[3,5]-Sigmatropic Shifts in the Photochemistry of 1-Allyl-naphthalen-2(1*H*)-ones

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Although the formation of a 2a,3,4,8b-tetrahydro-1,4-methanocyclobuta[*a*]naphthalen-2(1*H*)-one (**2**) in the photolysis of 1-methyl-1-(prop-2-enyl)-naphthalen-2(1*H*)-one (**5**) is confirmed by *X*-ray crystallography of the corresponding 7-bromo photoproduct (**3**), the available evidence does not support the previously made suggestion that this occurs *via* a [3,5]-sigmatropic shift; an alternative mechanism involving an arene–alkene exciplex is suggested.

Although a suprafacial [3,5]-sigmatropic shift is a symmetry-allowed photochemical process there are only two examples described in the literature.[1—3] As part of an investigation of the photochemistry of 1-allyl-naphthalen-2(1*H*)-ones we became interested in the generality of the [3,5]-sigmatropic shift which had been suggested as the initial step in the formation of (**1**) from the perfluorinated naphthalenone (**4**). This transformation also involves a [2 + 2]cycloaddition and a [1,3]-sigmatropic shift as outlined in Scheme 1. No evidence was provided as to the intermediate nature of molecules such as (B) and (C) and the structure of compound (**1**) was deduced largely on the basis of ^{19}F n.m.r. Thus it appeared worthwhile to obtain more evidence for the structure suggested and to determine if this highly unusual rearrangement was peculiar to the perfluorinated naphthalenone system.

The photolysis of (**5**) in cyclohexane (medium pressure mercury lamp, Pyrex filter) gave (**7**) (m.p. 72—73 °C), the result of a regiospecific [2 + 2]cycloaddition of the allyl group to the enone, as the major photoproduct, and in addition a compound (m.p. 66 °C) showing the absorption at 1780 cm^{-1} characteristic of a cyclobutanone; the products were formed in a ratio of 9 : 1. The minor product was isolated by the crystallisation of (**7**) from the crude photolysate and chromatography of the residue. Although the evidence available (i.r., n.m.r.) did suggest that this material had the structure (**2**), it was not completely unambiguous. For this reason an *X*-ray crystallographic study† was carried out on the corresponding minor photoproduct (**3**) (m.p. 81—82 °C) obtained from (**6**).

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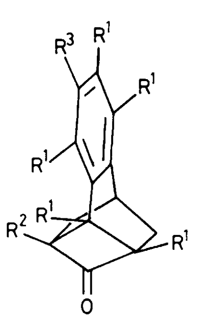
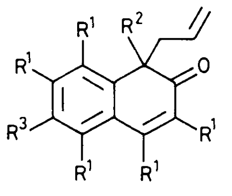
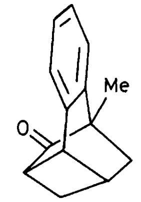
† *Crystal data* for (**3**): $C_{14}H_{13}BrO$, monoclinic, space group $P2_1/c$, a = 11.993(3), b = 7.875(3), c = 12.550(3) Å, β = 96.58(5)°; U = 1177.47 Å^3, Z = 4, μ(Mo-K_α) = 67.44 cm^{-1}. The structure was solved by direct methods and was refined by least square techniques to R = 0.073 and R_w = 0.089 for 1 013 reflections with $I > 3\sigma(I)$ collected on a Hilger and Watts Y290 diffractometer. Maximum shift/e.s.d. in any parameter was 5 × 10^{-3}. Number of variable parameters = 70. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



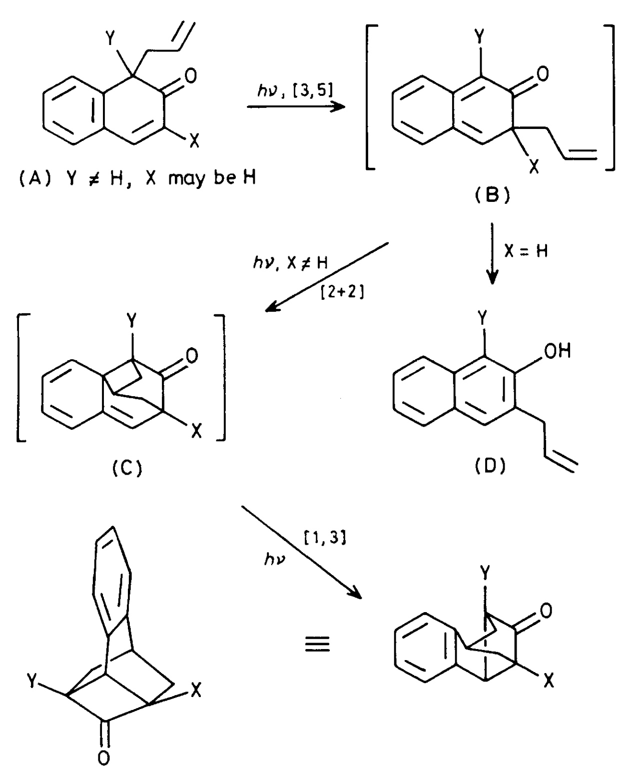
(1) R^1 = R^2 = R^3 = F
(2) R^1 = R^3 = H, R^2 = Me
(3) R^1 = H, R^2 = Me, R^3 = Br



(4) R^1 = R^2 = R^3 = F
(5) R^1 = R^3 = H, R^2 = Me
(6) R^1 = H, R^2 = Me, R^3 = Br



(7)



Scheme 1

The result of this study is shown in Figure 1 and confirms the assignment made on the basis of ^{19}F n.m.r.

