January, 1981] © *1981 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***54***, *301—302 (1981)* 301

Photochemical Reactions of Azidotriazines with Aromatic Substrates

Shigeru Tamura, Hisao Imaizumi, Yoji Hashida,* and Kohji Matsui*

Department of Synthetic Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376

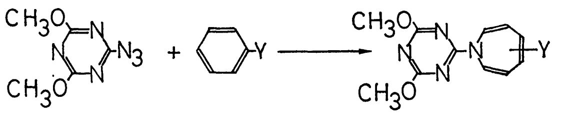
(Received May 14, 1980)

Synopsis. Triazinylnitrene generated photochemically from 2-azido-4,6-dimethoxy-1,3,5-triazine adds to the aromatic ring of alkylbenzenes and halobenzenes to give *N*-triazinylazepines.

Nitrene Chemistry has been extensively studied and is well established.[1] We have reported that the photolyses of azidotriazines in ketones[2,3] and nitriles[2,4] give 1:1 cycloaddition products of the triazinylnitrene and solvent molecule. In this paper we wish to describe the reactions of triazinylnitrene with several aromatic substrates to give *N*-triazinylazepines.

Results and Discussion

During the course of studies on photocycloadditions of triazinylnitrene to nitriles, we have found that irradiation of 2-azido-4,6-dimethoxy-1,3,5-triazine (**1a**) in phenylacetonitrile (**2d**) with a low-pressure mercury lamp resulted in the formation of *N*-(4,6-dimethoxy-1,3,5-triazin-2-yl)azepine (**3d**) in a 30% yield (Eq. 1). The structure of **3d** was indicated by its elemental composition and spectral properties. Similar photolyses of azidotriazine (**1a**) in several aromatic substrates also gave *N*-triazinylazepines (**3**); the details are listed in Table 1. Although various azepines have been isolated from the reactions of aromatic substrates with carboxynitrenes,[5—8] sulfonylnitrene,[9] and cyanonitrene,[10] *N*-triazinylazepine is a novel type of the isolable *N*-arylazepine.

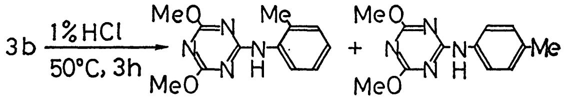


(1)

1a **2** **3**

a: $Y=C_2H_5$, b: $Y=CH_3$, c: $Y=H$, d: $Y=CH_2CN$, e: $Y=Cl$, f: $Y=F$, g: $Y=CF_3$.

Although attempts to determine the isomer distribution were unsuccessful, it is apparent that the *N*-triazinylazepines which were obtained are isomeric mixtures on the basis of the following. For example, the ^{1}H-NMR spectrum of crude triazinylazepine (**3b**) obtained from the reaction with toluene showed singlets at δ 1.85 and 4.00, ascribable to methyl and methoxyl protons respectively. The addition of ^{1}H-NMR shift reagent, however, caused splitting of each peak into two peaks, indicating that at least two isomeric azepines are involved in the crude product. In addition, thermal isomerization of **3b** in acidic solution gave *o*- and *p*-toluidino-1,3,5-triazines in a molar ratio of *ca.* 1:1 (Eq. 2): the ratio was determined by a direct comparison of its ^{1}H-NMR spectrum with those of authentic samples, which were prepared from the reactions of 2-chloro-4,6-dimethoxy-1,3,5-triazine with *o*- and *p*-toluidines.



(2)

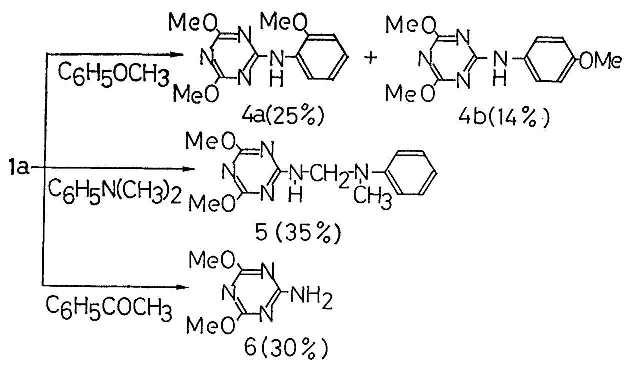
On the other hand, in the photoreactions of **1a** in anisole, *N*,*N*-dimethylaniline, and acetophenone, no azepine could be isolated as are shown in Scheme 1: the structures of (**4**), (**5**) and (**6**) were determined by spectral properties and mixed-melting-point tests with an authentic sample.[11]

In order to get an insight into a nature of triazinylnitrene, competitive reactions between benzene and monosubstituted benzene were performed (Table 2).

