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A PHOTOCHEMICAL SYNTHESIS OF TRICYCLO[6.1.0.$0^{4,9}$]NONADIENONES (HOMOSEMIBULLVALONES)

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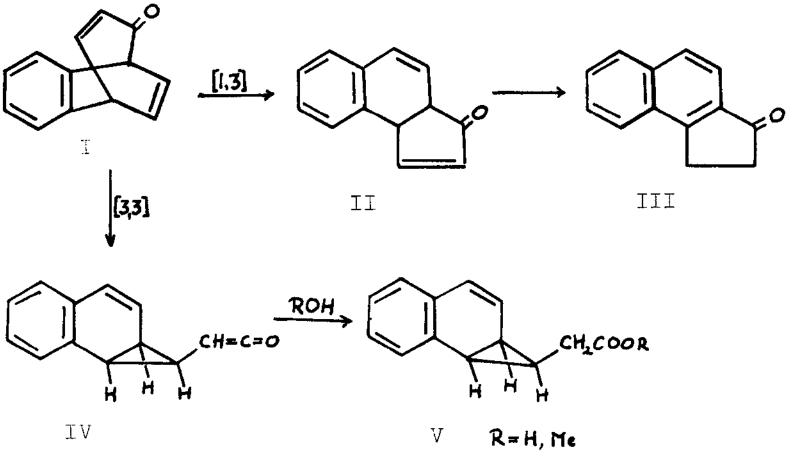
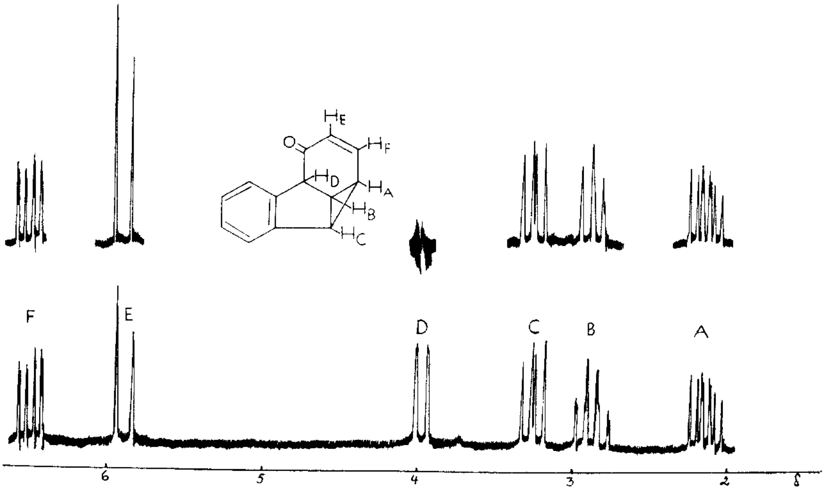
The direct irradiation of bicyclo[3.2.2]nonatrienones (e.g., I) has recently been shown to involve two distinct photorearrangements:[1] a 1,3 acyl migration to the dihydronaphthalene ketone II (isolated as III)[2] and a 3,3 sigmatropic shift to the benzonorcaradiene ketene IV (trapped as V by reaction with nucleophiles)[1,3]. A singlet excited state intermediate was shown to be the precursor in both cases.[1]

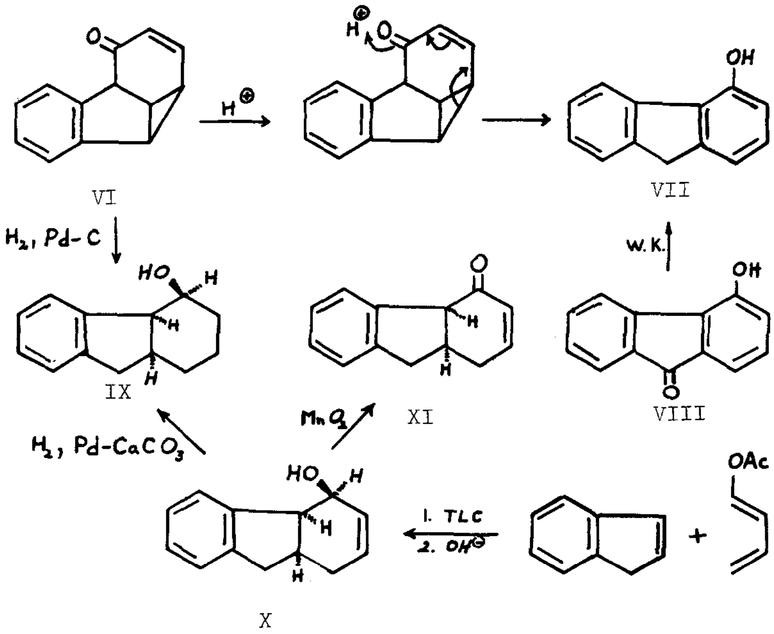


In the present communication we report a different photochemical transformation of ketone I upon sensitized excitation. Irradiation of an acetonitrile solution of ketone I in the presence of benzophenone (absorbing over 90% of incident light), followed by chromatography over silica gel, afforded a single crystalline product, mp 110°, in 47% yield.[5]

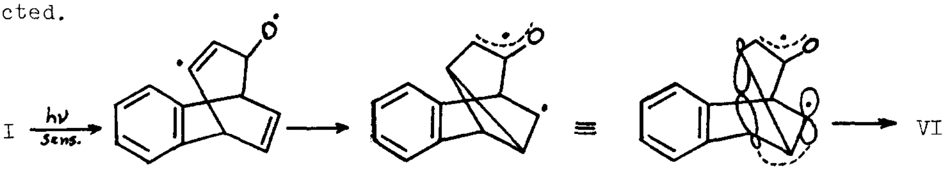
Fig. 1. NMR Spectrum of Photoproduct VI. Taken at 100 MHz in $CDCl_3$ Solution.



