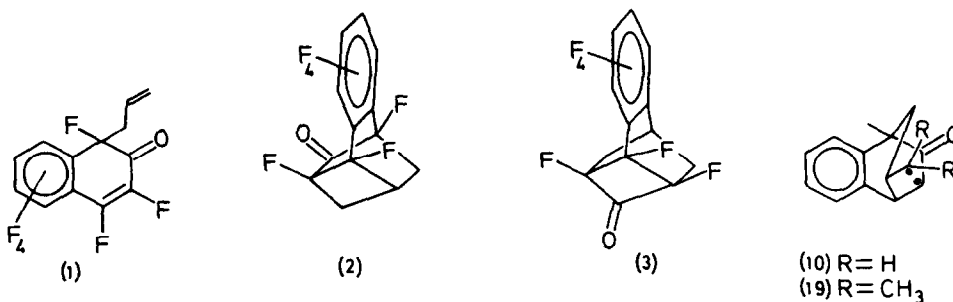


PHOTOCHEMISTRY OF 1-ALLYL-NAPHTHALEN-2(1H)-ONES : A REVISED MECHANISM FOR THE FORMATION OF
BENZOTRICYCLO[3.3.1.0^{2,7}]NONEN-8-ONES.

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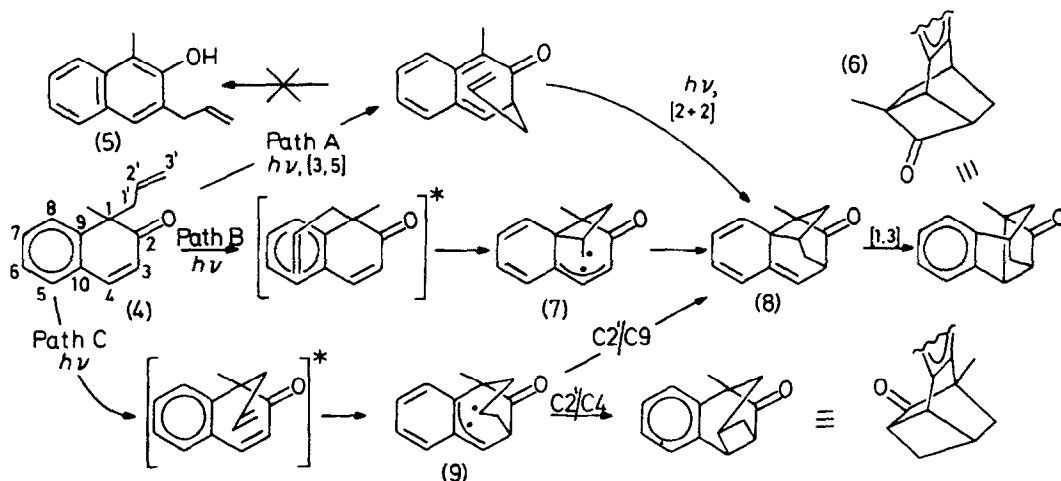
ABSTRACT: The photochemistry of a series of 1-alkenyl-naphthalen-2(1H)-ones suggests that the formation of benzotricyclo[3.3.1.0^{2,7}]nonen-8-ones involves an ambident benzyl radical which gives these products on ring closure at the endocyclic carbon; ring closure at the exocyclic carbon gives the normal [2+2] enone-olefin cycloaddition products.

The formation of a benzotricyclo[3.3.1.0^{2,7}]nonen-6-one, the product of an enone-olefin [2+2] cycloaddition, and a benzotricyclo[3.3.1.0^{2,7}]nonen-8-one on irradiation of 1-allyl-naphthalen-2(1H)-ones was first noted¹ for the 3-substituted compound (1) which gave (2) and (3) respectively. A mechanism (Scheme: Path A) involving an initial [3,5]-sigmatropic shift of the allyl group was suggested for the formation of (3). However the fact that the corresponding product was obtained² on irradiation of allyl-naphthalenones such as (4), which contained no substituent in the 3-position, without the concomitant formation of the 3-allyl substituted 2-naphthol (5) which should be formed in a highly competitive enolisation process in such cases, necessitated the formulation of an alternative mechanism. Thus it was suggested (Scheme: Path B) that the formation of the benzotricyclo[3.3.1.0^{2,7}]nonen-8-one (6) involved an intermediate arene-olefin exciplex which collapsed, with bond formation between C-2' and C-9, to the diradical (7). Ring closure at C-3 would give (8) which is common to both mechanisms.



