m, 1, vinyl H), 4.87 (1 H multiplet); ir (CCl_4) 1720, 1705, 1350, 1225, 1020 cm^{-1}.

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.24; H, 9.02.

8-Methyl-Δ^2,Δ^7-cyclodecadienone (5) and 8-methyl-Δ^3,Δ^7-cyclodecadienone (21).—A solution of 1.80 g of keto acetate **20** in 80 ml of triethylamine was warmed at 53° for 21 hr. The solvent was removed by rotary evaporation and the residue was dissolved in 50 ml of ether. A white flocculent precipitate (polymer?) formed that was removed by filtration. The ether solution was washed with water (two 20-ml portions), dried, and evaporated to give 1.08 g (82.0%) of yellow oil. The infrared spectrum indicated a mixture of α,β- and β,γ-unsaturated ketones: 1665 and 1630 and 1695 cm^{-1}, respectively. The ultraviolet spectra confirmed the presence of a conjugated enone: λ_{max} 265 nm. When the crude product was injected onto any one of several vpc columns, several products were formed from thermal rearrangement. The two major components were identified as tricyclic ketone **6** and bicyclic enone **22**.[10]

Photocyclization of Dienone 5.—Solutions of dienone **5** (0.1% in ether or hexane) were irradiated through a Pyrex filter in a 15-ml capacity quartz apparatus, under helium, with water cooling. Small samples were periodically withdrawn for uv analysis. Within 15 min, the absorption band at 265 nm had disappeared. After evaporation of the solvent, the volatile photoproduct was analyzed by glpc (150 ft × 0.01 in. Carbowax 20M) and by pmr spectroscopy. Quantitative glpc analysis showed that tricyclic ketones **6**, **7**, and **8** had been produced in the following yields: ether, 6:7:8 = 32:3:22; hexane, 6:7:8 = 60:6:30. In the experiment in ether, there were several additional, unidentified products. The hexane experiment was much cleaner, giving very little of any other product. Since we had found that dienone **5** undergoes thermal rearrangement upon attempted glpc analysis,[10] we also analyzed the crude photoproduct by pmr spectroscopy. Although the angular methyl singlets of tricyclic ketones **6** and **8** coincide when measured in CCl_4 or $CHCl_3$, they are separated by approximately 3 Hz in pyridine. Pmr analysis of the crude photoproduct in pyridine corraborated the glpc analysis.

In another experiment,[17] a 0.1% solution of dienone **5** in a 20:1 mixture of hexane–piperyline was irradiated in the same manner.

(16) R. I. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Wiley, New York, N. Y., 1956.

(17) This experiment was kindly performed by Dr. Ronald H. Starkey.

Pmr analysis showed that the 6:8 ratio in this experiment was 9:1.

cis,anti,cis-6-Methyltricyclo[5.3.0.0^{2,6}]decan-3-one (6) and *cis,syn,cis*-6-Methyltricyclo[5.3.0.0^{2,6}]decan-3-one (7).—These tricyclic ketones, needed for comparison with the photoproducts, were prepared as previously outlined.[4]

1-Methyltricyclo[4.4.0.0^{2,7}]decan-8-one (8).—This tricyclic ketone was prepared as previously outlined.[18]

(18) C. H. Heathcock, R. A. Badger, and J. W. Patterson, Jr., *J. Amer. Chem. Soc.*, **89**, 4133 (1967).

Registry No.—**5**, 32721-52-1; **11**, 21531-35-1; **12**, 21531-36-2; **13**, 21531-37-3; **14**, 21531-38-4; **15**, 21531-39-5; **16**, 21531-40-8; **17**, 32721-51-0; **18**, 32721-48-5; **19**, 32721-49-6; **20**, 32721-50-9; **26**, 32721-53-2.

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Stereochemistry of Alkaline Cleavage of Some Phospholanium Salts[1]

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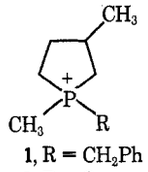
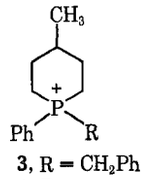
The geometric isomers of 1-benzyl-3-methyl-1-phenylphospholanium bromide (**5a** and **5b**) undergo hydroxide cleavage of benzyl which is accompanied by complete retention of configuration at phosphorus yielding pure isomers of 3-methyl-1-phenylphospholane 1-oxide (**6a** or **6b**). Cleavage of either isomer of 1,3-dimethyl-1-phenylphospholanium bromide (**7a** and **7b**) produces identical mixtures of cis and trans isomers of 1,3-dimethylphospholane 1-oxide (**2**). Base decomposition of the 3-methyl-1,1-diphenylphospholanium salt **8** yields a mixture of about equal parts of **6a** and **6b**.

