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THE PHOTOCHEMISTRY OF FENCHONE AND CAMPHENILONE IN METHANOL

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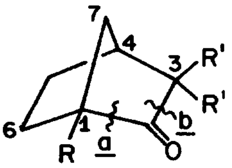
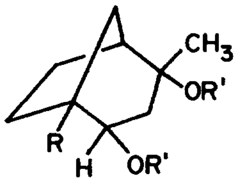
Yates and Fallis (1) have recently shown that the crystalline product formed on irradiation of fenchone (I) in aqueous ethanolic solution with sunlight (2) has structure II. An investigation of the products formed on irradiation of fenchone in methanol has now led to the elucidation of the origin of II and the discovery of a further example of the rare photoconversion of a five-membered cyclic ketone to a cyclic acetal (3,4).



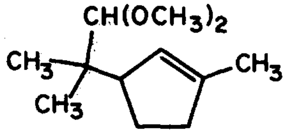
I, R = R' = CH_3
VIII, R = R' = H
XIV, R = H, R' = CH_3



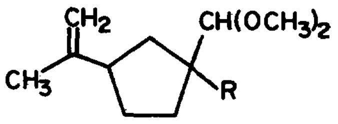
II, R = CH_3, R' = H
V, R = R' = CH_3
XVI, R = H, R' = CH_3

Irradiation of a 5% solution of (+)-fenchone in methanol containing 0.005% p-toluenesulfonic acid (5) in a quartz flask with a Hanovia 450-w. medium-pressure mercury arc lamp for 2-3 weeks gave two major products, III and IV, and two minor products, V and VI, salient features of whose p.m.r. spectra are given in Table 1.

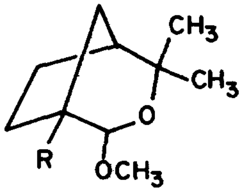
Compounds III and IV are dimethyl acetals of unsaturated aldehydes of a type well known to be formed on photolysis of cyclic ketones (6). They arise by cleavage of bonds a and b, respectively, in I; that aldehydes derived by cleavage of both of these bonds should be formed is in accord



III

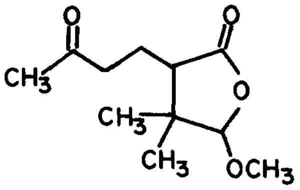


IV, R = CH_3;
XV, R = H

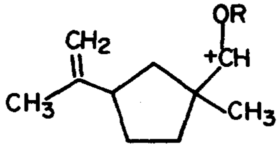


VI, R = CH_3;
XVII, R = H

with expectation in that C-1 and C-3 have the same degree of alkyl substitution (7). The position of the double bond in III was established by ozonolysis, which gave rise to the γ-lactone VII, as shown by a band at 5.65 μ in its infrared spectrum; the alternative formulation of the aldehyde arising by cleavage of bond a, in which the aldehyde hydrogen is transferred from the C-6 rather than the C-7 position in I, is excluded since this compound would give a δ-lactone on ozonolysis. The exclusive hydrogen abstraction from the C-7 position is in exact analogy with the case of norcamphor (VIII) (4,8,9).



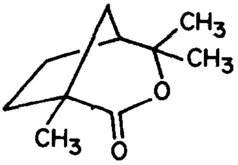
VII



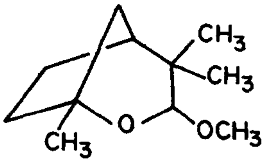
IX, R = CH_3;
X, R = H

Compound V was formed in low yield under the above conditions. However, on more prolonged irradiation or in more strongly acidic solution the yield of V increased while that of IV fell. This clearly suggested that V was formed from IV in an acid-catalyzed reaction, which was confirmed by the conversion of IV to V in acid medium in the dark. This reaction must proceed via formation of the cation IX and has ample precedent (10). It suggests very strongly that the diol II formed from fenchone in aqueous medium (1) arises from the cation X, which in turn is derived from the aldehyde corresponding to IV.

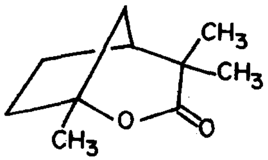
The structural assignment VI was confirmed by the independent synthesis of this compound by reduction of the lactone XI (11) with diisobutyl aluminum hydride to the corresponding hemiacetal (12) and treatment of this with methanol and p-toluenesulfonic acid. This product was a mixture of two compounds epimeric at the acetal carbon atom, as shown by two signals in its p.m.r. spectrum at δ 3.96 and 4.14 (ratio 2:1). The photochemical product VI from I had a single signal in this region at δ 3.96; on treatment with boiling acidic methanol it was converted to the mixture of epimers. It is significant that while VI arises by cleavage of bond b in I, no analogous product XII was formed that resulted from cleavage of bond a; this conclusion is based on comparison of the photolysis products with an authentic sample of XII, prepared by reduction of lactone XIII (11) followed by treatment with methanolic hydrogen chloride. It is suggested that VI is formed because of the disability attending the competing formation of unsaturated aldehyde in this case (4); the abstraction of a proton from C-4 is sterically prohibited, forcing the unfavorable abstraction from a methyl group. In the case of cleavage of bond a, a facile pathway for unsaturated aldehyde formation is available via abstraction of a C-7 hydrogen atom and the formation of XII is not competitive. This may be contrasted in turn with the case of camphor where aldehyde formation must involve abstraction of a C-6 rather than a C-7 hydrogen atom, and formation of products related to XII is observed (13).



XI



XII



XIII

Related observations have been made when camphenilone (XIV) is irradiated under similar conditions. Three products, XV, XVI and XVII (cf. Table 1) were observed, analogous to IV, V, and VI, respectively. No product analogous to III was detected; cleavage of bond b in XIV occurs to the exclusion of cleavage of bond a because of the higher degree of alkyl substitution at C-3 versus C-1 (7).

Table 1. P. M. R. SPECTRA OF PHOTOLYSIS PRODUCTS[a]

Compound	δ^{CCl_4}
III	0.74 and 0.76 (6), 1.72 (br s, 3), 3.42 (6), 3.82 (1), 5.23 (m, 1)
IV	0.96 (3), 1.69 (br s, 3), 3.42 (6), 3.85 (1), 4.60 (br s, 2)
V	1.07 (3), 1.23 (3), 2.86 (m, 1), 3.05 (3), 3.26 (3), 3.42 (m, 1)
VI	0.86 (6), 1.26 (3), 3.35 (3), 3.96 (1)
XV	1.72 (br s, 3), 3.23 (6), 4.03 (d, J 7 Hz, 1), 4.65 (m, 2)
XVI	1.24 (3), 3.04 (3), 3.22 (s + m, 4)
XVII	1.05 (3), 1.33 (3), 3.27 (3), 4.18 (br s, 1)

[a] Signals are singlets unless otherwise specified.

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