filtered off, washed with water, dried, and chromatographed on a silica gel column (100 g). Elution with a 1:1 chloroform and carbon tetrachloride mixture gives 0.6 g (40%) of quindoline IX, mp 322-324°C (from alcohol). IR spectrum: 2600-3200 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 225 (4.63); 264 (4.19); 3.13 nm (4.09). Found: C 85.0; H 6.2; N 9.3%; M^+ 298. $C_{21}H_{18}N_2$. Calculated: C 84.6; H 6.1; N 9.4%; M 298.

B) A mixture of 1.2 g (7 mmoles) of indolinone I, 2.8 g (15 mmoles) of benzylidenecyclohexanone VII and 3 g of ammonium carbonate is boiled for 5 h in 25 ml of acetic acid. The solvent is evaporated off and the residue treated with 50 ml of 10% NaOH. The precipitate is filtered off and chromatographed on a silica gel column (50 g). Elution with a 1:1 chloroform and carbon tetrachloride mixture gives 0.4 g (23%) of quindoline IX, which with respect to melting point and IR spectrum is identical with the compound obtained in experiment A.

1,1-Diaryl-3-methyl-10H-quindolines (Xa, b). A mixture of 5 mmoles of dihydroquindoline VIb,h and 1.5 g (47 mmoles) of sulfur is heated for 2 h at 240-260°C. The reaction mixture is dissolved in 30-50 ml of m-xylene, and chromatographed on a silica gel column (100 g). First, unreacted sulfur is eluted by carbon tetrachloride, and then quindolines Xa,b by a 1:1 carbon tetrachloride and chloroform mixture. Yield, 76 and 81%, respectively.

Xa. Dec. temp. >340°C. IR spectrum: 2600-3200 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 207 (4.65); 230 (4.68); 283 (4.89); 354 nm (4.24). Found: N 7.3%; M^+ 384. $C_{28}H_{20}N_2$. Calculated: N 7.3%; M 384.

Xb. Subl. Temp. >280°C. IR spectrum 2600-3200 cm^{-1}. (NH). UV spectrum, λ_{max} (log ε): 208 (4.63); 230 (4.67); 356 (4.90); 356 nm (4.21). Found: Cl 15.9; N 6.5%; M^+ 452. $C_{28}H_{18}Cl_2N_2$. Calculated: Cl 15.7; N 6.2%; M 452.

LITERATURE CITED

1. V. S. Velezheva, V. P. Sevodin, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 6, 847 (1979).
2. V. P. Sevodin, V. S. Velezheva, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 3, 368 (1981).
3. A. A. Polyakova and R. A. Khmel'nitskii, Mass Spectrometry in Organic Chemistry [in Russian], "Khimiya," Moscow (1972), p. 212.
4. E. Gellert and R.-H.E. Schlitler, Helv. Chim. Acta, 34, 642 (1951).

SYNTHESIS AND PROPERTIES OF sym-TRIAZINE DERIVATIVES.

3. ALKOXYLATION OF 2-ALKYL-4,6-BIS(TRICHLOROMETHYL)-sym-TRIAZINES CONTAINING HIGHER ALKYL RADICALS

V. I. Kelarev, Ammar Dibi,
and A. F. Lunin

UDC 547.491.8.07

Nucleophilic substitution reactions of trichloromethyl groups in 2-alkyl-4,6-bis-(trichloromethyl)-sym-triazines by alkoxy radicals were studied. It was shown that in the presence of sodium alcoholates, two CCl_3 groups are replaced, and the corresponding 2,4-dialkoxy-6-alkyl-sym-triazines are formed. The products of partial replacement, 2-alkoxy-4-trichloromethyl-6-alkyl-sym-triazines, were synthesized by heating the initial sym-triazines with alcohols in the presence of tertiary amines.

Only one paper [1] deals with alkoxylation of certain sym-triazines; in the reaction of 2,4,6-tris(trichloromethyl)-sym-triazine with sodium ethylate in ethanol, all of the CCl_3 groups are replaced, whereas partial replacement of these groups is obtained on heating with alcohols in the presence of triethylamine.

