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SYNTHESIS OF 2-ARYLOXY-4,6-BIS(4-CARBOXYPHENYL)-sym-TRIAZINES AND THEIR CHLORIDES

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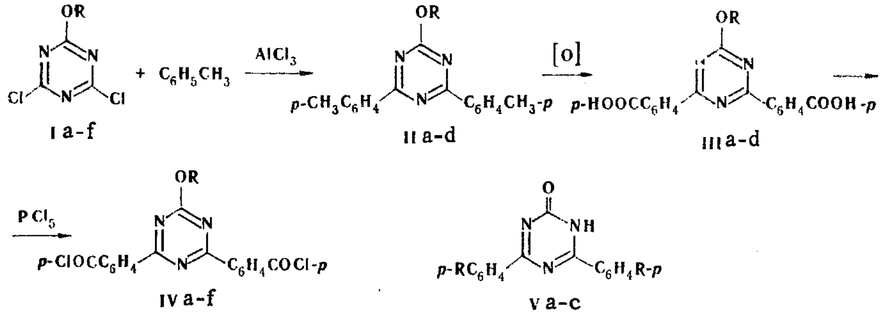
The peculiarities of the reaction of some substituted (in the benzene ring) 2,4-dichloro-6-aryloxy-sym-triazines with toluene under the conditions of the Friedel–Crafts reaction were investigated. Methods for the synthesis of 2-arloxy-4,6-bis(4-carboxyphenyl)-sym-triazines and their chlorides were developed. Cleavage of the ether bond to give a dihydro-sym-triazine structure occurs in the case of 2,4-dichloro-6-benzyloxy-sym-triazine.

We have previously [1] synthesized 2-phenoxy-4,6-bis(4-carboxyphenyl)-sym-triazine and have demonstrated the promising character of its use in the synthesis of heat-resistant polymers. A number of intermediates in the synthesis of such triazine-containing acids were described, and the peculiarities of the reaction of cyanuric acid chloride and its monosubstituted derivatives with toluene under the conditions of the Friedel–Crafts reaction were investigated [2]; it was shown that 2-phenoxy-4,6-bis(4-methylphenyl)-sym-triazine is formed in high yield.

In the present research we investigated the peculiarities of the reaction of toluene with aryloxy-substituted derivatives of dichloro-sym-triazine by the Friedel–Crafts reaction as a function of the structure of the substituent in the benzene ring, as well as the possibilities of the synthesis of sym-triazine-containing carboxylic acids and their chlorides on the basis of the compounds obtained:



I a $R=2\text{-}CH_3C_6H_4$, b $R=3\text{-}CH_3C_6H_4$, c $R=3\text{-}ClC_6H_4$, d $R=4\text{-}BrC_6H_4$, e $R=4\text{-}NO_2C_6H_4$, f $R=CH_2C_6H_5$, II a $R=2\text{-}CH_3C_6H_4$, b $R=3\text{-}CH_3C_6H_4$, c $R=3\text{-}ClC_6H_4$, d $R=4\text{-}BrC_6H_4$; III a $R=2\text{-}HOOCC_6H_4$, b $R=3\text{-}HOOCC_6H_4$, c $R=3\text{-}ClC_6H_4$, d $R=BrC_6H_4$; IV a $R=2\text{-}ClOCC_6H_4$, b $R=3\text{-}ClOCC_6H_4$, c $R=3\text{-}ClC_6H_4$, d $R=4\text{-}BrC_6H_4$; V a $R=CH_3$; b $R=COOH$, c $R=COCl$

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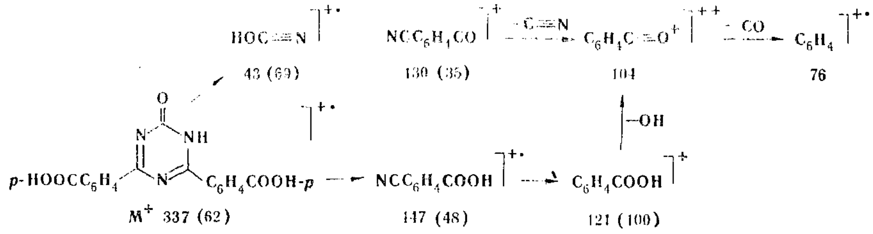
Various ring-substituted phenols and β-naphthol and benzyl alcohol were used to obtain Ia-f. The Friedel–Crafts reaction was accomplished in the presence of excess anhydrous aluminum chloride in dry toluene.

