Photolyses of 2-Azido-4-methoxy-6-(1-naphthyl)-1,3,5-triazines: Reactions of Singlet and Triplet 1,3,5-Triazinylnitrenes with Solvents

Tsuruji Goka, Haruo Shizuka,* and Kohji Matsui

Department of Chemistry, Gunma University, Kiryu, Gunma 376, Japan

Received July 19, 1977

Photochemical reactions of the title compounds with Me_2SO, acetone, and acetonitrile have been carried out. Photolyses of the triazinyl azides in acetone or acetonitrile gave the 1:1 cycloaddition products of the triazinylnitrene and the corresponding solvent molecule, aminotriazines, and unidentified polymeric products. In the case of Me_2SO, ylide, aminotriazine, and polymeric products were obtained. An electron-withdrawing substituent in the triazine nucleus accelerated the formation of addition product (or ylide) via the singlet nitrene. The chemical yields of the addition products varied depending upon solvents in the order of Me_2SO > acetone > acetonitrile. Aminotriazine is produced via the triplet nitrene.

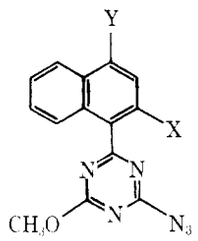
Recently, nitrene chemistry has been extensively studied and well established.[1] However, little is known about the triazinylnitrenes. Only the photocycloadditions of singlet triazinylnitrene with nitriles[2] and acetone[3] have been reported.

Triazine photochemistry involves interesting reactions: the photo-Smiles rearrangement,[4] the photo-Fries rearrangement,[5] the phototriazinilation,[6] and the intramolecular proton transfer in the excited state.[7] The 1,3,5-triazinyl group has an electron-withdrawing power, and formal charges at the nitrogen atoms of the triazine nucleus are very negative (ca. $-0.35 \sim -0.41$),[7] especially in the excited state. In addition, lone-pair electrons exist in the nitrogen atoms of the triazine nucleus. These electronic features may contribute to the photochemical reactions of triazines.

During the course of our studies on the triazine photochemistry, we have carried out the photolyses of 2-azido-4-methoxy-6-(1-naphthyl)-1,3,5-triazines in solution. This paper reports the reactions of singlet and triplet triazinylnitrenes with solvents (Me_2SO, acetone, and acetonitrile).

Results and Discussion

Preparation of 1,3,5-Triazine Derivatives. Azido-(1-naphthyl)-1,3,5-triazines employed are shown in Table I. Compounds **1, 2, 4,** and **5** were prepared by condensation of



1-Naphthylazido-1,3,5-triazines

the corresponding naphthalene derivatives with 2,4-dichloro-6-methoxy-1,3,5-triazine in the presence of $AlCl_3$ followed by treatment with sodium azide.[8] Compounds **3, 6, 7,** and **8** were synthesized by reactions of the corresponding 2- or 4-substituted 1-naphthylmagnesium bromide with cyanuric chloride followed by treatments with sodium methoxide and sodium azide.

Decomposition Quantum Yields of Azidotriazines. When the azidotriazines were irradiated with a high-pressure mercury lamp, a spectral change was observed with a lapse of time, suggesting that a clean photochemical reaction took place. The decomposition quantum yields of the azidotriazines were measured in cyclohexane at 254 nm using a low-pressure mercury lamp (Table II). Dissolved oxygen did not affect the quantum yields.

Photochemical Reactions of Azido-1,3,5-triazines. Reactions with Acetone. Photolyses of azidotriazines in acetone gave the 1:1 cycloaddition product of triazinylnitrene and acetone, the corresponding aminotriazine, and unidentified polymeric products depending upon the substituent Y in the naphthalene nucleus. These results are listed in Table III. The substituent in the naphthalene nucleus, especially the hydroxy group capable of forming an intramolecular hydrogen bond, was found to affect the photochemical reaction of azide. In the cases of compounds **1** and **2,** aminonaphthyltriazines which would result from the hydrogen-abstraction reaction by triplet nitrene were the major products, while in the cases of other azidotriazines cycloaddition products, which are considered to be produced via the electrophilic attack of singlet nitrene upon the carbonyl oxygen of acetone,[3] were the major product. It seems that the yield of the cycloaddition product increases with increasing the electron-withdrawing power of Y. That is, the electron-withdrawing substituent increases the electrophilic reactivity of singlet nitrene.

In the case of compound **1,** the reaction took place very selectively and the only product obtained was the corresponding amine resulting from the triplet nitrene. It is well known that an intramolecular hydrogen bond is formed in *o*-hydroxyaryltriazines. Therefore, in compound **1** a good coplanarity between two nuclei (naphthalene and triazine) would be expected due to the formation of the intramolecular hydrogen bond. This structure is responsible for an electron migration from the naphthalene ring to the triazine nucleus, and consequently the electrophilic reactivity of the singlet nitrene may decrease. As a result, the intersystem crossing $^1N \rightarrow {}^3N$ is dominant compared with the reaction of singlet nitrene with solvents.[9] Thus, instead of the photoproduct yielded from singlet nitrene, the product from triplet nitrene (aminotriazine) was obtained as the major product. In this case, however, an opposite effect which may decrease electron density at the proper nitrogen atom in the triazine nucleus through the intramolecular hydrogen bonding is also considered. However, the experimental results show that the former effect is predominant; the result described above may be one of a few examples of the remarkable effect of an intramolecular hydrogen bond upon photoreactivity.