The cis or the trans phosphonium salt of **1** will undergo cleavage with aqueous sodium hydroxide to afford the corresponding oxide **2** with complete retention of configuration at phosphorus.[2] Recently it was shown that the cis and trans isomers of 1-benzyl-4-methyl-1-phenylphosphorinanium bromide (**3**) are decomposed under the same conditions into nonidentical mixtures of the isomeric phosphine oxides (**4**).[3] For the latter study, the 1-phenyl rather than the 1-methyl compounds were chosen because of synthetic convenience.[4] Since Trippett, *et al.*,[5] report that the base cleavage results of *cis*-1-benzyl-1-phenyl-2,2,3,4,4-pentamethylphosphetanium bromide (**11**) are different from those of the trans isomer where the two compounds differ *configurationally*, we were cautioned against the assumption that the *substitutionally* different 1-methyl-1-benzyl- and 1-phenyl-1-benzylphospholanium salts (**1** and **5**, respectively) would behave identically. We were therefore prompted to investigate the stereochemistry of cleavage of the cis and trans isomers of **5** in order to determine conclusively that the dissimilarity in stereochemical behavior between **1** and **3** is indeed due to ring size and *not* differences in substitution at phosphorus.

The stereochemistry of base cleavage of the geometrical isomers of **7** was also investigated to enable a more confident correlation to be made between leaving group ability and stereochemistry of cleavage. Of the two stereochemical studies reported in the phospholane series, benzyl[2] and trichlorosiloxide[6] as leaving groups give, respectively, retention and inversion of configuration. We have now found that phenyl as a leaving group from *cis*- or *trans*-**7** provides identical mixtures of oxides. Since phosphine oxides are known to be configurationally stable toward aqueous sodium hydroxide,[2,3,6,7] it is plausible to assume that *cis*- and *trans*-**7** lead to a common intermediate preceding phosphine oxide (**2**) formation. In fact, we have found that, when either *cis*-**7** or *trans*-**7** are separately treated with 0.5 equiv of sodium hydroxide under cleavage conditions, the remaining undecomposed salt can be shown to consist of an approximate 1:1 mixture of cis and trans salts. Treatment of either *cis*- or *trans*-**7** with a trace of base at room temperature, however, was insufficient to produce stereomutation at phosphorus to a detectible extent.



1, R = CH_2Ph
2, R = O^-



3, R = CH_2Ph
4, R = O^-

Scheme I summarizes the stereochemical outcome of cleavage reactions of the five pure *P*-phenylphospholanium salts covered by this study.

The retention of configuration at phosphorus for **1** and **5** may be accounted for by (a) equatorial loss of benzyl *via* the conjugate base[8] of the initially formed phosphorane (**9**),[2] and/or (b) apical loss of benzyl from the conjugate base of **10** after an incomplete pseudorotational process.[9] If formed, **10** would be expected to lose benzyl *via* its conjugate base.[8] Placement of oxygen in the equatorial position of **10** can be

(1) This investigation was supported by National Science Foundation Grants No. GP-7407 and GP-25479. A preliminary account of a portion of this work is found in ref 6.

(2) (a) K. L. Marsi, *Chem. Commun.*, 846 (1968); (b) *J. Amer. Chem. Soc.*, **91**, 4724 (1969).

(3) K. L. Marsi and R. T. Clark, *J. Amer. Chem. Soc.*, **92**, 3791 (1970).

(4) G. Maerkl, *Angew. Chem., Int. Ed. Engl.*, **2**, 620 (1963).

(5) J. R. Corfield, J. R. Shutt, and S. Trippett, *Chem. Commun.*, 789 (1969). The *cis*- and *trans*-1-benzyl-1-methyl-2,2,3,4,4-pentamethylphosphetanium bromides are also reported to give nonidentical products on base cleavage. However, it should be noted that the results of this work are at variance with the work of Cremer, *et al.* (ref 12), on the same systems and under similar conditions.

(6) W. Egan, G. Chauviere, K. Mislow, R. T. Clark, and K. L. Marsi, *Chem. Commun.*, 733 (1970).

(7) K. F. Kumli, W. E. McEwen, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **81**, 3805 (1959). These references give a representative, but not exhaustive, list of such examples.

(8) W. E. McEwen in "Topics in Phosphorus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., Interscience, New York, N. Y., 1965, Chapter 1.

(9) K. Mislow, *Accounts Chem. Res.*, **3**, 321 (1970).