1045, 1060, 1090, 1125, 1175, 1265, 1320, 1385, 1430, 1465, 1515, 1575, 1610 cm^{-1}. PMR spectrum (DMSO): δ_{CH} 9.74 ppm. Found: C 21.3; H 1.0; N 50.0%; M 25 (by potentiometry). $C_4H_2N_8O_4$. Calculated: C 21.3; H 0.9; N 49.5%; M 226.

Reaction of N-Nitro-3-chlorotriazole with Triethylamine. A 2.4-ml sample of triethylamine was added to 1.2 g of N-nitrotriazole I in 5 ml of dry acetonitrile, and the solution was maintained at 20°C for 1 week. It was then diluted with water, acidified to pH 1, and extracted with ether. Removal of the ether gave 0.3 g of a solid product that was found to be a mixture of three compounds: IV (R_f 0.80; δ_{C-H} 9.45 ppm in DMSO), 3-nitro-5-chloro-1,2,4-triazole (X) (R_f 0.40 with reference spot), and 3-chloro-1,2,4-triazole (VII, δ_{C-H} 8.65 ppm in DMSO,* did not show up on the chromatogram). The IV:VII ratio was ≈10:1.

Reaction of N-Nitro-3-bromo-1,2,4-triazole (III) with Ferrous Sulfate and Sodium Hypophosphite. A 1-g sample of N-nitrotriazole III was heated at 50-60°C for 8 h with a solution of 2 g of ferrous sulfate in 20-25 ml of water, after which the solution was acidified and extracted with ether. The ether was removed by distillation to give 0.3 g of a substance which was found to be a mixture of V (R_f 0.66, δ_{CH} 9.42 ppm in DMSO), 3-nitro-5-bromo-1,2,4-triazole (XI, R_f 0.50 with a reference spot), and 3-bromotriazole VIII* (δ_{CH} 8.65 ppm in DMSO, did not show up on the chromatogram).

Similar results were obtained when triazoles II and III were heated with aqueous sodium hypophosphite solution.

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*When authentic samples of VII or VIII were added to the reaction products, the intensities of the corresponding signals in the PMR spectra increased.

REACTION OF CYANURYL CHLORIDE AND SOME OF ITS MONOSUBSTITUTED DERIVATIVES WITH TOLUENE

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The Friedel–Crafts reaction of cyanuryl chloride and some of its monosubstituted derivatives with toluene was studied. It is shown that the type and character of the substituent in the 6 position of the starting derivatives of cyanuryl chloride have a strong effect on the course of the reaction. The reaction of cyanuryl chloride and its phenyl and phenoxy derivatives with toluene leads smoothly to the formation of 2,4,6-tris- and 2-substituted 4,6-bis(4'-methylphenyl)-sym-triazines. 4,6-Bis(4'-methylphenyl)2-oxo-2,3-dihydro-sym-triazine is formed in the case of alkoxy-substituted cyanuryl chlorides. In the case of amino derivatives of cyanuryl chloride the reaction with toluene takes place only upon prolonged refluxing and gives the final products in low yields.

A great deal of attention has recently been directed to the synthesis of sym-triazine derivatives. Most study has been devoted to nucleophilic substitution reactions in cyanuryl chloride (Ia) and its mono- and disubstituted derivatives [1]. Not enough study has been devoted to the peculiarities of the behavior of the indicated compounds in Friedel–Crafts reactions. The literature contains only data on the products of the reaction of cyanuryl

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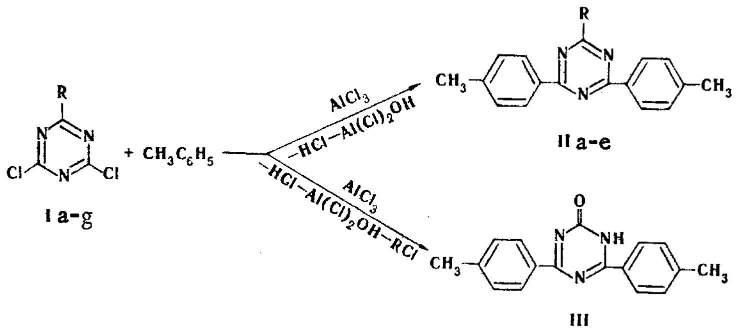
chloride with benzene [2] and of cyanuryl chloride and its aryl, amino, diphenylamino, and other derivatives with o-xylene [3] in the presence of aluminum chloride, whereas cheap and accessible compounds — intermediates in the synthesis of carboxylic acids and their diverse derivatives — can be synthesized by the indicated reaction.

