CHART I

Now we direct attention to entry 4 of Table I showing the efficiency undiminished by 0.1 M naphthalene. This is remarkable in that the energy of 4,4-diphenylcyclohexadienone triplet is 68.8 kcal./mole, 8 kcal./mole higher than for naphthalene triplet[4] (61 kcal./mole). Presently we restrict comment to a note of caution that absence of quenching by triplet acceptors is inconclusive evidence against a triplet mechanism; the triplet intermediate may react rapidly enough to preclude quenching.[5]

Finally, we provide evidence that the reacting triplet is n–π* rather than π–π*. The phosphorescence (i.e., triplet) emission spectrum of 4,4-diphenylcyclohexadienone in EPA at 77°K. is accompanied in Fig. 1 by that of benzophenone for comparison. (A) The vibrational pattern is characteristic of n–π* emission[6]; band separation averages 1647 cm.$^{-1}$ (ground state C=O or C=C stretching). (B) The dienone triplet energy (68.8 kcal./mole, 415-mμ O–O band) approximates that of benzophenone triplet (68.8 kcal./mole, 415-mμ O–O band), which has been assigned[4b,6] the n–π* structure. (The full argument depends on the singlet system energies. n–π* O–O 392 mμ, 73 kcal./mole vs. 375 mμ, 76 kcal./mole for $(C_6H_5)_2$C=O; π–π* 220 mμ, 129 kcal./mole, plus benzenoid absorption, vs. 248 mμ, 115 kcal./mole for $(C_6H_5)_2$C=O.) (C) The 77°K. lifetime was determined as ca. 0.5 msec., consonant with an n–π* assignment[7]; π–π* lifetimes are generally much longer.

Our conclusion that the lowest energy triplet is n–π* differs with Richards' suggestion[3] that the santonin rearrangement proceeds via a π–π* triplet.

(4) The role of triplets in a number of reactions has been nicely demonstrated: (a) G. S. Hammond, M. J. Turro, and P. A. Leermakers, J. Phys. Chem., 66, 1148 (1962); (b) G. S. Hammond and P. A. Leermakers, J. Am. Chem. Soc., 84, 207 (1962).

(5) Quenching via naphthalene triplet is especially inefficient. The 310–360-mμ filter used with naphthalene and dienone allowed 30 (±10) % of the light to be absorbed by naphthalene; here quantum yields of 0.29 resulted. This remarkable "uphill" sensitization may be due to slow naphthalene triplet to ground state degradation compared with the 8 kcal./mole uphill sensitization and rapid subsequent rearrangement of dienone. Alternatively, a nonvertical energy transfer as considered recently [G. S. Hammond and J. Saltiel, ibid., 85, 2515 (1963)] is possible. A most interesting rationale is singlet–triplet sensitization (intersystem crossing of an excited singlet naphthalene–ground state dienone collisional pair).

(6) M. Kasha, Radiation Res. Suppl., 2, 265 (1960).

(7) Cf. 0.85 msec. for MeCOEt and 1.26 msec. for Et$_2$CO vs. 0.95 × 10³ msec. for MeCO(β-naphthyl) reported by D. S. McClure [J. Chem. Phys., 17, 905 (1949)]; of these only the last is π–π* (cf. ref. 4b) while the first three are certainly n–π*. Benzophenone triplet lifetime is similarly short. The reliability of this generalization will be discussed in our full paper along with full referencing.

Finally, an n–π* intermediate being demonstrated, we comment that as for n–π* singlets, n–π* triplets of such unsaturated ketones should have an electron-rich π-system and more electron-rich β-carbons than in the ground state. That this rationalizes observed dienone photochemistry has already been indicated.[1,2] The molecular orbitals are depicted in Fig. 2. We note that n–π* excitation leads to an augmented 3,5-bond order, augmented more than for π–π* promotion.[8] This accords with the step postulated for this reaction wherein a 3,5-bond is formed by excited state III followed by electron demotion and cyclopropylcarbinyl carbonium rearrangement by zwitterion VI. Our earlier mechanism thus requires refinement by addition of two intersystem (singlet–triplet) crossing steps.

(8) The MO ordering and this conclusion depend on oxygen Coulomb integral choice dictated by the necessity of n–π* excitation being lowest as experimentally found. Discussion of this and other parameter choices in the ordinary and self-consistent calculations is deferred.

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The Structure and Stereochemistry of α-Caryophyllene Alcohol

Sir:

α-Caryophyllene alcohol is obtained along with clovene and caryolan-1-ol by sulfuric acid treatment of crude caryophyllene.[1] Added interest in α-alcohol arose from the finding that photolysis of its nitrite ester was accompanied by epimerization of the C–O bond.[2] The present work establishes the structure and stereochemistry of α-alcohol as 6[3] and shows that, contrary to reports in the literature,[1b] caryophyllene is not the progenitor. A novel feature was the use of nitrite photolysis (Barton reaction[4]) to introduce remote ketonic groups for degradation.

