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Photochemical Rearrangements of Cross-Conjugated Cyclohexadienones. II. Unsubstituted 1,4-Dien-3-ones[1]

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The photochemical rearrangements of unsubstituted 1,4-dien-3-ones in aqueous acidic media were studied using 4aβ,8α-dimethyl-5,6,7,8-tetrahydro-2(4aH)-naphthalenone (**9**) and androsta-1,4-dien-3-one-17β-ol acetate (**1a**). From the dienone **9**, the phenol **11**, the spiro ketone **12** and the hydroxy ketone **14** were all obtained under a variety of conditions. In 50% sulfuric acid or in refluxing 45% acetic acid the epimeric spiro ketone **13** was also formed. The cyclopropyl ketone **10** was shown to be a photochemical intermediate in the formation of the phenol **11**. It was also cleaved to a mixture of **12** and **13** by refluxing 45% acetic acid. The steroidal dienone **1a** in 45% acetic acid gave the phenols **19a** and **22a**, the spiro ketone **18**, and the hydroxy ketone **3a** in yields highly dependent on the temperature. The properties of the unsubstituted dienones are compared with those of the 4-methyl analogs, and mechanistic implications of the observed differences are discussed.

The photochemical properties of androsta-1,4-dien-3-one-17β-ol acetate (**1a**) in neutral media are known to be in marked contrast with those of the 4-methyl derivative **1b** and the closely related sesquiterpene santonin (**5**).[2] For example, whereas the 4-methyl derivatives undergo photochemical rearrangement in dioxane to a single "lumiproduct" (**2b** and **6**) in excellent yield,[2] the unsubstituted dienone **1a** rearranges to a complex mixture containing at least five ketones and four phenols.[3] In an effort to determine whether differences in the photochemical behavior of 1,4-dien-3-ones and their 4-methyl derivatives are exhibited in acidic media as well, we have examined the photochemical properties of a model compound, 4aβ,8α-dimethyl-5,6,7,8-tetrahydro-2(4aH)-naphthalenone (**9**),[4] in aqueous acidic media. The results of this study and their extension to the steroidal dienone **1a** are described in this communication.

The photochemical rearrangement of santonin (**5**) in aqueous acetic acid involves two distinct pathways in which both lumisantonin (**6**), the principal product in neutral media, and isophotosantoic lactone (**7**) are formed concurrently. Lumisantonin, in turn, undergoes further photochemical rearrangement in aqueous media to photosantonic acid (**8**). As outlined in Chart I, the 4-methyl steroidal dienone **1b** exhibits parallel behavior except that the secondary photoproduct from the lumiproduct **2b** is a phenol (**4b**).

The results from irradiation of the model dienone **9** in various acidic media are summarized in Table I. A

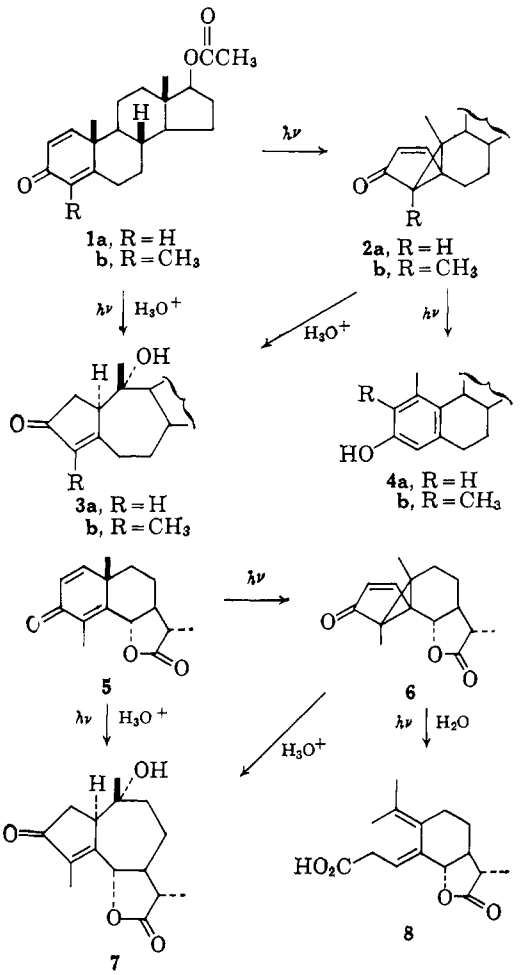
TABLE I

PHOTOCHEMICAL REARRANGEMENT OF 4aβ,8α-DIMETHYL-5,6,7,8-TETRAHYDRO-2(4aH)-NAPHTHALENONE (**9**)

		Yields, %			
Solvent, acid	Temp., °C.	Phenol **11**	Spiro ketone **12**	Spiro ketone **13**	Hydroxy ketone **14**
45% Acetic	20	29	16	None	19
45% Acetic	Reflux	29	16	5	16
45% Formic[a]	20	28	24	None	14
50% Sulfuric	15	40	9	9	7
Acetic	Reflux	43			

Pyrex filter used; yields adjusted for recovery of 33% of starting material.

CHART I



phenol (**11**) and *two* hydroxy ketones (**12** and **14**) were the principal products. An epimer (**13**) of the hydroxy ketone **12** was also formed in small yield under certain conditions.

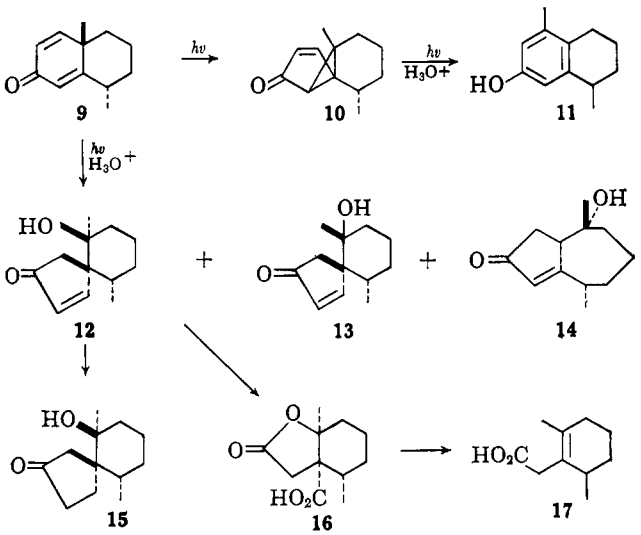
When the course of the irradiation was followed by gas chromatography, the presence of an intermediate product, not found at the end of the reaction, was detected. This intermediate was formed rapidly, being the first product to appear. It quickly reached and then maintained a steady-state concentration of about 10–15% of the total material until shortly after the last of the starting material had been consumed, at which time it also began to disappear. This intermediate could be isolated by interrupting the irradiation in acidic media before completion or, more conveniently, by brief irradiation of the dienone **9** in hexane. The

(1) (a) Presented in part before the Organic Division of the American Chemical Society at the 142nd National Meeting, Atlantic City, N. J., September 13, 1962; (b) for part I see P. J. Kropp and W. F. Erman, *Tetrahedron Letters*, 21 (1963).

(2) For a recent review of the photochemical rearrangements of cyclohexadienones see P. de Mayo and S. T. Reid, *Quart. Rev.* (London), **15**, 393 (1961). For recent establishment of the α-orientation of the C-11 methyl group of santonin and related compounds, see J. D. M. Asher and G. A. Sim, *Proc. Chem. Soc.*, 111 (1962).

