rate of flow of cold water through the quartz water jacket. The reaction mixture was then diluted with an equal volume of toluene, which dissolved a yellow polymeric material formed during the irradiation and concentrated to dryness under reduced pressure. Chromatography of the residue on activated silica gel gave, on elution with 500 ml. of hexane and 1000 ml. of 1:4 ether–hexane, a small amount of solid and an oily polymeric material which had no well-defined spectral characteristics.

Further elution with 1000 ml. each of 1:3 and 1:2 ether–hexane gave 0.20 g. of an unidentified oil which thin layer chromatography showed to be composed of one component. The n.m.r. spectrum of this material showed no vinyl protons which appeared to rule out the possibility of its being a spiro compound of the type VI ($R = CH_3$).

Finally, elution with 1000 ml. each of 2:1, 3:1, and 4:1 ether–hexane and with 1000 ml. of ether gave 1.34 g. (81%) of III as an oil which crystallized on standing, m.p. 96.5–98.0°. Recrystallization from diethyl ether gave colorless needles: m.p. 97.2–99.0°; λ_{max} 243 mμ (ϵ 13,300) and λ_{max} 2.90, 5.95, and 6.17 μ; n.m.r. spectrum (deuteriochloroform), τ 8.35 (m, 3, CH_3-3) and 9.09 (s, 3, CH_3-8).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.31; H, 9.37.

Acknowledgment.—Support of this research by a Frederick Gardner Cottrell grant-in-aid from the Research Corporation is gratefully acknowledged.

Photochemical Rearrangements of Cross-Conjugated Cyclohexadienones. V. A Model for the Santonin Series[1]

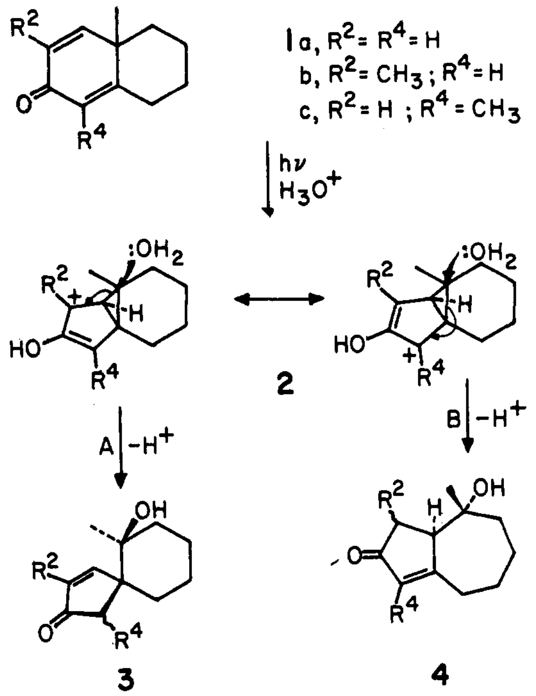
Paul J. Kropp

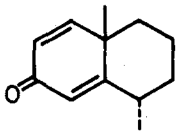
The Procter and Gamble Company, Miami Valley Laboratories, Cincinnati 39, Ohio

Received May 25, 1964

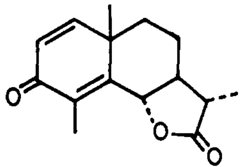
The principal course of the photochemical rearrangements of cross-conjugated cyclohexadienones of type **1** in aqueous, acidic media is hydroxy ketone formation; normally either a spiro ketone (**3**), a perhydroazulenone (**4**), or a mixture of the two is formed. In previous papers of this series, we reported that the type of hydroxy ketone photoproduct produced is influenced by the presence or absence of alkyl substituents on ring A of the dienone. Thus the 2-methyldienone **1b** (steroid numbering system) gave almost exclusively a spiro ketone (**3b**),[1] whereas the unsubstituted dienone **5** gave both a spiro ketone (type **3a**) and a perhydroazulenone (type **4a**) in approximately equal amounts.[2] Comparison of these results with the previous findings that the 4-methyldienones santonin (**6**)[3] and the steroid **7**[4] were converted predominantly to a perhydroazulenone (type **4c**) led to the conclusion that a cyclopropyl intermediate (**2**) is a common precursor to both types of product (with the direction of cleavage being controlled principally by the electronic effects of the substituents at C-2 and C-4).[2]

However, recent findings that the lactone ring of santonin markedly influences some of its photochemical[5a] and related chemical properties[5b] made it of interest to demonstrate that a bicyclic 4-methyldienone, lacking the additional rings of **6** and **7**, exhibits analogous behavior. This has now been found to be the case with the model dienone **1c**.

