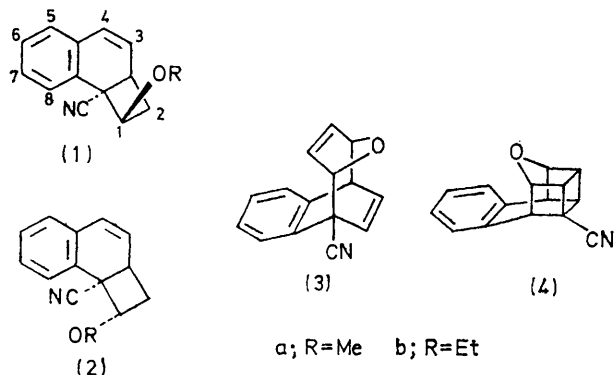


Photochemical Reactions of Aromatic Compounds. Part XXIII.¹ Photochemical Reactions of Alkyl Vinyl Ethers with 2-Naphthonitrile²

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Irradiation of 2-naphthonitrile (5) and an alkyl vinyl ether (6) at 313 nm gives only a single [2 + 2] cycloadduct, *endo*-2-alkoxy-1,2,2a,8b-tetrahydrocyclobuta[*a*]naphthalene-2a-carbonitrile (7), in 80–90% yield. On the other hand, irradiation through Pyrex (>280 nm) ultimately affords a cyclobutene, 4-alkoxy-2a,3,4,8b-tetrahydrocyclobuta[*a*]naphthalene-6-carbonitrile (8) (70%), as a main product, accompanied by various 1:1 adducts (9)–(12). Pyrolyses of the products (8) and (9) afford 10-alkoxy-5,6-dihydrobenzocyclo-octene-2-carbonitrile (10) in good yields; irradiation of (10) gives 8b-alkoxy-2a,3,4,8b-tetrahydrocyclobuta[*a*]naphthalene-7-carbonitrile (11) in quantitative yield. From a kinetic study, the formation of the adduct (7) is established as occurring from the lowest excited singlet state of the nitrile (5).

MUCH work has been carried out on photocycloadditions across aromatic rings which provide routes to various cyclic systems.^{3–12} Photocycloaddition of unsaturated compounds to naphthalenes exhibits interesting stereochemical aspects and solvent effects which have been discussed in terms of exciplexes.^{6–12} For example, stereoselectivity in the photoaddition of olefins to 1-naphthonitrile depends on the electronic nature of the olefin: more highly conjugated planar olefins such as phenyl vinyl ether and indene undergo *endo*-selective photocycloaddition,⁸ whereas such stereoselectivity is lacking in the photocycloaddition of alkyl vinyl ethers (6), which gives both *endo*- and *exo*-cycloadducts, (1)



and (2), in approximately equal amounts.⁹ These observations have been interpreted in terms of differences in stability between exciplex configurations: the former type of olefin may be expected to form more stable exciplexes possessing a sandwich-type structure. However, the stereochemical course of photocycloadditions to naphthonitriles is also affected by the position of the cyano-group: the photoaddition of furan to 1-naphthonitrile gives a [4 + 4] cycloadduct (3) with *anti*-configura-

¹ Part XXII, K. Mizuno, H. Okamoto, C. Pac, H. Sakurai, S. Murai, and N. Sonoda, *Chem. Letters*, 1975, 237.

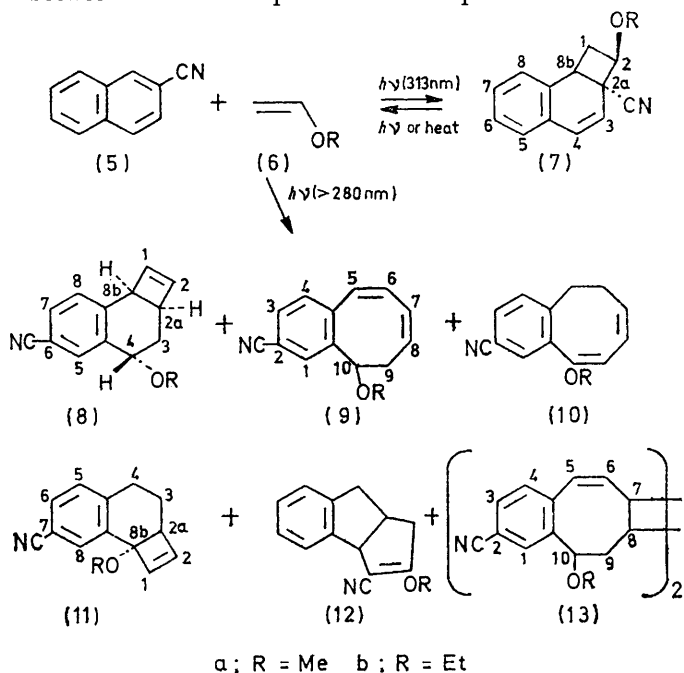
² Preliminary communication, K. Mizuno, C. Pac, and H. Sakurai, *J.C.S. Chem. Comm.*, 1973, 219.

³ D. Bryce-Smith, *Pure Appl. Chem.*, 1968, **16**, 47; J. Cornelisse, V. Y. Merritt, and R. Srinivasan, *J. Amer. Chem. Soc.*, 1973, **95**, 6197; J. Berridge, D. Bryce-Smith, and A. Gilbert, *J.C.S. Chem. Comm.*, 1974, 964; T. S. Cantrell, *Tetrahedron Letters*, 1974, 3959, and references cited therein.