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

(4) S. M. Bloom, *J. Am. Chem. Soc.*, **80**, 6280 (1958); *J. Org. Chem.*, **24**, 278 (1959).



intermediate was assigned the structure and stereochemistry **10** in analogy with lumisantonin (**6**).[5]

On hydrogenation over palladium-on-charcoal the intermediate absorbed one molar equivalent of hydrogen. The spectral properties of the intermediate [5.92 and 6.34 μ, 236 mμ (ϵ 6,100)] and the dihydro derivative (5.84 μ) agree well with those of lumisantonin (**6**) and dihydrolumisantonin.[5] The presence of one tertiary cyclopropyl hydrogen, required by the structure **10**, is confirmed by absorption at 1.677[6] and 12.00 μ.[7] The two vinyl protons appear in the n.m.r. spectrum as an ABX pattern consisting of two quartets (one proton each) at 2.62 and 4.22 τ (J_{AB} = 5.5, J_{AX} = 0.8, J_{BX} = 1.1 c.p.s.)—indicating stronger coupling of the cyclopropyl proton with the α-vinylic proton than with the β-proton.

In order to establish the role of the lumiproduct **10** in the over-all scheme, a solution of **10** in 45% acetic acid was irradiated at room temperature. The phenol **11**[8] was obtained in 63% yield[9]; no trace of the hydroxy ketones **12**, **13** or **14** could be detected by gas chromatography. Although unaffected by 45% acetic acid in the dark at room temperature, the lumiproduct **10** was cleaved under reflux to a mixture of the epimeric hydroxy ketones **12** (50% yield) and **13** (22% yield). Surprisingly, none of the other hydroxy ketone **14** or of the phenol **11** was formed.

The infrared spectra of the hydroxy ketones **12** and **13** are nearly identical—showing absorption at 5.84, 5.95 and 6.28 μ. The presence of a cyclopentenone unit was demonstrated, in the case of **12**, by conversion to a dihydro derivative having a single band in the carbonyl region at 5.76 μ. The phenomenon of two carbonyl stretching bands arising from a single chromophore has been observed previously for cyclopentenones which are unsubstituted at the α-vinylic position.[10] The substitution pattern on the cyclopentenone rings of **12** and **13** is clearly defined by their n.m.r. spectra. The α- and β-vinylic protons appear as an AB quartet consisting of doublets at 2.46 and 3.77 τ (J_{AB} = 6 c.p.s.) and the methylene protons appear as a second AB quartet with doublets at 7.29 and 7.91 τ (J_{AB} = 19 c.p.s.). Coupled with the lack of any secondary splitting of these patterns and the absence of any absorption attributable to an allylic proton, these data can be accommodated only by a cyclopentenone ring which is disubstituted at C-4.

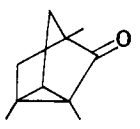
In support of the structural assignment **12**, ozonolysis of the ketone gave an acidic γ-lactone, λ_{max} 5.62, 5.70 and 5.85 μ,[11] which was assigned the structure **16**. On pyrolysis the sodium salt of the lactone-acid **16** underwent facile decarboxylation, forming a new unconjugated acid (λ_{max} 5.82 μ) with a molecular weight of 168 and an n.m.r. spectrum consistent with the structure 2,6-dimethyl-Δ^1-cyclohexeneacetic acid (**17**): 6.88 (two-proton singlet, α-methylene), 8.35 (three-proton singlet, 2-methyl) and 8.98 τ (three-proton doublet, J_{AB} = 7 c.p.s.; 6-methyl).

The striking similarity of the infrared, n.m.r. and mass spectra of the ketones **12** and **13** emphasizes their simple isomeric relationship, and their concurrent formation from the cyclopropyl ketone **10** suggests that they are epimeric only about the hydroxyl-bearing carbon—the stereochemical assignment at the spiro fusion following from that of **10**. Conclusive assignments at the hydroxyl-bearing carbon are complicated in the case of isomer **13** by the possibility that both conformational forms **13a** and **13b** are present in significant amounts.[12] The tentative assignments **12** and **13** for the major and minor products, respectively, are based primarily on the expected preferred formation of isomer **12** (see Discussion section).[14] These assignments have some support in the observation that the infrared hydroxyl absorption of the minor product (assigned structure **13**) shows a weak splitting[16] which is independent of concentration and is absent in the other isomer. A study of molecular models suggests that *intra*-molecular hydrogen bonding with the cyclopentenone ring

(5) (a) D. H. R. Barton, P. de Mayo and M. Shafiq, *J. Chem. Soc.*, 140 (1958); (b) D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger and L. J. Krebaum, *Helv. Chim. Acta*, **40**, 1732 (1957). For a description of the analogous lumiproduct **2a** see ref. 3.

(6) J. Meinwald, A. Lewis and P. G. Gassman, *J. Am. Chem. Soc.*, **84**, 977 (1962), report that a variety of newly synthesized bicyclo[3.1.0]hexanes having tertiary cyclopropyl hydrogens show characteristic first overtones in the 1.68-μ region.

(7) P. Yates and S. Danishefsky, *ibid.*, **84**, 879 (1962), note characteristic absorption in the 12-μ region for several nortricyclene derivatives—including the similarly-substituted ketone i, which absorbs at 12.05 μ.



i

(8) P. J. Kropp, *ibid.*, in press. The phenol **11** is also obtained as a minor product in the acid-catalyzed dienone–phenol rearrangement of the dienone **9**.

(9) A control experiment showed that the phenol **11** was subject to some decomposition under these conditions.

(10) (a) P. Yates, N. Yoda, W. Brown and B. Mann, *J. Am. Chem. Soc.*, **80**, 202 (1958); (b) P. Yates and L. L. Williams, *ibid.*, **80**, 5896 (1958); (c) R. Hirschmann, G. A. Bailey, R. Walker and J. M. Chemerda, *ibid.*, **81**, 2822 (1959). It was previously reported[10a] that the relative intensities of the two peaks are dependent upon the particular solvent used, but in a given solvent (chloroform was used for the dilution studies) are independent of concentration. We found, however, that in carbon disulfide the band at 5.95 μ was concentration dependent for both **12** and **13** (see Table IV).

(11) The appearance of two carbonyl stretching bands, arising from monomeric and dimeric forms, is common for carboxylic acids (*cf.* L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 165–166). The expected shift of relative intensities of the 5.70 and 5.85 μ bands in favor of the former was observed on dilution.

(12) However, isomer **12** probably exists predominantly in form **12a**, in which the severe interactions involving the two axial methyl substituents of **12b** (estimated ΔF of 6.7–7.5 kcal./mole[13]) are absent. The interactions involving the axial hydroxyl and vinylic groups of **12a** are approximately offset by the effect of the axial methylene carbon of **12b**.

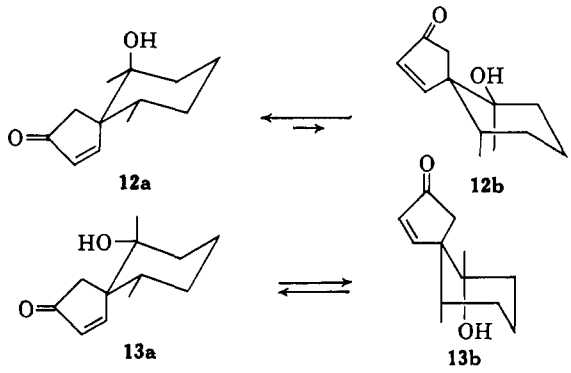
(13) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 236–237.

