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Reactions of Diazomethyl-1,3,5-triazines with Cyclohexane

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Synopsis. Diazomethyl-1,3,5-triazines reacted with cyclohexane thermally and photochemically to give cyclohexylmethyl-1,3,5-triazines as the major product. The reactions took place *via* a carbene intermediate; however, the hydrogen abstraction products (methyl-triazines) were not obtained in these cases.

There have been a number of studies of the reactions of aliphatic diazo compounds.[1] In recent years the reactions of diazoalkyl derivatives of heteroaromatics, such as triazole,[2] furan,[3–5] thiophene,[5,6] and pyridine,[6–8] have been investigated.

Diazomethyl-1,3,5-triazines have been known for a long time;[9–11] however, the thermal and photochemical reactions of diazomethyl-1,3,5-triazines have not yet been investigated.

On the other hand, the thermolysis and photolysis of diazomethyl-1,3,5-triazines may provide useful and convenient routes for the preparation of 1,3,5-triazine derivatives, which would otherwise be difficult to prepare.

This paper will report on the thermal and photochemical reactions of diazomethyl-triazines with cyclohexane.

Structure of Diazomethyl-1,3,5-triazines. 4,6-Dichloro-(1),[9,10] 4,6-dimethoxy- (2),[9] and 4,6-bis(dimethylamino)-2-diazomethyl-1,3,5-triazine (3)[10] are thermally stable; they can be purified by sublimation under reduced pressure. Generally, 2-diazomethyl nitrogen heteroaromatics are considered to exist in a diazomethyl-azomethine-triazole equilibrium. In the diazomethyl derivatives of pyridine, the equilibrium lies strongly on the side of triazole,[6–8,12] while in the derivatives of 1,3,5-triazine the triazole form is considered to be excluded on the basis of the mode of their reactions and the presence of the characteristic IR band of aliphatic diazo compound.[9]

The IR spectra of Compounds 1, 2, and 3 in KBr discs have a strong and sharp characteristic band near 2120 $\mathrm{cm^{-1}}$ assignable to the diazomethyl group, indicating that these compounds exist in the diazomethyl form in a solid state. In addition, the PMR spectra of Compounds 2 and 3 in CCl_4, $CDCl_3$, and DMSO-d_6 at 20 and 60 °C showed a signal assignable to $-OCH_3$ or $-N(CH_3)_2$ as a singlet in every case, in spite of the wide diversity in the nature of the solvent (see Table 1); this shows the absence of tautomeric triazole, which should possess two kinds of methoxyl or dimethylamino groups. Contrary to expectations, ordinary diazomethyl-1,3,5-triazines exist only in the diazomethyl form, not only in the solid state, but also in a solution, regardless of the solvent employed.

TABLE 1. PMR DATA OF DIAZOMETHYL-TRIAZINES

Solvent	Chemical Shift (δ)[a]			
	Compound 2		Compound 3	
	$-CHN_2$	$-OCH_3$	$-CHN_2$	$-N(CH_3)_2$
DMSO-d_6	5.9	3.9	5.4	3.0
CCl_4	5.2	4.0	4.0	3.1
$CDCl_3$	5.1	3.9	4.7	3.1

a) Measured at 20 °C using TMS as the internal standard.

In diazomethyl-1,3,5-triazines, electrons poured into the aromatic nucleus from the side chain should spread over the 3-ring nitrogen atoms; therefore, interaction between one of these nitrogen atoms and the terminal nitrogen atom of the side chain would be weaker than in the cases of diazines and pyridine. Thus, it may generally be said that an increase in the number of ring nitrogen atom prevents the formation of a stable bicyclic tautomer in azido, diazoalkyl, and related derivatives of nitrogen heteroaromatic compounds.

Reactions of Diazomethyl-1,3,5-triazines with Cyclohexane. When compound 2 was heated in cyclohexane at 180 °C, 2-cyclohexylmethyl-4,6-dimethoxy-1,3,5-triazine (yield, 12%) was obtained as the sole isolable product;[13] however, the corresponding methyl-triazine was not detected in the reaction mixture by tlc.

On the other hand, when a cyclohexane solution of Compound 2 was irradiated at 254 nm, several photoproducts were produced, along with one major product. The major product was 2-cyclohexylmethyl-4,6-dimethoxy-1,3,5-triazine (yield, 14%); in this case also, the corresponding methyl-triazine was not obtained. The monodiazomethyl-triazines are thermally stable (the decomposition point of Compound 2 is 190 °C, and that of Compound 3 is 195 °C); therefore, without irradiation they did not react with cyclohexane at room temperature. Since most of the 254 nm incident light is absorbed by diazomethyl-triazine, the photochemical reaction with cyclohexane should take place *via* a carbene intermediate formed by the decomposition of the excited diazomethyl-triazine, even though the presence of the corresponding carbene could not be confirmed when diazomethyl-triazines were irradiated at 254 nm in EPA at 77 K.[14] The formation of cyclohexylmethyl-triazine in the photochemical and thermal reactions can be understood in terms of the intermolecular insertion of the singlet triazinyl carbene.

