Photochemical Isomerization and Radical Fragmentation of 10-Hydroxymethyl-$\Delta^{1,9}$-2-octalone[1a]

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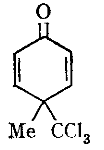
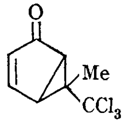
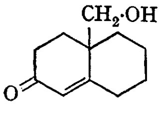
PREVIOUSLY,[1b] we have found that photochemical fragmentation of dienone (I) to give *p*-cresol was in competition with that isomerization which gave the lumi-product (II). Detailed kinetic studies showed that both processes originated from the same excited state of (I), identified as the $^3(n, \pi^*)$ state, and that the chemistry of this excited state is in accord with a diradical-like structure.[1] The use of photochemical fragmentation to probe the structure of excited states of ketones has now been demonstrated with 10-hydroxymethyl-$\Delta^{1,9}$-2-octalone, (III),[2] which reveals further the nature of the reactive excited state(s) of cyclohexenone derivatives.[3]



(I)



(II)



(III)

The photolysis of (III) was studied in dilute solution in chloroform, toluene, cumene, benzene, and t-butyl alcohol using a Hanovia 450 w high-pressure mercury lamp with Pyrex filters. Corex filters were used in some chloroform runs. The product mixture was quite rich in the first four solvents, as indicated by gas chromatographic analysis.† Two of the components were readily identified as the $\Delta^{1,9}$-2-octalone (IV) and the $\Delta^{9,10}$-2-octalone (V) by direct comparison‡ with independently prepared material.[4] In addition, the component corresponding to (IV) was isolated from the photochemical reaction mixture by preparative g.l.c. and its spectra were identical with the known compound. A minor product derived from further isomerization of (V) was recently shown to have structure (VI).[5] Compound (VII) was prepared from (IV) by the reaction with sodium hydride in tetrahydrofuran using the procedure of Büchi, Eschenmoser, *et al.*,[6] and was also shown to be present in the chloroform photolysis mixture.‡ The structure of (VII) was indicated by its method of synthesis, an i.r. carbonyl band at 1710 cm.$^{-1}$, a single vinyl hydrogen (5·4 p.p.m.) and other consistent n.m.r. resonances, and an end absorption in the ultraviolet.

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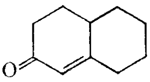
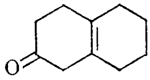
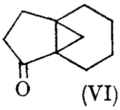
† F & M Model 810 Gas Chromatograph with flame ionization detector on a 6-ft. SE-30 column, 15% on Chromosorb W A/W, DMCS treated, at 150°. Benzil was used as an internal standard for the results given in the Table.

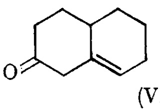
‡ Co-injection on two different columns.

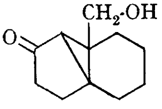
In contrast with the complex reaction mixtures in the other solvents, in t-butyl alcohol only one major product was observed (g.l.c.). After photolysis for more than 500 hr., there was still 50% of unreacted starting material, while comparable (and competitive) irradiations in the other solvents were usually complete in 10 hr. The product was isolated by preparative g.l.c. and shown to be the lumi-product (VIII). Infrared bands at 3550, 3400, and 1710 cm.$^{-1}$ indicated the presence of hydroxyl and carbonyl groups, with the stretching frequency of the latter as expected for a bicyclo[3,1,0]hexan-2-one.[7] The u.v. spectrum showed only end absorption with a shoulder at 223 mμ. The n.m.r. spectrum contained no vinyl hydrogen resonance, a broadened signal at 3·67 p.p.m. (2H) for the methylene protons of the hydroxymethylene group [same position as in (III)], and complex resonances between 1·0—2·7 p.p.m. The mass spectrum showed the molecular ion at m/e 180 and major fragments at m/e 149 and 150 [as also seen in (III)] indicating loss of the elements of CH_2O and CH_2OH, almost surely from the hydroxymethylene group.


(IV)


(V)

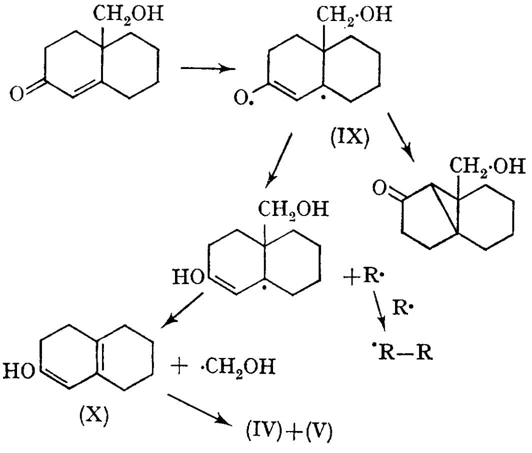

(VI)


(VII)


(VIII)

The Table gives the yields of the various products formed in each solvent in representative runs. Hexachloroethane was an additional product in chloroform (isolation and g.l.c. comparison‡) and bibenzyl was formed in toluene.‡ There is a major unidentified product (6·5%) in chloroform, and a component in toluene produced only on extended irradiation. Photolysis of (VIII) was studied in benzene, chloroform, and toluene. Compounds (IV–VII) were not formed in any solvent; bibenzyl and hexachloroethane were produced in toluene and chloroform, respectively, and a new unidentified product in toluene corresponded to the component formed from (III). Variable amounts of undistillable materials were formed in all except the t-butyl alcohol runs.