(14) As discussed below, the configurational assignment at C-10 analogous to that of isomer **12** was recently applied independently by Jeger and coworkers[15] to the spiro ketone **18** obtained from androsta-1,4-dien-3-one-17β-ol acetate (**1a**).

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

(16) Two sharp hydroxyl bands at 3600 and 3590 cm.$^{-1}$ were observed which were totally independent of concentration, remaining unchanged in intensity at dilutions at which both the anomalous carbonyl band discussed above and the broad intermolecularly bonded hydroxyl band were no longer observed.

would be possible in the case of **13a** (involving the equatorial hydroxyl group) but not for **12a**, the preferred conformational form for isomer **12**.[12]



The ultraviolet spectra of the ketones **12** and **13** (Table II) are surprisingly different for simple isomers. The position for the maximum of **13** is in good agreement with that of 4,5,5-trimethylcyclopentenone, which is reported to absorb at 221 mμ.[17] The cause for the bathochromic shift observed for **12** is not clear.

TABLE II
ULTRAVIOLET ABSORPTION DATA FOR KETONES 12 AND 13

	λ_{max}, mμ	
	12	13
Ethanol	232 (7000)	223 (7500)
Isoöctane	223 (6400)	216 (5800)

A third major product obtained in all of the runs was a hydroxy ketone to which the perhydroazulene structure **14** was assigned on the basis of spectral data and analogy with isophotosantonic lactone (**7**). It was never obtained in crystalline form and was separated from minor impurities only with great difficulty. However, purification by rechromatography several times on silica gel gave a colorless oil, λ_{max} 5.94 and 6.24 μ and λ_{max} 236 mμ (ε 13,000).[18] The n.m.r. spectrum indicated the presence of one α-vinylic proton (unresolved multiplet at 3.94 τ) but no β-vinylic protons. Hydrogenation over palladium-on-charcoal gave a dihydro derivative, λ_{max} 5.76 μ. These data are consistent with the presence of a β-substituted cyclopentenone unit, as required by the structural assignment **14**. The hydroxyl group could not be acetylated with acetic anhydride–pyridine, as expected for a tertiary alcohol.

Androsta-1,4-dien-3-one-17β-ol Acetate (1a).—With the results of the model study in hand, we turned next to the steroidal dienone **1a**. The results from the irradiation of **1a** in aqueous acetic acid at two temperatures are summarized in Table III.[19]

TABLE III
PHOTOCHEMICAL REARRANGEMENT OF ANDROSTA-1,4-DIEN-3-ONE-17β-OL ACETATE (1a) IN 45% ACETIC ACID

	Yields, %			
Temp., °C.	Phenol 19a	Phenol 22a	Spiro ketone 18	Hydroxy ketone 3a
20[a]	1	21	27	29
Reflux[b]	48	..	24	12

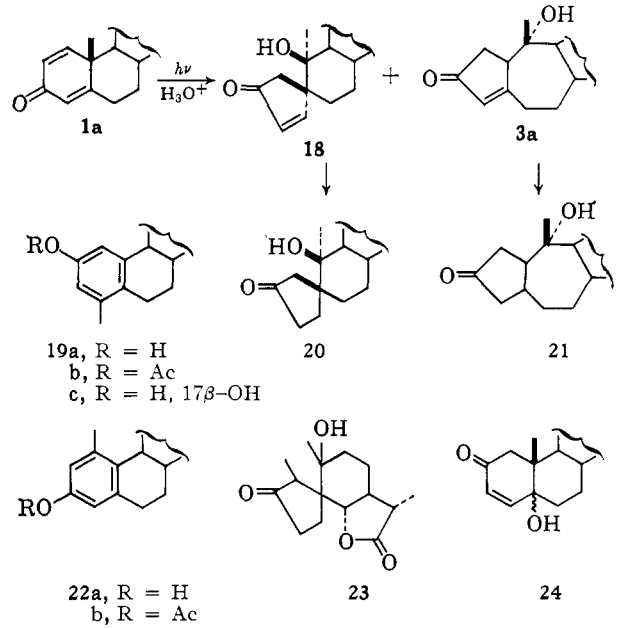
[a] Yields adjusted for 6% recovery of starting material. [b] Yields adjusted for 15% recovery of starting material.

(17) R. L. Frank, R. Armstrong, J. Kwiatek and H. A. Price, *J. Am. Chem. Soc.*, **70**, 1379 (1948).

(18) D. H. R. Barton and W. C. Taylor, *J. Chem. Soc.*, 2500 (1958), report similar data for a compound analogous with **14** obtained from photochemical rearrangement of prednisone acetate.

(19) Subsequent to the completion and initial publication[1] of our work, a report appeared describing the formation of the spiro ketone **18** and the phenol **19a** on irradiation of **1a** in refluxing aqueous acetic acid.[15] Irradiation at lower temperatures was not reported, however, nor was the hydroxy ketone **3a** described.

At either temperature two hydroxy ketones, **18** and **3a**, were obtained. Each of these gave a dihydro derivative (**20** and **21**) which had the characteristic cyclopentanone absorption at 5.75 μ. The structural assignments **18** and **3a** follow directly from the ultraviolet, infrared and n.m.r. spectra, which are identical in the appropriate regions with those of the corresponding hydroxy ketones **12** and **14** (see the Experimental section for details). The structural and configurational assignment **18** was recently corroborated in another laboratory.[19]



The major phenolic product formed at 20° was the 1-methylestradiol derivative **22a**,[3] which was identified by comparison of the diacetate **22b**[20] with a sample prepared by acid-catalyzed rearrangement of dienone **1a**. Also obtained in very low yield was the 2-hydroxy-4-methylestratriene **19a**,[3] which was characterized as its diacetate **19b**[3] and as the diol **19c**.[3,21] The melting point, infrared and ultraviolet spectra of the diol were identical with those of an authentic sample of **19c**.[21]

The photochemical properties of the dienone **1a** in 45% acetic acid showed a remarkable sensitivity to temperature which was not shared by the bicyclic dienone **9**. The phenol **19a**, which was formed only in trace amounts at 20°, became the major product at reflux. The yield of hydroxy ketone **3a** dropped appreciably at the higher temperature, and the yield of spiro ketone **18** was also somewhat decreased. As can be seen from Table I, the bicyclic system showed only minor variations with temperature.

Discussion

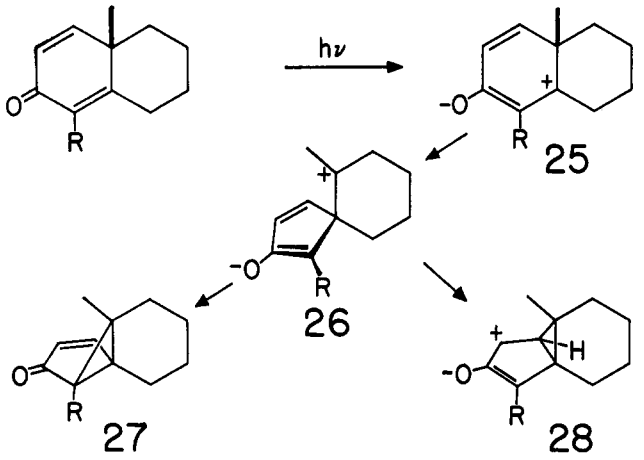
The present study has shown that unsubstituted 1,4-dien-3-ones exhibit photochemical behavior different from that of their 4-methyl derivatives in acidic media as well as in neutral solvents. Thus, whereas 4-methyl-1,4-dien-3-ones give only ketones of the type **30**,[2] the unsubstituted dienones give an approximately 1:1 mixture of ketones of the types **29** and **30**. The explanation for this difference between the two systems cannot lie in the properties of the lumiproducts **27**, since they are stable toward cold aqueous organic acids in the dark and are not converted to hydroxy ketones by the action of light. Even in rearrangements conducted at reflux tem-

(20) C. Djerassi, G. Rosenkranz, J. Romo, J. Pataki and St. Kaufmann, *J. Am. Chem. Soc.*, **72**, 4540 (1950).