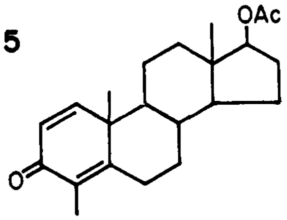




5



6



7

The dienone **1c**[6] was prepared by oxidation of the octalone **8**[6a,c,7] with 2,3-dichloro-5,6-dicyanobenzoquinone. Irradiation of **1c** in 45% acetic acid gave in 65–70% yield a hydroxy ketone to which the perhydroazulenone structure **4c** could be assigned on the basis of spectral data and by analogy to the formation of similar products from **6** and **7**. No evidence for the formation of any significant amount of the spiro ketone **3c** could be detected.

The hydroxy ketone **4c** exhibited typical absorption at 5.92 (conjugated C=O) and 6.14 μ (C=C) and at 242 mμ (ϵ 14,400). The n.m.r. spectrum verified the absence of any olefinic protons and showed the

---

[1] For part IV, see P. J. Kropp, *J. Am. Chem. Soc.*, in press.

[2] P. J. Kropp and W. F. Erman, *ibid.*, **85**, 2456 (1963).

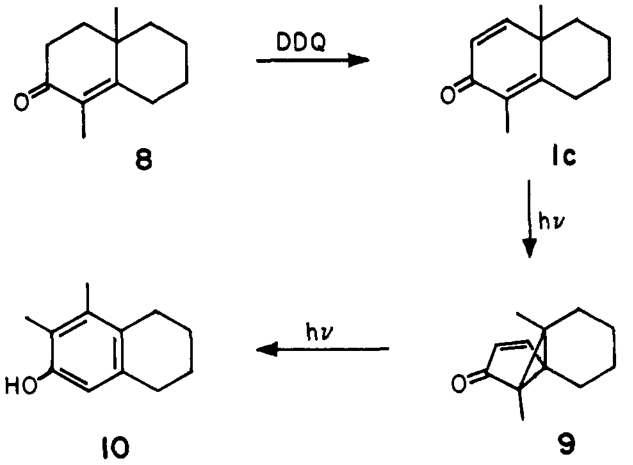
[3] D. H. R. Barton, P. de Mayo, and M. Shafiq, *J. Chem. Soc.*, 929 (1957); D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger, and L. J. Krebaum, *Helv. Chim. Acta*, **40**, 1732 (1957); J. D. M. Asher and G. A. Sim, *Proc. Chem. Soc.*, 111 (1962).

[4] K. Weinberg, E. C. Utzinger, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **43**, 236 (1960).

[5] (a) *Cf.* discussion in P. J. Kropp, *J. Am. Chem. Soc.*, **85**, 3779 (1963); (b) unpublished data from these laboratories.

[6] (a) F. D. Gunstone and R. M. Heggie, *J. Chem. Soc.*, 1437 (1952); (b) P. R. Hills and F. J. McQuillin, *ibid.*, 4060 (1953); (c) M. Yanagita and R. Futaki, *J. Org. Chem.*, **21**, 949 (1956); (d) M. Yanagita, S. Inayama, M. Hirakura, and F. Seki, *ibid.*, **23**, 690 (1958); (e) L. Mandell, D. Caine, and G. E. Kilpatrick, *J. Am. Chem. Soc.*, **83**, 4457 (1961).