Similarly, 2-diazomethyl-4,6-bis(dimethylamino)-1,3,5-triazine (3) reacted thermally and photochemically with cyclohexane to yield the corresponding cyclohexylmethyl-triazine as the sole isolable product (the yields were 10% and 16% respectively). The assumption that the thermal reaction of diazomethyl-triazines proceeds *via* a carbene intermediate may be supported by kinetic measurements of the reactions.

When diazomethyl-triazines were heated in hydrocarbons, an evolution of nitrogen was observed. Therefore, for the kinetic measurements, an increase in the volume of nitrogen evolved in various substrates was followed after a lapse of time; however, in the reaction with cyclohexane the kinetic runs were carried out by measureing the decrease in the intensity of the $-CHN_2$ IR band after heating in small, sealed glass tubes.[16] The first-order rate constants for the decomposition of Compound 2 are listed in Table 2.

TABLE 2. RATE CONSTANTS FOR THE DECOMPOSITION OF 2-DIAZOMETHYL-4,6-DIMETHOXY-1,3,5-TRIAZINE IN VARIOUS SUBSTRATES

Substrate	$k_1 \times 10^4$ (s^{-1})		
	180 °C	170 °C	160 °C
Cyclohexane	5.55	2.26	0.98
Decalin	3.25	1.43	0.41
Tetralin	2.57	—	—
Diphenyl ether	2.44	—	—

From Table 2 it is obvious that, in these reactions, there is little variation in the rate in spite of the wide diversity in the nature of the substrates, suggesting that the rate-determining step of these reactions is the loss of nitrogen to give a carbene species.

For a detailed discussion, the temperature dependence of the reaction constant was measured in decalin and cyclohexane; the activation parameters for the reactions are listed in Table 3.

TABLE 3. ACTIVATION PARAMETERS FOR THE DECOMPOSITION OF 2-DIAZOMETHYL-4,6-DIMETHOXY-1,3,5-TRIAZINE

Substrate	$\Delta H^{\neq}$ (kcal·mol^{-1})	$\Delta S^{\neq}$(170 °C) (cal·deg^{-1}·mol^{-1})
Cyclohexane	33.5	−0.4
Decalin	39.7	+12.7

The entropies of the activation of −0.4 and +12.7, which were comparable in magnitude to those of the reactions of other diazomethyl derivatives with similar substrates,[15] support the idea that the reaction is of the first order, involving the carbene intermediate.

Experimental

All the melting points are uncorrected. The assignments of the reaction products were performed by means of NMR, IR spectra, and elemental analyses. A low-pressure mercury lamp with a Vycor glass filter was used as the 254 nm radiation source.

Materials. The diazomethyl-triazines were prepared by the condensation of cyanuric chloride with diazomethane,[9,10] followed by treatment with sodium methoxide[9] or dimethylamine,[10] (Compound 1, mp 112—113 °C) (lit,[9,10] 111.5—112.5 °C) (Compound 2, mp 103—104 °C) (lit,[9] 105—106 °C) (Compound 3, mp 93—94 °C) (lit,[10] 94 °C). The reaction mixtures were concentrated, purified by column chromatography (silica-gel; benzene: acetone = 10: 1 by volume), and dried *in vacuo.* 2-Cyclohexylmethyl-4,6-dimethoxy-1,3,5-triazine. Viscous oil. Found: C, 60.85; H, 8.10; N, 17.92%. Calcd for $C_{12}H_{19}N_3O_2$: C, 60.73; H, 8.07; N, 17.71%. NMR (CCl_4), δ 1.0 (m, 11H), 2.55 (d, 2H), 4.0 (s, 6H). 2-Cyclohexylmethyl-4,6-bis(dimethylamino)-1,3,5-triazine, mp 58—58.5 °C (Ligroin). Found: C, 64.20; H, 9.52; N, 26.73%. Calcd for $C_{14}H_{25}N_5$: C, 63.84; H, 9.57; N, 26.59%. NMR (CCl_4), δ 1.6 (m, 11), 2.3 (d, 2H), 3.1 (s, 12). The procedures of the kinetic measurements were almost the same as those previously described.[16]

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13) In the thermal and photochemical reactions of diazomethyl-triazines with cyclohexane, cyclohexylmethyl-triazine can be said to be the major product in every case without taking a formation of a large amount of tarry matter into account. And all our trials have failed to obtain pure minor by-products by tlc, column or gas chromatography.

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