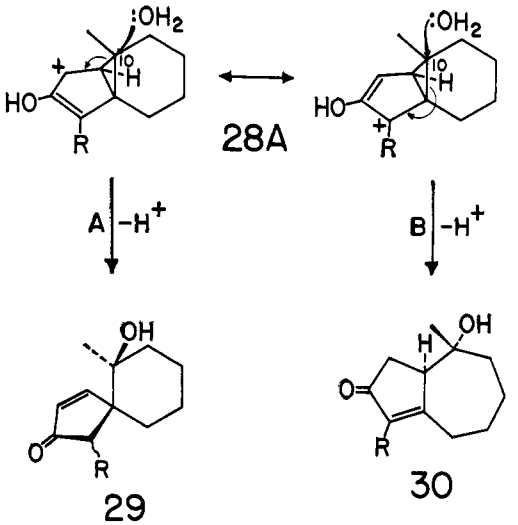
(21) R. L. Clarke, *ibid.*, **84**, 467 (1962). We are indebted to Dr. Clarke for supplying the infrared and ultraviolet spectra of **19c**.

peratures, acid-catalyzed cleavage of the lumiproducts must be only a minor factor. Such cleavage is quite slow (only 83% of ketone **10** consumed in 8 hr., as compared with the usual irradiation time of less than an hour), *and* **10** *fails to give any of the 5/7-fused ketone* **14**.[22] It should be noted that this latter behavior is in marked contrast with that of lumisantonin (**6**), which is cleaved under these conditions to isophotosantonic lactone (**7**).[5,23]

The observed stereoselective formation of both spiro and 5/7-fused ketonic photoproducts from unsubstituted 1,4-dien-3-ones introduces a new requirement in any mechanistic interpretation of the photochemical transformations of cross-conjugated cyclohexadienones. The formation of isophotosantonic lactone (**7**) and the related photoproducts from other 1,4-dien-3-ones has been accounted for previously in terms of an intermediate of the type **28**.[24] Using the polar state concept of product control in photochemical rearrangements,[25] the formation of the intermediate **28** can be represented as shown.[26] Internal alkylation involving either double bond of **26** would account for the formation of a lumiproduct **27**[27] or the intermediate **28**.[28]

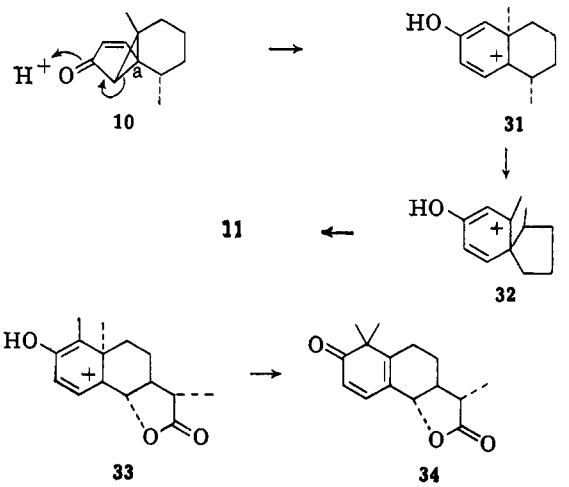


In acidic media protonation could occur at some stage to give a cation **28A**. As pointed out previously,[24] cleavage of one of the cyclopropyl bonds of **28A** with accompanying nucleophilic attack by water at C-10 would give a 5/7-fused ketone **30** which is stereochemically identical with isophotosantonic lactone (**7**).[2] Alternative cleavage as represented by path A would account for the formation of spiro ketones.[29] In the absence of a substituent at C-4 (*i.e.*, R = H), cleavage by either pathway with relatively equal facility would not be unexpected. The reason for the predominance of path B in the case of 4-methyl derivatives (R = CH_3) is not obvious. A study of Dreiding models reveals no severe steric interaction involving the 4-methyl group, but the possibility that the presence of the substituent causes unsymmetrical solvation of the intermediate, thus directing attack of solvent from the back side, cannot be eliminated. It is also possible that the methyl group provides some added stabilization for cleavage B through an inductive effect. From this picture it might be expected that 4-methyl-1,4-dien-3-ones also rearrange to some extent by path A.[30] The small amount of epimeric spiro ketone **13** which is formed by the irradiation of dienone **9** in refluxing 45% acetic acid possibly arises by simple acid-catalyzed cleavage of the lumiproduct **10**.



The photochemical conversion of the lumiproduct **10** to phenol **11** appears to involve initial cleavage of bond a, as depicted in Chart II. Rearrangement through the spiro

CHART II



intermediate **32** followed by further migration of the more highly substituted carbon of ring B has analogy in the dienone–phenol rearrangement.[4] The intermediacy of **31** has support in the recent discovery that the linearly conjugated dienone **34** is an intermediate in the transformation of lumisantonin (**6**) to

(22) Jeger and co-workers similarly report[18] that acid-catalyzed cleavage of **2a** gives a mixture of the spiro ketone **18** and the corresponding $\Delta^{9(10)}$-olefin. No evidence for the formation of **3a** is given.

(23) The cleavage of lumiproducts **27** (R = H) to spiro ketones has some analogy in the like cleavage of *dihydro*lumisantonin to the spiro ketone **23**.[5] However, dihydrolumiproducts unsubstituted at C-4, such as lumicholestenone or lumitestosterone acetate[15] (dihydro **2a**), undergo acid-catalyzed rearrangement to the hydroxy ketone **24** or the corresponding $\Delta^{3,5}$-olefin. *Cf.* W. W. Kwie, B. A. Shoulders and P. D. Gardner, *J. Am. Chem. Soc.*, **84**, 2268 (1962).

(24) H. E. Zimmerman and D. I. S.huster, *ibid.*, **84**, 4527 (1962).

(25) O. L. Chapman, A. I. Dutton and P. Fitton, Abstracts of Papers presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 9–14, 1962, p. 88Q.

(26) These rearrangements may well occur more concertedly than shown. It seems likely that the intermediates involved are electronically excited species (perhaps in high vibrational levels) rather than vibrationally excited ground state species, since the photochemical reactions of dienones and their lumiproducts generally do not parallel their thermal reactions.[15,24]

(27) The formation of dihydrolumiproducts from the photochemical rearrangements of 4-en-3-ones[15,23] can be represented similarly.

(28) For a fundamentally different approach to the formation of **27** and **28**, see ref. 24.

(29) Although a spiro ketone **29** could be formed stereoselectively by attack of water at C-10 concomitant with the rearrangement **25** → **26**, such a mode of formation would not appear to account for the suppression of spiro ketone formation in 4-methyl derivatives (see subsequent discussion).

(30) Indeed, K. Weinberg, E. C. Utzinger, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **43**, 236 (1960), report the formation in small yield of an "unidentified isomer" of **3b** from irradiation of the 4-methyl dienone **1b** in 45% acetic acid. The spectral data reported for this unidentified isomer are in close agreement with those of the spiro ketone **18**.

