

The Temperature Dependent Photochemistry of 1-Naphthyl Azide

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Abstract

Photolysis of 1-naphthyl azide in the presence of diethylamine at -60° or -78°C gives moderate yields of adducts derived from trapping of tricyclic azirines. These adducts are formed in very low yield on photolysis at room temperature.

The photochemistry of simple aryl azides in non-nucleophilic media is plagued by the very low yields of identifiable products formed. Photolysis of phenyl azide in cyclohexane gives mainly tar² although photolysis of this azide in diethylamine (DEA) gives good yields of 3H-azepine.³ Photolysis of 2-naphthyl azide also leads to efficient formation of adducts when photolyzed in the presence of DEA. This is not the case for 1-naphthyl azide (**1**) which gives only small amounts of 1-naphthyl amine **7** and azo compound **8**.⁴ Suschitzky, et. al.,⁵ have improved the yields of adducts with piperidine by adding TMEDA to complex with singlet 1-naphthyl nitrene (¹**2**). Unfortunately, TMEDA is ineffective at promoting adduct formation with DEA at 25°C.⁶ We have recently discovered that the photochemistry of phenyl azide is very highly temperature dependent.⁷ This has prompted the present study in which we are pleased to report that simply lowering the temperature of the photolysis of **1** with DEA leads to moderate yields of adducts.

Photolysis of **1** in methylcyclohexane containing 1.0M DEA at 35°C gives a 35% yield of **7**, a 4% yield of **8** and only a 3% yield of adduct **4** which is in reasonable agreement with the literature.⁴ The yield of **7** decreases as the temperature is lowered. In contrast, the yield of **4** increases steadily on cooling and reaches a maximum at -60° to -78°C (Table 1). The yields of **7** and **8** are much reduced at these temperatures leading to a very clean product mixture. A mixture of the isomeric diamines **4** and **6** is obtained at lower temperature (-100 to -130°C). However, upon further cooling to -160° or -196°C, the yields of adducts are tremendously reduced and azo compound **8** predominates. The photochemical reactions run between -100° and -196°C used a solvent mixture of 4:1 isopentane: cyclopentane which is much less viscous than methylcyclohexane at these temperatures.

The data can be interpreted with the aid of Scheme I. Photolysis of **1** leads to singlet 1-naphthyl nitrene (¹**2**) which rapidly rearranges to form tricyclic azirine **3**. Schrock and Schuster have shown that triplet 1-naphthyl nitrene (³**2**) is formed $\approx$ 2.5 μ s following photolysis of azide **1**.⁸ This presumably is the time interval required for **3** to revert to ¹**2**

The data can be interpreted with the aid of Scheme I. Photolysis of **1** leads to singlet 1-naphthyl nitrene (**1¹2**) which rapidly rearranges to form tricyclic azirine **3**. Schrock and Schuster have shown that triplet 1-naphthyl nitrene (**3²2**) is formed $\approx 2.5 \mu\text{s}$ following photolysis of azide **1**.⁸ This presumably is the time interval required for **3** to revert to **1¹2** (k_{32}) and to intersystem cross (ISC) to **3²2**. We speculate that at ambient temperatures $k_{32} \gg k_{34}$ (nucleophilic capture) hence the low yield of adduct **4**, but that on cooling these rate constants are more evenly balanced ($k_{32} \approx k_{34}$). Thus azirine **3** can be intercepted at -60° to -78°C . Dunkin⁹ has studied the matrix photochemistry of **1** and has detected two azirine photoproducts by infrared spectroscopy which have been attributed to **3** and **5**.⁹ Adduct **6** can be visualized as a trapping product of **5** at -100° and -130°C at which temperatures $k_{56} > k_{52}$. It is possible that the less stable azirine **5** is formed at higher temperatures but reverts to **1¹2** more rapidly than it can be trapped.