⁴ K. Mizuno, C. Pac, and H. Sakurai, *J.C.S. Perkin I*, 1974, 2360, and references cited therein.

⁵ D. Creed and R. A. Caldwell, *J. Amer. Chem. Soc.*, 1974, **96**, 7369; K. Mizuno, C. Pac, and H. Sakurai, *ibid.*, p. 2993 and references cited therein.

tion,¹⁰ but that to 2-naphthonitrile (5) occurs in the *syn*-direction to give a cage-like compound (4).¹¹ Thus, photocycloadditions of furan to the nitriles differ in both mode of addition and orientation, according to the position of the cyano-group. This behaviour probably reflects differences in configuration and chemical nature between the furan–naphthonitrile exciplexes.



SCHEME 1

Photocycloadditions of vinyl ethers to 2-naphthonitrile (5) would therefore be expected to differ from additions to

⁶ R. M. Bowman, T. R. Chamberlain, C.-W. Huang, and J. J. McCullough, *J. Amer. Chem. Soc.*, 1974, **96**, 692; N. C. Yang, J. Libman, and M. F. Savitzky, *ibid.*, 1972, **94**, 9226; N. C. Yang and J. Libman, *ibid.*, p. 9228 and references cited therein.

⁷ T. Teitei, P. J. Collins, and W. H. F. Sasse, *Austral. J. Chem.*, 1972, **25**, 171 and references cited therein.

⁸ C. Pac, K. Mizuno, T. Sugioka, and H. Sakurai, *Chem. Letters*, 1973, 187; K. Mizuno, C. Pac, and H. Sakurai, *J.C.S. Chem. Comm.*, 1974, 648.

⁹ C. Pac, T. Sugioka, K. Mizuno, and H. Sakurai, *Bull. Chem. Soc. Japan*, 1973, **46**, 238.

¹⁰ C. Pac, T. Sugioka, and H. Sakurai, *Chem. Letters*, 1972, 39.

¹¹ T. Sugioka, C. Pac, and H. Sakurai, *Chem. Letters*, 1972, 791.

¹² T. R. Chamberlain and J. J. McCullough, *Canad. J. Chem.*, 1973, **51**, 2578.

1-naphthonitrile in stereoselectivity and/or mode of addition. We have briefly reported² that the photoreaction of the nitrile (5) with the ethers (6) affords a single [2 + 2] cycloadduct (7) as a primary product, different from that from 1-naphthonitrile. We also mentioned that further irradiation of the solutions containing compounds (5)—(7) leads to accumulation of other products (8), (10), and (11), with concomitant consumption of (7). On the other hand, McCullough and his co-workers, in an independent study of the same photoreaction, isolated different products, (9a), (12a), and (13a), along with (7a).¹² This discrepancy prompted us to

products previously reported by both groups^{2,12} were isolated by careful column chromatography on silica gel; the product distribution is summarised in Table 1. However, yields of minor products (9)—(13) were poorly reproducible.

The structures of the products isolated were determined from their spectral properties and analytical data † and in some cases by chemical transformation. The skeletal arrangement of the adduct (7a) was readily determined by the n.m.r. spectrum, which shows the olefinic resonances as an AB quartet at δ 5.65 and 6.67 (J 10 Hz) and aliphatic ABCX signals at δ 2.35 (2 H, m),

TABLE 1
Product distribution of the photoreaction of the nitrile (5) with the ether (6b)^a

Filter ^b	Temp. (°C)	Conv. (%)	Yields (%)						
			(7b)	(8b)	(9b)	(10b)	(11b)	(12b)	(13)
(A)	20 ± 5	70	90 (76)	c	c	c	c	c	
(B)	20 ± 5	95	5	70 (46)	tr	tr	5	15 (8)	
(B)	20 ± 5	50 ^d	60	30	tr	tr	ca. 1	5	
(C)	0 ± 3	80	65	15	tr	tr	ca. 1	5	(10)
(C)	20 ± 5	40	40	25	15 (8)	tr	<1	10	(4)

^a A solution in benzene (4 ml) containing 0.05 g of (5) and 1 ml of (6b). Product distribution was determined by g.l.c. analyses and in parentheses are shown the isolated yields based on (5) consumed in the photoreaction of (5) and (6a) on a preparative scale.
^b See text. ^c Less than ca. 5% of combined yield; see text. ^d A neat solution of (6b) (4 ml) containing 0.05 g of (5).

reinvestigate the photoreaction of (5) with (6) in more detail. This paper describes the results, including product distribution under various conditions and a discussion of mechanism.