We have investigated the reaction of Ia and some of its monosubstituted derivatives with toluene under the conditions of the Friedel—Crafts reaction:



I **a** $R=Cl$; **b** $R=C_6H_5$; **c** $R=OC_6H_5$; **d** $R=N(C_6H_5)_2$; **e** $R=N(C_2H_5)_2$; **f** $R=OCH_3$; **g** $R=OC_2H_5$; II**a** $R=p\text{-}CH_3C_6H_4$; b $R=C_6H_5$; **c** $R=OC_6H_5$; **d** $R=N(OC_6H_5)_2$; **e** $R=N(C_2H_5)_2$

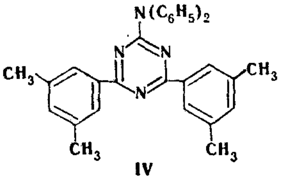
As expected, the type and character of the substituent in the 6 position of the starting 2,4-dichlorotriazines has a strong effect on the course of the electrophilic substitution reaction. The reaction of unsubstituted cyanuryl chloride with toluene leads smoothly to the formation of 2,4,6-tris(4'-methyphenyl)-sym-triazine (IIa). The formation of 2-phenyl-4,6-bis(4'-methylphenyl)-sym-triazine (IIb) also proceeds normally. However, in the case of monoalkoxy-substituted cyanuryl chloride 4,6-bis(4'-methylphenyl)-2-oxo-2,3-dihydro-sym-triazine (III) was obtained instead of the expected 2-alkoxy-4,6-bis(4'-methylphenyl)-sym-triazine. The formation of III is observed from both 2,4-dichloro-6-methoxy- and 2,4-dichloro-6-ethoxy-sym-triazines (If, g). This is evidently associated with the fact that splitting out of an alkyl halide, as in the cleavage of anisole [4], occurs in the reaction of the indicated compounds with toluene in the presence of aluminum chloride. It is interesting to note that the cleaving effect of aluminum chloride on the ether bond is not observed in the case of 2,4-dichloro-6-phenoxy-sym-triazine, and 2-phenoxy-4,6-bis(4'-methylphenyl)-sym-triazine (IIc) is formed.

Despite variations in the ratios of the starting components and prolonged refluxing (up to 30 h), we were unable to accomplish electrophilic substitution of the hydrogen atoms in toluene by monoamino derivatives of cyanuryl chloride containing diphenylamine, diethylamine, piperidine, and morpholine residues as substituents. Only the starting monoamino derivatives of cyanuryl chloride were isolated after decomposition of the reaction complex. Compounds IId and IIe were obtained in low yields only when the reflux time was increased to 50 h. This is probably associated with the fact that the formation of the complex of the electron-donor grouping of the amino substituent with aluminum chloride precedes the start of attack of the carbon atoms in the 2 and 4 positions of the starting cyanuryl chloride derivative. As a result of an increase in the conjugation of the electron density of the chlorine atoms with the overall electron density of the triazine ring, the capacity of the chloride ion for migration decreases, and realization of the electrophilic substitution reaction is hindered markedly.

When Id, e were used as the starting compounds, all of the components were added simultaneously, whereas in the case of cyanuryl chloride and its phenyl, phenoxy, and alkoxy derivatives the reaction proceeds so vigorously when the components are added simultaneously that it leads to ejection of the reaction mixture. In the latter cases solutions of Ia and its derivatives were therefore added dropwise to the heated reaction mixture. In the case of monoalkoxydichlorotriazines III is formed in good yield even when an equimolar amount of aluminum chloride is used. It has been shown [3] that 2,4-dichloro-6-diphenylamine-sym-triazine reacts with o-xylene in the presence of aluminum chloride when the mixture of the indicated components is refluxed for up to 25 h. The inability of toluene to react with the indicated dichlorotriazine under such conditions is associated with its lower electrophilicity as compared with o-xylene. As a confirmation of this, we carried out the reaction of 2,4-dichloro-6-diphenylamino-sym-triazine with m-xylene under similar conditions and obtained 2-phenylamino-4,6-bis(3',5'-dimethylphenyl)-sym-triazine (IV):

TABLE 1. Some Constants and Yields of the Products of the Reaction of Cyanuryl Chloride and Its Monosubstituted Derivatives with Toluene and m-Xylene