[7] F. J. McQuillin, *J. Chem. Soc.*, 528 (1955); J. K. Chakrabarti, P. Dutt, and P. C. Dutta, *ibid.*, 4978 (1956); M. Yanagita, M. Hirakura, and F. Seki, *J. Org. Chem.*, **23**, 841 (1958).



α-methyl substituent as a multiplet at τ 8.32 and the hydroxyl-bearing methyl group as a singlet at 9.08. Hydrogenation over palladium on charcoal gave a dihydro derivative which exhibited the typical cyclopentanone absorption at 5.75 μ.

Also formed in 6–7% yield on irradiation of dienone **1c** was the phenol **10**.[8] This is the expected product from the usual secondary pathway in acidic media involving initial photoisomerization of the dienone to a lumiproduct (**9**) followed by a second light-initiated rearrangement to **10**.[9]

Experimental[10]

1,4a-Dimethyl-4,4a,5,6,7,8-hexahydro-2(3H)-naphthalenone (8).—The general procedure of Poos, *et al.*,[11] was employed. To a solution of 39.0 g. (0.348 mole) of 2-methylcyclohexanone in 450 ml. of methanol was added dropwise under an atmosphere of nitrogen 166 ml. (0.356 mole) of 35% methanolic benzyltrimethylammonium hydroxide, followed by 29.9 g. (0.356 mole) of pent-1-en-3-one. The resulting solution was heated under reflux for 2 hr. The solution was then allowed to cool and 270 ml. of 3 *N* hydrochloric acid was added. After an additional 0.5-hr. reflux period, the solution was again cooled and extracted with four 150-ml. portions of ether. The combined ethereal extracts were dried over saturated sodium chloride solution and then anhydrous sodium sulfate and concentrated under reduced pressure on a rotary evaporator. Distillation of the residue gave 25.8 g. (41% yield) of colorless liquid: b.p. 74–78° at 0.4 mm.; λ_{max} 6.05 and 6.24 μ; λ_{max} 246 mμ (ε 16,000); n.m.r. spectrum, τ 8.76 (s,[12a] 3,[12b] CH$_3$-4a) and 8.20 (s, 3, CH$_3$-1); 2,4-dinitrophenylhydrazone, red platelets, m.p. 198–199° (lit.[6a] b.p., 99–100° at 1 mm., 2,4-dinitrophenylhydrazone m.p. 198–199°).

1,4a-Dimethyl-5,6,7,8-tetrahydro-2(4aH)-naphthalenone (1c). A. **Preparation.**—The general procedure of Burn, Kirk, and Petrow[13] was employed. A solution of 10.25 g. (57.5 mmoles) of octalone **8**, 14.32 g. (63 mmoles) of 2,3-dichloro-5,6-dicyanobenzoquinone, and 25 ml. of glacial acetic acid in 500 ml. of benzene was heated under reflux in an atmosphere of nitrogen for 32 hr. The reaction mixture was cooled to room temperature, filtered, and concentrated under reduced pressure on a rotary evaporator. The resulting amber oil was then filtered through 100 g. of activity II alumina with 1.25 l. of hexane and 4 l. of benzene to give 8.29 g. (82% yield) of a pale yellow oil which crystallized on refrigeration. Repeated low-temperature recrystallization from hexane gave colorless prisms: m.p. 40–40.5°; λ_{max} 6.02, 6.18, and 6.22 μ; λ_{max} 238 mμ (ε 11,000); n.m.r. spectrum, τ 3.24 and 3.78 (2d, 2, J_{AB} = 10 c.p.s., CH-4 and CH-3), 8.06 (s, 3, CH$_3$-1), and 8.74 (s, 3, CH$_3$-4a).