Asahina and Tsukamoto found that α-alcohol $(C_{15}H_{26}O$, m.p. 117°, [α]D 0°) was saturated, tricyclic, and contained an OH group.[1a] Recently we[2] showed the OH was secondary by oxidation to a 5-membered ketone (ν 1742 cm.$^{-1}$),[5] which has no enolizable hydrogens and which was converted to α-alcohol and to an epimer (epi-α-alcohol) by suitable reduction. In the n.m.r. spectra of various esters of α-alcohol and

(1) (a) Y. Asahina and T. Tsukamoto, J. Pharm. Soc. Japan, 434, 463 (1922); (b) J. Bell and G. G. Henderson, J. Chem. Soc., 1971 (1930); (c) D. H. R. Barton, T. Brunn, and A. S. Lindsey, ibid., 2210 (1952), and references cited there.

(2) A. Nickon, J. R. Mahajan, and F. J. McGuire, J. Org. Chem., 26, 3617 (1961).

(3) Workers at Glasgow University have independently arrived at the same structure by X-ray crystallography, and simultaneous publication was arranged [K. W. Gemmell, W. Parker, J. S. Roberts, and G. A. Sim, J. Am. Chem. Soc., 86, 1438 (1964)].

(4) (a) D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. M. Pechet, ibid., 82, 2640 (1960); (b) for a review see A. L. Nussbaum and C. H. Robinson, Tetrahedron, 17, 35 (1962).

(5) Unless stated otherwise, infrared spectra were taken in carbon tetrachloride, and n.m.r. spectra (60 Mc.) in deuteriochloroform, with peak positions (δ) expressed in p.p.m. downfield from internal tetramethylsilane.

1

2

3a, R = H
b, R = CH₃

4

5

6, R = OH; R' = H
7, R = H; R' = OH
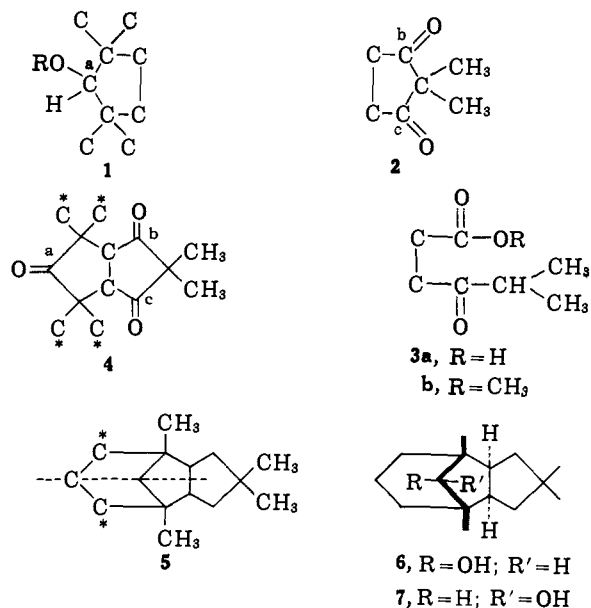
epi-α-alcohol (e.g., benzoate, 3,5-dinitrobenzoate, nitrite) the signal for the proton attached to the oxygenated carbon (carbon a) is a singlet. The adjacent centers are therefore fully substituted (partial structure 1, R = ester unit).

Previous work showed that α-alcohol nitrite and epi-α-alcohol nitrite are photorearranged to the same oximino alcohol, which was hydrolyzed to a keto alcohol (ν 1733 cm.$^{-1}$).[2,6] Oxidation with chromium trioxide now gave the related diketone ($C_{15}H_{22}O_2$, m.p. 98.5–99°, overlapping carbonyl bands at 1745 cm.$^{-1}$), which proved stable to hot alcoholic alkali and thereby excluded a 1,3-relationship of the two carbonyl groups. From the known structural requirements of the Barton reaction[4b] the second ketone group (carbonyl b) is in a 1,4-relationship to carbonyl a and the infrared data indicate that b is also in a 5-membered ring. To introduce a third function (carbonyl c) the keto alcohol was converted to its nitrite ($C_{15}H_{23}O_3N$, m.p. 73.5–74°), and photoisomerized in benzene. The derived keto oximino alcohol was hydrolyzed with acid to a diketo alcohol ($C_{15}H_{22}O_3$, ν 1751, 1706 cm.$^{-1}$ in CS_2, m.p. 149–149.5°) which was oxidized to the corresponding triketone ($C_{15}H_{20}O_3$, m.p. 132°, ν 1754, 1713 cm.$^{-1}$).