RESULTS

The product distributions in photoreactions of the nitrile (5) with the ethers (6) depend on the filters used, the concentrations of ethers, and the reaction temperature, but not on solvent. Irradiation of (5) containing an excess of (6a or b) at 313 nm afforded a single [2 + 2] cycloadduct (7a or b) in 80–90% yield.* When Pyrex glass was used as filter (transmission >280 nm) the adduct (7a or b) was initially produced, and further irradiation led to gradual accumulation of compounds (8a or b), (10a or b), (11a or b), and (12a or b), with concomitant consumption of (7a or b). Ultimately, when 90–95% of the nitrile (5) had been consumed, the adduct (7a or b) had almost disappeared, and (8a or b) was obtained in 70% yield. When a large excess of (6a or b) was used, the formation of (7a or b) was efficient and accumulation of the other products was slow. The dihydrobenzocyclo-octene (9a or b) was obtained only in a small amount at low conversion by irradiation through an aqueous solution of potassium hydrogen phthalate (transmission >300 nm) at 20 ± 5 °C. On the other hand, irradiation of a methanolic solution at 0 ± 3 °C through this filter solution gave a 2 : 2 adduct (13a or b), formed in lesser amounts at 20 ± 5 °C. Thus, all the

3.4 (1 H, dd), and 4.36 (1 H, dd). The *endo*-structure was assigned from the chemical shift of H-2 (δ 4.34), which is similar to that of H-1 (δ 4.40) of the *endo*-adduct (1a) rather than that of the *exo*-adduct (2a) (δ 4.09).⁹ The 1,2-dihydronaphthalene structure was supported by the u.v. spectrum [λ_{\max} 270 (ϵ 6 510) and 262 nm (6 480) in cyclohexane].¹³

The mass spectrum of the cyclobutene (8a) showed the parent peak at m/e 211 but different fragment peaks from those of (7a). The u.v. spectrum [λ_{\max} 280 (ϵ 380), 268 (510), and 260 nm (435)] did not correspond to a 1,2-dihydronaphthalene chromophore nor to an anisole chromophore, but was similar to that of benzonitrile. Moreover, (8a) exhibits i.r. absorption at 1 565 cm⁻¹, which is assignable to the stretching vibration of a cyclobutene double bond.¹⁴ In the n.m.r. spectrum the aromatic resonances appear as simple ABX signals at δ 7.10 (d, J 8 Hz), 7.26 (dd, J 8 and 1 Hz), and 7.65 (d, J 1 Hz) and the coupling constants between the olefinic protons (J 3 Hz) and between each olefinic proton and the adjacent methine proton (J 1 Hz) are consistent with a fused cyclobutene structure as shown by molecular models.¹⁵ Extensive double-irradiation experiments established that couplings of H-3_{ax} with H-4 (J 11.2 Hz) and H-2a (J 5.6 Hz) are very similar to those of axial-axial and axial-equatorial vicinal couplings respectively of cyclohexane derivatives, whereas those of H-3_{eq} with H-4 (J 4.5 Hz) and H-2a (J 3 Hz) are similar to values for equatorial-axial and equatorial-equatorial vicinal coup-

¹³ W. Hüchel, E. Ververa, and V. Wörfel, *Chem. Ber.*, 1957, **90**, 901; J. J. McCullough, *Canad. J. Chem.*, 1969, **757** and ref. 9.

¹⁴ L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' 2nd edn., Wiley, London, 1966, p. 37.

¹⁵ L. M. Jackmann and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, Braunschweig, 1969, p. 303.

* G.l.c. of the photolysate showed the presence of traces of other products, in amounts too small for unambiguous identification.

† Available as Supplementary Publication No. SUP 21514 (5 pp.). For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

lings, thus confirming the *trans*-relationship between H-4 and H-2a.¹⁶

Addition of the shift reagent Eu(fod)₃ caused the signal of only one of the aromatic protons to move rapidly downfield. Since co-ordination involving both the cyano- and methoxy-groups is expected this signal must be assigned to H-5, demonstrating the presence of the cyano-group at C-6. This structural assignment for (8a and b) was further supported both by thermal rearrangement of (8a and b) to (10a and b) and by photochemical formation of (8b) from (9b). The product (8a) could be that assigned a benzonorbornene structure by McCullough.¹²

The u.v. [λ_{max} (cyclohexane) 280 (ϵ 2 520) and 261 nm (2 320)] and i.r. spectra [ν_{max} (KBr) 2 250 and 1 635 cm^{-1}] of compound (10a) showed that it is a nitrile possessing a conjugated diene chromophore. The n.m.r. spectra showed that (10a and b) each had three aromatic protons (ABX spin system), three olefinic protons, and four aliphatic protons. The structures assigned are in good accord with the n.m.r. data. Moreover, irradiation of (10a and b) gave the cyclobutenes (11a and b) and acidic hydrolysis of (10b) occurred efficiently to give the enone (14) in good yield, again supporting the dienol ether structure. The ketone (14) shows an i.r. band at 1 673 cm^{-1} and an $n-\pi^*$ u.v. band at 325 nm (ϵ 245 in cyclohexane), both characteristic of an aromatic ketone. The structure of (14) was established by analysis of its n.m.r. spectrum; the chemical shifts of the two olefinic protons are almost identical [δ 5.55 (2 H, m)] and very similar to that of the olefinic protons of cyclo-octene (δ 5.54), indicating non-conjugation of the double bond with the carbonyl group. Double-irradiation experiments supported this assignment. The cyano-group was thus considered to be on the aromatic ring, and the position was readily determined to be C-3 by the chemical shift of the X proton in the ABX system of (14), which is considerably greater (δ 7.95) than that of (10a) (δ 7.71) unlike those of the A and B protons. This can be attributed to the deshielding effect of the carbonyl group in (14) on the *peri*-proton (X = H-4). From these results, we believe that the conjugated enone structure previously reported for (14) is erroneous.²

Spectral data and m.p.s of compounds (9a), (12a), and (13a) were essentially identical with those reported by McCullough *et al.*¹² We accept the structures assigned by them, which are in good accordance with the spectral properties.

