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PHOTOCHEMICAL, ACID, AND BASE CATALYZED REARRANGEMENT OF 5,10-DIMETHYL-5-HYDROXY-$\Delta^{1,9}$-2-OCTALONE*

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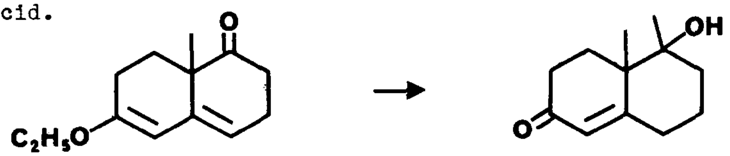
A recent communication by Schuster and Brizzolara (1) prompts us to report our results on the investigation of the photochemical rearrangement of 5,10-dimethyl-5-hydroxy-$\Delta^{1,9}$-2-octalone (1). In studying the photochemistry of compound 1, it was hoped that the presence of a hydroxyl group in an appropriate position would alter the course of the normal enone rearrangement and perhaps yield information as to the type of intermediate involved in these reactions.

The starting hydroxy-octalone (1) was synthesized in good yield by the addition of methyllithium to keto-enol ether 2 (2) followed by mild acid hydrolysis with oxalic acid.



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The pure hydroxy-octalone (1), mp 100-101°, mass peak 194, gave a good C,H analysis. Its infrared spectrum ($CHCl_3$) showed characteristic bands at 3615, 3475, 1660 and 1615 cm^{-1}. The nmr spectrum ($CDCl_3$) showed characteristic peaks at τ 8.77 (3H, singlet), 8.67 (3H, singlet) and 4.23 ppm (1H, singlet). The ultraviolet spectrum indicated one main absorption band: $\lambda_{max.}^{EtOH}$: 243 mμ (ε: 14,618).

The irradiation for 12 hr of compound 1 (500 mg) in dry t-butyl

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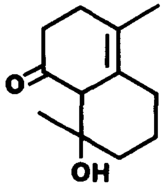
* This work was taken in part from the M.Sc. thesis submitted by J. Gauthier in March 1967.

alcohol (650 ml) using a Rayonet Photochemical Reactor (2537Å light) yielded, as shown by thin-layer chromatography (tlc), a complex mixture containing three main components. (The irradiation was carried out until the 1660 band in the infrared spectrum disappeared.)

After evaporation of the solvent *in vacuo*, the residue was taken up in ether and filtered through a short silica gel column which removed most of the tarry (possibly polymeric) material. The pale yellow oil thus obtained (*ca.* 50% of the product) was chromatographed on preparative tlc plates and yielded compounds 3 (8%), 4 (7%) and 5 (4%) in the pure state (3).



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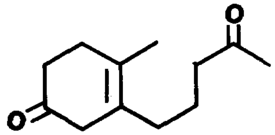

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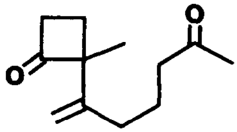

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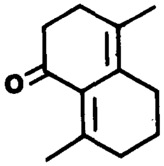
On the other hand, separation by preparative gas liquid chromatography (glc) gave compounds 6 (17%), 7 (4%) and 5 (7%) (4).



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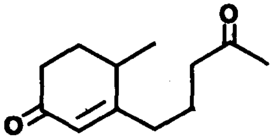

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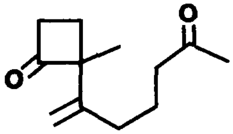

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It therefore seems reasonable to assume at this point that separation by preparative glc at 200° causes compound 3 to be dehydrated to dienone 6 and compound 4 to undergo isomerization to diketone 7.

Compound 3, a yellow oil, homogeneous on tlc, showed a mass peak of 194. Its infrared spectrum ($CHCl_3$) had characteristic bands at 3480 and 1704 cm^{-1}. The nmr spectrum ($CDCl_3$) showed characteristic peaks at τ 8.25 (3H, singlet) and 8.77 ppm (3H, singlet). No vinyl protons were present in the spectrum.

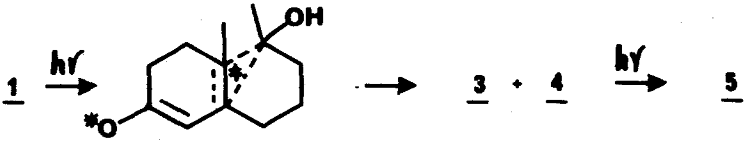
Compound 4, a yellow oil, homogeneous on tlc, showed a mass peak of 194. Its infrared spectrum ($CHCl_3$) had a characteristic carbonyl band at 1711 cm^{-1}. The nmr spectrum ($CDCl_3$), showed characteristic peaks at τ 7.20 (2H, unresolved multiplet), 7.57 (4H, two superimposed triplets J = 6.7 cps), 7.88 (3H, singlet) and 8.28 ppm (3H, singlet). No vinyl protons were present in the spectrum.

