BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(1), 238—239 (1974)

Photochemical Reaction of Halo-1,3,5-triazines: Photo-triazinylation

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(Received July 12, 1973)

Synopsis. Chloro-*s*-triazines or bromo-*s*-triazines containing halogen and/or methoxy substituents in the *s*-triazine nucleus gave the corresponding phenyl-*s*-triazines upon irradiation at 2537 Å in benzene.

It is known that some aryloxy-*s*-triazines rearrange photochemically to give *ortho* or/and *para* hydroxyaryl-*s*-triazines (photo-Fries rearrangement),[1] while aryloxy-*s*-triazines containing an *ortho* amino group give *ortho*-hydroxyarylamino-*s*-triazines on irradiation (photo-Smiles rearrangement);[2] these photochemical reactions are known to occur from the lowest excited singlet states of the corresponding molecules.

Recently, the photochemical reactions of haloarenes have been studied extensively; the photochemical primary processes in halobenzenes involve the fission of the C–Hal bond to give the phenyl radical and the halogen atom.[3] The photolysis of chlorobenzene in the gas phase orginates from the excited singlet state.[4] The photoarylations of aromatic compounds with haloarenes, such as halobenzenes[5–7] and *p*-halophenols,[8,9] proceed *via* a radical process. As for haloheteroaromatics, such as 2-iodothiazole,[10,11] 3-iodothiophen,[12] 3-iodobenzo[*b*]-thiophen,[13] and 3-iodopyridine,[14] similar photochemical reactions take place. However, no photochemical study of halo-*s*-triazine has yet been reported.

In the case of the *s*-triazine derivative, the photo-*s*-triazinylation of aromatic compounds with the halo-*s*-triazines was of interest from two points of view: the influence of the presence of three ring nitrogen atoms and the substituent effect upon the reaction. In addition, the photo-*s*-triazinylation of aromatic compounds with chloro-*s*-triazines will provide a useful and convenient method for the synthesis of aryl-*s*-triazines, since chloro-*s*-triazines containing various substituents in the *s*-triazine nucleus can readily be obtained from cyanuric chloride. This paper will report on the photo-*s*-triazinylation of benzene with halo-*s*-triazines.

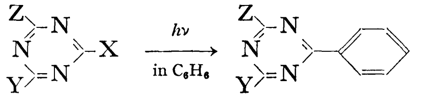
Experimental

A low-pressure mercury lamp was used as the 2537 Å radiation source. Table 1 lists the halo-*s*-triazines employed as the starting materials (No. 1—6).

After a long irradiation of benzene solutions of halo-*s*-triazines at 2537 Å, the reaction mixtures were evaporated, after which the photoproducts were separated and purified by column or thin-layer chromatography. The photoproducts were identified by means of elemental analyses, by a study of the IR, UV, and NMR spectra, and by a mixed-melting-point test with an authentic sample in some cases.

Results

In every case, the main product was found to be a phenylated *s*-triazine derivative, showing that the photoarylation of aromatic compound can be carried out using halo-*s*-triazine; Table 1 lists the photoproducts thus obtained (No. 6—9). The photoreaction of halo-*s*-triazines in benzene can be represented by the following general formula:



X = -Cl, -Br, Y, Z = -Cl, -Br, -OCH_3

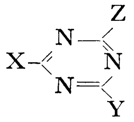
Thus, chloro- and bromo-*s*-triazines containing one, two, and three halogen atoms, and halo-*s*-triazines containing methoxyl groups in the *s*-triazine nucleus reacted photochemically with benzene to give the corresponding phenyl-*s*-triazines. However, when a phenyl group or an amino group, such as the *N*-methylanilino- or dimethylamino group, is present in the *s*-triazine nucleus, it was found to be very difficult for the photoreaction of halo-*s*-triazine to take place; therefore, derivatives containing more than two phenyl groups could not be obtained by the photoreaction of dihalo- or trihalo-*s*-triazines with benzene.

Generally, the progresses of these photoreactions were slow compared with those of photo-Fries rearrangements of aryloxy-*s*-triazines or photo-Smiles rearrangements of *O*-*s*-triazinyl-2-aminophenols; for example, the quantum yield for the product formation in the reaction of 2-chloro-4,6-dimethoxy-*s*-triazine with benzene was found to be 0.03 at the concentration of 3×10^{-3} M in benzene. In addition to the photoproducts mentioned above, the formation of hydrogen halide was observed, for example, in the photo-phenyldechlorination of chloro-dimethoxy-*s*-triazine, and the chemical yields of phenylated products in the photoreactions of 2-bromo-4,6-dimethoxy-*s*-triazine, 2-chloro-4,6-dimethoxy-*s*-triazine, 2,4-dichloro-6-methoxy-*s*-triazine, and cyanuric chloride were 21, 22, 20, and 19% respectively, at the concentration of 2×10^{-2} M in benzene at 2537 Å for 24 hr.

