

PHOTOCHEMICAL REACTIONS OF NAPHTHALENEDICARBOXIMIDES.
EFFECT OF ARENE STRUCTURE IN IMIDE COMPOUNDS ON REACTION WITH OLEFINS

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Photolyses of N-methylnaphthalenedicarboximides (1,8-NI, 2,3-NI, and 1,2-NI) with various olefins were investigated in benzene. The reaction pathways depended largely on the structure of arene moiety of the imides. The main reactions of 1,8-NI, 2,3-NI, and 1,2-NI were found as cyclobutane formation, oxetane formation, and insertion of olefin between the C(=O)-N bond of imide moiety, respectively.

The photochemistry of imide compounds has been the subject of intensive investigations.¹⁾ Concerning the photo-reaction with olefins, numerous works have been made for the reactions of mainly three types. (a) Oxetane formation of alicyclic imides²⁾ and phthalimides,³⁾ (b) insertion of the olefin between the C(=O)-N bond of phthalimides to form benzazepindiones,⁴⁾ and (c) alcohol-incorporated C-C coupling at the carbonyl carbon of phthalimides.⁵⁾ However, the imide compounds employed in the previous investigations have been confined to alicyclic imides and phthalimides, and no information have been reported on the effect of arene structure in the photochemistry of aromatic imides. Our studies have been focused on elucidation of the effect of extended π -conjugation system in the aromatic imides. Here we report the results of photo-reactions of three types of N-methylnaphthalenedicarboximides with olefins in benzene, in which the arene structure plays a crucial role in determining the reaction pathways. This new information undoubtedly show that there remain important problems to be uncovered in the photochemistry of imide.

Irradiation (aq.-CuSO₄ filtered 300-W high-pressure Hg-lamp) of a mixture of N-methyl-1,8-naphthalenedicarboximide (1,8-NI) and 2-methylpropene (1c) in N₂-purged benzene resulted in regiospecific cyclobutane formation at the 1,2-position in naphthalene ring of 1,8-NI (Table 1). The cyclobutane (2c) was isolated by chromatography and characterized by the elemental analysis and spectroscopic properties.⁶⁾ The cyclobutane (2c) decomposed quantitatively to the starting materials by heating or irradiation as expected⁷⁾ (Table 1). Yields and stabilities are summarized in Table 1 for the cyclobutanes obtained by the photo-reactions of 1,8-NI with various aliphatic and aromatic olefins. The results show the cyclobutane formation being characteristic for the reactions of 1,8-NI with aromatic olefins and ethylenes substituted by more than two alkyl groups. Cyclobutanes (2a,b) obtained in the reaction with 2,3-dimethyl-2-butene (1a) and 2-methyl-2-butene (1b) were highly unstable and decomposed to the starting materials even at room temperature. In the reaction with styrene (1f), two possible stereo-isomers

Table 1. Yields and Stabilities of Cyclobutanes (2a-f) from 1,8-NI and Olefins (1a-f) in Benzene

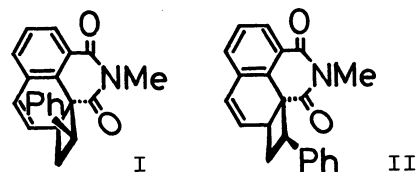
1,8-NI (36 mM) + 1a-f $\xrightleftharpoons[hv]{\Delta}$ 2a-f (1)

R ¹	R ²	R ³	R ⁴	1	Concn / M ^{a)}	2	Yield ^{b)} / %	Stability ^{c)}
Me	Me	Me	Me	1a	1.2	2a	60	X
Me	Me	Me	H	1b	1.4	2b	73 ^{d)}	X
Me	Me	H	H	1c	1.8	2c	68	O
n-C ₄ H ₉	H	H	H	1d	1.5	2d	0	—
Ph	Ph	H	H	1e	1.0	2e	67	O
Ph	H	H	H	1f	1.2	2f	79 (2:1) ^{e)}	O

a) 1 M = 1 mol dm⁻³. b) Yields were based on consumed 1,8-NI.

c) Thermal stability of 2a-f. X: Unstable at room temp; O: stable at room temp. d) Mixture of stereoisomers.

e) Ratio of stereoisomers (I:II).



of cyclobutanes (2f, I and II) were obtained with the ratio of 2:1 (I:II).

