Photochemical Cycloaddition of Benzophenone to 7-Methylenetetracyclo-[3.3.0.0.^{2,8}0^{4,6}]octan-3-one and its Alcohol Derivative

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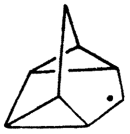
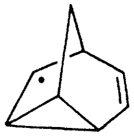
Summary Irradiation of benzophenone with 2,4-dimethyl- or 1,2,4-trimethyl-7-methylenetetracyclo[3.3.0.0.^{2,8}0^{4,6}]-octan-3-one affords oxetans (**3a**) and (**3b**), respectively, while irradiation with the alcohol derivative (**2**) affords a rearranged product (**5**) in addition to an oxetan.

Rearrangement of free radicals has been observed in reactions with low activation energies.[1] It was recently concluded[2] from product analysis and e.s.r. spectroscopy that of the radicals containing the bicyclo[3.2.1]octane skeleton (A), (B), and (C) the allyl radical (C) was the most stable while the radical (A) was not detected. We have shown previously that the products formed in the photocycloaddition of benzophenone to 1,5-dimethyl-6-methylene tricyclo[3.2.1.0^{2,7}]oct-3-en-8-one and its alcohol derivative result from the rearrangement of type (B) radicals which are formed before radicals of type (C).[3] We have now carried out the photoreactions of benzophenone with (**1a**), (**1b**), and a related alcohol derivative (**2**) in order to investigate the behaviour of the radical of type (A).



(A)



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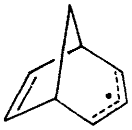
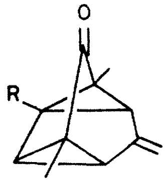
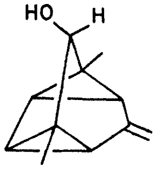


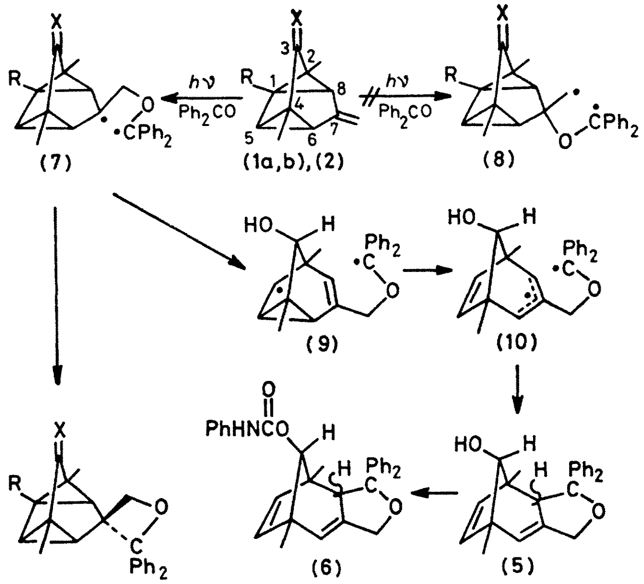
(C)



(1)a; R = H
b; R = Me



(2)



(3)a; R = H, X = O
b; R = Me, X = O
(4) R = H, X = H,OH

A solution of (**1a**) (0·05 M) in anhydrous benzene was irradiated (Rayonet-350 nm) at ambient temperature for 34 h in the presence of benzophenone (0·05 M), and the adduct (**3a**),† m.p. 160—161 °C, was obtained in 28% yield.‡ The trimethyl analogue (**1b**), which has an additional methyl group in the C-1 position afforded the adduct (**3b**),† m.p. 214—215 °C, in 26% yield under similar conditions. The carbonyl absorptions at 1710 cm^{-1} (**3a**) and 1692 cm^{-1} (**3b**) suggest that their skeletons are similar to that of (**1**). The chemical shifts of methylene groups at δ 4·51 (**3a**) and δ 4·42 and 4·47 (**3b**) indicate that the orientations of the benzophenone units in the adducts are as shown. W coupling (J 3·5 Hz)[4] between the protons of (**3b**) at 1·68 and 1·44 (overlapping the methyl signal) also supports the proposed structure. The stereochemical arrangement of the oxetan rings was deduced to be as shown from pseudo-contact n.m.r. spectra using Eu(fod)$_3$. These particular arrangements in oxetan formation may be due to steric effects. Since the yields of the photocycloadducts (**3a**) and (**3b**) were rather low, the photoreaction of (**1a**) was monitored by n.m.r. spectroscopy, but we could not detect any photoadducts other than benzpinacol.

