

with subsequent recombination of the benzoyl radical and a hydrogen atom. However, such a cage mechanism will not account for the formation of acetoin in the latter reaction. One must rule out acetaldehyde as an intermediate in this reaction since in one run acetaldehyde was added to an aqueous solution of pyruvic acid (molar ratio acetaldehyde to pyruvic acid 3:4) and its concentration was found not to decrease even after 50% conversion of pyruvic acid. One can account for the formation of acetoin from the intermediacy of a triplet hydroxymethyl carbene formed by cyclic concerted loss of CO₂¹ but no concrete evidence for this has yet been found.

One probably cannot account for the difference in products from the aqueous decompositions of the two acids as being due to different photochemically active excited states (*i.e.*, an $n-\pi^*$ triplet for pyruvic acid, a $\pi-\pi^*$ triplet for benzoylformic acid) since both the vibrational structure of the phosphorescence and the S_1-T_1 energy gaps indicate that in both cases the lowest (and hence chemically active) triplet is of the $n-\pi^*$ type.

An approach that we previously suggested¹ to explain the discrepancy in the result of irradiation of pyruvic acid in water and in organic solvents, that is, the species existing as aggregates in the organic solvents, may not

be entirely valid. While in benzene (where no photochemical reaction occurs) pyruvic acid is definitely dimeric¹ and even trimeric at higher concentrations,²³ it is monomeric in chloroform, a solvent in which photoreduction readily occurs without any significant amount of accompanying decarboxylation. Further investigation into the mechanism of aqueous photodecarboxylation of the ketoacids is in progress.

A most interesting and promising area of study is the gas phase photochemistry of pyruvic acid. Preliminary experiments reveal that pyruvic acid at low pressures photodecarboxylates (obviously not requiring the presence of water) quite cleanly to yield principally *acetaldehyde* rather than acetoin. The effect of added gases on the reaction, and the relevance of the mechanism of this reaction to those in solution, is currently being investigated.

Acknowledgment.—This work has been supported in part by a grant from the Petroleum Research Fund of the American Chemical Society.

(23) Molecular weights of pyruvic acid in benzene, methylene chloride, chloroform, and acetone indicate, respectively, trimer, dimer, monomer, and monomer. Apparatus utilizing vapor pressure measurements was employed, similar to that described by Neumayer.²⁴ We are indebted to Drs. B. H. Klanderma and O. E. Schupp of the Eastman Kodak Co. for performing these measurements.

(24) J. J. Neumayer, *Anal. Chim. Acta*, **20**, 519 (1959).

[CONTRIBUTION FROM THE PROCTER & GAMBLE CO., MIAMI VALLEY LABORATORIES, CINCINNATI 39, OHIO]

Photochemical Rearrangements of Cross-Conjugated Cyclohexadienones. III. An Example of Steric Control