Compound 5, a yellow oil, homogeneous on tlc, indicated a mass peak of 194. Its infrared spectrum ($CHCl_3$) had characteristic bands at 1769, 1710, 1636 and 912 cm^{-1}. The nmr spectrum ($CDCl_3$) showed characteristic peaks at τ 5.07 (1H, singlet), 5.24 (1H, singlet), 7.04 (2H, triplet J = 8.5 cps), 7.56 (2H, triplet J = 6.5 cps), 7.89 (3H, singlet) and 8.67 ppm (3H, singlet).

Compound 6, a white solid, mp 37-37.5°, gave a mass peak of 176. Its infrared spectrum ($CHCl_3$) showed characteristic bands at 1680, 1635 and 1580 cm^{-1}. The ultraviolet spectrum indicated two absorption bands: $\lambda_{max.}^{EtOH}$ 233mμ (ε: 15,448) and 301 mμ (ε: 4,341). The nmr spectrum ($CDCl_3$) showed characteristic peaks at τ 7.93 (3H, singlet) and 8.25 ppm (3H, singlet). No vinyl protons were present in the spectrum.

Compound 7, a yellow oil, homogeneous on tlc, gave a mass peak of 194. Its infrared spectrum ($CHCl_3$) showed characteristic bands at 1712, 1660 and 1620 cm^{-1}. The ultraviolet spectrum indicated one absorption band: $\lambda_{max.}^{EtOH}$ 237 mμ (ε: 11,378). The nmr spectrum ($CDCl_3$) showed characteristic peaks at τ 4.20 (1H, singlet), 7.86 (3H, singlet) and 8.81 ppm (3H, doublet J = 6.7 cps).

The formation of hydroxy-ketone 3 during the irradiation of compound 1 constitutes a novel rearrangement in the photochemistry of enones. This transformation could be rationalized by invoking a vinylogous retroaldol cleavage followed by an aldol cyclization. Such a behavior would be in accord with the intervention of a polar excited state or a polar intermediate in the late stages of the rearrangement as in dienone photochemistry (5). In this case, it would be expected that cyclization of the resulting intermediate 8 (* = -; ‡ = +) to compound 3 was in competition with protonation at carbon atom number 1 to yield diketone 4, the second photoproduct observed.



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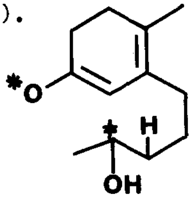
However, evidence put forward by Zimmerman (6) and Schuster (1) supports diradical-like intermediates in the photochemical rearrangement of enones. In the case of the transformation of 1 to 3, such an intermediate (8: * = ‡ = •) would be consistent with the observed result, and the formation of diketone 4 from the same intermediate would then require the intervention of a 1,5-hydrogen shift or two intermolecular hydrogen abstractions (disproportionation is also a possible but less likely process).



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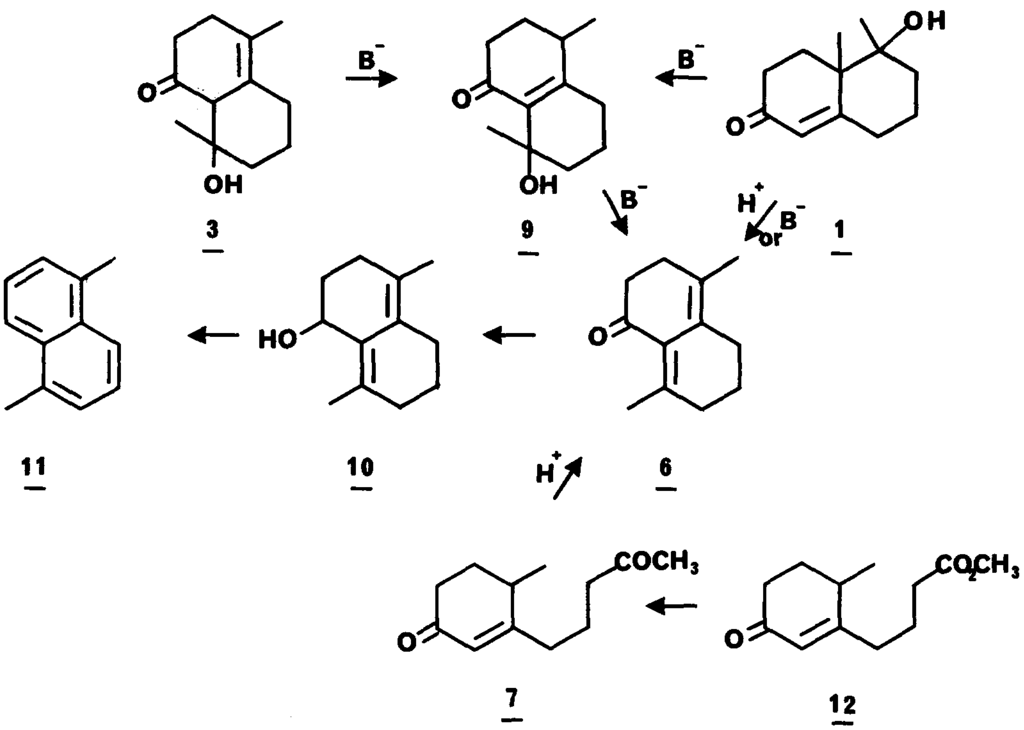
A reaction path in which diketone 4 would be reexcited and then cyclized to give compound 3 was eliminated since it was shown by tlc that no hydroxy-ketone 3 was formed upon the irradiation of 4 in t-butyl alcohol. On the other hand, as anticipated, a certain amount of the cyclobutanone derivative 5 was present. Such rearrangements of β,γ-unsaturated ketones have been reported in the literature(7).