The assumptions described above may be supported by the following facts that in the photolyses of azidotriazines in acetonitrile: (1) a cycloaddition product of triazinylnitrene and acetonitrile in a molar ratio of 1:1 is obtained when two substituents in the triazine nucleus are methoxyl groups;[2] (2) however, in the presence of benzophenone, which acts as a triplet sensitizer, only aminotriazine is obtained.[10] Similarly, only aminotriazine is obtained in the direct photolysis of 2-azido-4,6-bis(dimethylamino)triazine in acetonitrile,[10] indicating that the presence of two strong electron-donating

0022-3263/78/1943-1361$01.00/0

Table I. Derivatives of Azido-1-naphthyl-1,3,5-triazine

Registry no.	Compd	X	Y	Mp, °C	Anal., % Found	Anal., % Calcd	UV[e] λ_{max}, nm	UV[e] $\epsilon \times 10^{-4}$	NMR,[f] δ_{ppm}
59336-44-6	1	OH	H[a]	163–164[b]	C, 57.25 H, 3.44 N, 28.45	57.14 3.43 28.56	375	1.2	4.18 (s, 3 H), 7.60 (m, 5 H), 9.57 (d, 1 H), 13.9 (br)
59336-45-7	2	H	OH[a]	198–199[b]	C, 57.24 H, 3.44 N, 28.62	57.14 3.43 28.56	346	1.7	4.07 (s, 3 H), 7.07 (d, 2 H), 7.60 (m, 2 H), 8.40 (m, 2 H), 9.30 (m, 1 H), 11.15 (br, 1 H)
59336-46-8	3	H	H[a]	98–99[c]	C, 60.75 H, 3.64 N, 30.87	60.42 3.62 30.20	324	1.3	4.10 (s, 3 H), 7.57 (m, 3 H), 8.27 (m, 2 H), 8.40 (d, 1 H), 9.07 (m, 1 H)
65103-10-8	4	OCH_3	H	136–137[c]	C, 58.26 H, 3.92 N, 27.41	58.44 3.62 27.26	337	0.55	3.92 (s, 3 H), 4.13 (s, 3 H), 7.42 (m, 4 H), 7.88 (m, 2 H)
65103-11-9	5	H	OCH_3	109–110[d]	C, 58.04 H, 3.91 N, 27.48	58.44 3.92 27.26	346	2.0	3.95 (s, 3 H), 4.07 (s, 3 H), 6.73 (d, 1 H), 7.50 (m, 2 H), 8.38 (m, 2 H), 9.29 (m, 1 H)
65103-12-0	6	CH_3	H	88–89[c]	C, 61.33 H, 4.13 N, 28.51	61.63 4.14 28.76	308	0.39	2.40 (s, 3 H), 4.10 (s, 3 H), 7.47 (m, 4 H), 7.87 (m, 2 H)
65103-13-1	7	H	CH_3	131–132[d]	C, 61.40 H, 4.12 N, 28.46	61.63 4.14 28.76	332	1.4	2.73 (s, 3 H), 4.12 (s, 3 H), 7.50 (m, 3 H), 8.03 (m, 1 H), 8.30 (d, 1 H), 9.12 (m, 1 H)
65103-14-2	8	H	Cl	113–114[d]	C, 53.60 H, 2.89 N, 26.51	53.77 2.90 26.87	327	1.4	4.17 (s, 3 H), 7.62 (m, 3 H), 8.33 (m, 2 H), 9.10 (m, 1 H)

[a] Reference 8. [b] Solvent for recrystallization benzene. [c] Solvent for recrystallization ligroin. [d] Solvent for recrystallization benzene–ligroin. [e] Measured in cyclohexane. [f] Measured in $CDCl_3$.

Table II. Decomposition Quantum Yields Φ_{decomp} of Azido-(1-naphthyl)-1,3,5-triazines in Cyclohexane at 254 nm and 25 °C[a]

Compd	Substituent X	Substituent Y	Φ_{decomp}
1	OH	H	0.2 ± 0.1
2	H	OH	0.3 ± 0.1
3	H	H	0.2 ± 0.1
4	OCH_3	H	0.1 ± 0.1
5	H	OCH_3	0.4 ± 0.1
6	CH_3	H	0.7 ± 0.1
7	H	CH_3	0.4 ± 0.1
8	H	Cl	0.4 ± 0.1

[a] The quantum yields were measured in the initial stages of the photolyses (about 10% decomposition). The initial concentration of azidotriazines was 1×10^{-2} M in cyclohexane.

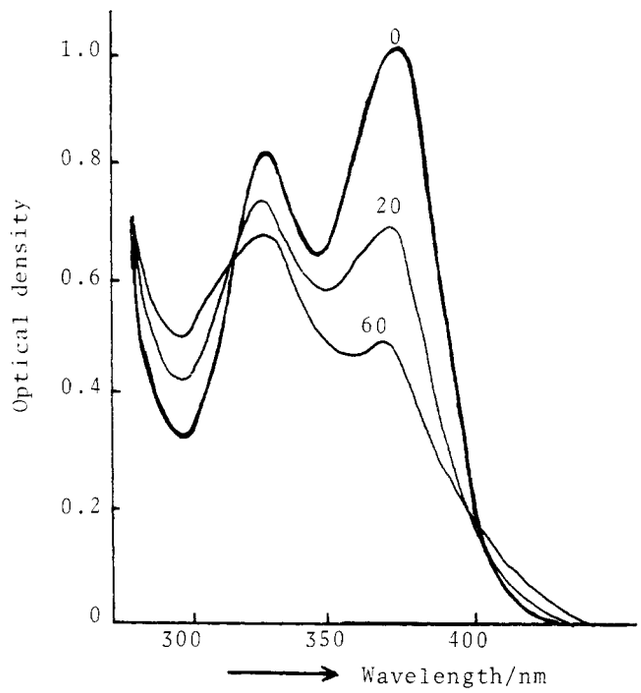


Figure 1. Spectral change of an acetonitrile solution of 2-azido-4-methoxy-6-(2-hydroxy-1-naphthyl)-1,3,5-triazine (1) by irradiation with a high-pressure mercury lamp. Numbers refer to time at a measurement in seconds.

groups in the triazine nucleus lowers the electrophilic reactivity of singlet nitrene very much. The cycloaddition product is known to result from the electrophilic attack of singlet triazinylnitrene upon the nitrogen atom of acetonitrile.[2]