(31) O. L. Chapman and L. F. Englert, submitted for publication.

photosantonic acid (**8**).[31] In this latter case rearrangement through a spiro intermediate is precluded by the presence of the *trans*-γ-lactone, since a highly strained *trans*-fusion of two five-membered rings would be involved in the spiro intermediate. A 1,2-methyl shift occurs instead. Phenol formation during irradiation of the steroidal dienone **1a** in acidic media, which shows the curious temperature effect noted above, is obviously much more complex and is currently under further study in this Laboratory.

Experimental[32]

Irradiation of 4aβ,8α-Dimethyl-5,6,7,8-tetrahydro-2(4aH)-naphthalenone (9).—Irradiations were carried out using an Hanovia 200-watt high pressure mercury vapor lamp. The lamp was placed in a Vycor water jacket which was, in turn, fitted inside a Pyrex reaction vessel of slightly larger diameter. The resulting annular space had a capacity of about 120 ml. and was employed as the reaction zone. Cold water was pumped through the water jacket during the photolysis at a rate sufficient to maintain the reaction mixture at a temperature of 20°. Vigorous stirring of the reaction mixture was effected by the introduction of a stream of nitrogen through a jet opening in the bottom of the outer jacket.

In a typical run a solution of 800 mg. of dienone **9**[4] in 100 ml. of 45% acetic acid was irradiated for 3 hr. Gas chromatographic analysis of aliquots of the reaction mixture removed at 0.5-hr. intervals showed that all of the cyclohexadienone had just been consumed at this time. The reaction mixture was diluted with an equal volume of toluene and then concentrated to dryness under reduced pressure on a rotary evaporator. Chromatography of the residue on 25 g. of silica gel gave, on elution with 1.25 l. of 1:1 hexane–benzene, 234 mg. (29% yield) of **4,8-dimethyl-5,6,7,8-tetrahydro-2-naphthol (11).**[8] Recrystallization from ether–hexane gave colorless prism clusters, m.p. 95–95.5°, which was undepressed on admixture with an authentic sample obtained by acid-catalyzed dienone–phenol rearrangement of **9**.[8]

Further elution with 1 l. each of benzene and 1:19 ether–benzene gave 202 mg. of oily material which was shown by gas chromatography to be a mixture of at least four components. Elution with 2 l. of 1:9 ether–benzene gave 141 mg. (16% yield) of **4aα,8α-dimethyl-1,5,6,7,8,8a-hexahydro-4aβ-hydroxy-4(4a → 8a,α)-*abeo*-2(4aH)-naphthalenone (12),**[33] m.p. 95–97°. Recrystallization from ether–hexane gave fine colorless needles, m.p. 98–99°; λ_{max} 2.74, 5.84, 5.95 and 6.28 μ, mol. wt. 194; n.m.r. spectrum: 2.46(d, 1)[34a] and 3.77(d, 1) (J_{AB} = 6, —CH=CH)[34b]; 7.29(d, 1) and 7.91(d, 1) (J_{AB} = 19, —CH_2C=O); 8.98(s, 3, CH_3COH); and 9.30 τ (d, 3, J_{AB} = 6.5, CH_3CH).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.25; H, 9.45.

Finally, elution with 2.5 l. of 1:1 ether–benzene gave 164 mg. (19% yield) of **4α,8β-dimethyl-4,5,6,7,8,8aα-hexahydro-8α-hydroxy-2(1H)-azulenone (14)** as an oil, which after rechromatography had λ_{max} 236 mμ (ε 13,000) and λ_{max} 2.74, 5.94 and 6.24 μ; n.m.r. spectrum: 3.94(m, 1, O=C—CH=C—), 8.80(d, 3, J_{AB} = 7, CH_3CH) and 9.04(s, 3, CH_3COH) τ; semicarbazone, colorless prisms, m.p. 204–205° dec.

Anal. Calcd. for $C_{13}H_{21}O_2N_3$: C, 62.12; H, 8.42; N, 16.72. Found: C, 61.95; H, 8.60; N, 16.45.

The results from irradiations conducted under various conditions are summarized in Table I. By far the cleanest products were obtained using 45% formic acid as solvent. When an irradiation similar to the one described above was carried out in refluxing 45% acetic acid, elution with 1 l. of 1:3 ether–benzene gave 44 mg. (5% yield) of **4aβ,8α-dimethyl-1,5,6,7,8,8a-hexahydro-4aα-hydroxy-4(4a → 8aα)-*abeo*-2(4aH)-naphthalenone (13),**[33] m.p. 88–90°. Recrystallization from ether–hexane gave fine colorless needles, m.p. 89.5–90.5°, mol. wt. 194; λ_{max} 2.74, 5.82, 5.92, and 6.28 μ; n.m.r. spectrum 2.32(d, 1) and 3.80(d, 1) (J_{AB} = 6, —CH=CH); 7.42(d, 1) and 8.04(d, 1) (J_{AB} = 18, —CH_2—C=O); 8.78(s, 3, CH_3—); and 9.38(d, 3, J_{AB} 6.5, CH_3CH) τ.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.95; H, 9.25.

Infrared Studies.—Spectra were determined on solutions of the epimeric ketones **12** and **13** in carbon disulfide using a Perkin–Elmer model 421 grating spectrophotometer. Ketone **12** had a sharp singlet at 3600 $cm.^{-1}$ and ketone **13** a sharp doublet at 3590 and 3600 $cm.^{-1}$ in addition to the broad intermolecularly bonded hydroxyl band at 3415 $cm.^{-1}$. The relative intensities of the two bands of the doublet for ketone **12** were unchanged with dilution down to 0.1%, at which point the 3415 $cm.^{-1}$ band had disappeared. The relative intensities of the carbonyl stretching bands of the two ketones for various concentrations are listed in Table IV.

TABLE IV

INFRARED DATA OF KETONES 12 AND 13 IN CARBON DISULFIDE AT VARIOUS CONCENTRATIONS

	Ketone 12	Ketone 13
1%		0.68[a]
0.5%	0.37	.25
.25%	.30	
.1%	.28	.07

[a] Ratio of optical densities of the bands at 5.84 and 5.95 μ.

Reactions of 4aα,8α-Dimethyl-1,5,6,7,8,8a-hexahydro-4aβ-hydroxy-4(4a → 8aα)-*abeo*-2(4aH)-naphthalenone (12). A. Hydrogenation.—A solution of 100 mg. of spiro ketone **12** in 10 ml. of absolute ethanol was stirred with 20 mg. of 10% palladium-on-charcoal in an atmosphere of hydrogen at atmospheric pressure. Hydrogen uptake ceased after 1.3 mol. equiv. The catalyst was removed by filtration and the solvent was evaporated under reduced pressure. Chromatography on 3 g. of silica gel gave, on elution with 400 ml. of 1:19 ether–benzene, 96 mg. (95% yield) of a colorless oil, λ_{max} 2.70 and 5.76 μ; semicarbazone, colorless prisms, m.p. 200–201°.

Anal. Calcd. for $C_{13}H_{23}O_2N_3$: C, 61.63; H, 9.25; N, 16.59. Found: C, 62.0; H, 9.25; N, 16.8.