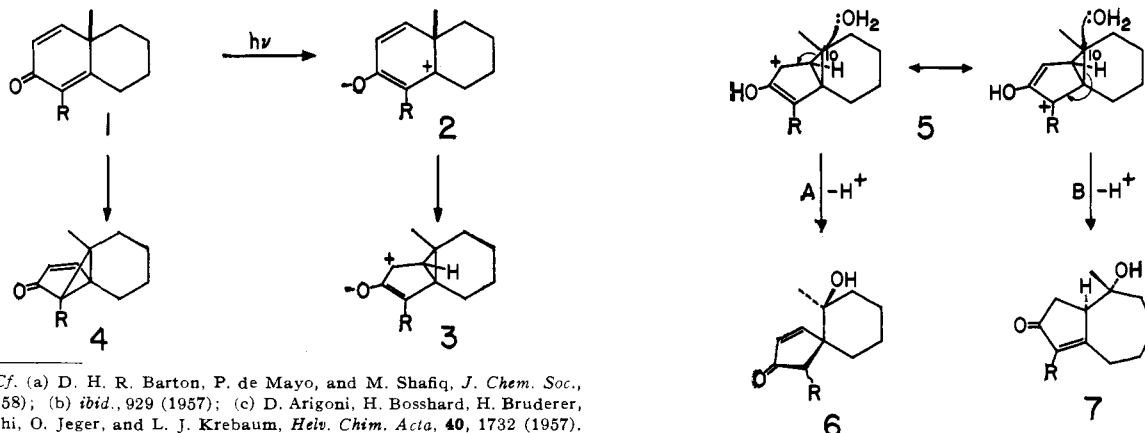
BY PAUL J. KROPP

RECEIVED JUNE 19, 1963

The photochemical behavior of the dienone **9** was examined in order to study the role of steric effects in photochemical rearrangements and to determine whether the marked influence of a 4-methyl substituent on the photochemical properties of 1,4-dien-3-ones can be attributed to steric factors. Irradiation of **9** in aqueous acidic media gave principally the *o*-cresol-type product **11a** and the 5/7-fused ketone **12**, accompanied by small amounts of the spiro ketone **10**. 1,4-Dien-3-ones of this type, unsubstituted at C-4, normally give *m*-cresol-type products and approximately equal amounts of spiro- (**6**) and 5/7-fused (**7**) hydroxy ketones in acidic media. Thus the properties of the dienone **9** are markedly influenced by steric factors. However, the behavior of **9** is not the same as that of 4-methyl-1,4-dien-3-ones; this suggests that the 4-methyl effect is not principally steric in origin.

Among the earliest photochemical rearrangements discovered were the light-induced transformations of the sesquiterpene santonin (**21**).¹ In recent years it has been found that almost all cross-conjugated cyclohexadienones undergo fascinating rearrangements under the influence of ultraviolet light. Moreover, all 1,4-dien-3-ones of the type **1** ($R = CH_3$), which bear a methyl substituent at C-4,² that have been studied to

date have been found to exhibit similar photochemical behavior.³ In neutral media they undergo facile isomerization to a cyclopropyl ketone **4** ($R = CH_3$), commonly known as a "lumiproduct." Lumiproduct formation occurs in aqueous acidic media as well, but under these conditions it is accompanied by a second reaction pathway leading to a hydroxy ketone **7** ($R = CH_3$) having a hydroazulene structure.



(1) Cf. (a) D. H. R. Barton, P. de Mayo, and M. Shafiq, *J. Chem. Soc.*, 140 (1958); (b) *ibid.*, 929 (1957); (c) D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger, and L. J. Krebaum, *Helv. Chim. Acta*, **40**, 1732 (1957).

(2) The steroid numbering system is used throughout the Discussion section.

(3) Cf. P. de Mayo and S. T. Reid, *Quart. Rev. (London)*, 393 (1961).

Quite surprisingly, removal of the 4-methyl substituent results in markedly different photochemical behavior. In neutral media the unsubstituted dienones **1** ($R = H$) give a complex mixture of ketonic and phenolic products, with a lumiprodukt **4** ($R = H$) being only one of many products formed.⁴ In aqueous acidic media the behavior of the unsubstituted dienones more closely resembles that of the 4-methyl analogs, as both the expected lumiprodukt **4** ($R = H$) and the 5/7-ketone **7** ($R = H$) are formed. However, the yield of 5/7-ketone is reduced by about one-half in this case, and a new ketone **6** ($R = H$), having a spiro structure, is formed in approximately equal yield.^{5,6}

The formation of the hydroxy ketone photoproducts **6** and **7** is generally accounted for in terms of a cyclopropyl intermediate **3**.⁷ In aqueous acidic media, **3**, or its protonated form **5**, could give rise to the spiro structure **6** or the 5/7-fused structure **7** by cleavage of either of two of the cyclopropyl bonds, with accompanying nucleophilic attack by solvent water at C-10. If the attack of water is assumed to occur from the side opposite to that of the particular cyclopropyl bond undergoing cleavage, the correct stereochemistry for the products **6**^{5,6} and **7**⁸ is predicted.