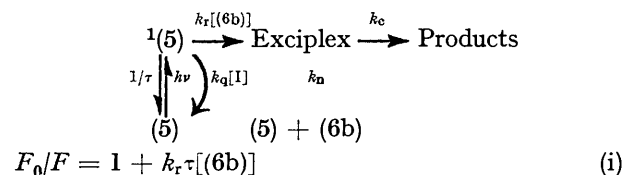
DISCUSSION

The adduct (7b) comprises nearly 90% of the primary products. Its formation was neither quenched by isoprene and oxygen nor sensitised by benzophenone and Michler's ketone, thus it probably occurs *via* the excited singlet state of (5). The singlet mechanism was unambiguously confirmed by kinetic results. Fluorescence of (5) was inefficiently but significantly quenched by (6b), the $k_r\tau$ values for air-saturated benzene solutions

* In the absence of isoprene, curved Stern-Volmer plots were obtained, owing to sensitised decomposition of (7b) by (5) (see later).

being 0.46 $\text{mol}^{-1} \text{dm}^3$ ($[(5)] = 1 \times 10^{-3} \text{mol dm}^{-3}$) and 0.24 $\text{mol}^{-1} \text{dm}^3$ ($[(5)] = 0.1 \text{mol dm}^{-3}$). The difference between the $k_r\tau$ values for dilute and concentrated solutions can be attributed to different lifetimes of (5) at different concentrations, since excimer formation must be taken into account in the case of a concentrated solution. In fact the fluorescence spectrum of a concentrated solution was markedly different from that of a dilute solution.

The quantum yields of disappearance of (5) [$\phi_{-(5)}$] and formation of (7b) [$\phi_{(7b)}$] for solutions in benzene in the presence of isoprene* at 313 nm were determined with varying concentrations of (6b). Thus, linear plots of $1/\phi_{-(5)}$ and $1/\phi_{(7b)}$ vs. $1/[6b]$ were obtained, from which the slopes and the intercepts were determined respectively as 8.7 mol dm^{-3} and 3.5 for $\phi_{-(5)}$, runs $\{[(5)] = 1.13 \times 10^{-3} \text{mol dm}^{-3}$ and 23.7 mol dm^{-3} and 4.6 for $\phi_{(7b)}$, runs $\{[(5)] = 0.1 \text{mol dm}^{-3}\}$. When these values and the quenching constants of isoprene ($k_q\tau$) were applied to equation (ii), the $k_r\tau$ values were calculated as 0.44 $\text{mol}^{-1} \text{dm}^3$ for $\phi_{-(5)}$ and 0.23 $\text{mol}^{-1} \text{dm}^3$ for $\phi_{(7b)}$, in excellent agreement with the values obtained from the fluorescence quenching studies on the corresponding solutions.



$$F_0/F = 1 + k_r\tau[(6b)] \quad (i)$$

$$1/\phi_{-(5)} \simeq 1/\phi_{(7b)} = (1 + k_a/k_c) \left\{ 1 + \frac{1 + k_q\tau[I]}{k_r\tau[(6b)]} \right\} \quad (ii)$$

$$k_q\tau[I] = 0.093; \quad k_q\tau = 3.1 \text{ mol}^{-1} \text{ dm}^3, \quad [I] = 0.03 \text{ mol dm}^{-3} \text{ for } \phi_{-(5)}$$

$$k_q\tau[I] = 0.170; \quad k_q\tau = 3.4 \text{ mol}^{-1} \text{ dm}^3, \quad [I] = 0.05 \text{ mol dm}^{-3} \text{ for } \phi_{(7b)}$$

Fluorescence quenching in polar solvents is much more effective than that for a solution in benzene (Table 2),

TABLE 2
Values of $k_r\tau$ from fluorescence quenching

Quencher (6b)	Adiabatic ionisation potential	Solvent ^a	$k_r\tau/dm^3 \text{ mol}^{-1}$
	8.49 ^b	PhH	0.46
		PhH ^c	0.24
		MeOH	3.88
		MeCN	2.98
		PhH	1.15 ^e
2,3-Dimethylbut-2-ene	8.05 ^d	MeOH	148 ^f
		MeCN	167 ^f

^a Air-saturated solution; $[(5)] = 1.1 \times 10^{-3} \text{mol dm}^{-3}$.
^b M. P. Niemczyk, N. E. Schore, and N. J. Turro, *Mol. Photochem.*, 1973, **5**, 69. ^c $[(5)] = 0.1 \text{mol dm}^{-3}$. ^d G. N. Taylor, *Chem. Phys. Letters*, 1971, **10**, 355. ^e Measured in this work.
^f See ref. 19a.

showing that k_r is greater in polar solvents, since lifetimes of (5) in methanol and cyclohexane are known to be

¹⁶ J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' vol. 2, Pergamon, London, 1966, p. 701.

almost identical.¹⁷ This solvent effect can be reasonably interpreted by assuming the intervention of an intermediate possessing charge-transfer character as suggested in a previous paper.⁹ Since such an intermediate (probably an exciplex)* is expected to be more stabilised in polar solvents than in less polar solvents, it would be predicted that values of k_f would increase with increase of solvent polarity. The exciplex intermediacy is further supported by the greater effectiveness of fluorescence quenching with 2,3-dimethylbut-2-ene, which possesses a lower ionisation potential (Table 2). Moreover, we observed that the fluorescence quenching by 2,3-dimethylbut-2-ene in a dilute solution in benzene was accompanied by enhancement of longer wavelength emission, due to the appearance of a new weak emission (exciplex emission) at longer wavelength (390–440 nm).

