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Photochemical Reactions of Bridged Polycyclic Ketones

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By photochemical reactions, the non-conjugated cyclic ketones which have hydrogens close to the carbonyl group undergo internal hydrogen transfer, thus giving cyclic tertiary alcohols.[*1,1)]

In this paper, we wish to report the results of our photochemical reactions of bridged polycyclic ketones (**1**, **2** and **3**),[2,3)] where the hydrogen extremely close to the carbonyl oxygen was not

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[*1] In these reactions, the hydrogen to be abstracted is usually γ-hydrogen. However, if by virtue of structure other hydrogens are closer to the excited carbonyl group, they will be transferred to the carbonyl group.[1f)]

1) a) H. Wehrli, M. S. Heller, K. Schaffner and O. Jeger, *Helv. Chim. Acta*, **44**, 2162 (1961). b) I. Iriarte, K. Schaffner and O. Jeger, *ibid.*, **46**, 1599 (1963). c) J. Fried and J. Brown, *Tetrahedron Lett.*, **1966**, 1677. d) E. Altenburger, H. Wehrli and K. Schaffner, *Helv. Chim. Acta*, **48**, 704 (1965). e) N. Sugiyama, K. Yamada and H. Aoyama, *Chem. Commun.*, **1968**, 1254. f) M. Barnard and N. C. Yang, *Proc. Chem. Soc.*, **1958**, 302.

2) P. Bruck, D. Thompson and S. Winstein, *Chem. Ind.* (London), **1960**, 405.

3) R. B. Woodward, T. Fukunaga and R. C. Kelly, *J. Amer. Chem. Soc.*, **86**, 3162 (1964).

abstracted.

When **1** in ethanol was irradiated in the n–π^* region of the carbonyl group, an unsaturated aldehyde (**4**) (α-cleavage product) was obtained. The structure of **4** was established by elemental analysis and by a study of its physical data. The NMR spectrum showed a triplet (1H) at δ 9.82 (the aldehyde proton) and a complex multiplet (2H) at δ 5.40 (the olefinic protons).

The irradiation of **2** under the same conditions also gave an α-cleavage product (**5**). On the other hand, **3** did not show any changes upon irradiation, but was recovered almost quantitatively.

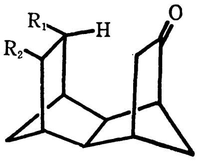
In any one of these three cases, no internal hydrogen transfer product could be detected. This may result from the stereoelectronic requirements for the hydrogen-abstraction step.*[2]

Experimental

Irradiation of 1. A solution of 700 mg of **1** in 50 m*l* of ethanol was irradiated for 6 hours under a nitrogen atmosphere. The light source was a 500-W high-pressure mercury lamp with a Pyrex filter. After the solvent had been removed, the residue was chromatographed on silica gel (70 g). Elution with benzene-*n*-hexane (8 : 2) gave the unreacted ketone (250 mg) and **4** (420 mg), which was distilled to give a colorless oil; bp 90°C/20 mmHg.

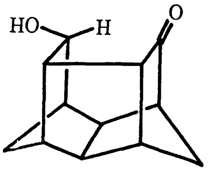
IR: (cm^{-1}, liq. film) 3040, 1608, 740 (*cis* -CH=CH-), 2750, 1720 (-CHO).

NMR: (δ, in $CDCl_3$) 5.40 (m, 2H, -CH=CH-), 9.84 (t, 1H, -CHO).

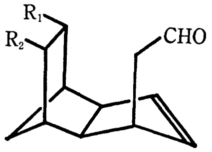


1: $R_1=R_2=H$

2: R_1, R_2=-O-



3



4: $R_1=R_2=H$

5: R_1, R_2=-O-

Fig. 1

Dimedone derivative of **4**: mp 170—173°C. Found: C, 76.71; H, 8.77%. Calcd for $C_{28}H_{38}O_4$: C, 76.67; H, 8.73%.

Irradiation of 2. A solution of 500 mg of **2** in 50 m*l* of ethanol was irradiated as above for 10 hr. The product was isolated by chromatography on silica gel and distilled to give a colorless oil (260 mg); bp 130°C/5 mmHg.

IR: (cm^{-1}, liq. film) 3050, 1610, 733 (*cis* -CH=CH-), 2740, 1720 (-CHO).

NMR: (δ, $CDCl_3$) 5.39 (m, 2H, -CH=CH-), 9.85 (t, 1H, -CHO).

Dimedone derivative of **5**: mp 167—170°C. Found: C, 74.30; H, 8.03%. Calcd for $C_{28}H_{36}O_5$: C, 74.30; H, 8.02%.

Irradiation of 3. A solution of 100 mg of **3** in 20 m*l* of ethanol was irradiated as above for 20 hr. No detectable quantities of products were found in the reaction mixture.

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*[2] Turror and Weiss have stated that, in the transition state of the photochemical hydrogen transfer reaction of alkyl ketones, the hydrogen to be abstracted needs to approach the halfvacant nonbonding orbital of the carbonyl oxygen atom.[4] However, these ketones, **1**, **2**, and **3**, cannot achieve the required transition state.

4) N. J. Turro and D. W. Weiss, *J. Amer. Chem. Soc.*, **90**, 2185 (1968). See also A. Padwa, E. Alexander and M. Niemcyzk, *ibid.*, **91**, 456 (1969) and F. P. Boer, T. W. Shannon and F. W. McLafferty, *ibid.*, **90**, 7239 (1968).