

Effect of Varying Wavelength on the Photorearrangements of Bicyclo[3,1,0]hexenones

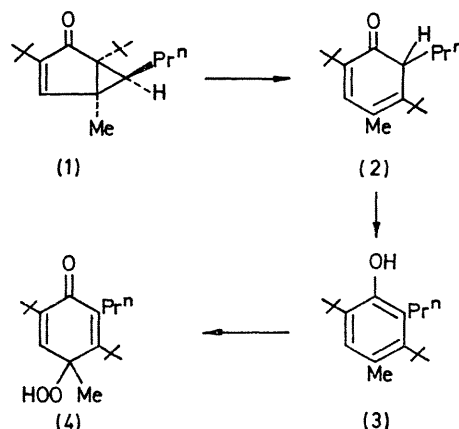
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Summary Irradiation of several bicyclo[3,1,0]hexenones through Pyrex filters caused rearrangements resulting principally from cleavage of an 'exocyclic' cyclopropane bond, while irradiation with short wavelength light gave much larger amounts of products resulting from cleavage of the 'endocyclic' cyclopropane bond.

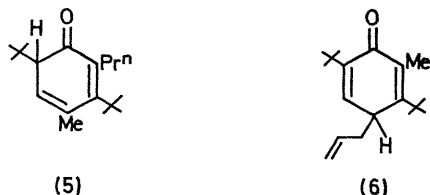
PHOTOCHEMICAL reactions normally proceed *via* the lowest excited singlet or triplet states of the photoexcited molecules.¹ Those molecules which are excited to higher states degrade rapidly to the lowest excited states before reacting further. For this reason, the few reactions in which photoexcitation by light of differing wavelengths give different products have aroused appreciable interest.² In this paper, we report that the products obtained from photorearrangements of bicyclo[3,1,0]hexenones can be markedly affected by the wavelength of the light employed. Surprisingly, the direction of the effect is opposite to that reported³ in an apparently closely similar reaction.

Irradiation of a cyclohexane solution of ketone (1) by a

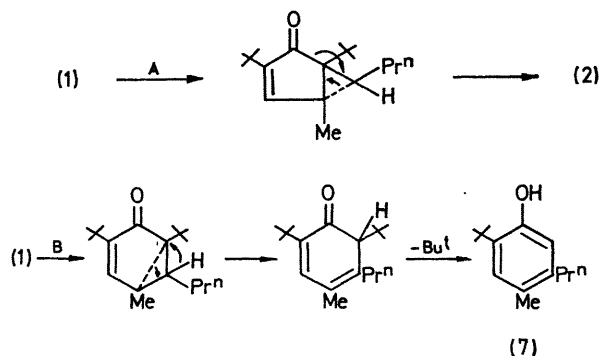


high pressure mercury lamp through a Corex or Pyrex filter, followed by evaporation at room temperature, gave a

product which appeared (g.l.c.) to be largely a single compound. The spectrum (λ_{\max} 6.10, 6.39 μm) and the u.v. spectrum [λ_{\max} (MeOH) 319 nm] of the product were typical of linearly conjugated cyclohexadienones.⁴ Although the spectra of the product were unchanged when it was stored for three weeks at -78° , the dienone peaks disappeared, to be replaced by typical phenolic absorptions, when the product was kept at room temperature, under nitrogen, for 48 h. No change in the g.l.c. of the product, however, occurred during that period.†



G.l.c. of the photolysis product yielded phenol (3) as an oil which was stable under nitrogen. Exposure to air rapidly oxidized (3) to the oxohydroperoxide (4), m.p. 104–106°, λ_{\max} 3.00, 6.20 μm , λ_{\max} (MeOH) 243 nm (log ϵ 4.08). The positions of the substituents in (4) were indicated by its n.m.r. spectrum (CCl_4) which showed singlets at τ 1.90 (1H, OOH), 3.39 (1H, HC=C=O), 8.55 (3H, quaternary -C-Me), 8.75 [9H, Bu^t at C(6)] and 8.52 [9H, Bu^t at C(3)], and triplets at τ 7.40 (2H, J 5.0 Hz, =C-CH₂-) and τ 9.17 (3H, J 5.5 Hz, CH₂CH₂Me). The unusually fast auto-oxidation of (3) can be ascribed to steric repulsion between the adjacent Me and Bu^t groups of (3); this is relieved on conversion into the non-planar (4).



The evidence given above strongly supports assignment of structure (2) for the initial product of photorearrangement of (1) although structure (5) is a formal possibility. Several enolizable cyclohexa-2,5-dienones have recently been identified,⁵ although they remain scarce and unstable molecules. The relative stability of (2) can be attributed to unfavourable interactions between adjacent Bu^t and Pr groups which would be planar in the phenol. The linearly conjugated cyclohexadienone (2), as expected,⁶ has a shorter lifetime than has the cross-conjugated dienone (6),^{5b} although the steric factors militating against aromatization are similar for both compounds.