The occurrence of paths A and B with approximately equal facility in the absence of a substituent at C-4 (*i.e.*, $R = H$) is not surprising. However, the nature of the effect of a 4-methyl substituent in causing path B to be highly favored over path A is not well understood. Two possibilities would seem both plausible and consistent with the available data: either an electronic effect, giving some added preferential stabilization to the transition state for path B, or a steric effect, involving hindrance to solvation of the intermediate **5** from the front side. This latter effect would direct the attack of water to the rear side and would, therefore, presumably favor cleavage by path B.

Little is known about steric effects in photochemical rearrangements. If the 4-methyl group effect is steric in origin (as described above), we should be able to observe similar effects in a model compound in which the approach of solvent to the front face of the molecule is prevented in much the same way as it might be prevented by a 4-methyl group. A satisfactory model would seem to be one bearing a 6β -methyl substituent, such as the dienone **9**.⁹ The 6β -methyl group appears to be isolated electronically from the dienone chromophore of ring A.¹⁰ It should, however, hinder seriously the approach of water at C-10 from the front side (as shown in **8a**¹¹) but not from the rear side. This should result in a marked predominance of path B, rather than

(4) H. Dutler, C. Ganter, H. Ryf, E. C. Utzinger, K. Weinberg, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2346 (1962).

(5) P. J. Kropp and W. F. Erman, *Tetrahedron Letters*, 21 (1963); *J. Am. Chem. Soc.*, **85**, 2456 (1963).

(6) C. Ganter, E. C. Utzinger, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2403 (1962).

(7) The present work is concerned only with the stereochemical consequences of the intervention of an intermediate with the structure **3**, and not with the precise details of its formation from **1**. For one approach to the formation of **3** see H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962). A somewhat different approach is presented in ref. 5.

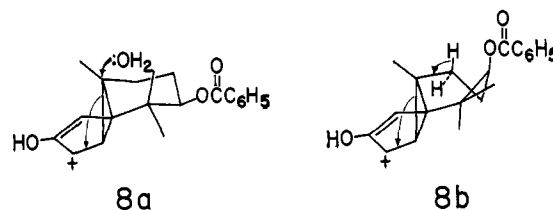
(8) J. D. M. Asher and G. A. Sim, *Proc. Chem. Soc.*, 111 (1962).

(9) B. R. Davis and T. G. Halsall, *J. Chem. Soc.*, 1833 (1962).

(10) A referee has called our attention to a report that 6α - and 6β -halo, nitro, and hydroxyl substituents influence the principal ultraviolet maxima of 4-en-3-ones [H. J. Ringold and A. Bowers, *Experientia*, **15**, 65 (1961)]. However, these authors found that a 6α - or 6β -methyl substituent, in contrast, exerts little or no effect.

(11) Of the two half-chair conformational forms available to ring B in the intermediate **8**, form **8a**, in which the benzoate group is equatorial, is probably preferred. Attack of water at C-10 from the front side of **8a**, as required for reaction by path A, should be hindered by the presence of the 6β -methyl substituent. Although this interaction would be relieved in the alternate form **8b**, path-A cleavage involving **8b** would also be unfavorable because of the accompanying development of a boat form in ring B.

the usual occurrence of both modes of cleavage with equal facility for dienones unsubstituted at C-4.