The yields of adducts **4** and **6** are negligible at -160° and -196°C . At these temperatures irreversible singlet to triplet ISC must be more rapid than azirine formation ($k_{\text{isc}} \gg k_{23}$ or k_{24} at -160° to -196°C) ISC has zero activation energy and will be favored over any process involving bond breaking and making at cryogenic temperatures.^{6,10}

It is possible to obtain adduct **4** at -196°C by photoisomerization of primary photoproduct **3²2** immobilized in a rigid glass. This is demonstrated in Table 2 which reveals that 1-naphthyl amine **7** is favored at low light intensities and short exposure times, whereas adduct **4** is the dominant product at high light intensity and long exposure time. The matrix photoisomerization of **3²2** (discovered by Dunkin⁹) is very facile because **3²2** has λ_{max} of 370 nm (where the absorption of **1** is weak, $\lambda_{\text{max}} \approx 300 \text{ nm}$) and can be readily pumped by the 366 nm line of a mercury discharge.

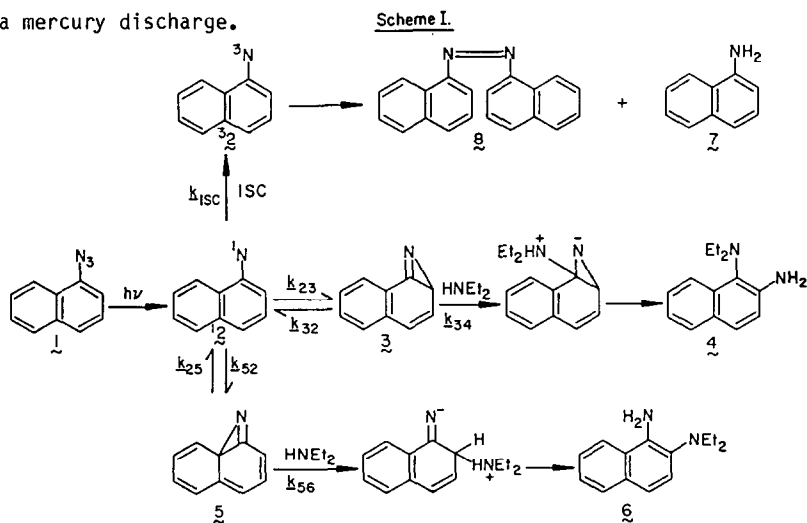


Table I. The distribution of products formed on photolysis of 0.04M 1-naphthyl azide (1) in the presence of 1.0M diethylamine at several temperatures^a

Temp (°C)	1 ^c	4 ^c	6 ^c	7 ^c	8 ^c
35 ^b	2	3	0	35	4
0 ^b	13	4	0	28	10
-20 ^b	13	19	0	20	5
-40 ^b	3	34	0	7	10
-60 ^b	7	50	0	4	0
-78 ^b	1	48	0	4	8
-100 ^c	0	39	18	5	0
-130 ^c	5	40	12	5	0
-160 ^c	24	2	0	4	31
-196 ^c	15	2	0	5	48

(a) Rayonet reactor with RPR 3500, 350 nm light source

(b) Methylcyclohexane, solvent (c) 4:1 isopentane:cyclopentane

(d) Percent yields are absolute relative to dicyclohexyl internal standard, $\pm 1\%$

Table II. The distribution of products formed on photolysis of 0.04M 1-naphthyl azide in 2-MTHF containing 1.0M diethylamine at -196° as

(a) a function of photolysis time (365 nm)^a

Time (min)	7	4	4/7
1	5.87	0	0
5	4.33	2.43	0.56
15	5.50	6.72	1.22
30	7.50	9.30	1.24
60	8.60	11.90	1.38

(b) as a function of light intensity (365 nm)^a

Light Intensity ^b	7	4	4/7
0.303	5	4	0.8
0.390	5	5	1.0
0.525	6	9	1.3
1.000	6	11	1.8

a) 1000 watt Hg-Xe lamp with CuSO₄ filter.

b) Light attenuation was achieved using neutral density filters from Oriel Corporation

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