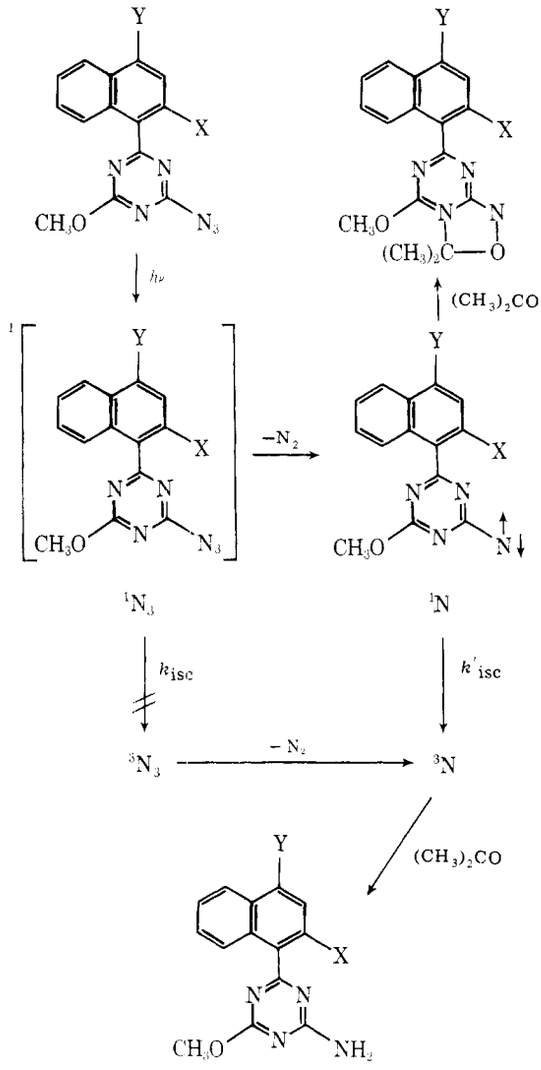
From quenching experiments, phenyl azide in the excited singlet state decomposes to the singlet nitrene and nitrogen ($^1\Sigma_g^+$).[11] By means of laser spectroscopy, it has been shown that the direct photodecomposition of 1-azidopyrene occurs through $^1N_3 \rightarrow {}^1N \rightarrow {}^3N$.[12] In the photolysis of 2-azido-4,6-dimethoxy-1,3,5-triazine in nitriles, the singlet mechanism occuring through $^1N_3 \rightarrow {}^1N \rightarrow$ adduct is also shown.[2]

Thus, the reaction pathway in the azidotriazine–acetone system is similarly accounted for by Scheme I, where ^1N and ^3N denote the singlet and triplet nitrenes, respectively. As for compound **1**, the intersystem crossing k'_{isc} is faster than the reaction of ^1N with acetone.

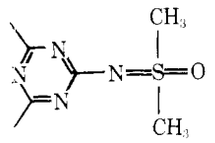
Photolyses of Azidotriazines in Me_2SO. In the photolyses of azido(1-naphthyl)triazines in Me_2SO, the corresponding ylide, aminotriazine, and unidentified polymeric products were obtained (Table IV).

In the cases of compounds **1** and **2**, both ylide and aminotriazine were obtained; however, in other cases no aminotriazine was detected. The photoproducts of ylide and aminotriazine seem to be yielded by the reactions of singlet and

Scheme I

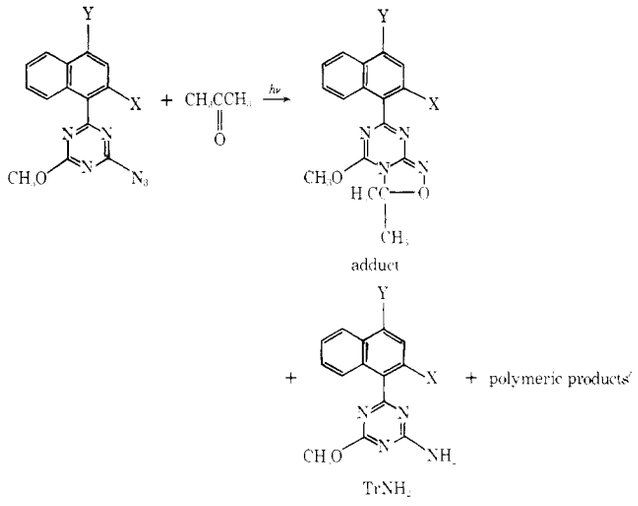


triplet nitrenes with Me_2SO, respectively. On the whole, the results in Table IV show that the photolysis in Me_2SO occurs in a pattern similar to that in acetone. However, the reaction of singlet nitrene with Me_2SO may proceed more readily than that in acetone. In Me_2SO, the reaction stopped at the stage of ylide instead of the cycloaddition product.[13] The combination between the ring nitrogen and oxygen atoms to give the cycloaddition product would be difficult because the ylides from Me_2SO are considered to exist as sulfoximine derivatives.[14]



Photolyses of Azidotriazines in Acetonitrile. The photolyses of azidotriazines in acetonitrile also gave the 1:1 cycloaddition product of triazinylnitrene and acetonitrile, aminotriazine, and unidentified polymeric products; however, the cycloaddition product was obtained only in the case of compound **4** as shown in Table V. In this case, two aromatic nuclei would be twisted toward each other very much by the steric hindrance due to the *o*-methoxyl group, resulting in a decrease in the electron migration from the naphthalene ring to the triazine nucleus; in addition this $-I$ effect of the naphthyl group would decrease the electron density of the triazine nucleus. Therefore, the main reaction product results from the singlet nitrene.

Table III. Photochemical Reactions of Azidotriazines in Acetone[a]



Compd	X	Y	% adduct	% $TrNH_2$
1	OH	H	*c*	43
2	H	OH	18	30
3	H	H	50	5
4	OCH_3	H	63	*c*
5	H	OCH_3	50	*c*
6	CH_3	H	31	8
7	H	CH_3	32	5
8	H	Cl	68	*c*

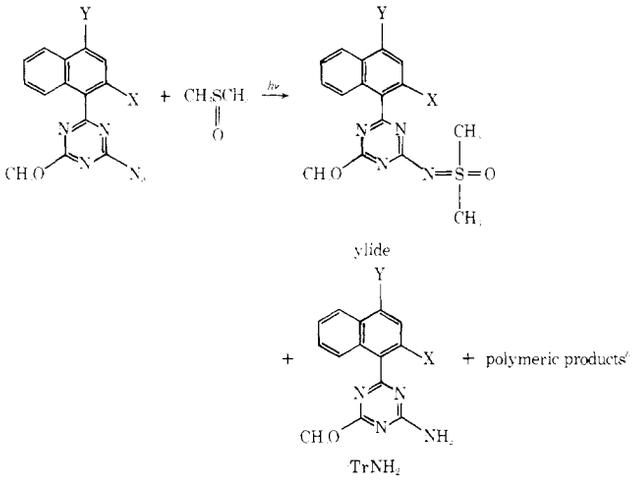
[a] Solutions of azidotriazines in acetone (0.1 g in 20 mL of acetone) were irradiated. Irradiation with a high-pressure mercury lamp was continued until the starting materials (azidotriazines) disappeared completely. It took about 2 days. [b] Unidentified dark brown polymeric products were produced in large amounts. [c] Undetected.