B. Ozonolysis.—The general procedure of Johnson, Rogier and Ackerman[35] was employed. Ozone was bubbled for 70 min. through a solution of 150 mg. of spiro ketone **12** in 36 ml. of ethyl acetate which was cooled with an ice-bath. To the solution were then added 10 ml. of acetic acid, 2.5 ml. of water and 1 ml. of 30% hydrogen peroxide. After standing 20 hr. at room temperature the resulting mixture was evaporated to dryness at reduced pressure. The last traces of acetic acid were removed by co-distillation with 100 ml. of toluene. The resulting residue was taken up in 500 ml. of ether and was extracted thoroughly with saturated sodium bicarbonate solution. The bicarbonate extracts were acidified and extracted three times with 100-ml. portions of ether. The combined ether fractions were dried over 50 ml. of saturated sodium chloride solution and then anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure gave 134 mg. (82% yield) of **1α-carboxy-2α,6α-dimethyl-2-hydroxycyclohexaneacetic acid γ-lactone (16),** m.p. 205–207.5°. Recrystallization from acetone–hexane gave colorless prisms, m.p. 211–212°; λ_{max} 5.62, 5.70 and 5.85 μ.[11]

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.35; H, 7.6.

A solution of 83 mg. of the lactone-acid **16** in 1 ml. of ethanol was added to 0.8 ml. of saturated sodium carbonate solution. The resulting mixture was evaporated to dryness under reduced pressure, and the residue was heated to 205–215° under an atmosphere of nitrogen for 0.5 hr. After being cooled to room temperature the reaction mixture was dissolved in 80 ml. of water and washed with 80 ml. of ether. The aqueous solution was then acidified with 4 ml. of 5% hydrochloric acid and extracted with three 80-ml. portions of ether. The combined ether extracts were dried over saturated sodium chloride solution and anhydrous sodium sulfate. Removal of solvent at reduced pressure gave 96 mg. of a colorless oil, which was chromatographed on 3 g. of silica gel. Elution with 300 ml. of benzene gave 47 mg. (73%

(32) Ultraviolet spectra were determined in absolute ethanol using a Cary model 14 spectrophotometer, and infrared spectra were obtained in 5% methylene chloride solution on a Perkin–Elmer Infracord spectrophotometer. Gas chromatographic separations were effected at 200° using a 5 ft. × 0.25 in. column containing 20% GE-silicone fluid 96 on 60/80 mesh fire brick. Melting points were determined on a micro-hotstage 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. Molecular weights were determined using a Bendix model 12-100 time-of-flight spectrometer. Optical rotations were obtained in chloroform solution. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

(33) The more conventionally derived name 6α,10α-dimethyl-6β-hydroxyspiro[4.5]dec-3-en-2-one fails to indicate the configurational assignment at the spiro fusion (C-5).

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

(35) W. S. Johnson, E. R. Rogier and J. Ackerman, *J. Am. Chem. Soc.*, **78**, 6322 (1956).

yield) of **2,6-dimethyl-Δ^1-cyclohexeneacetic acid (17)**. Final purification by short-path distillation at 122° and 0.1 mm. gave a colorless oil, λ_{max} 5.82 μ and 203 mμ (ϵ 6100), molecular weight 168; n.m.r. spectrum: 6.88(s, 2, $-CH_2C(=O)-$), 8.35(s, 3, $-C(=CCH_3)-$) and 8.98 (d, 3, J_{AB} = 7, CH_3CH) τ.

C. Attempted Acetylation.—Treatment of 55 mg. of spiro ketone **12** with 2 ml. of pyridine and 1 ml. of acetic anhydride overnight at room temperature resulted in total recovery of the starting ketone.

5α,8aα-Dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2(4aH)-naphthalenone (10). A. Preparation.—A solution of 4.00 g. of dienone **9** in 120 ml. of hexane was irradiated as described above for 25 min. The solvent was evaporated under reduced pressure and the resulting partially crystalline residue was chromatographed on 120 g. of silica gel. Elution with 1 l. each of hexane and 1:1 and 3:1 benzene–hexane gave 615 mg. of polymeric material. Further elution with 3 l. of benzene gave 400 mg. (10% yield) of ketone **10**. Final purification by short-path distillation at 0.2 mm. and 90° gave a colorless oil, λ_{max} 236 mμ (ϵ 6100), $\lambda_{max}^{CCl_4}$ 1.677 μ (ϵ 0.36); and λ_{max} 5.92, 6.34 and 12.00 μ; n.m.r. spectrum: 2.62(q, 1) and 4.22(q, 1) (J_{AB} = 5.5, J_{AX} = 0.8, J_{BX} = 1.1); 8.76(d, 3, J_{AB} = 7, CH_3CH-); and 8.82(s, 3, CH_3-) τ; semicarbazone, colorless platelets, m.p. 205–207°.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.7; H, 9.2.

Anal. Calcd. for $C_{13}H_{19}ON_3$: C, 66.92; H, 8.21; N, 18.01. Found: C, 66.55; H, 8.35; N, 17.75.

B. Irradiation.—A solution of 105 mg. of ketone **10** in 13 ml. of 45% acetic acid contained in a quartz flask and stirred with a magnetic stirring bar was irradiated for 5.5 hr. with a Hanovia type 30620 100-watt mercury lamp which was placed approximately 3 in. from the flask. The solution was then diluted with an equal volume of toluene and evaporated to dryness under reduced pressure. Co-distillation with toluene was repeated to remove the last traces of acetic acid. Chromatography of the resulting dark amber oil on 3 g. of silica gel gave, on elution with 400 ml. of 1:1 benzene–hexane, 66 mg. (63% yield) of crystalline 4,8-dimethyl-5,6,7,8-tetrahydro-2-naphthol (**11**).

C. Treatment with 45% Acetic Acid.—A solution of 54 mg. of ketone **10** in 7 ml. of 45% acetic acid was heated under reflux in an atmosphere of nitrogen for 8 hr. in the dark. It was then combined with 100 ml. of toluene, and the resulting mixture was evaporated to dryness under reduced pressure. Chromatography on 1.5 g. of silica gel gave, on elution with 75 ml. of 1:49 ether–benzene, 9 mg. (17% recovery) of starting ketone. Further elution with 150 ml. of 1:9 ether–benzene gave 25 mg. (50% yield) of crystalline spiro ketone **12**. Finally, elution with 125 ml. of 1:4 ether–benzene gave 12 mg. (22% yield) of crystalline spiro ketone **13**.

D. Hydrogenation.—A solution of 91 mg. of ketone **10** in 10 ml. of absolute ethanol was stirred with 30 mg. of 10% palladium-on-charcoal in an atmosphere of hydrogen. Hydrogen up-take ceased with 1.1 mol. equiv. Removal of the catalyst by filtration followed by evaporation of the solvent at reduced pressure gave a colorless oil, λ_{max} 5.84 μ; semicarbazone, colorless needles, m.p. 198–199°.

Anal. Calcd. for $C_{13}H_{21}ON_3$: C, 66.35; H, 9.00; N, 17.86. Found: C, 66.15; H, 8.95; N, 17.65.

Hydrogenation of 4α,8β-Dimethyl-4,5,6,7,8,8aα-hexahydro-8α-hydroxy-2(1H)-azulenone (14).—A solution of 25 mg. of hydroxy ketone **14** in 5 ml. of absolute ethanol was stirred with 10 mg. of 10% palladium-on-charcoal in an atmosphere of hydrogen at atmospheric pressure. A total of 1.1 mol. equiv. of hydrogen was absorbed. Removal of the catalyst by filtration and evaporation of the filtrate under reduced pressure gave 25 mg. of a colorless oil, λ_{max} 2.75 and 5.76 μ.