In relation to solvent effects on mechanistic pathways from exciplexes,^{6a,18} however, it is of interest that the systems (5)–(6) and (5)–2,3-dimethylbut-2-ene reveal very different solvent effects. In the latter case, the photoreaction of a methanolic solution gives solvent-incorporated adducts,^{19a} unlike the reaction in neat olefin,^{19b} and moreover the fluorescence quenching in methanol is one hundred times more effective than that in benzene, suggesting occurrence of a rapid electron-transfer reaction as established for some exciplex-forming systems.¹⁸ In contrast, the former system does not show such drastic solvent effects on both product distribution and the fluorescence quenching rate, implying negligible importance of electron-transfer reactions, even in polar media. The solvent effects can rather be interpreted in terms of solvation of a (5)–(6) exciplex depending on solvent polarity. In this regard, it is notable that the quantum yield (0.046) for disappearance of (5) in a dilute methanolic solution in the presence of 2.0 mol dm⁻³ of (6b) was significantly lower than that in a benzene solution (0.123), probably owing to solvation of the exciplex by methanol which leads to faster decay (greater k_n) in comparison with the decay in benzene. Alternatively, the lower quantum yield in methanol could be interpreted in terms of hydrogen bonding of a 1,4-diradical intermediate as has been discussed for Norrish type II photoelimination of ketones.²⁰ However, the intermediacy of a diradical is not consistent with the selective formation of the thermodynamically less stable (7) in both methanol and benzene.

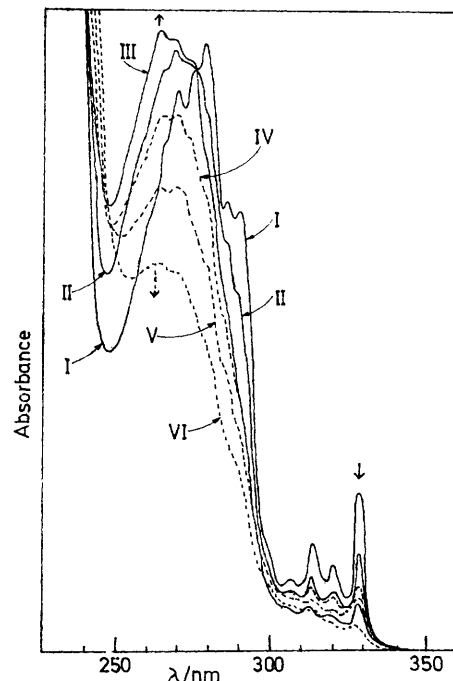
The change of the product distribution in irradiation through Pyrex is of mechanistic interest. This is shown dramatically by the u.v. spectra (Figure); irradiation at 313 nm of a dilute solution of (5) in cyclohexane containing (6b) resulted in a spectrum essentially identical with that of (7b), which rapidly collapsed to a spectrum similar to that of (8b) on further irradiation of the solution through Pyrex. We previously² ascribed this change to the photorearrangement of (7a and b); this

* A charge-transfer complex is not formed in the ground state, since the u.v. spectrum of (5) in the presence of (6b) is identical with that in the absence of (6b).

¹⁷ P. Lentz, H. Blume, and D. Schulte-Frohlinde, *Ber. Bunsengesellschaft Phys. Chem.*, 1970, **74**, 484.

has now been found to be erroneous, since (7a and b) are quantitatively decomposed into (5) and (6a or b) by either direct irradiation through Pyrex or sensitisation with benzophenone, Michler's ketone, and (5), but do not give compounds (8a and b) and the other products at all, even at –60 °C.

The change in product distribution is now thought to be due to continuous accumulation of the minor products during irradiation through Pyrex, as (7a or b) is decomposed in competition with its formation by light of longer



Spectral change of a cyclohexane solution containing the nitrile (5) (4.0×10^{-4} mol dm⁻³) and the ether (6b) (2.0 mol dm⁻³); solid line spectra: 313 nm irradiation for 0 (I), 20 (II), and 80 min (III); dotted line spectra: irradiation of mixture (III) through Pyrex for 50 (IV), 110 (V), and 180 min (VI)

wavelength than 280 nm. This interpretation is in good accord with the observations that irradiation at 313 nm or in the presence of a large excess of (6a or b) through Pyrex resulted in no appreciable or only a small change in product distribution, since (7a or b) is not appreciably photolysed at 313 nm or accumulates faster than it decomposes in the presence of a large excess of (6a or b) even during irradiation through Pyrex.

In order to elucidate the mechanistic pathways affording the minor products (ca. 5% of the primary products), photochemical and thermal interconversions were investigated; the results are shown in Scheme 2. Details of these reactions will be published elsewhere,

¹⁸ For a review see M. Ottolenghi, *Accounts Chem. Res.*, 1973, **153**.

¹⁹ (a) J. J. McCullough and W. S. Wu, *J.C.S. Chem. Comm.*, 1972, 1136; (b) T. S. Cantrell, *J. Amer. Chem. Soc.*, 1972, **94**, 5929.

