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PHOTOCHEMICAL REACTIONS OF NAPHTHYL-VINYL NON-CONJUGATED BICHROMOPHORIC SYSTEMS

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Abstract: 2-(1-Naphthyl)ethyl vinyl ether undergoes intramolecular 1,2-photocycloaddition whereas the 2-naphthyl isomer yields a product reflecting dimerisation and loss of the elements of acetylene: consistent with such diverse photochemistry, the addition of 2,3-dihydropyran to naphthalene produces only the 1,2-, 1',2'-regioisomer.

Although the photoaddition and photodimerisation processes of naphthalene derivatives, particularly those having alkoxy and cyano substituents, have been widely reported,[1] examples of photo-induced reactions of the parent hydrocarbon are sparse and cycloadditions of ethenes to the arene have only been described for cis and trans cyclo-octene,[2] acrylonitrile[3] and dichlorovinylene carbonate.[4] Further, there has only been one report of intramolecular photocycloaddition of an ethene to the naphthyl moiety and all of the systems studied had trimethylethenyl (electron donor) and cyanonaphthyl (electron acceptor) chromophores linked by the $-CH_2-O-CH_2-$ unit.[5] In order to gain information concerning the factors which control cycloadditions to naphthalene and to investigate the scope of the intramolecular process we have studied the effects on the photolability of naphthyl-vinyl bichromophoric systems of the structure of the intervening chain between the chromophores and the position of its attachment to the arene.

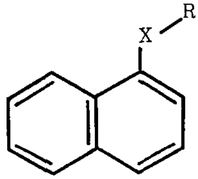
Irradiation of the bichromophores (1a-h) and (2a-h)[6] as 1% solutions in cyclohexane using either 254 nm radiation or wavelengths longer than 290 nm produced essentially similar results. These data and those from fluorescence spectral analysis of the bichromophores and their reduced derivatives are summarised in the Table. The photostability of the hydrocarbons (1a) and (2a) reflects the absence of significant quenching of the arene fluorescence by the vinyl chromophore in the two isomers but it would appear for some systems (e.g. (1e) and (2e)) that the reduced arene fluorescence intensity results to some extent from a "through bond" effect[7] involving the groups in the chain between the chromophores, whereas in others (e.g. (1b) and (1f)) clearly there is intramolecular interaction between the naphthyl and vinyl groups although only in the former case does this lead to intramolecular photo-cycloaddition.

TABLE

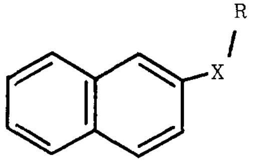
α Series			β Series		
Compound	Fluorescence Intensity^{a,b}	Result of Irradiation	Compound	Fluorescence Intensity^{a,c}	Result of Irradiation
1a	0.9	stable	2a	0.9	stable
1b	0.6	(8)	2b	0.85	$C_{26}H_{26}O_2$ compound
3b	1.0	-	4b	0.9	-
1c	0.9	(5)	2c	0.9	(6)
3c	0.9	-	4c	0.9	-
1d	0.75	stable	2d	0.6	stable
3d	0.9	-	4d	0.65	
1e	0.55	d	2e	0.4	d
3e	0.55	-	4e	0.4	-
1f	0.45	polymerisation	2f	0.4	polymerisation
3f	1.0	-	4f	0.7	-
1g	0.65	stable	2g	0.6	stable
3g	0.75	-	4g	0.85	-
1h	0.55	α-naphthol[e]	2h	0.9	β-naphthol[e]
3h	0.85	-	4h	1.0	-

(a) 2×10^{-4}M in iso-octane, (b) relative to (3a), (c) relative to (4a), wavelength of excitation at the absorption maximum of each system and comparisons of intensity made at the fluorescence maximum, (d) trace amounts of products detected by t.l.c. but not g.l.c., (e) small amounts of isomers of the bichromophore also detected.