The irradiation (Rayonet-350 nm) of benzophenone (0·1 M) with the alcohol derivative (**2**) (0·2 M) in anhydrous benzene for 7 h afforded (**4**),† m.p. 189—190 °C, in 4% yield only, together with the adduct (**5**). The product (**5**) was purified as its carbamate (**6**)† (13% yield from benzophenone) by reaction with phenyl isocyanate. Irradiation of (**6**) in the presence or absence of benzophenone did not afford (**5**), and we conclude that (**4**) and (**5**) are the primary photocycloadducts of benzophenone and (**2**). The configuration at the allylic hydrogen of (**6**) is not clear at the present stage.

The formation of the adducts (**3a**), (**3b**), (**4**), and (**5**) in these studies can be explained by a mechanism involving biradicals in the dicyclopropylcarbinyl system. The biradical (**7**) has been considered to be the intermediate[5] and may be produced either because it is more stable than (**8**), or from an initially formed complex of preferred orientation.[6] Compound (**7**) may be relatively long-lived because it derives from triplet benzophenone. Consequently, low-energy barrier processes other than radical combination to afford the oxetan, will participate in the reaction, and such processes may include rotation around a single bond and cyclopropylcarbinyl–allylcarbinyl radical rearrangement.[7] Thus, there are two competing reaction pathways available to (**7**), one giving (**3a**), (**3b**), and (**4**) by simple cyclization and another giving (**5**) by cyclization after rearrangement to (**10**). Compounds (**1a**) and (**1b**) do not afford a rearrangement product as (**2**) does, and the additional methyl group in the C-1 position of (**1b**) does not affect the rearrangement of (**7**; X = O) to the radicals (**9**) and/or (**10**). These facts are explained by resonance conjugation of the carbonyl group with the cyclopropane ring, which affects the energy barrier for the rearrangement of (**7**; X = O) to (**9**) and/or (**10**).[8]

Recently the kinetic data (E_a 5·9 kcal/mol; log A/s^{-1} 12·48) for the cyclopropylcarbinyl → allylcarbinyl radical rearrangement have been obtained from e.s.r. spectroscopy in the temperature range −120 to −145 °C.[9] However,

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† Satisfactory elemental analyses were obtained for all new compounds. Spectral data: (**3a**), ν_{max} (KBr), 1710 cm^{-1}; ^{1}H n.m.r., δ (CDCl$_3$), 1·03 (6H, s), 1·66 (2H, d, J 6·0 Hz), 2·32 (2H, d, J 6·0 Hz), 4·51 (2H, s), and 7·2—7·6 (10H, m); (**3b**) ν_{max} (KBr), 1692 cm^{-1}; δ (CDCl$_3$), 0·96 (3H, s), 1·01 (3H, s), 1·44 (3H, s), 1·44 (1H, d, J 3·5 Hz), 1·68 (1H, dd, J 6·0 and 3·5 Hz), 2·16 (1H, d, J 6·0 Hz), 4·42 (1H, d, J 6·0 Hz), 4·47 (1H, d, J 6·0 Hz), and 7·2—7·8 (10H, m); (**4**), δ (CDCl$_3$), 1·10 (6H, s), 1·34 (2H, d, J 6·0 Hz), 1·85 (2H, d, J 6·0 Hz), 3·47 (1H, s), 4·65 (2H, s), and 7·3—7·5 (10H, m); (**6**) δ (CDCl$_3$), 0·95 (3H, s), 1·08 (3H, s), 3·10 (1H, s), 4·15 (1H, d, J 12·0 Hz), 4·24 (1H, d, J 12·0 Hz), 4·76 (1H, s), 5·24 (1H, d, J 5·0 Hz), 5·34 (1H, s), 5·49 (1H, d, J 5·0 Hz), and 6·9—7·5 (15H, m). The chemical shifts for the OH group of (**4**) and the NH group of (**6**) are not given since they were not observed distinctly.

‡ The yields of photoadducts are based on the amounts of benzophenone used. Benzpinacol was also obtained in all photocycloaddition reactions.

the type (A) radical [which has the same skeleton as (**7**)] has not been detected even at −140 °C [2] These facts seem to suggest that the rearrangement of this radical is faster even than that of the simple cyclopropylcarbinyl radical itself The present results thus provide a novel example of the possible existence of a radical of type (A), rearrangement of which may be prevented by an electron-withdrawing substituent such as a carbonyl group

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