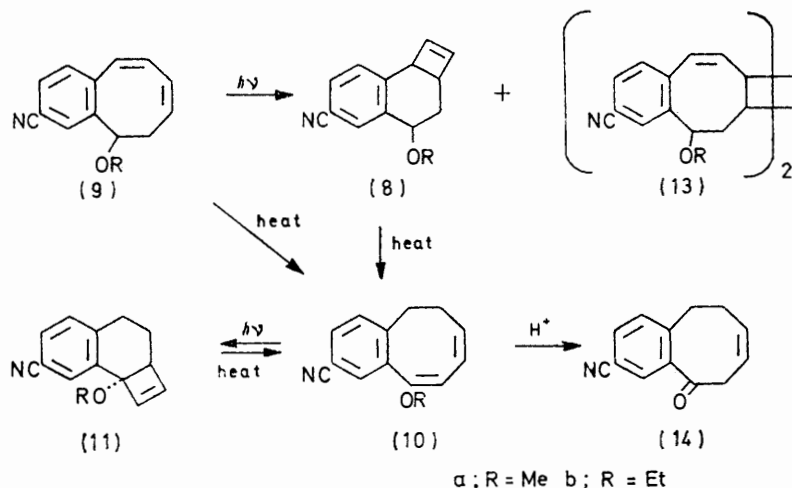
²⁰ P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Amer. Chem. Soc.*, 1972, **94**, 7480.

but some significant points will be discussed in relation to the mechanism of formation of these products.

None of the products (9), (10), and (12) is formed by secondary photoreactions of the other products. Compound (11) is evidently an artefact formed by photocyclisation of (10) since irradiation of the latter gave

(10), and (12) is not sensitised by benzophenone and Michler's ketone, suggesting the intermediacy of the excited singlet state of (5), though it is not clear whether or not these products are formed *via* an exciplex.

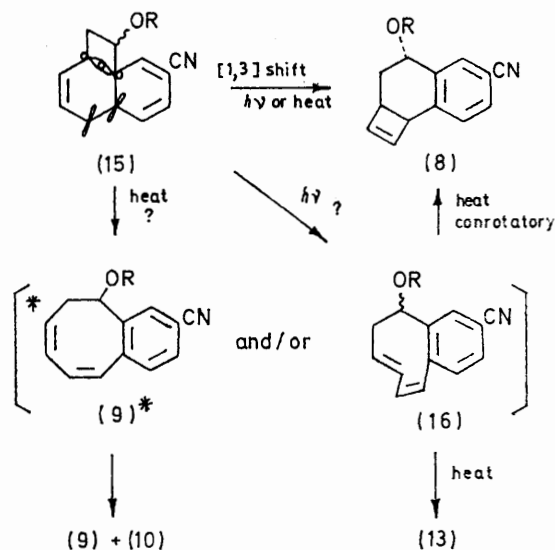
In summary, the $[\pi 2 + \pi 2]$ photocycloaddition of (6) to (5) occurs in a stereoselective manner unlike that to



SCHEME 2

(11) in quantitative yield. Likewise, (8) and (13) are formed by photochemical ring closure and dimerisation of (9); this was confirmed by irradiation of (9) in solution through Pyrex, giving (8) and (13) in good yield. Moreover, there is a remarkable temperature dependence of the ratio of the products (8) and (13): 0.5 : 1 at $0 \pm 3^\circ\text{C}$, 1.0 : 1 at $20 \pm 5^\circ\text{C}$, and 2.0 : 1 at $70 \pm 5^\circ\text{C}$, in good accord with the observation that the yield of (13) is higher at $0 \pm 3^\circ\text{C}$ than at $20 \pm 5^\circ\text{C}$. However, it is doubtful that all the product (8) formed from the photo-reaction of (5) with (6) is obtained by photocyclisation of (9), since the expected yield of (8) based on the (8) : (13) ratio never exceeds 50% at best (at $20 \pm 5^\circ\text{C}$),* and the observed yield is 70%. Therefore, (8) appears to be formed by another route as well. Since the products (8)–(10) have similar skeletons, their formation could be interpreted in terms of a common transient compound (15), which is formed by the photoaddition of (6) to the C(8)–C(8a) bond of (5); the intervention of vibrationally excited (9) arising from cleavage of the remaining single bond at this position in (15) provides a reasonable route to (9) and (10), since (9) thermally rearranged to (10) and/or the *cis, trans*-diene (16) generated by the bond cleavage would be a possible precursor of (8) and (13) by analogy with the thermal cyclisation and dimerisation of *cis, trans*-cyclo-octa-1,3-diene.²¹ Alternatively, formation of (8) could be explained in terms of a [1,3] sigmatropic shift of the naphthalene 8,8a-bond in (15). The mechanism for formation of (12) cannot be reasonably discussed at present. However, formation of compounds (8), (9),

1-naphthonitrile, but both the systems (5)–(6) and 1-naphthonitrile–(6) reveal similar solvent-dependent behaviour of quantum yields and fluorescence quenching rates, implying the intervention of exciplexes which have a similar charge-transfer nature but different configurational stabilities. Moreover, the photoreactions of (5)



SCHEME 3

with (6) could be of use for the preparation of various cyclic compounds, by suitable choice of filters and thermal or photochemical rearrangement of the photoproducts.

* Irradiation of (9) in the presence of (5) at $20 \pm 5^\circ\text{C}$ did not give (8) in appreciable amount, showing the absence of the sensitisation by (5).