The reactive state in the reaction may originate from the excited singlet state of halo-*s*-triazine, judging from the following reasons:

(1) The incident light at 2537 Å is absorbed by benzene (>99%), not by halo-*s*-triazine, under the experimental conditions described above. Therefore, the excited halo-*s*-triazine should be formed by the energy transfer from the excited benzene. The singlet-singlet energy transfer from the excited benzene to halo-*s*-triazine was confirmed by the measurements of the fluorescence quenching of benzene by halo-*s*-tri-

Table 1. Starting materials (halo-*s*-triazines) and photoproducts (phenyl-*s*-triazines)



No.	Z	Y	X	Mp (°C)	Anal. (%) Found C	H	N	Br	Calcd C	H	N	Br
1	CH_3O–	CH_3O–	Br–	122—123	27.73	3.16	18.97	—	27.29	2.73	19.10	—
2	CH_3O–	Br–	Br–	155—156	18.29	1.32	15.74	—	17.86	1.12	15.62	—
3	CH_3O–	CH_3O–	Cl–	79—80 (76—77)[a]	—	—	—	—	—	—	—	—
4	CH_3O–	Cl–	Cl–	91—92 (88—90)[a]	—	—	—	—	—	—	—	—
5	Cl–	Cl–	Cl–	145—146 (145.75)[b]	—	—	—	—	—	—	—	—
6	CH_3O–	CH_3O–	C_6H_5–	68—69(69)[c]	—	—	—	—	—	—	—	—
7	CH_3O–	Br–	C_6H_5–	76—77	45.12	3.45	15.50	30.25	45.15	3.04	15.79	30.03
8	CH_3O–	Cl–	C_6H_5–	75—76	54.12	3.71	18.82	—	54.17	3.61	18.96	—
9	Cl–	Cl–	C_6H_5–	121—122(120)[d]	—	—	—	—	—	—	—	—

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b) American Cyanamid Co., Cyanuric Chloride, *New Product Bulletin.*

c) Z. N. Pazenko and T. N. Lebedeva, *Ukr. Khim. Zh.*, **30**, 66—68 (1964); *Chem. Abstr.*, **60**, 12014e.

d) R. Hirt, H. Nidecker, and R. Berchtold, *Helv. Chim. Acta,* **33**, 1365 (1950).

azine; the intensity of the fluorescence decreased considerably with an increase in the concentration of halo-*s*-triazine.

(2) Very little effect of dissolved oxygen on the product formation was observed. This fact supports the singlet mechanism in the reaction, although an extremely fast triplet reaction can not be excluded.

When a solution of 2-bromo-4,6-dimethoxy-*s*-triazine in cumene was irradiated, dicumyl was obtained as a photoproduct, while the formation of acetone was observed when it was irradiated in 2-propanol, suggesting that the photoreaction of halo-*s*-triazines proceeded *via* a radical process involving an α-bond dissociation (C–X) into the halogen atom and the *s*-triazinyl radical. The triazinyl radical produced by the dissociation of excited singlet halo-*s*-triazine may attack the benzene molecule to give the final product *via* the intermediate, M. Figure 1 shows the schematic reaction mechanism of the photo-triazinylation of benzene by halo-*s*-triazine at 2537 Å, where B and B* are the ground and the lowest singlet excited states of benzene respectively, where RX and RX* denote the ground and the excited ($^1\pi\pi^*$) singlet states of halo-*s*-triazine respectively, and where X· and R· indicate the ground states of the halogen atom and the *s*-triazinyl radical respectively.

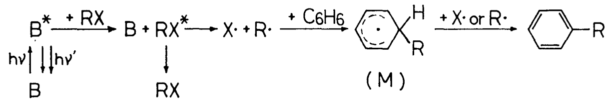

Fig. 1. Schematic reaction mechanism at 2537 Å.

The susbtituent effects on the reaction may suggest that the electronic structures in the excited states of halo-*s*-triazines (the nπ^* and $\pi\pi^*$ energy levels and the character of the lowest excited state) play an important role in the dissociation of the C–X bond Similar substituent effects were also observed in the case of the photo-Fries rearrangement of *s*-triazine derivatives.[15]

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