Table 1. *N*-Triazinylazepines (**3**)

Azepine	Yield %	Mp/°C(Solvent for recrystallization)	UV		MS $m/e(M^+)$	^{1}H-NMR, δ[c]	Found(Calcd), (%)		
			λ_{max}/nm	$\varepsilon\times10^{-4}$			C	H	N
3a	40(78)[a]	87—88 (C_6H_6-P.E.[b])	277 235	0.89 0.94	260	1.10(t, 3H), 2.15(q, 2H), 3.98(s, 6H), 5.50—6.50(m, 5H).	60.30 (59.99	6.49 6.20	21.83 21.52)
3b	24(72)	101—102 (P.E.)	276 236	0.95 0.90	246	1.85(s, 3H), 4.00(s, 6H), 5.55—6.40(m, 5H).	58.63 (58.53	5.71 5.73	22.86 22.75)
3c	40(55)	105—106 (C_6H_6-P.E.)	277 234	1.29 1.07	232	3.98(s, 6H), 5.50—6.32(m, 5H).	56.59 (56.88	5.15 5.21	24.02 24.13)
3d	30(35)	107—108 (C_6H_6)	277 209	1.47 1.92	271	3.20(s, 2H), 4.03(s, 6H), 5.40—6.50(m, 5H).	57.38 (57.56	4.80 4.83	25.56 25.81)
3e	20(25)	159—160 (C_6H_6-P.E.)	275 240	1.12 1.49	266	3.95(s, 6H), 5.70—6.50(m, 5H).[d]	49.69 (49.53	4.19 4.16	21.46 21.03)
3f	21(33)	117—118 (P.E.)	271 232	0.84 0.93	250	4.02(s, 6H), 5.50—6.67(m, 5H).	52.41 (52.80	4.47 4.43	22.10 22.39)
3g	15(23)	109—110 (P.E.)	277 231	1.27 1.36	300	4.01(s, 6H), 5.40—7.00(m, 5H).	48.30 (48.01	3.75 3.69	18.79 18.66)

a) Yields in parentheses were determined spectrophotometrically (see Experimental). b) P.E.: Petroleum ether. c) Unless otherwise noted, measurements were performed in $CDCl_3$. d) In DMSO-d_6.



Scheme 1.

Table 2. Relative rates for the reactions of 4,6-dimethoxy-1,3,5-triazinylnitrene with benzenes

Aromatic	Relative rate
Ethylbenzene	1.31
Toluene	1.96
Benzene	1.00
Phenylacetonitrile	0.98
Chlorobenzene	0.78
Fluorobenzene	1.10
(Trifluoromethyl)benzene	0.55

The Hammett plots using σ_p-values shows a satisfactory correlation: a least-squares treatment[12] gives an equation, $\log k_x = -0.67\,\sigma_p + 0.07$ with the correlation coefficient (r) of 0.94. The ρ value found is relatively low compared with that in the reaction of ethoxylcarbonylnitrene ($\rho = -1.32$),[13] indicating that the selectivity of triazinylnitrene toward substrate is relatively low. It has been well established[1] that azepines are obtained *via* singlet electrophilic nitrene. Thus, the lower selectivity of triazinylnitrene may be attributed to the electron-withdrawing nature of the triazine nucleus, which enhances the electrophilic reactivity of the nitrene.

On the other hand, the photolysis of 2-azido-4,6-bis(dimethylamino)-1,3,5-triazine (**1b**) in toluene yielded 2-amino-4,6-bis(dimethylamino)-1,3,5-triazine (40% yield), resulting from the hydrogen abstraction by triplet triazinylnitrene.[2] This is easily explained by assuming[2] that, in the photolysis of **1b** bearing highly electron donating dimethylamino groups, the intersystem crossing $^1N \rightarrow {}^3N$ becomes predominant path instead of the reaction of singlet nitrene.

