

ganic layer with 20% alkali, and worked up by acidification, extraction with benzene, drying over sodium sulfate, and distillation. Neutral products were recovered following removal of the chlorobenzene by distillation. The results of the various experiments are summarized in Table I.

TABLE I
ACTION OF ALUMINUM BROMIDE ON α -PHENETHYL ARYL ETHERS

Aryl group	α^{25}_D of the ether ^a	% yield of α -phenethyl-phenol	α^{25}_D of the alkylphenol ^a
Phenyl	22 ^b
Phenyl	- 3.30	20 ^c	0.30
2,6-Xylyl	0 ^d
<i>p</i> -Tolyl	-15.5 ^e	41 ^f	-6.10

^a All rotations are for the homogeneous material, $l = 1$ dm. ^b The neutral material, b.p. 160–170° (2 mm.), from this run contained 73.2% C, 5.2% H and 17.0% Cl. The expected dichlorodiphenylethane was probably contaminated with monochlorodiphenylethane and some phenolic product which had been incompletely extracted. ^c Neutral product from this run was optically inactive. ^d 94% of the theoretical quantity of 2,6-xylenol was formed.

Prepared from α -phenethyl chloride of rotation -51.5° . Using a value of 109° for optically pure α -phenethyl chloride (R. L. Burwell, A. D. Shields and H. Hart, *THIS JOURNAL*, **76**, 908 (1954)) and 17.1° for optically pure *o*- α -phenethyl-*p*-cresol,³ one calculates 75.5% retention of optical purity over the two-step process (ether synthesis and rearrangement). ^f From a run with *dl*-material the product was identified *via* the corresponding aryloxyacetic acid, m.p. 165–166°, neut. equiv. 270. *Anal.* Calcd. for $C_{17}H_{15}O_2$: C, 75.6; H, 6.7. Found: C, 75.5; H, 6.9.

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2,4-Dichloro-1,3,5-triazine

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Since mixed "trimerization" of trichloroacetonitrile and acetonitriles in the presence of anhydrous hydrogen chloride resulted in good yields of 2,4-bis-trichloromethyl-6-methyl-1,3,5-triazine,¹ the reaction was attempted with hydrogen cyanide and cyanogen chloride.

From a series of experiments carried out upon the reaction of hydrogen cyanide and cyanogen chloride, the following optimum conditions were found for the preparation of dichlorotriazine (see Experimental). The concurrent formation of monochlorotriazine was not established and in the light of Grundmann's experiments was not to be expected. However, cyanuric chloride was formed in small quantities. Dichlorotriazine is extremely reactive toward water and from preliminary observations it is believed that total rupture of the triazine ring occurs upon reacting with this solvent.

Experimental

Dichlorotriazine.—Three grams (0.082 mole) of dry hydrogen chloride was added to a mixture of 360 g. (6.0 moles) of cyanogen chloride and 81 g. (3.0 moles) hydrogen cyanide in a quart pop bottle. The bottle was capped and immersed in a 65° bath for 40 hours. The material in the bottle consisted of a clear liquid and an amorphous, brown solid. Distillation of the mixture from a 60° bath led to the recovery of 222 g. (3.6 moles) of cyanogen chloride and 64 g. (2.37 moles) of hydrogen cyanide. The residue from this distillation was leached with 250 ml. of benzene and filtered

(1) Grundmann, *et al.*, *Ann.*, **577**, 77 (1953).

from a dark-brown residue of 45 g. of amorphous solid. Distillation of the filtrate gave 35 g. (0.233 mole), 37% yield, of (7.8% conversion based upon HCN) dichlorotriazine boiling at 80–90° (40 mm.); 20 g. (0.108 mole) of cyanuric chloride distilling at 70–80° (1 mm.), and non-volatile residue of 5 g.

Anal. Calcd. for $C_3H_3N_3Cl_2$: C, 24.00; H, 0.67; N, 28.00; Cl, 47.34. Found: C, 24.82; H, 1.07; N, 25.6; Cl, 46.34.

Reaction of dichlorotriazine with excess aniline gave 2,4-bisphenylamino-1,3,5-triazine in 95% yield; m.p. 292–295°; mixture melting point with an authentic sample 292–294°. (2,4-Bisphenylamino-1,3,5-triazine was prepared from 1,5-diphenylbiguanide and methyl formate in the usual manner.²)

Anal. Calcd. for $C_{15}H_{13}N_5$: C, 68.4; H, 4.92; N, 26.6. Found: C, 68.4; H, 5.06; N, 26.8.

Spectroscopic data upon dichlorotriazine will appear in a future issue of the *J. Chem. Phys.*

(2) Rackman, *ibid.*, **367**, 163 (1910).

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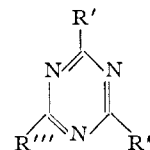
Basic Substituted Triazines

BY BRUCE W. HORROM

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Many amino and alkoxy triazines have been made by the reaction of cyanuric chloride with amines and alcohols. Only two instances where tri-substituted products have been obtained from diamines appear to have been reported.^{1,2}

The present paper reports the preparation of four new basic derivatives (I, II, III and IV) of cyanuric acid, three of which resulted from displacement of all three chlorine atoms of cyanuric chloride. In the fourth compound (I), one chlorine remained unreacted.



I, $R' = R'' = -HNCH_2CH_2CH_2N$ O; $R''' = Cl$

II, $R' = R'' = R''' = -HNCH_2CH_2CH_2N$ O

III, $R' = R'' = R''' = -OCH_2CH_2CH_2N$ O · HCl

IV, $R' = R'' = R''' = -OCH_2CH_2N(CH_3)_2 \cdot CH_3I$

Experimental

2,4-Di-(γ -morpholinopropylamino)-6-chloro-*s*-triazine (I) and 2,4,6-Tri-(γ -morpholinopropylamino)-*s*-triazine (II).—Cyanuric chloride (14.5 g., 0.079 mole) in 200 cc. of dry benzene was added dropwise with stirring to γ -morpholinopropylamine (43.2 g., 0.3 mole) and triethylamine (30.3 g., 0.3 mole) in 250 cc. of dry benzene. The temperature of the mixture was not allowed to rise above 35°. After the mixture was stirred at room temperature overnight it was refluxed for six hours and filtered warm. The benzene was removed by distillation, the semi-solid residue was triturated with ether and removed by filtration. The solid weighed 15 g. (47.5%), m.p. 148–151°. Three recrystallizations from methanol gave m.p. 154–155°.

Anal. Calcd. for $C_{17}H_{30}N_7ClO_2$ (I): C, 51.05; H, 7.56; N, 24.61; Cl, 8.86. Found: C, 51.16; H, 7.75; N, 24.95; Cl, 8.96.

(1) H. S. Mosher and F. C. Whitmore, *THIS JOURNAL*, **67**, 662 (1945).

(2) W. O. Foye and A. E. Buckpitt, *J. Am. Pharm. Assoc.*, **41**, 385 (1952).