B. **Irradiation.**—A solution of 553 mg. of dienone **1c** in 150 ml. of 45% acetic acid was irradiated for 30 min. at 25° using a Hanovia 200-w. high-pressure mercury lamp and the apparatus previously described.[2] The resulting solution was concentrated to dryness on a rotary evaporator under reduced pressure, and the residue was chromatographed on 16.5 g. of silica gel. Elution with 750 ml. of 1:1 benzene–hexane gave 36 mg. (6.5% yield) of **3,4-dimethyl-5,6,7,8-tetrahydro-2-naphthol (10)**, m.p. 108–115°. Recrystallization from hexane gave colorless prisms, m.p. 116–118°, which was unchanged on admixture with an authentic sample of **10**.[8]

Continued elution with 1 l. of 3:1 benzene–hexane, 600 ml. of benzene, 1 l. of 1:19 ether–benzene, and 300 ml. of 1:9 ether–benzene gave 108 mg. of a colorless oil which was shown by gas chromatography to consist of at least five components. Continued elution with 3.3 l. of 1:3 ether–benzene gave 399 mg. (65% yield) of **3,8β-dimethyl-4,5,6,7,8,8aα-hexahydro-8α-hydroxy-2(1H)-azulenone (4c)** as a colorless oil. Further purification by short-path distillation at 131–133° and 0.15 mm. gave a colorless viscous oil which crystallized on standing. Recrystallization from ether–hexane gave colorless needles: m.p. 82.5–83.5° and 100.5–102°; λ_{max} 2.78, 5.92, and 6.14 μ; λ_{max} 242 mμ (ε 14,400); n.m.r. spectrum, τ 8.32 (m, 3, CH$_3$-3) and 9.08 (s, 3, CH$_3$-8β).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.85; H, 9.28.

Similarly irradiation of a solution of 269 mg. of dienone **1c** in 120 ml. of 45% acetic acid for 2 hr. with a Hanau NK 6/20 low-pressure mercury lamp gave the phenol **10** and the ketone **4c** in yields of 6 and 70%, respectively.

Treatment of a solution of 56 mg. of the above analytically pure ketone **4c** in 10 ml. of absolute ethanol with 10 mg. of 10% palladium on charcoal in a hydrogen atmosphere resulted in the absorption of 1.1 equiv. of hydrogen and produced a **dihydro derivative**, m.p. 85–90°. Recrystallization from ether–hexane gave long colorless needles: m.p. 90.5–91.5; λ_{max} 2.75 and 5.75 μ.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.42; H, 10.42.

---

[8] W. Cocker, *J. Chem. Soc.*, 36 (1946).

[9] It should be noted that santonin is exceptional from other cyclohexadienones in that it does not give a phenolic photoproduct. This anomalous behavior can be ascribed to strain introduced by the *trans*-fused γ-lactone ring in the spiro intermediate normally involved in phenol formation. A more complete discussion is given in ref. 2 and 5a.

[10] Ultraviolet spectra were determined in absolute ethanol with a Cary Model 14 spectrophotometer, and infrared spectra were obtained in 5% methylene chloride solution with a Perkin-Elmer Infracord spectrophotometer. Melting points were determined on a micro hot stage and are calibrated and corrected. Nuclear magnetic resonance spectra were obtained in deuteriochloroform solution with a Varian Model A-60 spectrometer, using tetramethylsilane as an internal standard. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

[11] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

[12] (a) Multiplicity (s = singlet, d = doublet, and m = multiplet); (b) integration.

[13] D. Burn, D. N. Kirk, and V. Petrow, *Proc. Chem. Soc.*, 14 (1960).

Diels–Alder Reactions of Acyclic Fluoro Ketones

WILLIAM J. LINN

Contribution No. 975 from the Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware

Received May 11, 1964

The use of carbonyl compounds as dienophiles in the Diels–Alder reaction is limited. Formaldehyde adds to 2-methyl-1,3-pentadiene at 185° but not to butadiene.[1] At 150°, chloral participates in the diene reaction, but here again no adduct forms with butadiene.[2] However, the exceptionally reactive hexafluorocyclobutanone and butadiene combine to give a normal Diels–Alder adduct below 0°.[3]

---

[1] T. L. Gresham and T. R. Steadman, *J. Am. Chem. Soc.*, **71**, 737 (1949).

[2] W. J. Dale and A. J. Sisti, *ibid.*, **76**, 81 (1954).

[3] D. C. England, *ibid.*, **83**, 2205 (1961).