It is interesting to note that some acid and base catalyzed rearrangements similar to the transformation 1 → 3 had been observed by Swaminathan and co-workers (8) and were explained in terms of a vinylogous retroaldol-aldol condensation mechanism.

In order to ascertain the similarity between the photochemical and acid or base catalyzed processes, and also in the hope of obtaining reference material to firmly establish the structures of the photoproducts, these ground-state rearrangements of compound 1 were studied.

Treatment of hydroxy-octalone 1, either with p-toluenesulfonic acid in refluxing benzene or sodium t-butoxide in t-butyl alcohol at room temperature gave the dienone 6 in very good yield (9).

In the case of the base catalyzed reaction, the use of a 0.2% solution of sodium methoxide in methanol at 60° permitted the isolation of intermediate 9 (10) as a separable mixture of two isomers. The mixture, when heated in the presence of a greater amount of the same base, was converted into the dienone 6 (11).



In order to establish unambiguously the skeleton of these rearranged products, dienone 6 was reduced with lithium aluminum hydride to the corresponding hydroxy-diene 10 (12) which was then dehydrogenated over selenium powder at 300° to yield 1,5-dimethyl naphthalene (11). Compound 11 was identical in all respects (mixed mp, mass spectrum, nmr, uv, ir and tlc) with an authentic sample.

Finally, as it became obvious that the enol or enolate forms of photoproducts 3 and 4 were also intermediates in the acid and base catalyzed rearrangements of hydroxy-octalone 1, photoproduct 3 was treated with a 0.04% solution of sodium methoxide in methanol at 35° to yield the conjugated intermediate 9 (13) thus correlating both structures. On the other hand, an unambiguous synthesis of diketone 7 was achieved in four steps starting from the known keto-ester 12 (14); the synthetic diketone was identical in all respects (tlc, ir, uv and nmr) with the conjugated diketone isolated via preparative glc from the photolysis mixture. It, also, was converted in the presence of p-toluenesulfonic acid in benzene to the dienone 6 (15) thus relating both compounds. These results combined with the spectroscopic data obtained therefore conclusively establish the structures of the isolated photoproducts. Further work is presently underway in our laboratory to determine the mechanistic details of this new photochemical rearrangement.

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REFERENCES

1. D.I. Schuster and D.F. Brizzolara, Chem. Comm., 1158 (1967).
2. C.B.C. Boyce and J.S. Whitehurst, J. Chem. Soc., 2680 (1960).
3. A control experiment has shown that compound 1 is stable under the reaction conditions in the absence of light.
4. A fourth fraction (5%) consisting of a mixture was also isolated but has not as yet been investigated.
5. For a recent discussion, see P.J. Kropp in "Organic Photochemistry", Volume I ed. O.L. Chapman, Marcel Dekker, New York, 1967.
6. H.E. Zimmerman, R.G. Lewis, J.J. McCullough, A. Padwa, S.W. Staley and M. Semmelhack, J. Am. Chem. Soc., 88, 159, 1965 (1966).
7. D.I. Schuster, M. Axelrod and J. Auerbach, Tetrahedron Letters, 1911 (1963).
8. a) S. Swaminathan, J.P. Hohn and S. Ramachandran, Tetrahedron Letters, 729 (1962); b) S. Swaminathan, R.K. Natarajan, S. Ramachandran and S.K. Sankarappa, J. Org. Chem., 31, 656 (1966).
9. Identity was shown by tlc, ir, uv, nmr and mixed mp.
10. The structure was established by ir, uv, nmr, mass spectrometry and dehydration to dienone 6.
11. Identity was shown by tlc, ir and nmr.
12. The structure was established by elemental analysis, ir, uv, nmr and mass spectrometry.
13. Identity was shown by tlc, ir, uv, nmr and mass spectrometry.
14. M.S. Newman and A.B. Mekler, J. Am. Chem. Soc., 82, 4039 (1960).
15. Identity was shown by tlc, ir, and uv.