The following evidence establishes that carbonyls b and c are in the same ring and separated from each other by one carbon that carries two methyl groups (part structure 2). Alkaline cleavage of the diketo alcohol gave a noncrystalline hydroxy keto acid, which was oxidized (CrO₃) to the related diketo acid ($C_{15}H_{22}O_4$, m.p. 129–130°, ν in CS_2 3400–3030, 1748, 1701 cm.$^{-1}$; methyl ester, b.p. 145–155° (0.1 mm.), ν in CS_2 1748, 1730, 1704 cm.$^{-1}$). This diketo acid (part structure 3a) was also obtained by alkaline cleavage of the triketone. The methyl ester (3b) contains three enolizable hydrogens (2.49 D incorporated by treatment with sodium methoxide in methanol-d) and its n.m.r. spectrum indicated an isopropyl ketone unit (a six-proton doublet at δ 1.23 assigned to the gem-dimethyl group and a one-proton septet at δ 2.76

(6) In the photorearrangement it is the α-epimer that undergoes configurational change so that the keto alcohol has its OH in the epi configuration (ref. 2).

assigned to the adjacent methine hydrogen; $J \cong 7.5$ c.p.s.). The facts require that the fragments 1 and 2 have two atoms in common and .uniquely define their mode of attachment as that illustrated for the triketone by the C_{14} fragment 4.

The n.m.r. of all the tricyclic compounds reveal the presence of four quaternary methyl groups. In α-alcohol and epi-α-alcohol (and their esters), and in the ketone, the diketo alcohol, and the triketone two of the methyl groups are equivalent. For example, the methyl signals in α-alcohol appear as singlets at δ 0.87 (6H), 0.90 (3H), and 1.05 (3H). It follows that the 15th carbon as well as two of the starred carbons of skeleton 4 must be part of the third ring, which itself must be symmetrically disposed (as in 5) to account for the equivalence of the bridgehead methyl groups.[7]

The two intramolecular photorearrangements that functionalize centers b and c are possible only if the five-membered rings have a cis fusion and have the junction hydrogens projecting away from the hydroxylated carbon bridge (6 and 7). The configuration of the OH group in α-alcohol (6) and in epi-α-alcohol (7) follow, from earlier findings.[2]

When commercial caryophyllene was treated in ether with D_2SO_4 the derived α-alcohol contained 2.73 D. The absorption patterns in the 1395–1360 cm.$^{-1}$ region of the infrared spectra (taken in CCl_4 or KBr) and in the δ 0.8–1.1 region of the n.m.r. spectra are identical in detail with those regions in the spectra of nondeuterated α-alcohol. These results establish the absence of the structural unit $-CH_2D$, which would have formed had α-alcohol arisen from caryophyllene. Humulene[8] is the only other constituent present in sufficient quantity to account for the α-alcohol produced.[9,10] Mechanistic studies of the cyclization and of various aspects of the nitrite photolyses are in progress.

(7) The equivalence of the two ring-junction hydrogens (singlet at δ 3.06) is also evident in the n.m.r. of the diketo alcohol.

(8) S. Dev, Tetrahedron, 9, 1 (1960); V. Benesova, V. Herout, and F. Sorm, Collection Czech. Chem. Commun., 26, 1832 (1961); M. D. Sutherland and O. J. Waters, Australian J. Chem., 14, 596 (1961), and references cited there.

(9) The commercial caryophyllene ordinarily contained ca. 10–15% humulene and traces of several unknown components (total <5%). Typical yields of α-alcohol were 3–5%.

(10) On acid hydration of humulene S. Dev [Current Sci. (India), 20, 296 (1951)] obtained an alcohol (m.p. 116°) which he suggested might be α-caryophyllene alcohol. Dr. Dev kindly sent us his compound and we confirmed its identity with α-alcohol by melting point, mixture melting point, and infrared spectral comparisons.

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The Structure of α-Caryophyllene Alcohol

Sir:

Discordant reports concerning α-caryophyllene alcohol[1] prompted us to reinvestigate the source and struc-

(1) Y. Asahina and T. Tsukamoto, J. Pharm. Soc. Japan, 484, 463 (1922); E. Deussen, J. prakt. Chem., 114, 121 (1926); J. Bell and G. G. Henderson, J. Chem. Soc., 1971 (1930); L. Ruzicka and D. T. Gibson, Helv. Chim. Acta, 14, 573 (1931); D. H. R. Barton, T. Bruun, and A. S. Lindsey, J. Chem. Soc., 2210 (1952); D. H. R. Barton and A. Nickon, ibid., 4665 (1954).