Although in the photolyses of azido(1-naphthyl)triazines in acetone, Me_2SO, and acetonitrile the addition product and/or aminotriazine was obtained as the major product in every case, the yield of the major product varied depending upon the solvent employed. Overall, the highest yields of addition products were obtained with Me_2SO, while acetonitrile gave the highest yields of amines. This difference in reactivity among the solvents employed may be attributed to a difference in the electron-donating power of solvents; for example, the sulfur atom in Me_2SO would be more electron donating than the oxygen atom in acetone (the 3p lone pair electrons of the sulfur atom should be much more electron donating than the 2p lone pair electrons of the oxygen atom). Thus, the electrophilic attack by singlet triazinylnitrene upon the sulfur atom of Me_2SO would take place more readily than that upon the carbonyl oxygen atom of acetone. As for acetone and acetonitrile, the former would be more electron donating in accord with their ionization potentials; the ionization potential of acetonitrile is known to be 1.23 eV[15] and that of acetone is 9.69 eV.[16] Thus, when compound **4** was irradiated in a mixture of Me_2SO, acetone, and acetonitrile, although all products obtained were resulted from the singlet triazinylnitrene, the yields of the addition products varied in the following order with respect to the solvents, supporting the assumption described above:

$$Me_2SO > \text{acetone} > \text{acetonitrile}$$

In conclusion, the reactions of singlet and triplet triazinylnitrenes produced by the photolyses of azido(1-naphthyl)triazines can be explained reasonably by Scheme II, where T-N_3 is the starting material, ^3D the triplet sensitizer

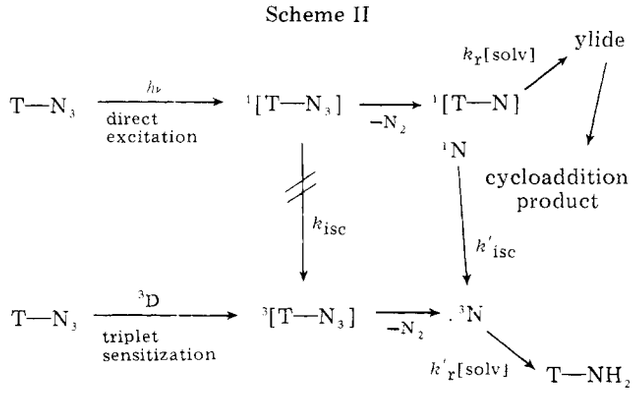
Table IV. Photochemical Reactions of Azidotriazines in Me_2SO[a]



Compd	X	Y	% ylide	% $TrNH_2$
1	OH	H	30	25
2	H	OH	25	27
3	H	H	55	c
4	OCH_3	H	43	c
5	H	OCH_3	54	c
6	CH_3	H	50	c
7	H	CH_3	54	c
8	H	Cl	63	c

[a] Solutions of azidotriazines in Me_2SO (2.0 g in 20 mL of Me_2SO) were irradiated with a high-pressure mercury lamp for 2 days; however 25–30% of the starting materials (azidotriazines) were recovered. [b] Unidentified polymeric products were produced in small amounts. [c] Undetected.

Scheme II



(e.g., benzophenone), and ^1N and ^3N the singlet and triplet triazinylnitrenes, respectively.

The overall reaction is governed by the relative rate of the electrophilic attack (k_r[solv]) to that of intersystem crossing k'_{isc},[9] which depends upon the electronic property of the substituent in the naphthalene nucleus on one hand and the electron-donating power of the solvent on the other hand.

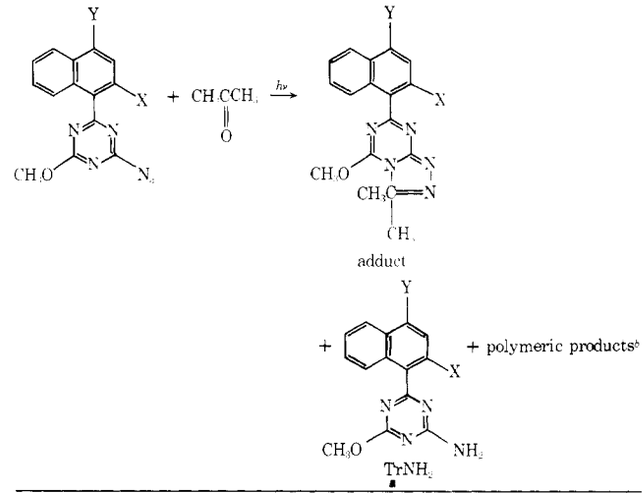
Thus, when k_r[solv] > k'_{isc}, the cycloaddition product or ylide is the major product, while aminotriazine becomes the main product when k_r[solv] < k'_{isc}.

Experimental Section

All the melting points are uncorrected. The identification of the reaction products was performed by means of NMR, IR, UV, and MS spectra, by elemental analyses, and by a mixed melting point test with an authentic sample.

Materials. A typical preparation by the Friedel–Crafts reaction of chlorotriazines with naphthalene derivatives is shown in the case of compound **4.** Compounds **1, 2,** and **5** were prepared by treating the corresponding chlorotriazine derivatives with sodium azide.[8]

Table V. Photochemical Reactions of Azidotriazines in Acetonitrile[a]



Compd	X	Y	% adduct	% $TrNH_2$
1	OH	H	c	30
2	H	OH	c	21
3	H	H	c	25
4	OCH_3	H	23	6

[a] Solutions of azidotriazines in acetonitrile (2.0 g in 20 mL of acetonitrile) were irradiated with a high-pressure mercury lamp for 1 week; however 45–50% of the starting materials (azidotriazines) were recovered. [b] Unidentified dark brown polymeric products were produced in large amounts. [c] Undetected.