Androsta-1,4-dien-3-one-17β-ol Acetate (1a).—Following the general procedure of Burn, Kirk and Petrow,[36] a solution of 4.00 g. (12.1 mmoles) of testosterone acetate and 3.16 g. (13.9 mmoles, 1.15 mol. equiv.) of 2,3-dicyano-4,5-dichlorobenzoquinone in 200 ml. of benzene was heated under reflux in an atmosphere of nitrogen for 17 hr. The amber solution was cooled to about 10° and white precipitate was removed by filtration. The filtrate was evaporated to dryness under reduced pressure, and the residue was chromatographed on 120 g. of activity II alumina. Elution with benzene and 1:1 benzene–ether gave 3.92 g. (99% yield) of dienone, m.p. 148–149°. Recrystallization from ether–pentane gave colorless needles, m.p. 150–151.5°, reported[37] 151–152°.

Irradiation of Androsta-1,4-dien-3-one-17β-ol Acetate (1a). A. In Refluxing 45% Acetic Acid.—A solution of 1.50 g. of dienone **1a** in 100 ml. of 45% acetic acid heated under reflux was irradiated for 15 min. as described above, and the resulting residue was chromatographed on 48 g. of silica gel. Elution with 4.5 l. of 1:99 ether–benzene gave 613 mg. (41% yield) of **2,17β-dihydroxy-4-methyl-1,3,5(10)-estratriene 17-acetate (19a)**.[3] Recrystallization from acetone–hexane gave colorless needles, m.p. 208–209°, $[\alpha]^{26}D$ +47° (*c* 0.53), λ_{max} 282 mμ (ϵ 2,200); λ_{max} 2.70, 5.82, 6.22 and 11.54 μ; n.m.r. spectrum: 3.31(m, 1) and 3.43(m, 1) (CH-1 and CH-3), 5.24(m, 1, CH-17), 7.84(s, 3, CH_3-19), 7.96(s, 3, 17-$OCOCH_3$) and 9.18(s, 3, CH_3-18) τ.

Anal. Calcd. for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59. Found: C, 76.95; H, 8.55.

Elution with 3 l. of 1:19 ether–benzene gave 223 mg. (15% recovery) of starting dienone **1a**. Elution with 4.5 l. of 1:9 and 2 l. of 1:3 ether–benzene gave 333 mg. (24% yield) of **1(10 → 5β)-*abeo*-androst-3-en-2-one-10β,17β-diol 17-acetate (18)**, m.p. 217.5–218.5°. Recrystallization from acetone–hexane gave colorless needles, m.p. 218–219°, $[\alpha]^{29}D$ +29° (*c* 0.76), λ_{max} 232 mμ (ϵ 7,300); λ_{max} 2.70, 5.80, 5.85, 5.96 and 6.30 μ; n.m.r. spectrum: 2.22(d, 1) and 3.86(d, 1) (J_{AB} = 6, $CH=CH-C(=O)-$; 5.36(m, 1, CH-17); 7.18(d, 1, J_{AB} = 19, half of $-CH_2C(=O)-$ quartet); 7.95(s, 3, 17-$OCOCH_3$); 9.04(s, 3, CH_3-19); and 9.16(s, 3, CH_3-18) τ.

Anal. Calcd. for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 72.7; H, 8.65.

Finally, elution with 7 l. of 1:1 ether–benzene gave 174 mg. (12% yield) of **9aβ-methyl-19-nor-A-nor-B-homo-10α-androst-3-en-2-on-9aα,17β-diol 17-acetate (3a)**, m.p. 224–227°. Recrystallization from acetone–hexane gave colorless needles, m.p. 228–229°, $[\alpha]^{27.5}D$ + 83° (*c* 0.82), λ_{max} 236 mμ (ϵ 12,800); λ_{max} 2.80, 5.78, 5.90 and 6.22 μ; n.m.r. spectrum: 4.05(m, 1, $O=C-CH=C-$), 5.35(m, 1, CH-17), 7.94(s, 3, 17-$OCOCH_3$), 9.07(s, 3, CH_3-19), 9.16(s, 3, CH_3-18).

Anal. Calcd. for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 72.55; H, 8.75.

B. In 45% Acetic Acid at 20°.—A solution of 1.18 g. of dienone **1a** in 125 ml. of 45% acetic acid was irradiated as described for dienone **9** above for 6 hr. at 20°. The solution was then neutralized with sodium carbonate and extracted three times with 100-ml. portions of ethyl acetate. The combined extracts were dried over saturated sodium chloride and anhydrous sodium sulfate. Removal of the solvent at reduced pressure gave 1.21 g. of an amber oil, which was chromatographed on 36 g. of silica gel. Elution with 3.3 l. of 1:99 ether–benzene gave 233 mg. (21% yield) of **1-methylestradiol 17-acetate (22a)**,[3] m.p. 174–176°. Recrystallization from acetone–hexane gave colorless needle clusters, m.p. 176–177°, $[\alpha]^{27}D$ +127° (*c* 0.56), λ_{max} 283 mμ (ϵ 1,880); λ_{max} 2.78, 5.80, 6.22, 6.30 and 11.52 μ; n.m.r. spectrum: 3.52(m, 2, CH-2 and CH-4), 5.26(m, 1, CH-17), 7.72(s, 3, CH_3-19), 7.94(s, 3, 17-$OCOCH_3$) and 9.12(s, 3, CH_3-18).

Elution with 0.5 l. of 2:98 ether–benzene gave 11 mg. (1%) of phenol **19a**. Elution with 1 l. each of 2:98 and 1:19 ether–benzene gave 93 mg. of non-crystalline materials. Further elution with 1.2 l. of 1:19 ether–benzene gave 74 mg. (6% recovery) of starting dienone **1a**. Elution with 3.6 l. of 1:9 and 1.8 l. of 1:3 ether–benzene gave 313 mg. (27% yield) of spiro ketone **18**. Finally, elution with 4.8 l. of 1:1 ether–benzene gave 339 mg. (29% yield) of hydroxy ketone **3a**.

1(10 → 5β)-*abeo*-androstan-2-one-10β,17β-diol 17-Acetate (20).—A solution of 63 mg. of spiro ketone **18** in 10 ml. of absolute ethanol was stirred with 20 mg. of 10% palladium-on-charcoal in an atmosphere of nitrogen at atmospheric pressure. A total of 1.1 mol. equiv. of hydrogen was absorbed. Removal of the catalyst by filtration and evaporation of the solvent at reduced pressure gave 64 mg. of colorless needles, m.p. 175–181°. Recrystallization from acetone–hexane gave long colorless needles, m.p. 185–186°, $[\alpha]^{29}D$ +32° (*c* 0.76), λ_{max} 2.72 and 5.74 μ.

Anal. Calcd. for $C_{21}H_{32}O_4$: C, 72.38; H, 9.26. Found: C, 72.35; H, 9.2.

9aβ-Methyl-19-nor-A-nor-B-homo-10α-androstan-2-one-9aα,17β-diol 17-Acetate (21).—A solution of 75 mg. of hydroxy ketone **3a** in 10 ml. of absolute ethanol was stirred with 20 mg. of 10% palladium-on-charcoal in an atmosphere of hydrogen at atmospheric pressure. Hydrogen uptake ceased with 1.1 mol. equiv. Removal of catalyst by filtration and evaporation of the solvent under reduced pressure gave 75 mg. of colorless blades, m.p. 199–200°. Recrystallization from acetone–hexane gave fine colorless prisms, m.p. 203–204° with conversion to long colorless needles prior to melting, λ_{max} 2.74 and 5.75 μ, $[\alpha]^{29}D$ +77° (*c* 0.56).

