Photochemical Cycloaddition of Barbaralone with Benzophenone

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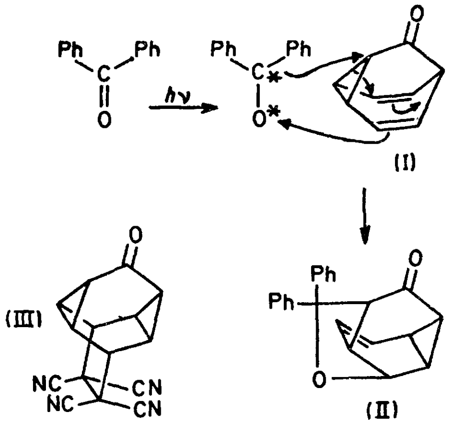
Summary Irradiation of barbaralone (I) in the presence of benzophenone afforded an addition product (II), whose structure was elucidated on the basis of spectral data.

Previously, it was reported that the direct irradiation of tricyclo[3,3,1,$0^{2,8}$]nona-3,6-diene-9-one (barbaralone) (I) resulted in cheletropic decarbonylation arising from the n–π^* singlet state to give cyclo-octatetraene.[1] We now describe a novel cycloaddition of (I) with benzophenone.

When a solution of (I) (0·08 M) in benzene was irradiated (350 nm) for 16 h in the presence of benzophenone (0·8 M). an adduct (II),† m.p. 200—201°, was obtained (89%). Fluorenone or xanthone did not add to (I) under similar conditions. An attempted thermolysis of (II) by heating in $CDCl_3$ (sealed tube) at 200° for 1 h, resulted in recovery of the adduct. The n.m.r. data of (II) are consistent with the structure shown, which possesses two olefinic protons, and rule out other structures originated from ($2_\pi + 2_\pi$), ($2_\sigma + 2_\pi$) or ($2_\pi + 2_\pi + 2_\pi$) cycloaddition.

Although the available evidence does not allow us to distinguish between a concerted and a stepwise process for the formation of (II), radical addition of the n–π^* triplet state of benzophenone seems preferable to the concerted ($2_\sigma + 2_\pi + 2_\pi + 2_\pi$) cycloaddition.[2]



Attempted cycloadditions of (I) with cyclopentadiene and dimethyl acetylenedicarboxylate resulted in recovery of (I), while heating of (I) with tetracyanoethylene in benzene at 40° for 30 h gave an adduct,† m.p. > 350° (decomp.), (92%). The n.m.r. data support the symmetrical structure (III) for the adduct. Such a homo Diels-Alder reaction,[3] *i.e.*, ($2_\pi + 2_\pi + 2_\pi$) process was reported in the cycloaddition of barbaralane with tetracyanoethylene.[4]

(*Received*, 13*th June* 1972; *Com.* 1031.)

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† Elemental analyses and spectral data were satisfactory for (II) and (III).

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[3] H. E. Zimmerman, and G. L. Grunewald, *J. Amer. Chem. Soc.*, 1964, **86**, 1434.

[4] H. Musso, *Angew. Chem. Internat. Edn.*, 1968, **7**, 306.