

Photochemical Reactions of *N*-Alkyl- and *N*-Aryl-1,4-dihydro-1,4-iminonaphthalene Derivatives

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Upon irradiation *N*-alkyl- and *N*-aryl-1,4-dihydro-1,4-iminonaphthalene derivatives undergo photoisomerization to give mainly azatricycloundecatetraene and/or naphthalene derivatives depending upon the substituents on the nitrogen atom and the aromatic ring.

The photoisomerization of 1,4-dihydro-1,4-iminonaphthalene derivatives has been established by Prinzbach *et al.*¹ and Swenton *et al.*² the *N*-acyl derivatives led to benz[*d*]azepine or benzofulvene derivatives depending upon the multiplicity of the reactive state. We report here contrasting results for the photoisomerization of the *N*-alkyl and *N*-aryl derivatives, which leads to the corresponding azatricycloundecatetraene and naphthalene derivatives as the major products. This may reflect the intramolecular interaction between the lone-pair electrons associated with the nitrogen atom and the π electrons on the benzene ring in the excited state.³

The starting 1,4-dihydro-1,4-iminonaphthalenes (**1a–f**) were synthesized by Diels–Alder reactions between pyrrole derivatives and the appropriate benzyne generated by the reaction of *o*-dihalogenoarenes with butyl-lithium.⁴ The new compounds (**1b–f**) were fully characterized.

Irradiation of the *N*-methyl (**1a**) or *N*-*t*-butyl (**1b**) derivatives in cyclohexane under similar conditions to those used by Swenton *et al.*² gave only naphthalene (**2a**) in 44 and 30% yields respectively. Similar irradiation of the *N*-phenyl derivative (**1c**) also gave naphthalene (26%), together with a new product (30%) which was assigned the tricyclic structure (**3c**),[†] and a small amount (8%) of the amine (**4c**). Similarly

the *N*-*p*-methoxyphenyl derivative (**1d**) gave naphthalene and (**3d**) in 53 and 32% yields respectively. Interestingly even the *N*-methyl derivative (**1e**) which contained four methyl substituents on the aromatic ring of the naphthalene unit photoisomerized like the *N*-phenyl derivatives, and tetramethylnaphthalene (**2e**) and the tricyclic compound (**3e**) were obtained in 14 and 10% yields respectively. In contrast, the *N*-methyl-hexamethyl derivative (**1f**) did not give the naphthalene (**2f**) but gave (**3f**) in 25% yield along with a small amount of the benz[*d*]azepine derivative (**5f**) (3% yield). These results are summarized in Table 1 and Scheme 1.

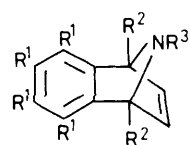
The naphthalenes (**2a**) and (**2e**) may be derived by a mechanism involving a cheletropic reaction in which a nitrene should be formed simultaneously.⁵ In accord with this expectation *N*-(*p*-methoxyphenyl)cyclohexylamine, which corresponds to the product of reaction between the nitrene

Table 1. Formation of naphthalenes (**2**) and tricyclic compounds (**3**) from 1,4-dihydro-1,4-iminonaphthalenes (**1**).

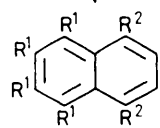
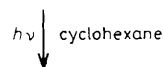
(1)	R ¹	R ²	R ³	% Yield ^a		
				(2)	(3)	Other products
a	H	H	Me	44 ^b	—	—
b	H	H	Bu ^t	30 ^b	—	(4b), tr. ^d
c	H	H	Ph	26 ^b	30	(4c), 8
d	H	H	<i>p</i> -MeOC ₆ H ₄	53 ^b	32	(A), ^c tr.
e	Me	H	Me	14 ^c	10	—
f	Me	Me	Me	—	25	(5f), 3

^a Yields are for isolated, purified materials. ^b (**2a**). ^c (**2e**). ^d Trace. ^e (A) = *N*-(*p*-methoxyphenyl)cyclohexylamine.

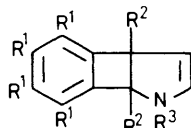
[†] The structures of (**3c–f**) were based on mass, i.r., and n.m.r. spectroscopy as well as elemental analyses. The following selected spectral data for (**3e**) are typical: *m/z* 213 (85%, *M*⁺), 198(47), 187(100, *M*⁺ – C₂H₂), 172 (65), and 157 (33); ¹H n.m.r. δ (90 MHz; CDCl₃), 2.14 (3H, s), 2.15 (3H, s), 2.21 (6H, s), 2.74 (3H, s), 4.20 (1H, d, *J* 3.5 Hz), 4.47 (1H, dd, *J* 3.5 and 1.8 Hz), 6.06 (1H, dd, *J* 1.8 and 2.6 Hz), and 6.45 (1H, d, *J* 2.6 Hz); ¹³C n.m.r. δ 151.6, 144.0, 138.0, 135.3, 132.7, 129.4, 128.1, 122.6, 71.9, 52.4, 43.7, 16.9, 16.3, 15.7, and 15.6; i.r. (KBr) 3120, 3040, and 1595 cm⁻¹.



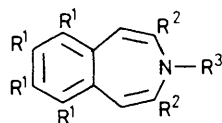
(1), a-f



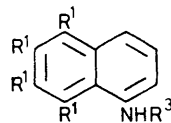
(2), a,e



(3), c-f

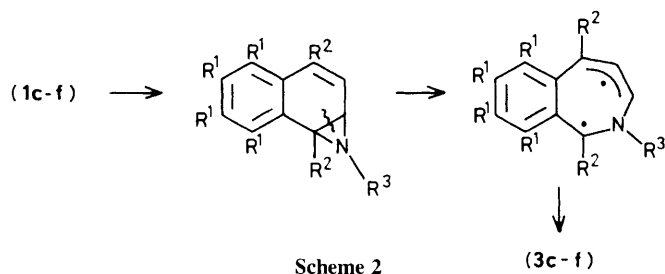


(5), f



(4), b, c

Scheme 1



Scheme 2

and the solvent cyclohexane,⁶ was detected by gas chromatography-mass spectroscopy in the reaction of (1d).

As a possible route to the tricyclic compounds (3c-f) we propose photochemical 1,3-rearrangement followed by cleavage of the aziridine ring, as shown in Scheme 2.

Upon irradiation of (1e) in acetone, (2e) but no (3e) was obtained, whereas in acetonitrile (2e) and (3e) were efficiently produced in 47 and 14% yields respectively. The acetone-sensitization result is in sharp contrast to results for the *N*-acyl derivatives² and suggests that the tricyclic products (3c-f) are derived from the singlet excited states.

Thus, our results clearly show that the photoisomerization of *N*-alkyl- and *N*-aryl-1,4-dihydro-1,4-iminonaphthalene derivatives differs from that of the *N*-acyl compounds, and an electronic effect dependent on the substituents on the nitrogen atom and the aromatic moiety controls the reaction mode.

We thank the Ministry of Education of Japan for a Grant-in-aid for Scientific Research and Dr M. Yoshifuji of Tokyo University for n.m.r. spectra.

Received, 30th August 1984; Com. 1242

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