²¹ A. Padwa, W. Koehn, J. Masaracchia, C. L. Osborn, and D. J. Trecker, *J. Amer. Chem. Soc.*, 1971, **93**, 3633.

EXPERIMENTAL

Materials.—Commercial thiophen-free benzene was washed with sulphuric acid until no further colouration of the acid layer took place, then with water, and distilled from sodium. Reagent grade methanol was distilled from calcium hydride. Ethyl vinyl ether (Nakarai Chemicals) was distilled over calcium chloride under nitrogen before use. Methyl vinyl ether (Tokyo Kasei) was distilled from a gas cylinder before use. 2-Naphthonitrile (Tokyo Kasei) was purified by vacuum distillation and subsequent recrystallisation from hexane (m.p. 66–67 °C).

General.—N.m.r. spectra were obtained with a Hitachi-Perkin-Elmer R24 spectrophotometer (60 MHz) and a JEOL JNM JS-100 instrument (100 MHz) for solutions in carbon tetrachloride or deuteriochloroform containing tetramethylsilane as internal standard, i.r. spectra with a Hitachi EPI-S2 spectrophotometer, u.v. spectra with a Hitachi 124 spectrophotometer, and fluorescence spectra with a Hitachi MPF-2A spectrofluorimeter. Yields and product ratios were determined by g.l.c. with a Shimadzu GC-2C machine equipped with a flame-ionisation detector (column of 5% Ucon Oil LB-550X on Celite 545; 0.75 or 1.5 m; 160 °C). M.p.s were measured for samples in capillaries.

Quantum Yields.—(a) The solutions were prepared by dissolving the nitrile (5) (1.13×10^{-3} mol dm⁻³), the ether (6b) ($0.8\text{--}4.0$ mol dm⁻³), and isoprene (0.03 mol dm⁻³) in benzene or methanol. Monochromatic light at 313 nm was obtained from a high-pressure mercury arc (450 W) by passage through a Toshiba UV-D25 glass filter and aqueous potassium chromate (0.2 g dm⁻³; 10 mm path length). The light intensity (I_0) was determined by potassium ferrioxalate actinometry to be 2.01×10^{-7} einstein cm⁻² min⁻¹. Sample solutions placed in an optical cell ($10 \times 10 \times 45$ mm) were irradiated and the decrease of absorbance at 316 nm (A) was monitored. Plots of $\ln(e^A - 1)$ vs. irradiation time (t /min) were linear. Quantum yields for the disappearance of (5) [$\phi_{(5)}$] were obtained from the slopes of the lines by applying the equation $\ln(e^A - 1) = -1000 \epsilon \phi_{(5)} I_0 t + C$, where ϵ is the molar absorption coefficient of (5) at 316 nm (8.9×10^2 dm² mol⁻¹) and C is a constant. In all the runs, conversions were less than 10%.

(b) The quantum yields for formation of (7b) [$\phi_{(7b)}$] were determined for solutions in benzene 0.1 mol dm⁻³ in (5), 0.05 mol dm⁻³ in isoprene, and $0.5\text{--}4.0$ mol dm⁻³ in (6b). Relative quantum yields were obtained by using a 'merry-go-round' apparatus immersed in water at 20 ± 2 °C. Light filtered through the filter (A) (see later) was used to irradiate samples (4 ml) in matched Pyrex tubes. After irradiation, *p*-methoxybenzophenone (internal standard) was added to each irradiated solution and the amounts of (7b) formed were determined by g.l.c. analysis. The absolute quantum yield in the presence of 4.0 mol dm⁻³ of (6b) was 0.097 . In all the runs, conversions were less than 5%.

Photoreactions of 2-Naphthonitrile with Alkyl Vinyl Ethers.—**General procedures.** Irradiation was carried out with an Eikosha PIH 300 W high-pressure mercury arc at room temperature. The following filters were employed: (A) 5.0×10^{-4} mol dm⁻³ aqueous potassium chromate in a Pyrex vessel (10 mm path length; 313 nm), (B) Pyrex (>280 nm), and (C) 2.4×10^{-2} mol dm⁻³ aqueous potassium hydrogen phthalate in a Pyrex vessel (10 mm path length; >300 nm). In control runs, a solution in benzene (4 ml) containing the nitrile (5) (0.05 g) and the ether (6b) (1 ml) or a solution of (5) (0.05 g) in (6b) (4 ml) was irradiated and the

photolysate was analysed by g.l.c. Oxygen-free nitrogen was bubbled through the solutions for 30 min before irradiation. In preparative experiments, a solution in benzene or methanol (200 ml) containing (5) and (6a or b) was irradiated for 20–50 h. The solvent and the excess of (6a or b) were removed, and the residue was subjected to column chromatography over silica gel (Merck Kieselgel 60) with benzene-hexane as eluant. After elution of unchanged (5) with benzene-hexane (1 : 3), compounds (12a or b), (9a or b), (7a or b), (10a or b), and (11a or b) were isolated in sequence by elution with 1 : 2, 1 : 1.8, 1 : 1, 3 : 2 and 4 : 1 solvent mixtures, respectively. Since the procedures for the photo-reactions of (5) with (6a) and with (6b) were almost identical, only the former reaction is described.