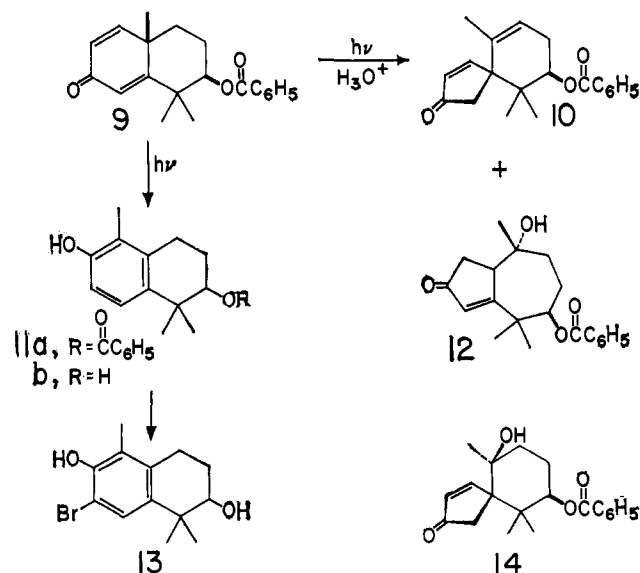


With this thought in mind, the photochemical behavior of dienone **9** was investigated. The results of this study are summarized in Table I. It will be noted

TABLE I
PHOTOCHEMICAL REARRANGEMENT OF DIENONE **9**

	Yields, %		
	Ketone 12	Ketone 10	Phenol 11a
45% formic acid	37	14	15
45% acetic acid	15	5	23

that the predominant product was the hydroxy ketone **12**, formed by path B. A very small amount of material which had spectral properties consistent with those expected for the spiro-fused hydroxy ketone **14** was also isolated, but lack of sufficient material prevented complete characterization of this product. Thus the 6β -methyl substituent appears to hinder seriously the approach of solvent at C-10 from the front side of the molecule. However, although the normal path-A product **14** is not formed in significant yield, a path-A-type cleavage does still occur, giving the keto olefin **10** in moderate yield. Products of this type have not been obtained previously from either unsubstituted 1,4-dien-3-ones or their 4-methyl analogs in aqueous acidic media.¹² Thus in the event of hindrance to solvent attack at C-10, spiro ketone formation still occurs to some extent, but with accompanying loss of a proton at C-9 apparently replacing the usual attack of water at C-10 (see **8b**).



The formation of no more than negligible amounts of spiro ketone **14** and the definite predominance of the path-B product **12** over the keto olefin **10** indicate that steric factors can play an important role in the photochemical behavior of cyclohexadienones. Moreover, shielding of the molecule from front-side attack at C-10 can influence the relative occurrence of A- and B-type

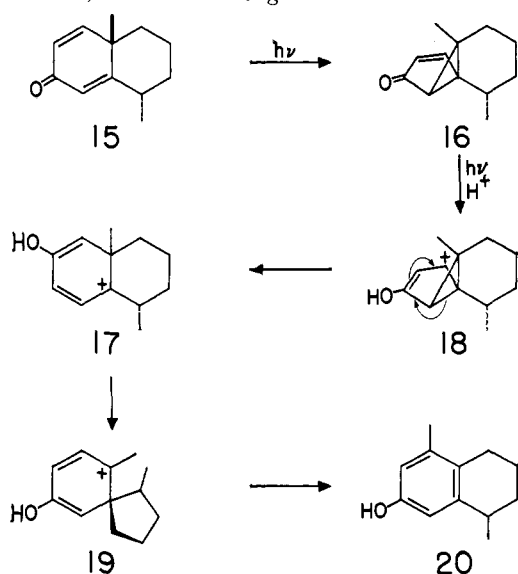
(12) However, an analogous product was obtained in low (2%) yield from irradiation of androsta-1,4-dien-3-one-17 β -ol acetate in glacial acetic acid; see ref. 6.

cleavage. However, the formation of a significant amount of path-A product in the form of the keto olefin **10** is quite different from the behavior of the 4-methyl-dienones, which are reported to form only 5/7-fused ketones.^{1,3} It would appear that the "4-methyl effect" is not principally steric in origin and is probably due to electronic factors.