I. M. Gubkin Moscow Institute of Petrochemical and Gas Industry, Moscow 117917. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1674-1677, December, 1984. Original article submitted October 17, 1983.

0009-3122/84/2012-1380$08.50

TABLE 1. Alkoxy- and Dialkoxy sym-Triazine Derivatives

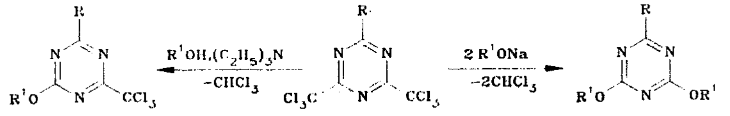
Compound	R	R^1	Mp* or bp, °C (gPa)	n_D^{20}	R$_f$ (system solvents)	Found, %				Empirical formula	Calculated, %				Yield, %
						C	H	Cl	N		C	H	Cl	N	
IIa	n-C_5H_{11}	CH_3	145—147 (1,33)	1,4791	0,81 (A)	56,7	8,1	—	20,0	$C_{10}H_{17}N_3O_2$	56,9	8,1	—	19,9	76
IIb	n-C_5H_{11}	C_2H_5	169—170 (1,33)	1,4780	0,70 (A)	60,3	8,8	—	17,4	$C_{12}H_{21}N_3O_2$	60,2	8,8	—	17,6	83
IIc	n-$C_{12}H_{25}$	CH_3	38—40†	—	0,71 (A)	66,1	9,9	—	13,5	$C_{17}H_{31}N_3O_2$	66,0	10,0	—	13,6	74
IId	n-$C_{17}H_{35}$	CH_3	50—51,5	—	0,60 (A)	69,5	10,8	—	11,0	$C_{22}H_{41}N_3O_2$	69,6	10,8	—	11,1	72
IIe	n-$C_{17}H_{35}$	C_2H_5	44—45	—	0,65 (B)	70,9	11,0	—	10,5	$C_{24}H_{45}N_3O_2$	70,8	11,1	—	10,3	75
IIIa	n-C_5H_{11}	CH_3	154—156 (2,66)	1,5182	0,88 (B)	40,1	4,7	35,5	14,2	$C_{10}H_{14}Cl_3N_3O$	40,2	4,7	35,7	14,1	79
IIIb	n-C_5H_{11}	C_2H_5	179—180 (1,33)	1,5098	0,80 (B)	42,2	5,1	34,3	13,3	$C_{11}H_{16}Cl_3N_3O$	42,2	5,1	34,1	13,4	73
IIIc	n-$C_{10}H_{21}$	C_2H_5	oil	1,5054	0,72 (A)	50,2	9,1	27,6	10,9	$C_{16}H_{26}Cl_3N_3O$	50,2	9,2	27,8	11,0	71
IIId	n-$C_{12}H_{25}$	C_2H_5	42—43,5	—	0,74 (B)	52,5	7,3	26,0	10,1	$C_{18}H_{30}Cl_3N_3O$	52,6	7,3	25,9	10,2	74
IIIe	n-$C_{10}H_{21}$	CH_2CH_2CN	oil	1,5135	0,68 (B)	50,1	6,2	26,0	19,8	$C_{17}H_{25}Cl_3N_4O$	50,1	6,1	26,1	13,7	56
IIIf	n-$C_{10}H_{21}$	$CH_2CH_2NO_2$	oil	1,5208	0,55 (B)	50,0	5,8	24,7	13,0	$C_{16}H_{25}Cl_3N_4O$	49,8	5,8	24,9	13,0	52

---

*Compounds IId,e were recrystallized from aqueous ethanol, IIId from a 2:1 acetone and water mixture. Compounds IIIc-f were purified chromatographically on columns with Al_2O_3.

†Bp 194-195°C (2.66).