Compound	mp, °C (solvent)	IR spectrum, ν, cm⁻¹	Found, %			Empirical formula	Calc., %			Yield, %
			C	H	N		C	H	N	
IIa	270—271 (dioxane)	3050 (=CH); 1620, 1590, 1530, 1510 (conjug. C=N and phenyl); 810 (para position)	81,7	5,8	11,7	$C_{24}H_{21}N_3$	82,0	6,0	12,0	50,0
IIb	216—218 (dioxane)	1620, 1600, 1530 (conjug. C=N and phenyl); 820, 850 (para position)	81,5	5,4	12,1	$C_{23}H_{19}N_3$	81,9	5,7	12,5	41,3
IIc	172—174 (dioxane)	1590, 1570, 1530 (conjug. C=N and phenyl); 1210, 1180, 1150 (COC), 810 (para position)	78,5	5,1	11,3	$C_{23}H_{19}N_3O$	78,2	5,4	11,9	70,0
IId	193—195 (acetone)	1610, 1590, 1520, 1500 (conjug. C=N and phenyl) 850, 810 (para position)	80,9	5,3	13,0	$C_{29}H_{24}N_4$	81,3	5,7	13,1	21,2
IIe	223—226 (acetone)	1610, 1560, 1540, 1510 (conjug. C=N and phenyl); 810 para position	75,3	7,1	17,2	$C_{21}H_{24}N_4$	75,9	7,3	16,9	6,4
III	320—322 DMF	1690 (CO); 3230, 3320 (NH); 3050 (=CH); 1610, 1590, 1550, 1520 (conjug. C=N and phenyl)	73,4	5,6	14,9	$C_{17}H_{15}N_3O$	73,6	5,5	15,2	80,0
IV	212—215 (CCl_4)	1610, 1450 (conjug. C=N and phenyl); 790, 760 meta position	80,9	6,4	12,4	$C_{31}H_{28}N_4$	81,5	6,2	12,3	26,3



IV

The compounds obtained are finely crystalline, odorless, white or slightly yellowish powders (IIa-d, III) and dark-green powders (IIe, IV). Compound III is soluble only in amide solvents and m-cresol, IIa-d are also soluble in dioxane but only slightly soluble in acetone, and IIe and IV are soluble in acetone and chlorine-containing hydrocarbons; the solutions of the latter are bright-green.

The synthesized compounds may find application as intermediates in the synthesis of aldehydes, carboxylic acids, and their various derivatives.

EXPERIMENTAL

Cyanuryl chloride was purified by two recrystallizations from CCl_4 and had mp 146°C. The phenyl, phenoxy, alkoxy, and amino derivatives of cyanuryl chloride were obtained by the methods in [5-11]. The toluene and xylene were purified and dried by the method in [12]. The IR spectrum of mineral oil suspensions and KBr pellets of the compounds were recorded with a UR-20 spectrometer; the IR spectra of IIe and IV were obtained from CCl_4 films.

2,4,6-Tris(4'-methylphenyl)-sym-triazine (IIa). A solution of 11.06 g (0.06 mole) of cyanuryl chloride in 40 ml of dry toluene was added dropwise with stirring at 100-110°C to a suspension of 47.5 g (0.36 mole) of aluminum chloride in 60 ml of dry toluene, and the mixture was refluxed for 8 h. It was then cooled and poured into a mixture of 300 g of ice and 80 ml of concentrated HCl. The reaction product was subjected to steam distillation, washed thoroughly with hot water, acetone, and methanol, and dried at 100°C to give 10.6 g (50%) of IIa.

Compounds IIb, c were similarly obtained. The synthesis of 2-diphenylamino- and 2-diethylamino-4,6-bis(4'-methylphenyl)-sym-triazines (IId, e) was carried out similarly; however, a sixfold excess of aluminum chloride was used, all of the components were added simultaneously, and the reaction mixtures were refluxed for 50 h.

4,6-Bis(4'-methylphenyl)-2-oxo-2,3-dihydro-sym-triazine (III). A solution of 9 g (0.05 mole) of 2,4-dichloro-6-methoxy-sym-triazine in 50 ml of dry toluene was added dropwise with stirring at 100°C to a suspension of 13.3 g (0.1 mole) of aluminum chloride in 50 ml of dry toluene, and the mixture was refluxed for 10 h. It was then cooled and worked up as in the preparation of IIa to give 11.0 g (80%) of III. Compound III was obtained in 32% yield from 2,4-dichloro-6-ethoxy-symtriazine under similar conditions.

2-Diphenylamino-4,6-bis(3,5-dimethylphenyl)-sym-triazine (IV). A mixture of 7.93 g (0.025 mole) of 2,4-dichloro-6-diphenylamino-sym-triazine, 40 g (0.3 mole) of aluminum chloride, and 150 ml of m-xylene was refluxed for 25 h, after which it was cooled, and the resulting complex was decomposed with a mixture of ice and hydrochloric acid. The product was isolated by steam distillation, washed with hot water, 30 ml of acetone, and 120 ml of ether, reprecipitated twice from dioxane solution by the addition of ether, and dried at 100°C to give 3 g (26%) of IV.

The purification of IIe was carried out in the same way as the purification of IV.

The properties of the compounds obtained are presented in Table 1.

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