The results above indicate a competition between rearrangement to form the lumi-ketone (VIII) and fragmentation to unsaturated ketones with formal loss of the elements of CH_2O. Mechanistically, the reactive excited state behaves as expected for a diradical species, (IX). As shown in the Scheme, (IX) can abstract hydrogen from a suitable solvent donor (chloroform, toluene, cumene), followed by fragmentation to $\cdot CH_2OH$ and the enol (X). Formation of solvent products of type R–R argues strongly for this formulation. t-Butyl alcohol is not reactive toward hydrogen abstraction, hence in this solvent the competitive rearrangement pathway is dominant, as seen in analogous rearrangements.[8] The benzene results are puzzling, as hydrogen abstraction is surely unimportant from this solvent.[1b] Perhaps the starting material (III) or the lumi-ketone (VIII) serves as the hydrogen source in this case.



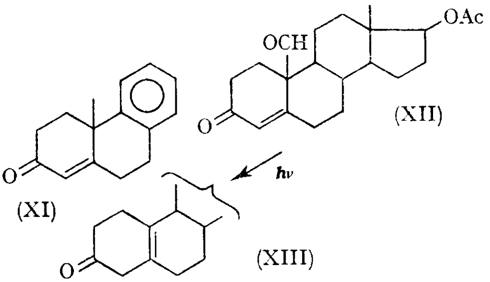
The reactions reported here are mechanistically related to the competition between pinacol

TABLE

Products† *from photolysis of* 10-*hydroxymethyl*-Δ^{1,9}-2-*octalone* (III)

Solvent	Time (hr.)	Yields (%) (III)	(IV)	(V)	(VI)	(VII)	(VIII)
$CHCl_3$	4	26	22	2·3	2·5	6·3	3·4
Toluene	10	17	—	8·7	1·3	—	13
Cumene	10	25	—	9·0	1·9	—	7·8
Benzene	10	23	—	10	1·3	—	16
Bu^{t}OH	300	25	—	—	—	—	45

formation and isomerization to the lumi-ketone reported for the enone (XI) by Zimmerman, *et al.*[8c] In both systems (III) and (XI), the results seem best understood on the basis of a competition between hydrogen abstraction and rearrangement by a diradical-like excited state. In the case of (XI), the excited state has been clearly established to be a triplet state, probably (but not necessarily) with an n,π^* configuration.[8c] The possibility that more than one excited state may be involved in these reactions cannot be rigorously excluded on the basis of the available evidence presented in this or the earlier study.[8c]



(XI) (XII) (XIII)

Finally, the fragmentation reaction reported here is formally analogous to the photoconversion of (XII) into (XIII) recently reported by Jeger and his co-workers.[9] In the case of (XII), however, the fragmenting group (CH=O) is part of the chromophore being excited, which is not the case with the CH_2OH group in (III). Thus, the fragmentation of (XII) may proceed by a totally different mechanism from that of (III). Indeed, decarbonylation of other 10-formyl steroid derivatives is a ready process in the absence of an additional carbonyl group when the formyl group is attached to a saturated backbone as well as in the presence of a $\beta\gamma$ carbon–carbon double bond.[10] The yield of the fragmentation product (XIII) (15%) is also low in comparison with that of other products (55%) retaining the formyl group.

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[1] (a) Previous Paper (Part XI) in this series on the photochemistry of unsaturated ketones in solution, I. S. Krull and D. I. Schuster, *Tetrahedron Letters*, 1967, in the press. (b) D. J. Patel and D. I. Schuster, *J. Amer. Chem. Soc.*, 1967, **89**, 184.

[2] Prepared by modifications of the procedures of L. S. Minckler, A. S. Hussey, and R. H. Baker, *J. Amer. Chem. Soc.*, 1956, **78**, 1009; and G. Stork, P. Rosen, N. Goldman, R. V. Coombs, and J. Tsuji, *ibid.*, 1965, **87**, 275. The systematic nomenclature for this compound would be 2,3,4,4a,5,6,7,8-octahydro-4a-hydroxymethylnaphthalen-2-one.

[3] For a recent discussion with pertinent references, see P. J. Kropp in "Organic Photochemistry", Volume 1, ed. O.L. Chapman, Marcel Dekker, New York, 1967.

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[10] J. Hill, J. Iriarte, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 1966, **49**, 292.