Experimental

Materials. The azidotriazines (**1**) were prepared according to the procedure given in a previous paper.[14]

Irradiation. Let us take as example the photolysis of **1a** in toluene: A solution containing **1a** (2.00 g, 11.0 mmol) in toluene (20 ml) was irradiated for 48 h. After removal of the solvent, the residue was chromatographed on a silica-gel column using benzene–acetone mixture (10:1, v/v) as an eluent to yield crude azepine (**3b**). Recrystallization of crude **3b** from petroleum ether gave 0.65 g of white needles **3b** listed in Table 1.

Irradiations of **1a** in anisole, *N*,*N*-dimethylaniline, and acetophenone solutions were carried out in the same way to yield **4**, **5**, and **6**, respectively.

4a: mp 135—137 °C; MS *m*/*e* 262(M$^+$); ^{1}H-NMR (DMSO-d_6) δ 3.97 (s, 3H), 4.03(s, 6H), 7.00—8.20(m, 4H), 8.85 (s, 1H). Found: C, 55.01; H, 5.36; N, 21.46%.

4b: mp 138—139 °C; MS *m*/*e* 262(M$^+$); ^{1}H-NMR(CDCl$_3$), δ 3.80(s, 3H), 3.98(s, 6H), 6.80—7.68(m, 4H), 8.35(s, 1H). Found: C, 55.48; H, 5.37; N, 21.56%. Calcd for $C_{12}H_{14}N_4O_3$: C, 54.95; H, 5.38; N, 21.36%.

5: mp 118—119 °C; MS *m*/*e* 275(M$^+$); ^{1}H-NMR(CDCl$_3$), δ 3.04(s, 3H), 3.98(s, 6H), 5.15(d, 2H), 6.55(t, 1H), 6.70—7.46(m, 5H). Found: C, 56.59; H, 5.92; N, 25.20%. Calcd for $C_{13}H_{17}N_5O_2$: C, 56.71; H, 6.18; N, 25.44%.

Competitive Reactions. After irradiation in a mixed solvent of benzene and monosubstituted benzene (1:1 in volume), known amounts of azobenzene were added into the solution as an internal standard. The products were separated by silica gel TLC using benzene–acetone mixture (20:1, in a typical run) as the developing solvent. From the chromatogram, each product was extracted and diluted with methanol to a fixed volume; then the extinction was measured spectrophotometrically.

References

1) a) "Nitrenes," ed by W. Lwowski, Interscience, New York, N.Y. (1970); b) "The Chemistry of the Azido Group," ed by S. Patai, Wiley, New York, N.Y. (1971), and references cited therein.

2) T. Goka, H. Shizuka, and K. Matsui, *J. Org. Chem.*, **43**, 1361 (1978).

3) R. Kayama, H. Shizuka, S. Sekiguchi, and K. Matsui, *Bull. Chem. Soc. Jpn.*, **48**, 3309 (1975).

4) H. Yamada, H. Shizuka, and K. Matsui, *J. Org. Chem.*, **40**, 1351 (1975).

5) J. W. Baldwin and R. A. Smith, *J. Org. Chem.*, **32**, 3511 (1967).

6) W. Lwowski, T. J. Maricich, and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **85**, 1200 (1963).

7) R. J. Cotter and W. F. Beach, *J. Org. Chem.*, **29**, 751 (1964).

8) K. Hafner and C. König, *Angew. Chem.*, **75**, 89 (1963).

9) R. A. Abramovitch and V. Uma, *J. Chem. Soc., Chem. Commun.*, **1968**, 797.

10) F. D. Marsh and H. E. Simmons, *J. Am. Chem. Soc.*, **87**, 3529 (1965).

11) J. Thurston, J. Dudley, D. Kaiser, K. Hechenbleicker, F. Schaefer, and D. Holm-Hansen, *J. Am. Chem. Soc.*, **73**, 2981 (1951).

12) The CH$_2$CN group was omitted from our calculations, since its substituent constant is unavailable.

13) J. E. Baldwin and R. A. Smith, *J. Am. Chem. Soc.*, **89**, 1886 (1967).

14) R. Kayama, S. Hasunuma, S. Sekiguchi, and K. Matsui, *Bull. Chem. Soc. Jpn.*, **47**, 2825 (1974).