In addition to the typical benzoate absorption at 5.88 μ ,¹³ the hydroxy ketone **12** has strong infrared absorption at both 5.92 and 6.30 μ , characteristic of α,β -unsaturated ketones of type **7** ($R = H$).⁵ The n.m.r. spectrum shows a single vinylic proton at 3.76 τ —consistent with the presence of a β -substituted cyclopentenone.¹⁴ By analogy with the formation of similar products from all of the 1,4-dien-3-ones previously studied,^{1,3,5} the structure **12** was assigned.

The infrared spectrum of the keto olefin **10** shows carbonyl absorption at 5.82 μ with a shoulder at 5.94 and only weak olefinic absorption at 6.24—characteristic of the cyclopentenone moiety of spiro ketones of type **6**.^{5,6} The α -vinylic proton of the cyclopentenone ring appears in the n.m.r. spectrum as half of an AB quartet at 3.74 τ (J_{AB} 5.5 c.p.s.)¹⁵ and the methylene protons appear as a second AB quartet at 7.08 and 7.52 τ (J_{AB} 11.5 c.p.s.).^{5,12,14} The single vinylic proton of the B ring appears at 4.44 τ , and the C-10 methyl group at 8.46 τ .¹⁴ The absence of any additional splitting of either the α -methylene protons or the vinylic protons of ring A indicates that the cyclopentenone ring is disubstituted at the γ -position.

Phenol Formation.—In addition to the steric effects described above involving the formation of ketonic photoproducts, the photochemical behavior of the dienone **9** exhibits another steric effect that is quite significant mechanistically. This involves the second reaction pathway mentioned earlier which always accompanies hydroxy ketone formation in aqueous acidic media—namely, the formation of a lumiprotect (4). Actually, the lumiprotect itself is seldom isolated from the reaction mixture because it is photochemically labile and under the irradiation conditions undergoes a second light-catalyzed rearrangement to a phenol or a closely related photoproduct. Unsubstituted dienones (e.g., **15**) normally give *m*-cresol-type products (e.g., **20**). By contrast, the dienone **9** gave the *o*-cresol **11a**. This



(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Second Ed., John Wiley and Sons, New York, N. Y., 1958, p. 78.

(14) Cf. L. M. Jackman, "Applications of Nuclear Magnetic Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, pp. 50-65.

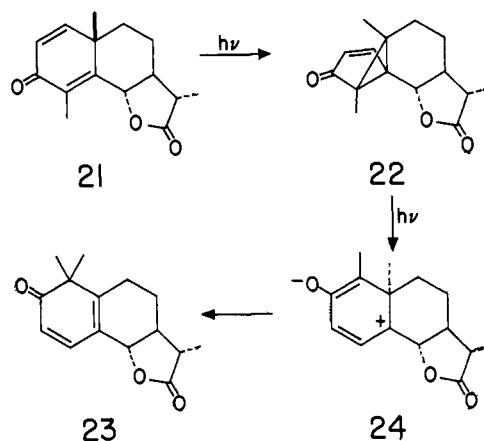
(15) The β -vinylic proton appears with the five aromatic protons.

departure of **9** from the usual pattern of *m*-cresol formation provides an important insight into the mechanistic pathway for phenol formation.

The intermediacy of a lumiprotect in phenol formation has been demonstrated, for example, in the case of the dienone **15**.⁵ Under irradiation in 45% acetic acid **15** is rapidly isomerized to the lumiprotect **16**. This ketone builds up to and maintains a steady-state concentration of 10-15% of the total material until the last of the dienone **15** is consumed, at which time it also begins to disappear. Irradiation of pure **16** under the same conditions gives the phenol **20** as the exclusive isolable product. This latter transformation is direct and does not involve reversion to the dienone **15**.