Considering these data, we decided to study in greater detail the alkoxylation reactions of certain 2-alkyl-4,6-bis(trichloromethyl)-sym-triazines (Ia-c) which have already been previously synthesized by us [2]. We found that on boiling sym-triazines Ia,c,d with a small excess of sodium alcoholate in the corresponding alcohol, the two CCl_3 groups become replaced, and 2,4-dialkoxy-6-alkyl-sym-triazines (IIa-e) are formed.



IIIa-f Ia-d IIa-e

We found that, in general, below 40-45°C, no replacement of the trichloromethyl groups occurs. For example, after heating triazine Ia with sodium ethylate for 12 h at 35-40°C, only the initial triazine Ia was isolated from the reaction mixture; at 50-55°C, the yield of triazine IIa after 6 h was 35% (together with unreacted Ia) and only after 12 h was a yield of 82% attained.

By using sodium alcoholates as the bases, we were unable to carry out a gradual replacement of one CCl_3 group only, and to synthesize thus 2-alkoxy-4-chloromethyl-6-alkyl-sym-triazines (IIIa-f). Despite attempts to vary the reaction conditions, i.e., the amount of sodium alcoholate and temperature, not even traces of these compounds were detected in the reaction mixture. For example, after boiling sym-triazine Ic for 3 h with one equivalent of sodium methylate in methanol, only dialkoxy derivatives IIc (yield 44%) and the initial azine Ic were found in the reaction products.

Monoalkoxy-sym-triazines IIIa-f were obtained by alkoxylation of triazines Ia-c with an excess of alcohol in the presence of tertiary amines, triethylamine or N-ethylpiperidine, in a yield of 71-79% (see Table 1). Monoalkoxy-sym-triazines IIIa,b were also synthesized in a yield of 58 and 52%, respectively, by using equimolar amounts of the alcohol; in these cases, dioxane, benzene, or DMFA were used as the solvent. Monoalkoxy derivatives of IIIe,f were obtained under similar conditions from alcohols containing electron acceptor groups (NO_2, CN) in β-position. It should be noted that in the presence of tertiary amines, in all cases monoalkoxy derivatives were obtained as the sole reaction products; under these conditions it is impossible to replace the two CCl_3 groups by the alkoxy radicals, even by prolonged (72-80 h) boiling of the reagents.

In the IR spectra of compounds II and III intense narrow absorption bands are observed in the 1235-1222 cm^{-1} region, as well as several bands of variable intensity in the 1080-1025 cm^{-1} region that are due to asymmetric and symmetric stretching vibrations, respectively, of the C—O—C fragment, which is characteristic of alkoxy derivatives of sym-triazine [3] (Table 2).

EXPERIMENTAL

The IR spectra were run on the UR-20 spectrophotometer in mineral oil and PMR spectra on the Tesla BS-487C (80 MHz) spectrometer with HMDS as internal standard, the composition of the reaction mixture and the purity of the compounds were determined by TLC on Al_2O_3 activity grade II according to Brockman, in benzene—methanol 30:1 (A) and benzene—methanol 20:1 (B) systems of solvents. The development was carried out with iodine vapors.

The initial 2-alkyl-4,6-bis(trichloromethyl)-sym-triazines (Ia-d) were previously synthesized [2].

2,4-Dialkoxy-6-alkyl-sym-triazines (IIa-e). A solution of 15 mmoles of the corresponding sym-triazine Ia, c, d in 10 ml of alcohol is added with stirring to a solution of sodium alcoholate prepared from 0.76 g (33 mmoles) of sodium in 40 ml of absolute methanol or ethanol. The reaction mixture is boiled with stirring for 2 h, cooled to 20°C, and poured into 200 ml of water. The reaction products are extracted with ether (3 × 40 ml), the extract is washed with water to neutrality, dried over $MgSO_4$, and evaporated under reduced pressure. The residue is either distilled in vacuo in an inert gas atmosphere (IIa-c), or crystallized from an aqueous alcohol (IId,e).