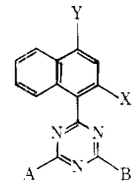
2-Azido-4-methoxy-6-(2-methoxy-1-naphthyl)-1,3,5-triazine (4). A solution of 45.0 g (0.29 mol) of β-methoxynaphthalene in 300 mL of chloroform was added drop by drop into a mixture of 52.0 g (0.29 mol) of 2,4-dichloro-6-methoxy-1,3,5-triazine, 38.8 g (0.29 mol) of powdered aluminium chloride, and 800 mL of chloroform at room temperature. The mixture was stirred at 40 °C for 24 h; then the reaction mixture was poured into 1 L of ice water containing 250 mL of a concentrated hydrochloric acid solution. After the chloroform layer was washed with water, chloroform was distilled off, and the residue was purified by column chromatography on silica gel using a mixture of benzene and ligroin (10:1 by volume) to give an analytical sample of 2-chloro-4-methoxy-6-(2-methoxy-1-naphthyl)-1,3,5-triazine in a yield of 24%: mp 142–143 °C.

A solution of 7.8 g (0.116 mol) of sodium azide in 60 mL of water was added drop by drop into a solution of 10 g (0.033 mol) of 2-chloro-4-methoxy-6-(2-methoxy-1-naphthyl)-1,3,5-triazine in 300 mL of dioxane at room temperature. After stirring at 45 °C for 7 h, the reaction mixture was poured into 1 L of water. The precipitate thus obtained was filtered, dried, and purified by recrystallization from lingoin to give an analytical sample of compound **4** in a yield of 98%: mp 136–137 °C.

A typical preparation by the Grignard reaction of 1-naphthylmagnesium halides with chlorotriazines is shown in the case of compound **6.** A solution obtained by the reaction of 30.0 g (0.136 mol) of 2-methyl-1-bromonaphthalene with 3.30 g (0.136 mol) of magnesium in a mixture of 250 mL of diethyl ether and 150 mL of tetrahydrofuran was added drop by drop into a solution of 25.0 g (0.136 mol) of cyanuric chloride in 350 mL of diethyl ether at room temperature. After stirring for 5 h at room temperature, the mixture was poured into 1 L of ice water containing 200 mL of concentrated hydrochloric acid. The ether layer was washed with water, then the solvent was removed by distillation and the residue was purified by column chromatography on silica gel using a mixture of benzene and ligroin (2:1 by volume) to give 2,4-dichloro-6-(2-methyl-1-naphthyl)-1,3,5-triazine in a yield of 23%: mp 141–142 °C.

A solution obtained by dissolving 0.4 g (0.0174 mol) of sodium in 50 mL of methanol was added drop by drop into a solution of 5.0 g (0.0174 mol) of 2,4-dichloro-6-(2-methyl-1-naphthyl)-1,3,5-triazine in a mixture of methanol (50 mL) and dioxane (100 mL). The reaction mixture was stirred for 2 h at room temperature, then was poured into 500 mL of ice water and extracted with chloroform. After the solvent was removed by distillation, the reaction product was purified by

Table VI. Derivatives of Chloro(1-naphthyl)-1,3,5-triazine



Registry no.	A	B	X	Y	Mp, °C	Solvent for recrystallization	Anal., % Found C	Found H	Found N	Calcd C	Calcd H	Calcd N
65103-15-3	OCH_3	Cl	OCH_3	H	142–143	Ligroin	59.95	4.03	13.75	59.70	3.98	13.93
65103-16-4	OCH_3	Cl	H	OCH_3	135–136	Benzene–ligroin	59.57	4.15	14.11	59.70	3.98	13.93
65103-17-5	Cl	Cl	CH_3	H	141–142	Ligroin	58.10	3.22	14.28	57.93	3.10	14.48
4446-43-9	Cl	Cl	H	CH_3	173–174	Benzene–ligroin	57.78	3.33	14.56	57.93	3.10	14.43
65103-18-6	OCH_3	Cl	CH_3	H	90–91	Ligroin	63.24	4.43	14.63	63.05	4.20	14.71
65103-19-7	OCH_3	Cl	H	CH_3	132–133	Benzene–ligroin	63.03	4.35	14.57	63.05	4.20	14.71
65103-20-0	Cl	Cl	H	Cl	135–136	Benzene–ligroin	50.43	2.05	13.66	50.24	1.93	13.53
65102-89-8	OCH_3	Cl	H	Cl	120–121	Benzene–ligroin	54.83	3.12	13.84	54.90	2.94	13.73

Table VII. 2-Amino-4-methoxy-6-(2- or 4-substituted-1-naphthyl)-1,3,5-triazines

Registry no.	X	Y	Mp, °C	Solvent for recrystallization	Anal., % Found C	Found H	Found N	Calcd. C	Calcd. H	Calcd. N	MS, *m/e*
65102-90-1	OH	H	225–226	Benzene	62.80	4.67	20.78	62.68	4.51	20.89	268
65121-39-3	H	OH	215–216	Benzene	62.97	4.60	20.71	62.68	4.51	20.89	268
65102-91-2	H	H	220–221	Benzene	66.35	4.71	22.01	66.65	4.79	22.21	252
65102-92-3	OCH_3	H	221–222	Benzene	63.98	4.87	19.51	63.82	5.00	19.85	282
65102-93-4	CH_3	H	218–219	Benzene	67.98	5.31	20.96	67.65	5.30	21.04	266
65102-94-5	H	CH_3	220–221	Benzene	67.92	5.28	20.78	67.65	5.30	21.04	266

Table VIII. 1:1 Adducts of 4-Methoxy-6-(2- or 4-substituted-1-naphthyl)-1,3,5-triazin-2-ylnitrene and Acetone or Acetonitrile