The formation of **20** apparently involves cleavage of one of the cyclopropyl bonds of **16** and protonation to give a cationic intermediate **17**.⁵ Further rearrangement of **17** to **20** is then pictured as occurring through the spiro intermediate **19**. This latter step has ample analogy in the acid-catalyzed dienone-phenol rearrangement.¹⁶

Now if a rearrangement of the type represented by $17 \rightarrow 19$ is indeed involved in the conversion of lumiprotects to phenols, one should be able to test this by obtaining different products from systems in which the formation of a spiro intermediate of the type **19** is, for one reason or another, prevented. A case in point is the recent observation that lumisantonin (**22**), which does not give a phenolic photoproduct, rearranges instead to the linearly conjugated dienone **23**.¹⁷ This ketone apparently arises from the intermediate **24** by 1,2-methyl migration rather than the usual rearrangement through a spiro intermediate. The presence of the *trans*- γ -lactone in this case prevents spiran formation, since the resulting spiro intermediate would require the highly strained *trans* fusion of two five-membered rings.^{18,19}



The dienone **9** represents a second system in which rearrangement through a spiro intermediate cannot be a possible step in the formation of the phenolic photoproduct. This conclusion is based on the recent observation of Davis and Halsall⁹ that acid-catalyzed rearrangement of the hydroxy ketone **25** gave the phenol **11b** in 86% yield. The further rearrangement of the initially formed cationic intermediate **26** by a 1,2-methyl migration

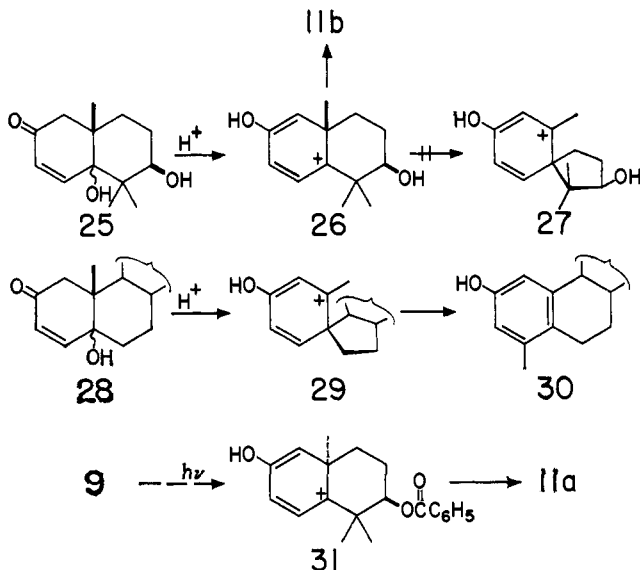
(16) S. M. Bloom, *J. Am. Chem. Soc.*, **80**, 6280 (1958). The phenolic product formed is always the isomer arising from migration of the more highly substituted carbon of the spiro intermediate.

(17) O. L. Chapman and L. Englert, unpublished observation. On further irradiation in aqueous media **23** is converted to photosantonin acid.

(18) The occurrence of 1,2-methyl migration in preference to rearrangement through a spiro intermediate cannot be attributed to the presence of the 4-methyl substituent in santonin since the lumiprotect from the analogous 4-methyl-androsta-1,4-dien-3-one-17 β -ol acetate gives a phenolic photoproduct.⁴

(19) An acid-catalyzed rearrangement through a spiro intermediate has been observed with a dienone bearing a 6 α ,7 α -(*cis*-fused)- γ -lactone; see M. Hirakura and M. Yanagita, *J. Org. Chem.*, **27**, 2948 (1962).

tion rather than by the expected rearrangement through a spiro intermediate¹⁶ (27 in this case) under these conditions is surprising. This resistance to the formation of the spiro intermediate 27 is probably attributable to a combination of unfavorable steric interactions in 27 involving (a) the methyl substituent of ring A and the 6 β -methyl group, (b) the 6 α -methyl group and the C-4 hydrogen, and (c) increased eclipsing of the 6 β - and 7 β -substituents in the formation of a five-membered ring. Under the same experimental conditions the hydroxy ketone 28, in which these steric factors are absent, is transformed to the phenol 30 through a spiro intermediate 29.⁹



