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Photolyses of Azidotriazines in Organic Nitro Compounds

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Synopsis. Triazinylnitrenes were found to be inert towards nitro compounds. They afforded the products derived from the combination of two molecules of the starting materials.

Nitrene chemistry has been extensively studied and well established.[1] Recently, we reported some photochemical reactions of azidotriazines in aprotic solvents such as nitriles,[2] acetone,[3] and DMSO;[4] triazinyl nitrene reacts with nitriles and acetone to yield a cycloaddition product, while its reaction with DMSO give an ylide. We now wish to report the photochemical reaction of azidotriazines in nitro compounds.

Experimental

Azidotriazines (**1**) were prepared by treating the corresponding chlorotriazines with sodium azide[5] (Table 1).

The experimental produre was almost the same as those described previously.[2-4]

TABLE 1. 4,6-DISUBSTITUTED 2-AZIDO-1,3,5-TRIAZINE[a]

Compound	Substituent 4-	Substituent 6-	Mp(°C)	Solvent for recryst.
1a	OMe	OMe	85—85.5[b]	Ligroin
1b	OEt	OEt	31—32	Petroleum ether
1c	O-*i*-Pr	O-*i*-Pr	30—31	Petroleum ether
1d	OMe	NMe_2	116—117	Ligroin
1e	NMe_2	NMe_2	106—107[b]	Benzene

a) Satisfactory chemical analyses (±0.5%) were obtained for all compounds. b) Ref. 5.

Results and Discussion

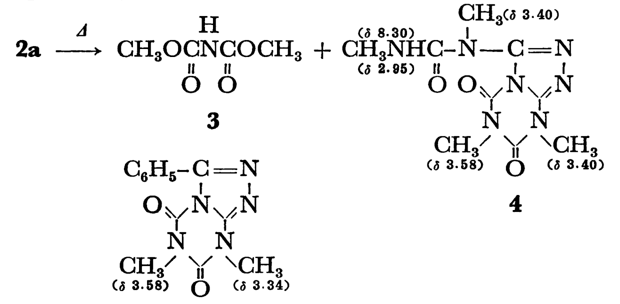
Photolyses of 2-Azido-4,6-dimethoxy-1,3,5-triazine (1a) in Nitro Compounds. When 2-azido-4,6-dimethoxy-1,3,5-triazine (**1a**) was irradiated in several nitro compounds, the same photoproduct (**2a**) was obtained regardless of the solvents employed (Table 2).

TABLE 2. THE PHOTOCHEMICAL REACTIONS OF 2-AZIDO-4,6-DIMETHOXY-1,3,5-TRIAZINE

Solvent	Yield (%) of **2a**
$MeNO_2$	26
$EtNO_2$	32
i-$PrNO_2$	40
$PhNO_2$	23

The mass spectrum of **2a** has a parent peak at *m/e* 311. The PMR spectrum indicates the presence of one active hydrogen atom and 4 kinds of methyl groups, each of which was observed as a singlet.

2g gave a dimethylester (**3**)[6] of dimethyl iminodicarbonate and **4** upon heating in cumene at 190 °C, indicating that **2a** has a skeleton of **4**. The structure of **4** was assigned on the basis of its mass spectrum and by a comparison of its PMR spectrum to those of the known compound (**5**).[2]



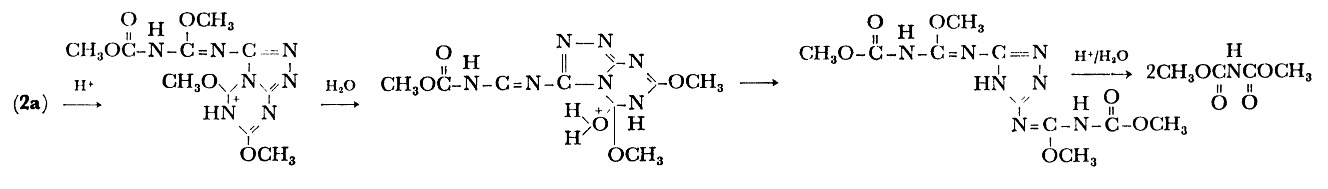
Moreover, **2a** gave **3** as the major product in a very good yield (1 mol of **2a** gave 1.7 mol of **3**) when treated with diluted hydrochloric acid at 40 °C. The results suggest that i) in **2a** the methyl groups in the triazine ring exist as methoxyl groups, and ii) **2a** does not have a aromatic stabilization, because ordinary 1,3,5-triazine derivatives are known to be stable to a treatment with dilute acid.