2-Methoxy(ethoxy)-4-trichloromethyl-6-alkyl-sym-triazines (IIIa-d). A mixture of 12 mmoles of sym-triazine Ia-d and 3.45 g (36 mmoles) of dry triethylamine in 40 ml of absolute alcohol is boiled with stirring for 8 h, and then evaporated at reduced pressure. In the prep-

TABLE 2. Spectral Characteristics of Compounds IIa-e, IIIa-f

Compound	PMR spectrum, δ, ppm				IR spectrum, cm^{-1}							
					νC—H	triazine ring vibrations				δC—H	νC—O	other vibrations
	CH_3 (t)	CH_2 (m)	CH_2—Ar (t)	OR'		ν	—†	γ‡	β‡			
IIa	1,16 (3H)	1,22—2,11 (6H)	2,84 (2H)	3,68 (6H, s)	2970, 2935, 2865	1555, 1412	1105, 995	812	705	1470, 1375, 1360	1235, 1075, 1030	735 (CH_2)
IIb	1,14 (3H)	1,30—2,08 (6H)	2,92 (2H)	1,20 (6H, t); 4,24 (4H, q)	2965, 2940, 2865, 2815	1565, 1415	1112, 990	815	705	1460, 1375, 1362	1230, 1080, 1035	720 (CH_2)
IIc	1,16 (3H)	1,22—2,04 (20H)	2,86 (2H)	3,67 (6H, s)	2970, 2940, 2860	1560, 1405	1115	810	715	1470, 1375, 1355	1222, 1075, 1030	720 (CH_2)
IId	1,12 (3H)	1,27—2,15 (30H)	2,94 (2H)	3,73 (6H, s)	2975, 2945, 2870	1555, 1415	1110, 1005	810	712	1465, 1370, 1350	1232, 1085, 1035	725 (CH_2)
IIe	1,14 (3H)	1,31—2,12 (30H)	2,84 (2H)	1,22 (6H, t); 4,12 (4H, q)	2970, 2945, 2875	1560, 1410	1110, 1000	812	705	1470, 1465, 1350	1230, 1075, 1032	725 (CH_2)
IIIa	1,08 (3H)	1,18—1,90 (6H)	2,84 (2H)	3,58 (3H, s)	2960, 2950, 2865	1550, 1410	1105, 992	805	710	1465, 1370, 1355	1235, 1072, 1025	785 (C—Cl), 720 (CH_2)
IIIb	1,10 (3H)	1,28—1,90 (6H)	2,82 (2H)	1,18 (3H, t); 4,08 (2H, q)	2970, 2935, 2860	1552, 1405	1110, 1005	810	715	1472, 1378, 1350	1225, 1075, 1030	780 (C—Cl), 725 (CH_2)
IIIc	1,08 (3H)	1,24—2,12 (16H)	2,88 (2H)	1,14 (3H, t); 4,10 (2H, q)	2960, 2940, 2875, 2825	1550, 1410	1112, 1005	815	710	1465, 1370, 1355	1225, 1070, 1050	780 (C—Cl), 720 (CH_2)
IIId	1,14 (3H)	1,30—2,18 (20H)	2,92 (2H)	1,20 (3H, t); 4,20 (2H, q)	2970, 2955, 2875, 2815	1545, 1405	1110, 995	812	705	1470, 1365	1225, 1070	785 (C—Cl), 725 (CH_2)
IIIe	1,16 (3H)	1,25—2,08 (16H)	2,82 (2H)	3,12 (2H, t); 4,78 (2H, t)	2965, 2935, 2865	1540, 1410	1105, 990	810	712	1465, 1370, 1355	1225, 1075, 1050	2225 (CN), 785 (C—Cl), 725 (CH_2)
IIIf	1,12 (3H)	1,26—2,02 (16H)	2,94 (2H)	3,26 (2H, t); 4,84 (2H, t)	2970, 2940, 2860	1545, 1410	1105, 1010	810	715	1470, 1365, 1355	1222, 1080, 1035	1570, 1380 (NO_2), 780 (C—Cl), 720 (CH_2)

---

*Solvent for compounds IIa,b, IIIa,b,e — $CDCl_3$; for IIc, IIIc,f — CD_3OD; IId,e, IIId — DMSO-D_6.