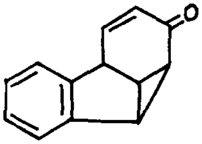
The spectroscopic data indicate structure VI for the photoproduct.[6] This assignment has been confirmed by nmr decoupling experiments[7] (shown in part in fig. 1) and by the following chemical evidence. Treatment of VI with refluxing ethanolic HCl (10%) gave a 72% yield of 4-fluorenol (VII), mp 108°, which was identical to an authentic sample prepared[8] by Wolff-Kishner reduction of 4-hydroxy-9-fluorenone (VIII). Moreover, reduction of VI over palladium on carbon catalyst resulted in the uptake of 3 equivalents of hydrogen to give the alcohol IX, mp 112-113°.[9] The identical alcohol was obtained by reduction over palladium on calcium carbonate of the allylic alcohol X, mp 91° which has in turn been independently synthesized by the alkaline hydrolysis of the principal Diels-Alder adduct of indene with 1-acetoxybutadiene.[10]



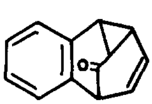
The mechanism of the photochemical formation of ketone VI may involve a special case of the known di-π-methane rearrangement[11] in which one of the participating double bonds is conjugated to a carbonyl group; one possible pathway is depicted.



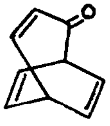
It should be noted that the a priori possibility of formation of two other isomers by related types of rearrangements[11,12] i.e., ketones XII and XIII[13] was not observed.



XII



XIII



XIV

Preliminary results of the photosensitized transformation of the simple bicyclononatrienone XIV[14] indicate that a similar rearrangement takes place.[15] Thus, the sensitized irradiation of bicyclo[3.2.2]nonatrienones appears to provide a general route to the synthesis of the previously unknown tricyclo[$6.1.0.0^{4,9}$] nonadienone[16] ("homosemibullvalone") system and clearly demonstrates the specificity of the particular di-π-methane pathway favored for such systems.

References

1) A. S. Kende, Z. Goldschmidt and P. T. Izzo, *J. Am. Chem. Soc.*, November (1969).

2) J. Ciabattoni, J. E. Crowley and A. S. Kende, *ibid.*, **89**, 2778 (1967).

3) O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen and H. E. Wright, *ibid.*, November (1969).

4) 140 w Hanovia medium pressure mercury lamp, under N_2, pyrex filter.

5) All new compounds have been characterized by ir, uv, nmr, mass spectrum and satisfactory analytical data.

6) Compound VI: ν_{max}^{KBr} 1670 cm^{-1}; λ_{max}^{EtOH} (nm) 250 (ϵ 2718); 290 (2123), 330 (s) (498).

7) We gratefully acknowledge the aid of Dr. John E. Lancaster, (American Cyanamid Co., Stamford, Conn.) for the nmr high-resolution spectra and decoupling experiments.

8) cf. H. L. Pan and T. L. Fletcher, *J. Org. Chem.*, **25**, 1106 (1960); P. H. Grantham, E. K. Weisburger and J. H. Weisburger, *ibid.*, **26**, 1008 (1961).

9) The stereochemistry was tentatively assigned on the basis of a preferred attack from the less hindered side of the molecule.

10) Preparative tlc of the crude adduct of indene with a mixture of *cis* and *trans* 1-acetoxybutadiene gave almost exclusively a single compound. Its formulation as X-acetate rests upon the nmr spectra of allylic alcohol and its MnO_2 oxidation product, XI, and is consistent with *endo*-addition of the *trans* acetoxydiene to indene as the major pathway.

11) H. E. Zimmerman and P. S. Mariano, *J. Am. Chem. Soc.*, **91**, 1718 (1969).

12) E. G., J. Ipaktschi, *Tetrahedron Letters*, 215, 2153 (1969); E. Baggiolini, K. Schaffner and O. Jeger, *Chem. Comm.*, 1103 (1969).

13) Ketone XIII has been prepared by another route (unpublished results with P. T. Izzo) to be reported shortly.

14) M. J.Goldstein and B. G. Odell, *J. Am. Chem. Soc.*, **89**, 6539 (1967).

15) Nmr spectrum of the oily product resembles that of ketone VI except for two vinyl proton multiplets at δ 5.43 and 5.75 instead of the aromatic protons and additional splitting of proton 1 and 4 signals; λ_{max}^{EtOH} (nm) 245 (ϵ 4752) 280 (3281), 330 (453).

16) However, other derivatives of this tricyclic system have been described previously by C. G. Cardenas, B. A. Shoulders and P. D. Gardner, *J. Org. Chem.*, **32**, 1220 (1967). See also H. R. Ward and E. Karafiath, *J. Am. Chem. Soc.*, **90**, 2193 (1968).