In order to define the factors affecting the course of these rearrangements, a series of 1-allyl-naphthalen-2(1H)-ones, in which the substitution pattern of the olefin and the length of the carbon chain joining it to the naphthalenone system were both varied, was synthesised and photolysed. The results of this study show that although a [3,5]-allyl shift is not involved, neither is the formation of the two tricyclic products the result of competitive enone-olefin and arene-olefin exciplex formation. Instead, it now appears that both products are formed (Scheme: Path C) via the same exciplex and that it is, surprisingly, the ambident

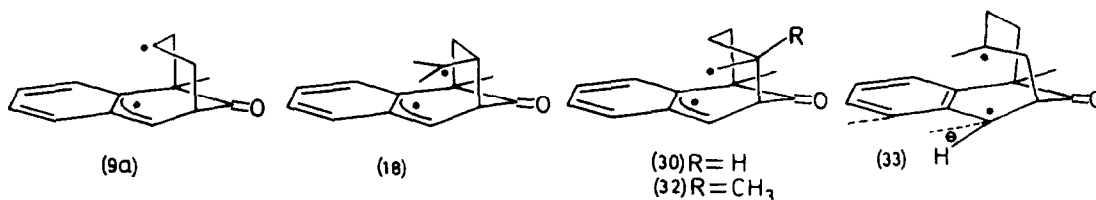
behaviour of the benzyl radical (9) formed from this exciplex which leads to the formation of two products.



Scheme

It is clear from the proposed mechanism that only a diradical such as (9), formed by initial bond formation at C-3 can couple at C-9 and thus lead ultimately to (6). If the alternative diradical (10), resulting from initial bond formation at C-4 is preferred for any reason, or if ring closure at C-9 becomes more difficult relative to closure at C-4, then tricyclo[3.3.1.0^{2,7}]nonen-8-ones such as (6) will be formed in smaller amounts if at all. Although in some of the cases discussed below it is clear that the exciplex with the opposite orientation of enone and olefin is involved, the factors outlined above still form a basis for an understanding of the course of the reaction.

The photochemical behaviour of (4), (11), (12) and (13) is as described in the Scheme (Path C). Regioselective exciplex formation is followed by collapse to the diradical (9) in which the delocalised benzylic radical is symmetrically disposed relative to the other radical centre (9a). Ring closure of this diradical leads to the products observed.



The photolysis of (14) gives a benzotricyclo[3.3.1.0^{2,7}]nonen-6-one (15) and a benzotricyclo[4.2.1.0^{3,8}]nonen-7-one (16) but only a trace of the cyclobutanone (17) (i.r. 1771 cm⁻¹). The formation of (16) the result of a [2+2] enone-olefin cycloaddition whose regiochemistry is the opposite of that leading to (15), is thus associated with a reduction in the amount of cyclobutanone formed. The diradical (18) which may be involved in the formation of (16) and which has the potential to lead to C-3'/C-9 ring closure, should close exclusively through C-3'/C-4 bond formation as the tertiary radical is held significantly

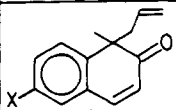
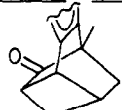
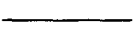

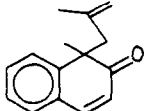

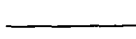

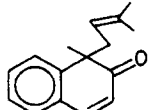
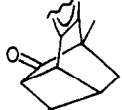

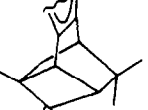
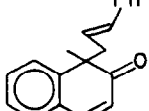




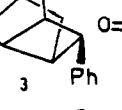


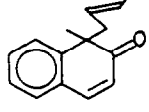

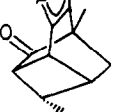
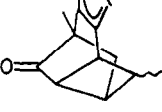
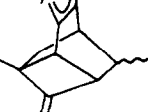
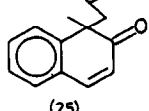
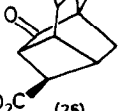