We found that the presence of substituents (a methyl group, halo groups, and a nitro group) in the benzene ring of Ia-e has a definite effect on how the electrophilic substitution proceeds. Thus when substituents of the first type are present in the benzene ring, the reaction of Ia-d leads smoothly to structures IIa-d; under identical substitution conditions the yields of IIa-d increase in the order in which the electron-donor properties of the substituents increase. This is probably associated with the corresponding redistribution of the electron densities of the starting compounds, which leads to an increase in the labilities of the chlorine atoms in the 2,4-positions of the triazine ring, which reaches a maximum in the case of Id; this is confirmed by its maximal yield. When a substituent of the second type is present (Ie), opposite redistribution of the electron density and a decrease in the labilities of the chlorine atoms occur, inasmuch as even prolonged (>50 h) refluxing of the reaction mixture does not lead to realization of structure II; starting Ie was isolated after decomposition of the reaction complex.

Resinous products that we were unable to identify are formed in the case of prolonged refluxing of Ig under the investigated conditions. On the basis of IIa-d we were able to synthesize the corresponding di- and tricarboxylic acids IIIa-d and their chlorides IVa-d. Oxidation of the methyl groups of II was carried out with a chromic mixture as in [1]. Chlorides IV were obtained by the reaction of III with phosphorus pentachloride in dry carbon tetrachloride.

As in the case of alkoxy derivatives of dichlorotriazines, instead of the expected 2-benzyloxy-4,6-bis(4-methylphenyl)-sym-triazine, the reaction of If with toluene gave 35.1% 4,6-bis-(4-methylphenyl)-2-oxo-2,3-dihydro-sym-triazine (Va), the melting point (322-323°C) and other characteristics of which are in agreement with the literature data [2]. Consequently, sym-triazine structures that contain an $-OCH_2Ar$ substituent in the 6 position of the triazine ring are also unstable under the conditions of the Friedel–Crafts reaction. Under the influence of aluminum chloride the ether bond is cleaved with the isolation of the corresponding chloride and the formation of an oxodihydro-sym-triazine structure. Oxo acid Vb and its chloride Vc were obtained on the basis of Va under conditions similar to those described above. The fragmentation peaks observed in the mass spectrum of Vb confirm its structure. A possible fragmentation scheme is presented below.



Vb

The II-V synthesized in this way are white, pale-pink, and light-yellow powders. Acids IIIa-d and Vb are quite soluble in dimethylformamide (DMF), N-methylpyrrolidone, and DMSO, the intermediates (IIa-d) in their synthesis are also soluble in hot chloroform and dioxane, and chlorides IVa-d and Vb-c are soluble in ordinary organic solvents. The structures and individuality of II-V were confirmed by the results of elementary analysis and data from the IR and PMR spectra and TLC (Tables 1 and 2). The assignment of the frequencies in the IR and PMR spectra was made in accordance with [3, 4].

Four intense absorption bands at 1495-1615 cm^{-1}, which are characteristic for the stretching vibrations of conjugated C=C and C=N bonds, are observed in the IR spectra of the synthesized compounds; the presence of five absorption bands in the indicated region of the spectrum of Vb is probably associated with its structural peculiarities. Because of the presence in the spectra of IIIa-d and Vb of an intense broad OH_{acid} absorption band at 2980-3300 cm, CH_{arom} bands of weak intensity do not show up at 3035-3120 cm^{-1}. An interesting feature of the IR spectra of III-V is the appearance of stretching vibrations of a C=O group in the case of acids in the form of one narrow intense band, whereas two bands appear in the case of the chlorides; this is also characteristic for the chlorides of other sym-triazine-containing carboxylic acids [5]. Another peculiarity of the IR spectra is the presence of a broad absorption band at 1270-1310 cm^{-1} in the case of the acids; this is probably the result