Anal. Calcd. for $C_{21}H_{32}O_4$: C, 72.38; H, 9.26. Found: C, 72.5; H, 9.2.

2,17β-Dihydroxy-4-methyl-1,3,5(10)-estratriene Diacetate (19b).—Acetylation of 152 mg. of the phenol **19a** with a 2:1 mixture of pyridine–acetic anhydride overnight at room temperature

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

(37) H. H. Inhoffen, G. Zühlsdorff and Huang-Minlon, *Chem. Ber.*, **73**, 451 (1940).

gave 179 mg. of colorless needles, m.p. 144–146°. Recrystallization from acetone–hexane gave colorless prisms, m.p. 142–143°, $[\alpha]^{28}D$ +53° (*c* 0.72); λ_{max} 5.68, 5.78, 6.24 and 11.04 μ; λ_{max} 267 mμ (ϵ 800); n.m.r. spectrum: 3.17(m, 1, CH-1), 3.31(m, 1, CH-3), 5.32(m, 1, CH-17), 7.78(s, 3), 7.83(s, 3), 8.00(s, 3), and 9.22(s, 3, CH_3-18) τ.

Anal. Calcd. for $C_{23}H_{30}O_4$: C, 74.56; H, 8.16. Found: C, 74.8; H, 8.25.

2,17β-Dihydroxy-4-methyl-1,3,5(10)-estratriene (19c).—A solution of 59 mg. of diacetate **19b** and 2 ml. of 40% sodium hydroxide in 10 ml. of methanol and 1 ml. of water was heated under reflux in an atmosphere of nitrogen for 1 hr. The solution was concentrated on a rotary evaporator, acidified with concentrated hydrochloric acid, and extracted with three 50-ml. portions of ethyl acetate. The organic extracts were combined, washed with 50 ml. of saturated sodium bicarbonate solution and 50 ml. of saturated sodium chloride solution, then dried over anhydrous sodium sulfate. Removal of solvent at reduced pressure gave 47 mg. of needles. Recrystallization from acetonitrile gave colorless needles, m.p. 256–258°, reported[21] m.p. 257–259°; λ_{max}^{KBr} 3.05, 6.30, 11.78 μ; λ_{max} 281–286 mμ (ϵ 2100). The infrared and ultraviolet spectra were identical with those of an authentic sample.[21]

1-Methylestradiol Diacetate (22b).—Treatment of a portion of the 1-methylestradiol 17-acetate described above with a 2:1 mixture of pyridine–acetic anhydride overnight at room temperature gave, after recrystallization from methanol, colorless blades, m.p. 178–180°, $[\alpha]^{26}D$ +112° (*c* 0.78), λ_{max} 5.72 and 5.82 μ, and λ_{max} 269 (ϵ 580); reported[20]: 178–180°, $[\alpha]^{20}D$ 111°, λ_{max} 268 (ϵ 340).

For the preparation of an authentic sample, 200 mg. of androsta-1,4-dien-3-one-17β-ol acetate (**1a**) was treated with 5 ml. of 50% sulfuric acid at 100° for 30 min. according to the general procedure of Dreiding, Pummer and Tomasewski.[38] The reaction mixture was then neutralized with saturated sodium bicarbonate solution and extracted with four 50-ml. portions of ethyl acetate. The combined extracts were dried over saturated sodium chloride solution and anhydrous sodium sulfate and evaporated to dryness under reduced pressure to give 223 mg. of an amber oil. Acetylation by the pyridine–acetic anhydride procedure gave 242 mg. of a semicrystalline amber solid, which was chromatographed on 9 g. of silica gel. Elution with 400 ml. of 1:99 ether–benzene gave 93 mg. of a colorless oil, which crystallized when seeded with a specimen of the above diacetate. Recrystallization from ether–hexane and then methanol gave colorless blades, m.p. 178–180°. The melting point was unchanged on admixture with the material described above.

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(38) A. S. Dreiding, W. J. Pummer and A. J. Tomasewski, *J. Am. Chem. Soc.*, **75**, 3159 (1953).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION AND REFINERY CHEMICALS DEPARTMENT, ORGANIC CHEMICALS DIVISION, AMERICAN CYANAMID CO., STAMFORD, CONN.]

Some Aspects of the Chemistry of Cyclopolyphosphines

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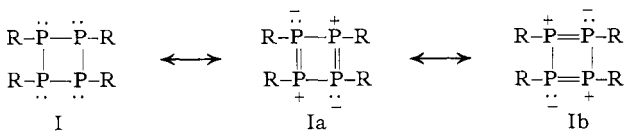
Several new cyclotetraphosphines, $(RP)_4$, have been synthesized by the reduction of primary dihalophosphines with magnesium, the dehydration of primary phosphine oxides, and by methods already reported in the literature. The dehydration reaction constitutes the first example of the formation of a P–P bond by loss of water. The vapor phase ultraviolet spectra of alkylcyclotetraphosphines have been found to be characteristic of the ring and different from that of cyclopentaphosphines, $(RP)_5$. Evidence is presented for the existence of two tetraphenylcyclotetraphosphines, $(C_6H_5P)_4$, and for the nonexistence of $(C_6H_5P)_2$.

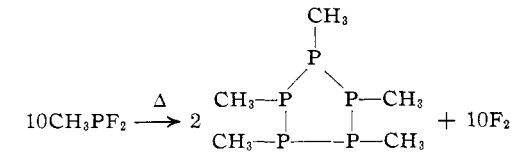
As has been suggested by Mahler and Burg,[1] cyclotetraphosphines (tetraphosphetanes) might well be expected to exhibit electron delocalization and, perhaps, aromatic character through the contribution of resonance structures such as Ia and Ib. Presumably, these



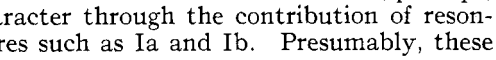
I Ia Ib

structures would involve pπ–dπ bonding and would result in significant departures from normal phosphine behavior. This should be apparent both in the physical and chemical properties of cyclopolyphosphines. Because of the obviously interesting properties of these compounds, we have initiated a study of this area, the results of which are reported here.

Alkylcyclopolyphosphines.—A few alkylcyclopolyphosphines have been reported in the literature. Pentamethylcyclopentaphosphine has been synthesized by heating methyldifluorophosphine.[2] Issleib and co-



workers have prepared tetraethylcyclotetraphosphine[3a] and tetracyclohexylcyclotetraphosphine[3b] by reaction of the alkylphosphine and alkyldichlorophosphine in refluxing toluene.



Burg has made the trifluoromethyl tetramer and pentamer by reduction of trifluoromethyldiiodophosphine with mercury.[1] The former compound has also been prepared in low yield by the reaction of trifluoromethyl radicals with elemental phosphorus.[4]

Tetra-*n*-butylcyclotetraphosphine has been prepared by Rauhut and Semsel of this Laboratory[5] by the reaction of *n*-butylmagnesium bromide, *n*-butyl bromide, and phosphorus.

Synthetic Methods.—A summary of our synthetic routes to alkylcyclopolyphosphines is given in Fig. 1 and in Table I. It will be noted that the preparations involving the dehydration of a phosphine oxide and the reduction of a primary dichlorophosphine with magnesium are new as are several of the compounds prepared. A detailed discussion of the above synthetic methods follows.

The reaction of a primary phosphine with the corresponding dihalophosphine is the simplest method of preparing cyclopolyphosphines.

The dihalophosphines may best be obtained by chlorination of the primary phosphine with phosgene[6] or alter-

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