(a) **With filter (A).** A solution in benzene containing (5) (1.0 g) and (6a) (30 g) was irradiated at 20 ± 5 °C for 40 h. Column chromatography afforded starting material (5) (0.3 g), endo-2-methoxy-1,2,2a,8b-tetrahydrocyclobuta[a]naphthalene-2a-carbonitrile (7a) (0.73 g, 76%), m.p. 71.5–72.5 °C (from hexane), and small amounts of other products (ca. 0.1 g).

(b) **With filter (B).** A solution in benzene containing (5) (2.0 g) and (6a) (30 g) was irradiated at ambient temperature for 50 h. Column chromatography afforded the nitrile (5) (0.1 g), 3,3a,4,8b-tetrahydro-2-methoxycyclopent[a]indene-1-carbonitrile (12a) (0.2 g, 8%), m.p. 89.5–92 °C (from hexane), 2a,3,4,8b-tetrahydro-4-methoxycyclobuta[a]naphthalene-6-carbonitrile (8a) (1.2 g, 46%), m.p. 50–51 °C (from hexane), 5,6-dihydro-10-methoxybenzocyclo-octene-2-carbonitrile (10a) (ca. 0.02 g), m.p. 106.5–108 °C (from methanol), 2a,3,4,8b-tetrahydro-8b-methoxycyclobuta[a]naphthalene-7-carbonitrile (11a) (0.1 g, 4%), m.p. 92–93 °C (from hexane), and a mixture of adducts.

(c) **With filter (C).** A methanolic solution containing (5) (2.0 g) and (6a) (30 g) was irradiated at ambient temperature for 20 h. During irradiation a solid was precipitated, and was filtered off to yield the cyclobutabis(benzocyclo-octene) (13a) (0.05 g, 4%), m.p. 290–300 °C (decomp.) (from benzene). After evaporation of methanol and the excess of (6a), column chromatography gave the nitrile (5) (1.1 g), compound (12a) (ca. 0.1 g), 9,10-dihydro-10-methoxybenzocyclo-octene-2-carbonitrile (9a) (0.1 g, 8%), m.p. 108–110 °C (from hexane), and compounds (8) (ca. 0.25 g) and (7a) (ca. 0.4 g).

Photolyses and Pyrolyses of the Adducts (7a and b).—A solution in methanol or benzene solution of (7a or b) (0.1 g in 4 ml) in a Pyrex tube was irradiated with a high-pressure mercury arc (300 W). During the irradiation, g.l.c. analyses of the photolysate were carried out at 1 h intervals for the initial 5 h; it was found that the amount of nitrile (5) increased linearly with disappearance of (7a or b) and no other compounds were formed at 100% conversion.

Irradiation of a solution in benzene of (7a or b) (0.01 g) in the presence of (5) (0.03 g), benzophenone (0.03 g), or Michler's ketone (0.03 g) for less than 2 h also resulted in complete decomposition to (5). Pyrolyses of (7a or b) at 230–250 °C again gave (5).

Pyrolyses of the Adducts (8a and b).—On heating crystalline (8a or b) (0.1 g) at 200–210 °C for 1 h under nitrogen, a brownish material was obtained, which was chromatographed on silica gel. Elution with benzene-hexane (1 : 2; 500 ml) gave the benzocyclo-octene (10a or b) (ca. 70 mg, 70%), and further elution afforded brownish glassy materials which were not identified.

Pyrolyses of the Adducts (9a and b).—Crystalline (9a or b)

(0.01 g) in a Pyrex tube was degassed and heated at 280 ± 5 °C for 15 min; the n.m.r. spectrum of the resultant mixture showed formation of (10a or b) in *ca.* 70% yield.

Irradiation of the Adduct (9b).—A solution in benzene of (9b) (0.01 g in 5 ml) in a Pyrex tube at 0 ± 3 °C for 6 h, at 20 ± 5 °C for 3 h, or at 70 ± 5 °C for 30 min was irradiated with a high-pressure mercury arc. During the irradiation, g.l.c. analyses of the photolysate were carried out at 30 min intervals; it was found that compound (8b) was formed linearly with disappearance of (9b) but the total yields were decreased. After irradiation, removal of solvent left a solid which was shown to consist of (8b) and (13b) by the n.m.r. spectra *ca.* (ratios 1 : 2, 1 : 1, and 2 : 1 respectively).

Irradiation of the Benzocyclo-octenes (10a and b).—An ethereal solution of (10a) (0.2 g in 100 ml) in a Pyrex vessel was irradiated with a high-pressure mercury arc for 5 h. After irradiation, removal of solvent left an oil containing

(11a) and a small amount of (10a); subsequent chromatography afforded pure (11a) (0.18 g). Similarly, irradiation of (10b) afforded (11b) quantitatively, but the product did not solidify, even on storage in a refrigerator for 2 months.

Acid-catalysed Hydrolysis of the Benzocyclo-octene (10b).—To ethanolic hydrochloric acid (0.1N; 100 ml) was added an ethanolic solution of (10b) (0.2 g) and the solution was left for a week at an ambient temperature. After removal of two-thirds of the solvent, the solution was extracted with ether. The extract was washed with saturated aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride, dried (MgSO_4), and evaporated. The brownish residue was chromatographed on silica gel to afford 3-cyano-9,10-dihydrobenzocyclo-octen-5(6H)-one (14) (0.12 g), m.p. 106.5—107.5 °C (from methanol).

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