† Addition of a drop of sulphuric acid, or of sodium methoxide solution, to a methanol solution of the initial product resulted in almost instantaneous loss of the 319 nm peak, which was replaced by peaks at 280–290 nm.

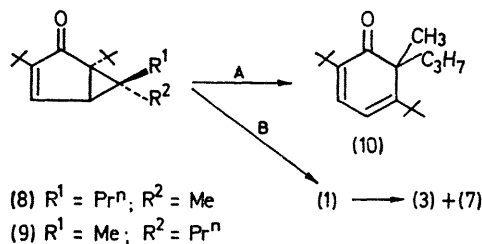
‡ Essentially the same results are obtained from either isomer.

§ The ratio of products obtained from the processes reported in this paper were unaffected by temperature changes within the range 15–40°.

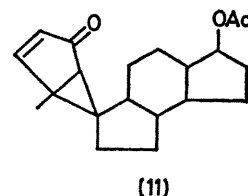
Formation of (2) can be rationalized by process A, in which formal cleavage of the 'exocyclic' cyclopropane bond *a* occurs. This mechanism was previously proposed for formation of linearly conjugated dienones from other bicyclo[3,1,0]hexenones.⁷

When a cyclohexane solution of (1) was irradiated by a 2537 Å light source, the product consisted almost entirely of two components in the ratio 4:5. The products were isolated by g.l.c. and identified as (3) (the major component) and 4-methyl-5-propyl-2-*t*-butylphenol (7). Compound (7) can be obtained by process B in which the (formal) first step is cleavage of the 'endocyclic' cyclopropane bond *b*.⁸

A similar influence of the wavelength of the light employed is found in the photorearrangements of the bicyclohexenones (8) and (9).^{7,†} Irradiation of (8) or (9) with



2537 Å light initially gives (10), the product of process A, and (1), the product of process B, in the ratio 1.2:1. Continued irradiation results in further photorearrangements of (1), as described above, but the ratio of the products of processes A and B remains essentially constant. Irradiation of (8) or (9) through a Pyrex filter gives principally the products of process A, as previously reported.⁷ It does, however, give minor amounts of (1) and other products of process B. The ratio of process A to process B is 3.4:1.‡



For these molecules, therefore, it appears that a $\pi \rightarrow \pi^*$ excitation is more likely to result in cleavage of the 'endocyclic' bond than is an $n \rightarrow \pi^*$ transition. Swiss workers, however, have reported that in photorearrangements of (11) the long-wavelength $n \rightarrow \pi^*$ excitation gives products of processes A and B in *ca.* 11:1 ratio while the shorter-wavelength $\pi \rightarrow \pi^*$ excitation gives the same products in the ratio 6.5:1.³

In both our observations and those of the Jeger-Schaffner group, the $n \rightarrow \pi^*$ excitation results in a higher proportion of the reaction going through the principal rearrangement process, while the $\pi \rightarrow \pi^*$ excitation results in a larger proportion of side reactions. A clear explanation for the

effects of differing wave lengths on these reactions however, is not available.

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¹ N. J. Turro, 'Molecular Photochemistry', W. A. Benjamin, New York, 1965, p. 5.

² E. F. Ullman, *Accounts Chem. Res.*, 1968, **1**, 353.

³ J. Frei, C. Ganter, D. Kägi, K. Kocsis, M. Miljkovic, A. Siewinski, R. Wenger, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 1966, **49**, 1049.

⁴ E.g., C. Ganter, F. Greuter, D. Kägi, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 1964, **69**, 627; H. Hart, P. M. Collins, and A. J. Waring, *J. Amer. Chem. Soc.*, 1966, **88**, 1005; B. Miller, *ibid.*, 1970, **92**, 6246.

⁵ E.g. (a) A. A. Volod'kin and V. V. Ershov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1962, 2022; (b) B. Miller, *J. Amer. Chem. Soc.*, 1967, **89**, 1685; (c) T. Matsuura and K. Ogura, *Tetrahedron*, 1968, **24**, 6157.

⁶ B. Miller in "Mechanisms of Molecular Migrations", vol. 1, ed. B. S. Thyagarajan, Interscience, New York, 1968, p. 248.

⁷ B. Miller, *J. Amer. Chem. Soc.*, 1967, **89**, 1678.

⁸ The precise stage at which the Bu^t group is lost is not known, but loss of Bu^t groups from very similar compounds occurs during acid-catalysed formation of analogues of (7) from cyclohexa-2,5-dienones. B. Miller and K. Margulies, *J. Amer. Chem. Soc.*, 1965, **87**, 5106.