If, then, the formation of phenolic photoproducts from dienones in acidic media involves an intermediate of the type 31, irradiation of dienone 9 should give the phenol benzoate 11a, formed from 31 by 1,2-methyl migration.²⁰ Indeed, the phenolic product obtained²¹ gave, on saponification, a diol with strong infrared absorption at 12.38 μ and an AB quartet with J_{AB} 9 c.p.s. in the aromatic region of the n.m.r. spectrum. These data indicate the presence of two adjacent aromatic hydrogens^{13,14} and are consistent with the *o*-cresol structure 11. Moreover, the material had a melting point and other spectral data identical with those reported for the diol 11b.⁹ Finally, treatment with an excess of bromine gave a monobromo derivative with the same physical constants as reported for the bromophenol 13.⁹

Thus light-induced rearrangement of the dienone 9 gave results markedly different from those normally encountered with similar 1,4-dien-3-ones.⁵ These differences are those which would be expected from steric effects introduced by the presence of the B-ring substituents of 9 and are additional support for the intermediacy of structures of the types 5 and 31 in the photochemical transformations of dienones related to 1.

(20) Essentially the same steric interactions invoked to account for the failure of 26 to rearrange through the spiro intermediate 27 would be present in the spiro intermediate from 31. It should also be noted that the formation of phenol 20 from 16 suggests that interaction (a), involving the methyl substituents of rings A and B, by itself is not sufficient to prevent the formation of spiro intermediates.

(21) The lumiprotect related to 4 was not isolated in this case. However, a similar product is formed from 3 β -acetoxytanosta-5,8-dien-7-one, in which the ring adjacent to the dienone chromophore has the same substitution pattern as ring B of 9. See D. H. R. Barton, J. F. McGhie, and M. Rosenberger, *J. Chem. Soc.*, 1215 (1961).

Additional work designed to elucidate further these mechanistic concepts is in progress.

Experimental²²

Rearrangement of 7 β -Hydroxy-4 α ,8,8,2-trimethyl-5,6,7,8-tetrahydro-2(4aH)-naphthalenone Benzoate (9). A. In 45% Formic Acid.—A solution of 500 mg. of dienone 9⁹ in 100 ml. of 45% formic acid was irradiated for 2 hr. at 20° using a Hanovia 200-w. high-pressure mercury lamp and the apparatus previously described.⁵ The reaction mixture was neutralized with sodium carbonate and extracted with three 100-ml. portions of ethyl acetate. The combined organic extracts were dried over saturated sodium chloride solution and anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure gave 586 mg. of an amber oil, which was chromatographed on 15 g. of alumina (Woelm, activity II). Elution with 450 ml. of 1:3 benzene-hexane gave 72 mg. (14% yield) of 6 β -hydroxy-5,5,8a-trimethyl-4a,5,6,7-tetrahydro-1(8a \rightarrow 4a β)abeo-2(1H)-naphthalenone benzoate (10), m.p. 128–130°. Recrystallization from ether-hexane gave colorless prisms, m.p. 130–131°; λ_{max} 5.82, 5.94 (shoulder), 6.24, and 6.30 μ ; and λ_{max} 228 m μ (ϵ 17,800); n.m.r. spectrum: 3.74 (d, ^{23a}1, ^{23b} J_{AB} 5.5, ^{23c}CH-3), 4.44 (m, 1, CH-8), 4.72 (m, 1, CH-6), 7.08, and 7.52 (2d, 2, J_{AB} 11.5, CH₂-1), 8.46 (m, 3, CH₂-8), and 8.90 and 9.02 τ (2s, 6, 2CH₃-5).

Anal. Calcd. for C₂₀H₂₂O₃: C, 77.39; H, 7.14. Found: C, 77.40; H, 7.28.