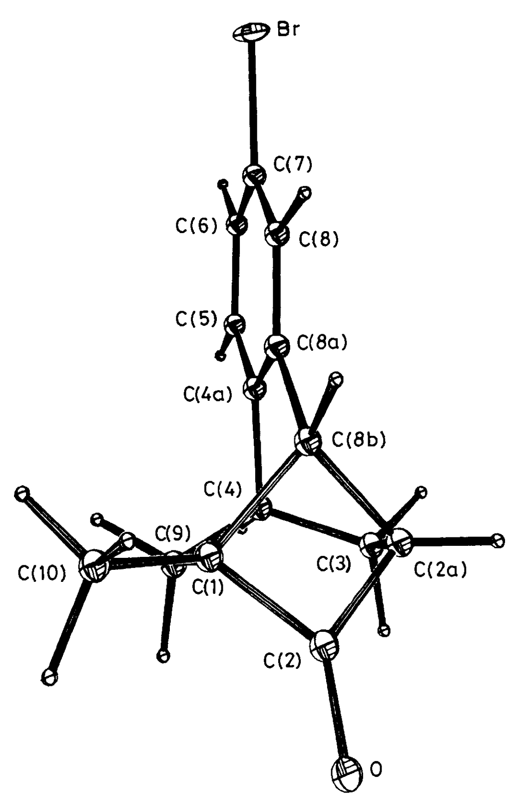
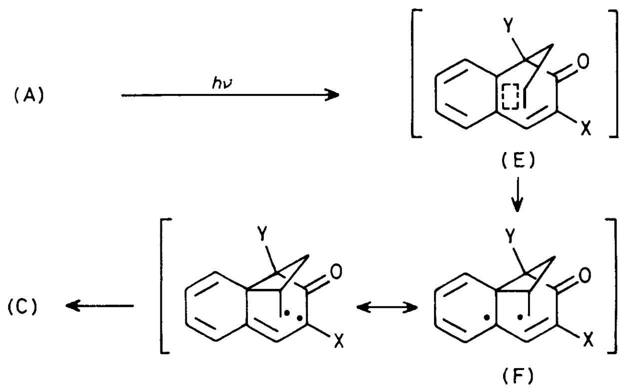
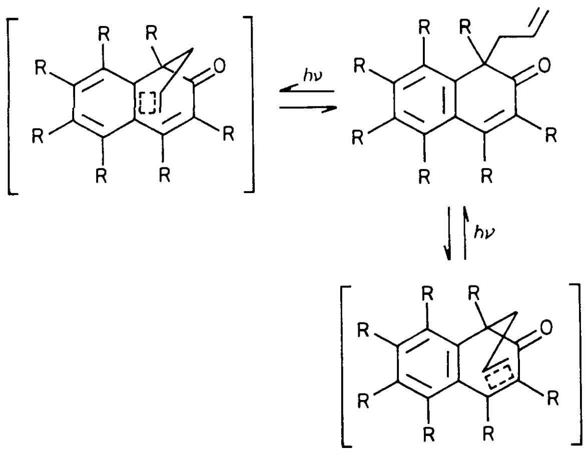


Figure 1. The structure of 1-methyl-7-bromo-2a,3,4,8b-tetrahydro-1,4-methanocyclobuta[*a*]naphthalen-2(1*H*)-one (**3**).



Scheme 2

The suggested mechanism for this process requires some comment. In the case of the perfluorinated naphthalenone (**4**) (Scheme 1, X = Y = F) the key [3,5]-shift results in the formation of the α,α-disubstituted keto tautomer (B) of a naphthol and so a subsequent [2 + 2]cycloaddition is not unreasonable. However, although the corresponding product obtained from (**5**) (Scheme 1, Y = Me, X = H) would be expected to tautomerise rapidly to the exclusion of, or at least competitively with, the [2 + 2]cycloaddition process, we have seen no evidence for the formation of 1-methyl-3-(prop-2-enyl)-2-naphthol (D; Y = Me) during the photolysis of (**5**). The first reported example of a [3,5]-sigmatropic shift also involved the formation of the keto tautomer of a phenol which could, and did, isomerise. There does exist the formal possibility of a photochemically mediated equilibration of (B; X = H) and (D) which would allow the ultimate conversion of the latter to (C). To exclude this possibility, (D; Y = Me) was synthesised, but did not afford any (**2**) on photolysis under the conditions used here. It would appear then that although there is no doubt as to the identity of the minor photoproduct, its formation does not involve a [3,5]-sigmatropic shift. The possibility that (**2**) is formed by further photochemical



Scheme 3

reactions of (**7**) may also be excluded as (**2**) is not formed even on prolonged exposure to the conditions used here. Compound (**1**) has been shown[3] to be similarly unreactive.

An alternative mechanism (Scheme 2) involves the formation of an arene–alkene exciplex (E) which collapses to the diradical (F); this can undergo radical coupling to give (C), the formation of (**2**) being completed by the [1,3]-shift already postulated. Such a mechanism would also explain the significantly higher yield of the cyclobutanone in the case of the perfluorinated naphthalenone (**4**) (Scheme 3, Ṙ = F) as the formation of the arene–alkene exciplex would be expected to be more favoured in this case owing to a stronger donor–acceptor interaction.

Received, 28th May 1985; Com. 740

References

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3 G. M. Brooke, R. S. Matthews, and N. S. Robson, *J. Fluorine Chem.*, 1980, **16**, 461.