TABLE 1. Some Properties and Yields of Triazines II-V

Compound	mp,^{a} °C	R_f	Found, %			Empirical formula	Calc., %			Yield, %
			C	H	N		C	H	N	
IIa	164—165	0,74^b	78,2	5,9	11,3	$C_{24}H_{21}N_3O$	78,5	5,7	11,4	22
IIb	155—156	0,73^b	78,0	5,3	11,5	$C_{24}H_{21}N_3O$	78,5	5,7	11,4	35
IIc	159—160	0,72^b	70,9	5,0	10,4	$C_{23}H_{18}ClN_3O$	71,2	4,7	10,8	41
IId	189—190	0,71^b	63,5	4,5	10,2	$C_{23}H_{18}BrN_3O$	63,9	4,2	9,8	50
IIIa	317—318		62,8	3,6	8,5	$C_{24}H_{15}N_3O_7$	63,0	3,3	9,1	16
IIIb	327—328		63,4	3,4	8,6	$C_{24}H_{15}N_3O_7$	63,0	3,3	9,1	34
IIIc	324—325		61,9	3,0	9,4	$C_{23}H_{14}ClN_3O_5$	61,6	3,2	9,4	24
IIId	285—287		55,7	2,9	8,4	$C_{23}H_{14}BrN_3O_5$	56,1	2,8	8,5	26
IVa	60—61	0,62^c	57,9	2,1	8,0	$C_{24}H_{12}Cl_3N_3O_4$	56,2	2,3	8,2	50
IVb	69—70	0,61^c	56,3	2,6	7,9	$C_{24}H_{12}Cl_3N_3O_4$	56,2	2,3	8,2	55
IVc	66—67	0,66^b	57,5	2,2	8,5	$C_{23}H_{12}Cl_3N_3O_3$	57,1	2,5	8,7	48
IVd	68—69	0,74^b	52,5	2,5	8,4	$C_{23}H_{12}BrCl_2N_3O_3$	52,2	2,3	7,9	48
Vb	350—352		60,1	3,0	12,2	$C_{17}H_{11}N_3O_5$	60,5	3,3	12,4	50
Vc	66—67	0,68^b	54,9	2,0	11,4	$C_{17}H_9Cl_2N_3O_5$	54,6	2,4	11,2	91

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[a] Crystallization solvents: dioxane for IIa-d, DMF—water (5:1) for IIIa-d and Vb, benzene for IVa,b and Vc, and petroleum ether for IVc,d. [b] Chloroform—petroleum ether (3:1). [c] Chloroform—petroleum ether (1:1).

TABLE 2. IR Spectra of II-V

Compound	IR spectrum, ν, cm^{-1}					
	C = O, COCl	aromatic C=C & C=N	arom. CH	aromatic C—O—C	acid OH	other absorption bands*
IIa		1610, 1580, 1540, 1510	3080, 3065	1300, 1290, 1250, 1185, 1045, 1020		810, 795, 753, 705
IIb		1600, 1575, 1540, 1510	3065, 3035	1300, 1235, 1210, 1190, 1040, 1020		810, 755, 740
IIc		1615, 1585, 1550, 1515	3120, 3095	1300, 1290, 1275, 1225, 1182, 1040		809, 785, 740, 710
IId		1615, 1590, 1545, 1525	3090, 3060	1300, 1270, 1200, 1070, 1012		855, 845, 805
IIIa	1695	1610, 1580, 1560, 1515		1303—1280, 1185, 1025	3300—3000	815, 875, 735
IIIb	1690	1595, 1585, 1550, 1510		1300—1280, 1185, 1022	3300—3000	820, 783, 730
IIIc	1685	1598, 1575, 1555, 1510		1300—1280, 1180, 1023	3300—3010	880, 820, 785, 730
IIId	1690	1600, 1580, 1550, 1505		1300—1280, 1175, 1023	3300—2980	875, 815
IVa	1770, 1735	1600, 1575, 1520, 1495	3100, 3070	1300, 1258, 1240, 1200, 1020		850, 810, 735
IVb	1760, 1735	1575, 1550, 1520, 1500	3100, 3050	1300, 1255, 1195, 1010		850, 815, 745, 725
IVc	1780, 1750	1615, 1585, 1530, 1500	3110, 3065	1260, 1200, 1180, 1020		810, 745, 725
IVd	1775, 1740	1600, 1582, 1550, 1525	3110, 3070	1260, 1240, 1200, 1020, 1005		860, 810, 725
Vb	1685	1600, 1580, 1550, 1545, 1505		1310—1270, 1175, 1025	3280—2990	860, 820
Vc	1775, 1745	1610, 1580, 1530, 1500	3110, 3060	1268, 1200, 1050, 1020		855, 805

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*The absorption regions that are characteristic for the deformation vibrations of o-, m-, and p-substituted benzenes and the sym-triazine ring are presented.

of superimposition of the stretching and deformation vibrations of the OH and CO groups.