Elution with 750 ml. of 1:1 benzene-hexane gave 75 mg. (15% yield) of 6-hydroxy-1,5,5-trimethyl-5,6,7,8-tetrahydro-2-naphthol 6-benzoate (11a), m.p. 133–136°. Recrystallization from ether-hexane gave colorless prisms, m.p. 139–140°, λ_{max} 225 (ϵ 20,000) and 275–281 m μ (ϵ 2500); λ_{max} 2.76, 5.86, 6.24, and 12.38 μ .

Anal. Calcd. for C₂₀H₂₂O₃: C, 77.39; H, 7.14. Found: C, 77.33; H, 7.41.

Finally, elution with 1:3 ether-benzene through ethyl acetate gave a total of 195 mg. (37% yield) of 5 β ,8 α -dihydroxy-4,4,8 β -trimethyl-4,5,6,7,8,8a α -hexahydro-2(1H)-azulenone 5-benzoate (12), m.p. 155–160°. Recrystallization from acetone-hexane gave fine colorless needles, m.p. 166–167°; λ_{max} 2.75, 5.88, 5.92, 6.30 μ ; and λ_{max} 233 m μ (ϵ 26,600); n.m.r. spectrum: 3.76 (m, 1 CH-3), 4.76 (t, 1, J_{AB} = 6, CH-5), 8.48 (s, 3, CH₂-8), and 8.74 and 9.02 τ (2s, 6, 2CH₃-4).

Anal. Calcd. for C₂₀H₂₄O₄: C, 73.14; H, 7.37. Found: C, 73.06; H, 7.52.

B. In 45% Acetic Acid.—A solution of 680 mg. of dienone 9 in 135 ml. of 45% acetic acid was irradiated as described above for 75 min. A copious yellow precipitate (218 mg.) which formed was removed by filtration. The filtrate was treated as described above. Chromatography of the resulting amber oil (560 mg.) on 15 g. of activity II alumina gave 34 mg. (5% yield) of the spiro ketone 10, 153 mg. (23% yield) of the phenol 11a, and 110 mg. (15% yield) of the ketone 12. Chromatography of the precipitate afforded no recognizable material.

6-Hydroxy-1,5,5-trimethyl-5,6,7,8-tetrahydro-2-naphthol (11b).—Saponification of the phenol benzoate 11a by treatment with 4% aqueous methanolic potassium hydroxide under reflux for 0.5 hr. gave the diol 11b, which crystallized from benzene as colorless prisms, m.p. 176–177°, λ_{max} 279 (ϵ 1850) and 285 m μ (ϵ 1750), λ_{min} 251 m μ (ϵ 400), and λ_{max}^{KB} 12.28; n.m.r. spectrum: 2.88 and 3.30 (2d, 2, J_{AB} 9, CH-4 and CH-3), 6.24 (t, 1, CH-6), 7.86 (m, 3, CH₂-1), and 8.68 and 8.70 τ (2s, 6, 2CH₃-5); reported⁹ m.p. 174–175°, λ_{max} 279 (ϵ 1800), and λ_{min} 249 m μ (ϵ 350).

3-Bromo-6-hydroxy-1,5,5-trimethyl-5,6,7,8-tetrahydro-2-naphthol (13).—Treatment of a portion of the diol 11b with an excess of bromine as described previously⁹ gave a monobromo derivative which crystallized from ether-hexane as colorless prisms, m.p. 134–136°, λ_{max} 287 m μ (ϵ 2200), and λ_{min} 256 m μ (ϵ 510); reported⁹ for 13 m.p. 135–136°, λ_{max} 286 m μ (ϵ 2250), and λ_{min} 254 m μ (ϵ 410).

Acknowledgments.—The author expresses his gratitude to Dr. W. F. Erman for his interest during the course of this work and to Mr. H. C. Kretschmar for able technical assistance.

(22) 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; n.m.r. 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.

(23) (a) Multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet); (b) integration; (c) coupling constants given in c.p.s.