Formation of the naphthols from (1h) and (2h) and that of the aldehydes (5) and (6) from (1c) and (2c) respectively has precedence (refs. 8 and 9 respectively) but the marked difference in the photochemical behaviour of (1b) and (2b) is unexpected. The product ($C_{26}H_{26}O_2$ requires 370.1930, found 370.1933)[10] from the latter reflects dimerisation of the bichromophore and loss of the elements of acetylene and while this process is not readily envisaged, the ^{1}H n.m.r. spectrum is consistent with structure (7) in which the vinyl but not the naphthyl chromophores are involved in the photoreaction. The fluorescence spectra of (2b) and (4b) indicate little excited state interaction between the S_1 arene and vinyl group in this system. In marked contrast there is appreciable quenching of the arene fluorescence by the vinyl group in (1b) and this is reflected in the efficient (Φ = 0.5) intramolecular cycloaddition of this system to give (8) [δ values ($CDCl_3$, 220 MHz) 7.4-7.0 (4H, m), 6.35 (1H, dd, J's = 10 and 1Hz), 5.85 (1H, dd, J's = 10 and 5Hz), 2.9 (1H, dd + fine splitting, J's = 5 and 1Hz), 4.59 (1H, dd + fine splitting, J's = 5.5 and 5Hz), 4.5-4.25 (2H, m), 2.35 (2H, m), and 2.3-2.0 p.p.m. (2H, m). $C_{14}H_{14}O$ requires M^+ 198.1045, found 198.1045].[10] The formation of (8) is not appreciably affected by change in solvent polarity and is considered to arise from the singlet state since the cycloaddition is appreciably quenched (63%) from irradiation of solutions of (1b) degassed under xenon which is known to increase triplet populations. Such marked differences between the photoreactions and degree of excited state interaction of the chromophores of (1b) and (2b) may reflect a higher charge density of the 1- than at the 2-position for the S_1 state of naphthalene. For such a situation, the vinyl group of the enol ether of (1b) may conveniently be aligned to yield (8) whereas for (2b) this orientation would be considerably restricted by the unit connecting the chromophores.

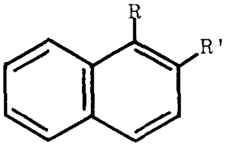


(1) R=$-CH=CH_2$
(3) R=C_2H_5



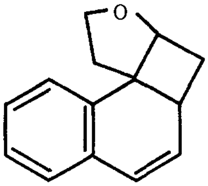
(2) R=$-CH=CH_2$
(4) R=C_2H_5

a, X = $-(CH_2)_3-$
b, X = $-(CH_2)_2-O-$
c, X = $-CH_2-O-$
d, X = $-CH_2-O-CH_2-$
e, X = $-CH_2COO-$
f, X = $-CH_2-OCO-$
g, X = $-COOCH_2-$
h, X = $-OCOCH_2-$

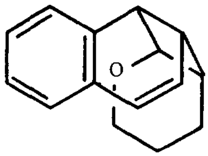


(5) R = $-CH_2CHO$, R'=H
(6) R=H, R' = $-CH_2CHO$

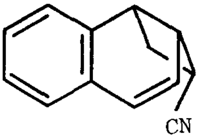
$(2\text{-Nap-CH}_2\text{-CH}_2\text{-O})_2\text{CHCH}_3$
(7)



(8)



(9)



(10)

In the absence of charge density data for S_1 naphthalene we have further examined the possibility of operation of such a directing influence by study of the intermolecular photoreaction of naphthalene with enol ethers. Irradiation of the arene with ethyl vinyl ether gave several products in very low yield but the reaction with 2,3-dihydropyran is regio- and stereo-specific giving (9) as the sole primary photoproduct.[11] [δ values ($CDCl_3$ 220 MHz)

7.4-6.95 (4H, m), 6.42 (1H, dd, J's = 10 and 1Hz), 5.92 (1H, dd, J's = 10 and 4.5Hz), 4.48 (1H, dd + fine splitting, J's = 6.5 and 2Hz), 3.74 (1H, dd, J's = 9 and 6.5 Hz), 3.62 (1H, m), 3.31 (2H, m), 2.88 (1H, dd + minor splitting), 2.0 - 1.6 (2H, m), and 1.6 - 1.0 p.p.m. (2H, m). $C_{15}H_{16}O$ requires M^+ 212.1202, found 212.1196].[10] It thus appears that the specificity of the intra- and inter-molecular reactions of naphthalene-ethene systems results from similar controlling factors and it is most satisfying to note that formation of the major cycloadduct (10) from naphthalene and acrylonitrile is also consistent with a higher charge density at the 1- than the 2-position of the S_1 arene and this gives predictability to its cycloaddition reactions.

References and Notes

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10. The P.C.M.U., Harwell, are thanked for accurate mass measurements and 220 MHz spectra.
11. The adduct (9) rapidly reaches a photostationary state and is converted into the naphthalene-2,3-dihydropyran 1,4- 1',2'-cycloadduct isomer (m.p. 116-117°C).

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