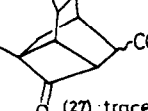
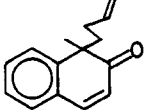


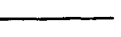
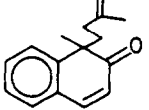
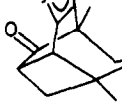


SUBSTRATE	[2+2] CYCLOADDITION PRODUCTS		CYCLOBUTANONES
 (4) X = H (11) X = Br (12) X = OCH ₃	 X = H: 10 X = Br, OCH ₃ : 7		 X = H, Br, OCH ₃ : 1
 (13)	 17		 †
 (14)	 (15): 5	 (16): 1	 (17): trace
 (20)	 7  3  1  1	 3  1	
 (21)	 (22): 7  (22a): 1	 (23): trace	 (24): trace
 (25)	 MeO ₂ C (26)		 (27): trace
 (28)		 (29)	
 (31)	 † 1	 2	

Table. The relative amounts given for the photoproducts were obtained using ¹H-NMR following photolysis of the parent naphthalenone in methanol using a Rayonet reactor equipped with 254 nm lamps and a pyrex filter. All compounds, with the exception of those obtained in trace amounts, were characterized by ¹H and ¹³C-NMR, IR and, in one case, X-ray crystallography; satisfactory elemental analyses were also obtained for all compounds with the exception of those marked thus (+), which could not be separated from the major product and, again, those obtained in trace amounts.

closer to the C-4 end of the ambident benzylic radical by the rigid structure of the diradical. In addition the diradical corresponding to (9) is now competing with the tertiary/ α -keto diradical (19) and this will also limit the opportunities for cyclobutanone formation. The trend is even more pronounced in the case of (20) as the two stereoisomers of both regioisomeric [2+2] photoadducts are formed without any detectable trace of a cyclobutanone. The naphthalenone (21) behaves in an intermediate way giving (22) and (22a) as major products together with traces of the other two compounds. The behaviour of (25) is, however, atypical in that although the formation of the [2+2] adduct is regiospecific, only a barely detectable amount of the cyclobutanone (27) (i.r. 1777 cm^{-1}) is formed. This may be rationalised in terms of the exciplex collapsing by exclusive C4/C2' bond formation.

The addition of an extra carbon to the chain connecting enone and olefin has a dramatic effect on the regiochemistry of the [2+2] cycloaddition process. Thus the photolysis of (28) leads exclusively to (29) in a complete inversion of the regiochemistry observed on photolysis of (4). The diradical (30), which may be involved in the formation of (29) and which could lead to closure at C-9, involves a primary radical which is held much closer to the C-4 end of the potentially ambident benzyl radical and thus it is not surprising that products resulting from C-4'/C-9 closure are not observed. The formation of both regioisomeric [2+2] adducts on photolysis of (31) is expected on the basis of frontier orbital considerations and its failure to form any cyclobutanone is again understandable in terms of the structure of the diradicals involved: (32), for example, would not be expected to close at C-9 for the reasons outlined above. The situation for the other important diradical is less clear as it has greater conformational freedom due to the presence of a seven-membered ring. However in the conformation (33) which holds the two radical centres closest together the ambident benzyl radical is almost symmetrically disposed relative to the other radical as was the case for (9a); the difference between (33) and (9a), and indeed all the other radicals discussed above, is that its structure is such that the benzene ring and a trigonal C-4 cannot be coplanar ($\theta = 20\text{-}30^\circ$, depending on the precise conformation adopted) and as a consequence significant resonance involving the radical and the aromatic system is unlikely. The failure of (28) and (31) to form cyclobutanones suggests that arene-olefin exciplexes are not involved in their formation as in both the alkene and arene groups are linked by a three-carbon chain, an arrangement which has been found to be most effective in promoting intramolecular arene-olefin interactions.³

Thus the evidence suggests that the formation of cyclobutanones on photolysis of allyl-naphthalen-2(1H)-ones involves a variation of the enone-olefin exciplex/diradical mechanism which relies on the ambident reactivity of a benzyl radical allowing ring closure at an endocyclic carbon.

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