Irradiation of N-methyl-2,3-naphthalenedi-carboximide (2,3-NI) and 1,1-diphenylethylene (1e) in benzene gave oxetane (3) as the main product, together with naphthoazepindione (4) as the minor one (Eq. 2). The oxetane (3)⁸⁾ decomposed to 5 by heating or by acid. The reaction of 2,3-NI and 1f in benzene gave alcoholic isomers (6a: 40%, 6b: 28%) possibly by decomposition of the oxetane precursor (7). The results show the oxetane formation being characteristic for the reaction of 2,3-NI with aromatic olefins.

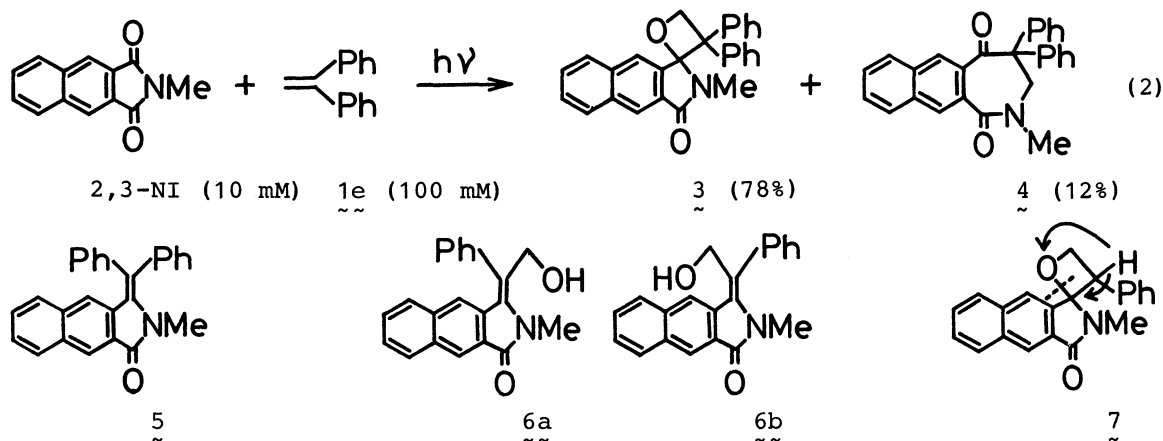


Table 2. Yields of Naphthoazepindione (8a-e, 9a-e) from 1,2-NI and Olefins (1b-f) in Benzene

1,2-NI (10 mM)			1b-f (100 mM)			8a-e ~~~~~		9a-e ~~~~~	
R ¹	R ²	R ³	1 ~~~	8 ~~~	Yield ^{a)} / %	9 ~~~	Yield ^{a)} / %		
Me	Me	Me	1b ~~~	8a ~~~	46	9a ~~~	31		
Me	Me	H	1c ~~~	8b ~~~	53	9b ~~~	46		
n-C ₄ H ₉	H	H	1d ~~~	8c ~~~	0	9c ~~~	0		
Ph	Ph	H	1e ~~~	8d ~~~	54	9d ~~~	21		
Ph	H	H	1f ~~~	8e ~~~	41	9e ~~~	38		

a) Yields were based on consumed 1,2-NI.

On irradiation with aliphatic olefins 2,3-NI was less reactive; i.g., no reaction was observed in the photolysis of 2,3-NI with 1c or 1-hexene (1d), and reaction with 1b only gave a mixture of unidentified minor products.

Irradiation of N-methyl-1,2-naphthalenedicarboximide (1,2-NI) with various aliphatic and aromatic olefins formed exclusively naphthoazepindiones (8 and 9); i.e., insertion of the olefin between the C(=O)-N bond of imide moiety (Table 2). The structure of 9 was suggested from the low chemical shift of proton H^a which was observed as ortho and meta coupled double doublets at δ 8.3-8.6.⁹⁾ Molecular models indicate that this proton should be deshielded by the proximate ketone carbonyl group. The corresponding proton in 8 was observed relatively higher field region.¹⁰⁾ The yield of 8 was generally higher than that of 9.