Registry no.	Substituent X	Substituent Y	Mp, °C	Solvent for recrystallization	Anal., % Found	Anal., % Calcd	MS, *m/e*	NMR, δ_{ppm}
					Acetone			
65102-95-6	H	OH	221–222	Benzene	C, 62.96 H, 5.16 N, 17.59	62.95 4.97 17.28	324	[a]1.73 (s, 6 H), 4.15 (s, 3 H), 6.98 (d, 1 H), 7.57 (m, 2 H), 8.33 (m, 3 H), 9.22 (m, 1 H)
65102-96-7	H	H	177–178	Benzene	C, 66.70 H, 5.24 N, 18.42	66.22 5.23 18.17	308	[a]1.75 (s, 6 H), 4.12 (s, 3 H), 7.58 (m, 3 H), 8.07 (m, 3 H), 8.93 (m, 1 H)
65102-97-8	OCH_3	H	196–197	Benzene	C, 64.02 H, 5.32 N, 16.62	63.89 5.36 16.58	338	[a]1.77 (s, 6 H), 3.93 (s, 3 H), 3.98 (s, 3 H), 7.95 (m, 6 H)
65102-98-9	H	OCH_3	173–174	Benzene	C, 63.40 H, 5.41 N, 16.57	63.89 5.36 16.58	338	[b]1.78 (s, 6 H), 4.03 (s, 3 H), 4.13 (s, 3 H), 6.83 (d, 1 H), 7.52 (m, 2 H), 8.38 (m, 2 H), 9.33 (m, 1 H)
65102-99-0	CH_3	H	147–148	Benzene	C, 67.09 H, 5.72 N, 17.81	67.06 5.63 17.38	322	[b]1.83 (s, 6 H), 2.52 (s, 3 H), 4.00 (s, 3 H), 7.42 (m, 3 H), 7.80 (m, 3 H)
65103-00-6	H	CH_3	167–168	Benzene	C, 67.15 H, 5.61 N, 17.42	67.06 5.63 17.38	322	[b]1.80 (s, 6 H), 2.72 (s, 3 H), 4.13 (s, 3 H), 7.42 (m, 3 H, 8.08 (m, 2 H), 9.17 (m, 1 H)
65103-01-7	H	Cl	145–146	Benzene	C, 59.83 H, 4.45 N, 16.55	59.57 4.41 16.34	342	[b]1.83 (s, 6 H), 4.18 (s, 3 H), 7.66 (m, 3 H), 8.33 (m, 2 H), 9.20 (m, 1 H)
					Acetonitrile			
65103-02-8	OCH_3	H	135–136	Benzene	C, 63.24 H, 4.73 N, 21.61	63.54 4.70 21.80	321	[a]3.22 (s, 3 H), 3.87 (s, 3 H), 3.95 (s, 3 H), 7.50 (m, 5 H), 8.05 (m, 1 H)

recrystallization from ligroin to give an analytical sample of 2-chloro-4-methoxy-6-(2-methyl-1-naphthyl)-1,3,5-triazine (mp 90–91 °C) in a yield of 84%.

2-Chloro-4-methoxy-6-(2-methyl-1-naphthyl)-1,3,5-triazine was treated with sodium azide in a manner similar to that of described above to give the corresponding azido-1,3,5-triazine in a yield of 92% (mp 88–89 °C).

Analytical data of new compounds of chlorotriazine type were listed in Table VI.

Acetone and Me_2SO (G.R. grade) were used without further puri-

Table IX. Photochemical Reaction Products (Ylides) of 2-Azido-4-methoxy-6-(2- or 4-substituted-1-naphthyl)-1,3,5-triazines with Me_2SO

Registry no.	X	Y	Mp, °C	Solvent for recrystallization	Anal., % Found	Anal., % Calcd	MS, *m/e*	NMR (Me_2SO-d_6), δ_{ppm}
65103-03-9	OH	H	214–215	Acetone	C, 55.69 H, 4.67 N, 16.25	55.80 4.68 16.27	344	3.50 (s, 6 H), 4.06 (s, 3 H), 7.75 (m, 6 H), 9.27 (m, 1 H)
65103-04-0	H	OH	152–153	Benzene	C, 55.71 H, 4.42 N, 16.36	55.80 4.68 16.27	344	3.55 (s, 6 H), 4.02 (s, 3 H), 7.03 (m, 1 H), 7.58 (m, 2 H), 8.27 (m, 2 H), 9.25 (m, 1 H), 10.83 (m, 1 H)
65121-40-6	H	H	164–165	Benzene–ligroin	C, 58.89 H, 5.21 N, 17.63	58.52 4.91 17.06	328	3.58 (s, 6 H), 4.03 (s, 3 H), 7.63 (m, 3 H), 8.08 (m, 3 H), 9.13 (m, 1 H)
65103-05-1	OCH_3	H	193–194	Benzene	C, 57.15 H, 5.05 N, 15.54	56.97 5.06 15.63	358	3.53 (s, 6 H), 3.90 (s, 3 H), 3.98 (s, 3 H), 7.50 (m, 4 H), 8.10 (m, 1 H), 9.15 (m, 1 H)
65103-06-2	H	OCH_3	194–195	Benzene	C, 57.43 H, 5.10 N, 15.65	56.97 5.06 15.63	358	3.55 (s, 6 H), 4.00 (s, 3 H), 4.05 (s, 3 H), 7.12 (d, 2 H), 7.58 (m, 2 H), 8.30 (m, 2 H), 9.17 (m, 1 H)
65103-07-3	CH_3	H	218–219	Benzene	C, 59.43 H, 5.47 N, 16.45	59.63 5.30 16.36	342	2.33 (s, 3 H), 3.52 (s, 6 H), 3.98 (s, 3 H), 7.50 (m, 4 H), 7.97 (m, 2 H)
65103-08-4	H	CH_3	219–220	Benzene	C, 59.56 H, 5.30 N, 16.42	59.63 5.30 16.36	342	2.76 (s, 3 H), 3.58 (s, 6 H), 4.03 (s, 3 H), 7.60 (m, 3 H), 8.13 (d, 2 H), 9.00 (m, 1 H)
65103-09-5	H	Cl	140–141	Benzene	C, 53.10 H, 4.33 N, 15.40	52.96 4.17 15.44	362	3.58 (s, 6 H), 4.05 (s, 3 H), 7.80 (m, 3 H), 8.20 (m, 2 H), 9.05 (m, 1 H)

fication. Acetonitrile (reagent grade) was purified by the usual method.[17] Cyclohexane (G.R. grade) was further purified by passing it through a silica gel column and by distillation.