Sample PMR spectra were recorded for IIa, IIIa-d, IVa,c, and Va-c. Chemical shifts of phenyl protons (7.13-8.35 ppm), as well as protons of the COOH group (10.26-11.43 ppm) in the case of acids IIIa-d and Vb, which confirm their structure, were observed in the spectra of all of the enumerated compounds.

The carboxylic acids and the chlorides synthesized in this way may find application as polycondensed monomers in the synthesis of polytriazines.

EXPERIMENTAL

The starting monosubstituted derivatives (Ia-f) of cyanuric acid chloride were synthesized by the methods in [6-8]. The toluene and carbon tetrachloride were purified and dried by the method in [9]. The individuality of all of the synthesized compounds were verified by TLC on Silufol UV-254 plates with development by means of iodine vapors or by UV irradiation (the eluents and R_f values are presented in Table 1). The mass spectrum of Vb was recorded with an MKh-1320 spectrometer. The IR spectra of mineral oil suspensions of the compounds (or of a KBr pellet in the case of IIIc) were recorded with a UR-20 spectrometer. The PMR spectra of solutions of IIa, IIIa-d, and Va,b in d_6-DMSO and of solutions of IVa,c and Vc in CH_2Cl_2 were recorded with a Perkin-Elmer spectrometer (60 MHz) with tetramethylsilane as the external standard at 30°C.

2-(2-Methylphenoxy)-4,6-bis(4-methylphenyl)-sym-triazine (IIa). A solution of 12.85 g (0.05 mole) of 2,4-dichloro-6-(2-methylphenoxy)-sym-triazine in 40 ml of dry toluene was added with stirring at 100-110°C to a suspension of 26.7 g (0.2 mole) of aluminum chloride in 40 ml of dry toluene, and the mixture was then refluxed for 8 h. It was cooled and poured over a mixture of 250 g of ice and 70 ml of concentrated HCl. The decomposition product was subjected to steam distillation, washed thoroughly with hot water and methanol, and dried at 80°C. Recrystallization from dioxane gave 4 g (22%) of IIa.

Compounds IIb-d and Va were similarly synthesized.

4,6-Bis(4-carboxyphenyl)-2-oxo-2,3-dihydro-sym-triazine (Vb). A 16-g (0.16 mole) sample of concentrated H_2SO_4 was added slowly with vigorous stirring at 80-100°C to a mixture of 3 g (10.3 mmole) of 4,6-bis(4-methylphenyl)-2-oxo-2,3-dihydro-sym-triazine (Va), 5.9 g (20 mmole) of potassium dichromate, and 9 g of water, and the reaction mixture was refluxed with stirring for 8 h. It was then cooled, diluted with 40 g of water, and filtered by means of a glass filter. The precipitate on the filter was washed thoroughly with water, transferred to a separatory flask, refluxed for 5 min with 2 g of sodium hydroxide and 3 g of activated charcoal in water, and filtered hot. The filtrate was acidified to pH 4 with hydrochloric acid, and the precipitated flakes were removed by filtration, washed thoroughly with water, and dried to give 1.8 g (50%) of Vb.

The synthesis of carboxylic acids IIIa-d was realized similarly; in the case of triacids IIIa,b the amounts of potassium dichromate, sulfuric acid, and water were increased by a factor of 1.5.

4,6-Bis(4-carboxyphenyl)-2-oxo-2,3-dihydro-sym-triazine Chloride (Vc). A mixture of 1 g (3 mmole) of oxo acid Vb and 1.4 g (6.7 mmole) of phosphorus pentachloride in 20 ml of dry carbon tetrachloride was refluxed for 10 h, after which the hot mixture was filtered. The filtrate was evaporated, and the dry residue was recrystallized from petroleum ether to give 1 g (91%) of chloride Vc in the form of a pale-yellow finely crystalline powder.

Chlorides IVa-d were similarly synthesized; in the case of trichlorides IVa,b 3.3 mole of phosphorus pentachloride was used per mole of the acid.

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