Effects of Substituents in Triazine Nucleus. Substituents in the triazine nucleus were found to affect the photochemical reactions of azidotriazines in nitro compounds (Table 3). The physical and analytical data of compounds (**2**) are collected in Table 4. In the cases of azidotriazines (**1d** and **1e**), in which the electron-donating NMe_2 groups are found, the corresponding reactions did not take place. In addition, when **1b** was irradiated in the presence of benzophenone, the corresponding aminotriazine was obtained in 18% yield. These results clearly suggest that the reaction to give **2a** involves singlet triazinylnitrene, which has an electrophilic character.[1,4] In the reactions of azidotriazine (**1b**) containing OEt groups, a similar photoproduct was also obtained. On the other hand, the yield

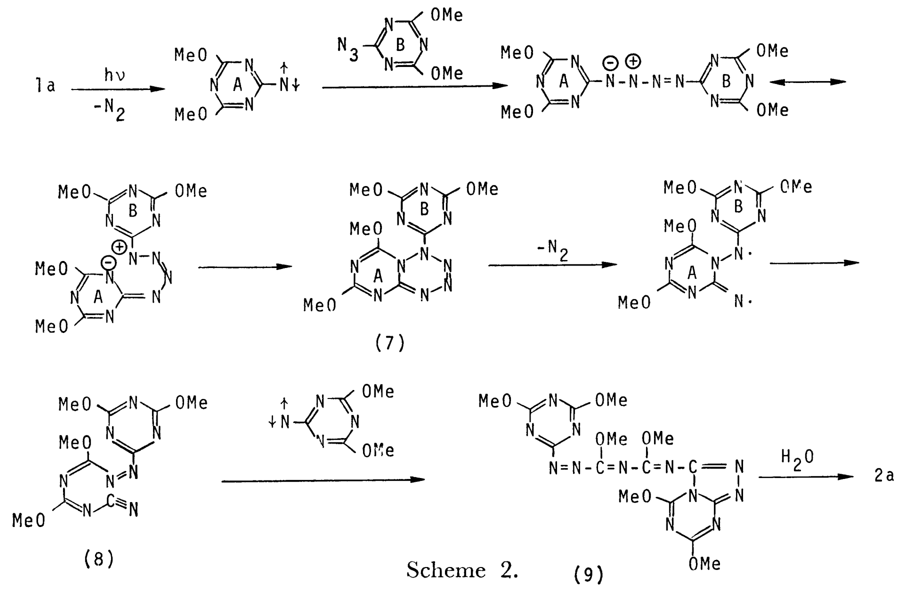
TABLE 3. THE PHOTOCHEMICAL REACTIONS OF AZIDOTRIAZINES

Azidotriazine	Condition	Yield(%) of **2**(product)
1a	a)	26 (**2a**)
1b	a)	19 (**2b**)
1b	b)	6 (**2b**)
1b	c)	26 (**2b**)
1c	a)	15 (**2c**)
1c	b)	5 (**2c**)
1c	d)	2 (**2c**)
1d	a)	—
1e	a)	—

a) Irradiation was performed in nitroethane. b) Neat sample was irradiated. c) Irradiation was performed in water. d) Irradiation was performed in nitroethane under bubbling oxygen.



Scheme 1.

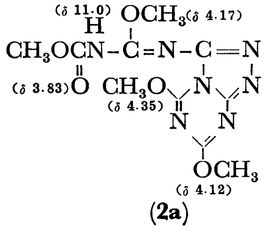


Scheme 2.

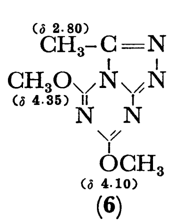
Table 4. The physical and analytical data of compounds (**2**)

2	Mp(°C)	Solvent for recryst.	Found (Calcd)%			MS m/e
			C	H	N	
2a	198—199	Chloroform	38.65 (38.59	4.55 4.21	31.97 31.50)	311
2b	184—185	Benzene	45.98 (45.77	5.95 5.76	26.91 26.69)	367
2c	162—163	Benzene	51.37 (51.05	7.12 6.90	29.36 23.15)	423

of photoproduct increased considerably when a small amount of water was added into the reaction mixture, showing that water participates in the reaction. From the results described above and a comparison of the PMR data of **2** with those of the known compound (**6**),[2] the constitution of **2a** was assumed to be as shown below:



(**2a**)



(**6**)

A probable process of the decomposition of **2a** in the presence of hydrochloric acid is shown in Scheme 1.

On the other hand, in the reactions of azidotriazine (**1c**) in nitroethane in the presence of oxygen, a remarkable decrease in the yield of the photoproduct was observed (Table 3), indicating that the reaction involves the radical process.

Although several pathways could account for the formation of **2**, the most likely one is shown in Scheme 2. That is, singlet triazinylnitrene produced by the photolysis of azidotriazine electrophilically attacks upon the terminal nitrogen of azido group[7] to yield an ylide which cyclizes to give a pentazine (**7**). Then the intermediate (**7**) gives a derivative of nitrile (**8**) under a cleavage of nitrogen and a ring opening of the triazine nucleus (A). Electrophilic attack of singlet triazinylnitrene may occur not only at the azido group but also at the nitrile group of **8**. However, the nucleophilic reactivity of the –CN group in **8** would be much higher than that of the azido group of **1a**, because the –CN group is attached to a conjugated position involving two strong +R(–OCH$_3$) groups, while the azido group is connected to the electron-withdrawing triazine nucleus. Therefore, electrophilic attack of the singlet triazinyl nitrene should occur upon the –CN group preferentially to give a cycloaddition product (**9**). Finally, the product (**9**) hydrolyzes by water to give the final product (**2a**).

References

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

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7) Electron density at the terminal nitrogen is calculated to be the highest (Ref. 1, Chap. 1).