†"Rocking" ring vibrations.

‡β — In-plane deformational ring vibrations; γ — extraplanar deformational ring vibrations.

paration of compounds IIIa,b, the residue is distilled *in vacuo* in an inert gas atmosphere. In the preparation of compounds IIIc,d, the residue is chromatographed on a column with Al_2O_3 (3.5 × 50 cm) and eluted with 30:1 benzene–methanol mixture. After removal of the solvents, IIIc is obtained as a viscous light-yellow oil, and IIId as an oil which crystallizes on keeping the material in cold.

2-(β-Cyanoethoxy)-4-trichloromethyl-6-n-decyl-sym-triazine (IIIe). A mixture of 3.2 g (7 mmoles) of triazine Ib, 0.5 g (7 mmoles) of ethylene cyanohydrin and 1.7 g (17 mmoles) of dry triethylamine in 20 ml of dry dioxane is boiled with stirring for 6 h, and then evaporated in vacuo. The residue is chromatographed on a column with Al_2O_3 (3.5 × 30 cm), and eluted by a 30:1 benzene–methanol mixture. After removal of the solvents, compound IIIe is obtained as a dark-yellow uncrystallizable oil.

2-(β-Nitroethoxy)-4-trichloromethyl-6-N-decyl-sym-triazine (IIIf) is obtained similarly as a viscous light-green oil.

LITERATURE CITED

1. E. Kober, J. Org. Chem., 25, 1728 (1960).
2. Ammar Dibi, Candidate Chemical Sciences Dissertation, the Moscow Institute of Petrochemical and Gas Industry, Moscow (1983).
3. P. A. Perov, A. T. Gerasimova, P. A. Kudryashov, and N. A. Sokova, Izv. Vuzov, Khim. i Khim. Tekhnol., 25, 1196 (1982).

SYNTHESIS AND PROPERTIES OF sym-TRIAZINE DERIVATIVES.

2.* SYNTHESIS OF AMINO-sym-TRIAZINES CONTAINING FRAGMENTS OF STERICALLY HINDERED PHENOL

O. V. Malova, T. P. Vishnyakova, I. A. Golubeva,
V. I. Kelarev, and A. F. Lunin

UDC 547.491.8.04:543.422.4

The reaction of mono- and dichloro-sym-triazines with 4-hydroxy-3,5-di-tert-butylaniline was studied. N-substituted derivatives of 2,4,6-triamino-sym-triazine were synthesized, containing fragments of sterically hindered phenol.

In recent years, researchers are paying increasing attention to nitrogen containing derivatives of sterically hindered phenols, which are effective antioxidants for various materials, biologically active agents, and intermediates for their synthesis [2]. However, many compounds of this type have insufficient thermal stability and lose their effectiveness above 150°C [3, 4]. It would therefore be very interesting to try to increase the thermal stability of phenolic type antioxidants by using a sym-triazine ring as a thermostable binding unit, to which fragments of a sterically hindered phenol are attached, which impart antioxidizing properties to the entire molecule. In the literature [5-8] uncorrelated data are reported on the use of sym-triazine derivatives as antioxidants, thermo- and light stabilizers for polymeric materials and lubricants.

To search for new antioxidants in the above series of compounds, we carried out a synthesis of N-substituted derivatives of amino-sym-triazine, containing not only the fragments of the screened phenol, but also alkylamine and arylamine substituents (III, IV). As the starting material for the preparation of compounds of this type, we chose cyanuryl chloride (1,3,5-trichloro-sym-triazine).

The synthesis of the amino derivatives of sym-triazine (III, IV) was carried out in two stages. In the first stage, by reacting cyanuryl chloride with isobutylamine, N-methyl-N-

---

*For article 1, see [1].

I. M. Gubkin Moscow Institute of Petrochemical and Gas Industry, Moscow 117917. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1678-1682, December, 1984. Original article submitted December 1, 1983.