Thus, we found three types of photochemical reactions of naphthalenedicarboximides with olefins. Type (i): cycloaddition to the aromatic C=C bond (cyclobutane formation), type (ii): addition to the carbonyl C=O bond (oxetane formation), and type (iii): insertion of olefin between the C(=O)-N bond of imide moiety. The predominant types of reaction were found to depend largely upon the arene structure, and the positions attacked by olefins are indicated by arrows in Fig. 1, in which big arrows indicate the predominant reaction sites. Although phthalimides were reported to proceed the type (iii) reaction in general⁴⁾ and

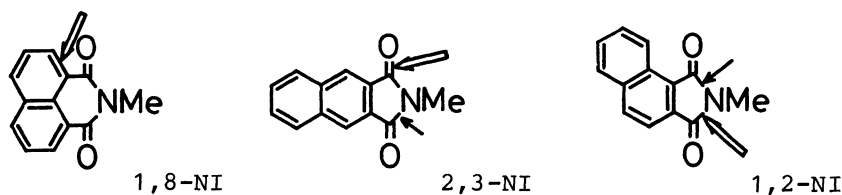


Fig. 1.

oxetanes were obtained only in a few cases,³⁾ the reaction of imide proceeds to two different directions when its fused ring system is altered from benzene to naphthalene; i.e., type (ii) (oxetane formation) reaction predominates in photolyses of 2,3-NI and type (iii) reaction in the case of 1,2-NI. The variation of the imide-ring size is accompanied by the alteration of the arene structure; i.e., five membered ring for 1,2- and 2,3-NI's and six membered ring for 1,8-NI. A conjugated five-membered imide ring may be required for the type (iii) reaction because the analogous reaction was not observed in the photolyses of 1,8-NI with all of olefins investigated.

Extension of our new observations and detailed studies are now in progress.

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- 6) 2c: ¹³C NMR (CDCl₃) δ 26.5 (q), 26.6 (q), 27.0 (q), 29.8 (d), 41.4 (t), 51.7 (s), 52.1 (s), 123.6 (d), 124.8 (s), 127.1 (d), 127.4 (d), 130.3 (d), 131.2 (s), 132.3 (d), 132.3 (d), 164.8 (s, imide), 175.1 (s, imide); ¹H NMR (CDCl₃) δ 0.94 (s, 3H), 0.97 (s, 3H), 1.82 (dd, 1H, J = 3.3, 13.0 Hz), 2.64 (dd, 1H, J = 10.3, 13.0 Hz), 3.34 (s, 3H, NMe), 3.78 (m, 1H), 6.11 (dd, 1H, J = 4.3, 10.6 Hz), 6.49 (dd, 1H, J = 1.6, 10.6 Hz), 7.1-7.4 (m, 2H), 7.8-8.0 (m, 1H); IR (KBr) 1715, 1665 (imide), 1424, 1365, 1292, 1138, 763 cm⁻¹.
- 7) J. J. McCullough, W. K. MacInnis, C. J. L. Look, and R. Faggiani, J. Am. Chem. Soc., 104, 4644 (1982).
- 8) 3a: ¹H NMR (CDCl₃) δ 2.66 (s, 3H, NMe), 5.43 (d, 1H, J = 7.0 Hz), 5.57 (d, 1H, J = 7.0 Hz), 6.9-8.0 (m, 15H), 8.24 (s, 1H); IR 1705 (amide), 1570, 962, 700 cm⁻¹; MS (m/e, %) 389 (2, M⁺), 359 (100, M⁺-CH₂O).
- 9) 9b: ¹H NMR (CDCl₃) δ 0.8-1.7 (coalesced br s, 6H, CMe₂), 2.9-3.2 (coalesced br s, 1H), 3.30 (s, 3H, NMe), 3.7-4.2 (coalesced br s, 1H), 7.3-8.0 (m, 5H), 8.48 (dd, 1H, J = 3.9, 8.0 Hz); IR (KBr) 1705 (ketone), 1648 (amide), 1475, 1403, 842, 774 cm⁻¹.
- 10) 8b: ¹H NMR (CDCl₃) δ 1.28 (s, 6H, CMe₂), 3.23 (s, 3H, NMe), 3.42 (s, 2H, CH₂), 7.4-8.1 (m, 6H); IR (KBr) 1708 (ketone), 1652 (amide), 1392, 1088, 778 cm⁻¹.

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