Light Source and Actinometry. A high-pressure mercury lamp (a Richosa 100-W UVL-100HA) was used for photolyses. Nitrogen gas was bubbled through the solutions during the photolyses. A low-pressure mercury lamp (30 W) with a Vycor glass filter was used as the 254-nm radiation source. The decomposition quantum yields for the starting materials were measured in cyclohexane at 254 nm and 25 °C. Actinometry was carried out using a ferric oxalate solution (0.006 M).[18]

Reaction Products. After a long irradiation of solutions of azidotriazines in acetone, acetonitrile, and Me_2SO with a high-pressure mercury lamp (see the Tables III–V), the reaction mixtures were evaporated. Then the photoproducts were separated and purified by column chromatography on silica gel using a mixture of benzene and acetone as the developing solvent (the ratio of the two solvents was changed depending upon the photoproducts obtained).

2-Amino-4-methoxy-6-(2- or 4-substituted-1-naphthyl)-1,3,5-triazines. Analytical data of aminotriazines were listed in Table VII. These compounds were also confirmed by a mixed melting point test with authentic samples prepared by condensation of the corresponding chlorotriazines with ammonia under pressure.

Adducts of Triazinylnitrene and Acetone, Acetonitrile, or Me_2SO. Analytical data of the adducts were listed in Tables VIII and IX.

Adducts of Triazinylnitrene and Acetone. A typical example is noted below in the case of the adduct of acetone and methoxy(1-naphthyl)triazinylnitrene (X = Y = H); *m/e* of 308 agrees with the predicted value. NMR spectra support the constitution proposed: δ 1.75 (2-CH_3), 4.12 (-OCH_3), 7.58 and 8.07 (aromatic protons, 6 H), 8.93 (H of 8-position of the naphthalene nucleus, 1 H). IR spectrum of this compound (measured in potassium disk) lacks a peak of carbonyl group.

Adducts of Triazinylnitrene and Acetonitrile. MS and NMR spectra support the proposed structure: *m/e* 321; NMR δ 3.22 (-CH_3), 3.87 (-OCH_3), 3.95 (-OCH_3), 7.50 (aromatic protons, 5 H), 8.05 (H of 8-position of the naphthalene nucleus, 1 H). IR spectrum of this adduct lacks a peak of -C≡N group.

Adducts of Triazinylnitrene and Me_2SO. A typical example is noted below in the case of the adduct of (4-methyl-1-naphthyl)triazinylnitrene and Me_2SO (X = H, Y = -CH_3): *m/e* of 342 agrees with the predicted value. NMR spectra [δ 2.76 (-CH_3), 3.58 (2-CH_3), 4.03 (-OCH_3), 7.60 and 8.13 (aromatic protons), 9.00 (H of 8-position of the naphthalene nucleus)] agree with the constitution proposed. IR spectrum of this compound involves peaks assignable to SO group (1015 cm^{-1}) and triazine nucleus (820 cm^{-1}).

Registry No.—Acetone, 67-64-1; acetonitrile, 75-05-8; Me_2SO, 67-68-5; β-methoxynaphthalene, 93-04-9; 2,4-dichloro-6-methoxy-1,3,5-triazene, 3638-04-8; sodium azide, 26628-22-8; 2-methyl-1-bromonaphthalene, 2586-62-1; cyanuric chloride, 108-77-0; 1-bromonaphthalene, 90-11-9; 1-bromo-4-methylnaphthalene, 6627-78-7; 1-bromo-4-chloronaphthalene, 53220-82-9.

References and Notes

(1) W. Lwowski, Ed., "Nitrenes", Interscience, New York, N.Y., 1970; S. Patai, Ed., "The Chemistry of the Azido Group", Wiley, New York, N.Y., 1971, and references concerning nitrenes are cited therein.
(2) H. Yamada, H. Shizuka, and K. Matsui, *J. Org. Chem.*, **40**, 1351 (1975).
(3) R. Kayama, H. Shizuka, S. Sekiguchi, and K. Matsui, *Bull. Chem. Soc. Jpn.*, **48**, 3309 (1975).
(4) H. Shizuka, N. Maeno, and K. Matsui, *Mol. Photochem.*, **4**, 335 (1972); K. Matsui, N. Maeno, S. Suzuki, H. Shizuka, and T. Morita, *Tetrahedron Lett.*, 1467 (1970).
(5) H. Shizuka, T. Kanai, T. Morita, Y. Ohto and K. Matsui, *Tetrahedron*, **27**, 4021 (1971); Y. Ohto, H. Shizuka, S. Sekiguchi, and K. Matsui, *Bull, Chem. Soc. Jpn.*, **47**, 1209 (1974); K. Tsutsumi, K. Matsui, and H. Shizuka, *Mol. Photochem.*, **7**, 325 (1976).
(6) Y. Yamada, H. Shizuka, S. Sekiguchi, and K. Matsui, *Bull. Chem. Soc. Jpn.*, **47**, 238 (1974).
(7) H. Shizuka, K. Matsui, T. Okamura, and I. Tanaka, *J. Phys. Chem.*, **79**, 2731 (1975); H. Shizuka, K. Matsui, Y. Hirata, and I. Tanaka, *J. Phys. Chem.*, **80**, 2070 (1976); **81**, 2243 (1977).
(8) S. Tsunoda, Y. Hashida, S. Sekiguchi, and K. Matsui, *Bull. Chem. Soc. Jpn.*, **49**, 487 (1976).
(9) There is a possibility that the rate constants k'_{isc} in the intersystem crossing $^1N \rightarrow {}^3N$ may be affected by the substituents of the nitrene or the solvents used. It is, therefore, difficult to make quantitative analyses of the reactions, since the k'_{isc} values are unknown. However, it may be possible to discuss the reactivity of nitrene with solvents qualitatively.
(10) T. Goka, H. Shizuka, and K. Matsui, presented at the 36th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1977.
(11) R. Reiser and L. J. Leyshon, *J. Am. Chem. Soc.*, **93**, 4051 (1971).
(12) M. Sumitani, S. Nagakura, and K. Yoshihara, *Bull. Chem. Soc. Jpn.*, **49**, 2995 (1976).
(13) K. Fujinuma, S. Sekiguchi, and K. Matsui, The 35th Annual Meeting of the

