

THE REACTION OF BENZOPHENONE TRIPLETS WITH
NORBORNADIENE AND QUADRICYCLENE

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One of the best documented reactions of organic photochemistry involves the conversion of a norbornadiene to the corresponding quadricyclene system.¹ Sensitisation of the reaction is possible and Hammond has shown that with aromatic ketone and aldehyde triplet sensitisers a photostationary state between norbornadiene (1) and quadricyclene (2) is established, the position of which depends on the triplet energy of the donor.^{2,3} This was interpreted in terms of a non-spectroscopic excitation of 2 to either the Franck-Condon triplet of 1 or a biradical 3; the different internal energies of 1 and 2 thus accounted for the importance of the donor triplet energy on the position of the photostationary state.¹ Kubota, Shima and Sakurai⁴ have recently reported that the 1:1 adducts of benzophenone and norbornadiene 4, 5 and 6 are formed in 32%, 15% and 3% yields respectively. These workers proposed that the adducts are formed via the intermediacy of interconverting biradicals of types 7, 8 and 9 which are formed by attack of benzophenone triplet on ground state norbornadiene.

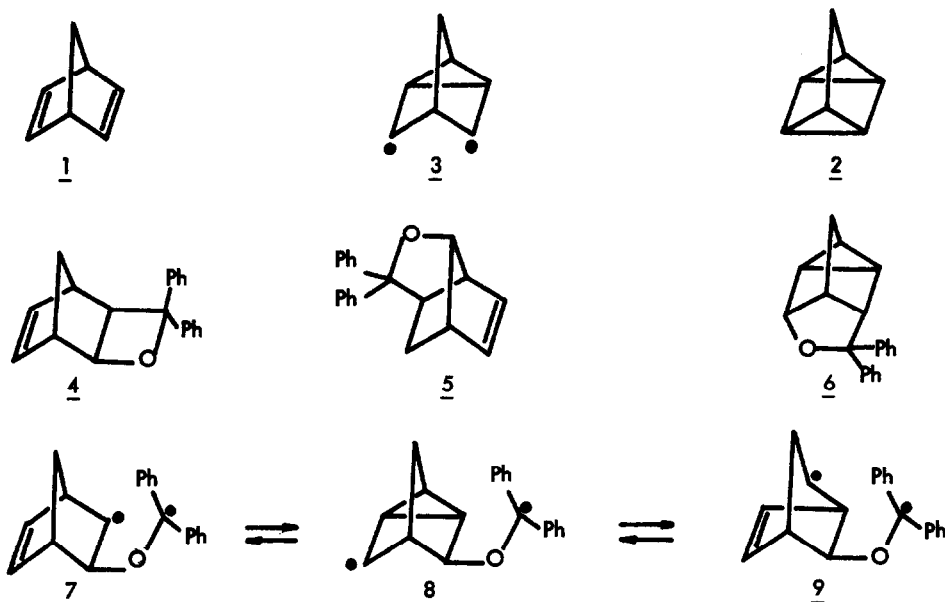
An interest in the mechanism of energy transfer in ketone sensitised reactions⁵ had led us to investigate the reaction of the norbornadiene/quadricyclene system with benzophenone. The work by the Japanese group prompts us to describe our own results which show that the adducts are not formed by addition of benzophenone triplet to norbornadiene.

Deoxygenated benzene solutions containing norbornadiene (0.02M) and benzophenone (0.014M) were irradiated in pyrex with a 100w medium pressure mercury arc and the reaction monitored by g.l.c. and t.l.c. After 20 minutes the formation of quadricyclene (2) and two unknown products could be detected and after 18

¹) Substantial amounts of the starting material were consumed in side reactions.³

hours all the benzophenone had been consumed. The two unknowns, separated by dry column chromatography on alumina, were isolated in 61% and 26% yields and identified as the oxetane 4 and the ether 5 respectively. A similar reaction with quadricyclene (0.02M) and benzophenone (0.014M) in benzene gave only 4 and 5 in essentially the same isolated yields, 55% and 26% respectively.²⁾ The same products (nmr. and mass spectra) were also obtained using ether or isopentane as solvent although the reactions were not as clean.

Clearly 4 and 5 are the products of *exo* attack of benzophenone triplet on norbornadiene and/or



quadricyclene leading to the set of biradicals 7, 8 and 9. Evidence that in fact benzophenone triplet adds only to quadricyclene and not to norbornadiene was obtained as follows: degassed 0.011M solutions of benzophenone in neat norbornadiene were irradiated on a conventional "merry-go-round" apparatus in sealed pyrex tubes. The changes in concentration of benzophenone and quadricyclene with time are shown in Fig. 1.³⁾ There was initially no decay of benzophenone and the quadricyclene production was pseudo-zero order. After approximately 100 minutes, decay of benzophenone and a decrease in the rate of quadricyclene formation

²⁾ Our structural assignments are in complete agreement with those of Kubota et al.⁴ We did not isolate the minor adduct 6.

³⁾ n-Nonane and 2-naphthaldehyde, added before and after irradiation respectively, were employed as g.l.c. standards.

became apparent.⁴⁾ This indicates that the loss of benzophenone as adduct does not involve norbornadiene. Therefore, since the biradical adducts 7, 8 and 9, which experiment shows are derived from quadricyclene, lead to adducts, they cannot be formed from norbornadiene.

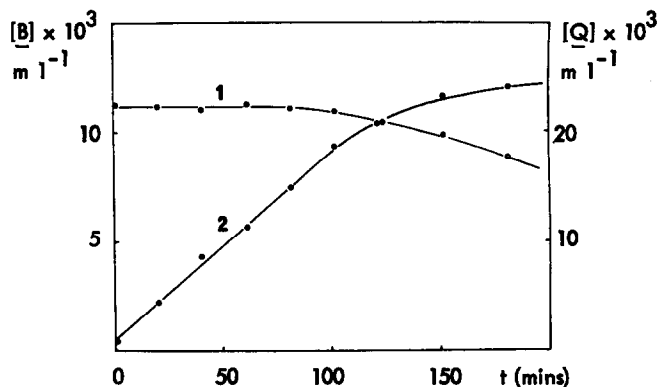


Fig. 1. Change in concentration with time of benzophenone (B; curve 1) and quadricyclene (Q; curve 2) on irradiation of benzophenone (0.011 M) in neat norbornadiene.

Thus, we conclude that a) the benzophenone sensitised conversion of 1 to 2 involves collisional energy transfer or complex formation which does not lead to biradical and b) benzophenone triplet reacts with 2, at least in part, to form a Schenk-like biradical, perhaps via complex formation. This is to our knowledge the first example of attack of a ketone triplet on a strained saturated hydrocarbon.

A possible alternative mechanism for the process resulting in the conversion of quadricyclene to norbornadiene via aromatic ketone and aldehyde sensitisation would appear to be one involving the fragmentation of intermediate adduct biradicals of type 7. Further work concerning this possibility is in progress.

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⁴⁾The experiment was repeated using a different apparatus and 313 nm light. The decay of benzophenone commenced much later (100 hours) but at the same quadricyclene concentration ($1.8 \times 10^{-2}M$).

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