Chemical Society of Japan, Hiratsuka, 1976.
(14) C. R. Johnson and C. W. Schroeck, *J. Am. Chem. Soc.*, **95**, 7418 (1973).
(15) R. F. Lake and H. Thompson, *Proc. R. Soc. London, Ser. A*, **317**, 187 (1970).
(16) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).
(17) A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Troops, Jr., "Organic Solvents", Interscience, New York, N.Y., 1955, p 435.
(18) C. G. Hatchard and C. A. Parker, *Proc. R. Ser. London, Ser. A*, **235**, 518 (1956); for details, see the following reference: P. de Mayo and H. Shizuka in "Creation and Detection of the Excited State", Vol. 4, W. R. Ware, Ed., Marcel Dekker, New York, N.Y., 1976, Chapter 4.

Methylation of Protomeric Ambident Nucleophiles with Methyl Fluorosulfonate: A Regiospecific Reaction

Peter Beak,* Jae-keun Lee, and B. Gary McKinnie

Roger Adams Laboratory, University of Illinois at Urbana-Champaign, Urbana Illinois 61801

Received October 6, 1977

Methylation of 15 protomeric ambident nucleophiles with methyl fluorosulfonate has been found to occur regiospecifically at the heteroatom remote from the mobile proton. In most cases the fluorosulfonate salts thus obtained can be isolated, identified by ^{1}H NMR spectroscopy, and converted to the neutral methylated derivatives by aqueous base. The compounds studied include five of the nine possible systems X=YZH ⇄ HXY=Z, in which Y is carbon and X and Z are oxygen, nitrogen, and/or sulfur. In 12 cases the reaction is synthetically useful, although it is sometimes necessary to remove the excess methyl fluorosulfonate prior to treatment with base. Three cases give mixtures of methylated products, a result established for the case of 2-pyridone to be due to proton transfer from the initial regiospecifically formed salt.

The alkylation of protomeric tautomers is of interest in a wide variety of chemical and biochemical studies.[1,2] More detailed understanding and better control of such reactions would be useful.

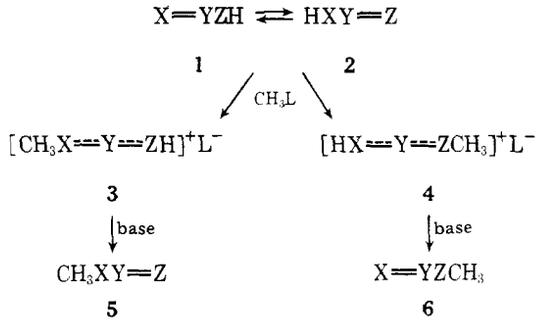
A generalized case is shown in Scheme I for methylation of the ambident protomeric nucleophiles **1** and **2** to give the salts **3** and **4**. Reaction of **3** and **4** with a base would provide the methylated isomers **5** and **6**. It is well-recognized that there is not necessarily any correspondence between the relative amounts of the protomeric reactants, **1** and **2**, and the isomeric products, **3** and **4** or **5** and **6**. Recent analyses of such reactions have been appropriately cautious.[1,3-6]

If X and Z are heteroatoms, proton transfer would be expected to be several orders of magnitude more rapid than methylation, and the relative rates of formation of **3** and **4** would then be determined solely by the relative transition-state energies leading to these cations.[7,8] If **3** and **4** are stable under the conditions of their formation, subsequent deprotonation would provide **5** and **6** in a ratio which has been determined by the relative transition-state energies leading to **3** and **4**. Reaction profiles showing product control under the Curtin–Hammett principle[7] in which the ratios of **3** and **4** could be greater or less than one are illustrated in Figure 1.

Nonetheless, the possibility does exist that there might be a circumstantial relationship between the ground-state energies of **1** and **2** and the transition states for their alkylation. For example, the bonding features which make **1** of lower energy than **2** could persist in the respective transition states (Figure 1a). In that case, cation **3** would be predominant and the subsequent isomer **5**, in which the alkyl group is attached to the heteroatom remote from the mobile proton in the major tautomer, would be produced after proton removal by a base. While this guide would be at best a *qualitative* indication of the position of alkylation, it is interesting that if the transition-state energy difference were >2 kcal/mol (at 25 °C) an effectively regiospecific alkylation of the tautomeric system would result. Formally the proton would appear to be a directing group if the profile of Figure 1a were followed. In fact, a number of cases exist which follow such a qualitative course.[1,3,5,9]

It should be emphasized that quantitative correlation of the

Scheme I



tautomeric ratio and the ratio of alkylated products is neither expected[6,7] nor observed, as careful studies of 5-nitroimidazole by Ridd[3] and of 3-hydroxyisothiazole by Crow[4] have shown. Moreover, our above suggestion of possible qualitative generality for the reaction path of Figure 1a might well be considered naive by the following argument. If isomers **1** and **2** undergo protonation to give a common product, the difference in the ground-state energies of **1** and **2** can be considered to reflect the difference in basicity of the atoms X and Z. If that basicity difference reflects a parallel difference in the nucleophilicity of these atoms in the respective transition states for alkylation, the suggested regiospecificity would not be observed.[3,10] On a practical level, the assumptions that the salts **3** and **4** will be stable and that the neutral tautomers will be reactive nucleophiles might not be valid.

In order to explore the possibility that the pathway of Figure 1a could be followed for more than a few cases, we have investigated the reactions of 15 protomeric ambident nucleophiles and methyl fluorosulfonate.[11] This highly reactive readily soluble methylating agent was chosen to maximize the possibilities that transition states would reflect the ground-state energies of the tautomers and that the reaction could be driven, and the initially formed salts stabilized, by precipitation from a nonpolar solution. In general, the regiospecific course suggested by Figure 1a is followed, although synthetic complications arise due to the instabilities of the initially formed salts to the reaction conditions for three cases.[12-14]

0022-3263/78/1943-1367$01.00/0