Anal. Calcd. for $C_{15}H_{22}O_{10}$: C, 49.72; H, 6.12. Found: C, 49.72; H, 6.07.

Methyl 4,6-*O*-Benzylidene-α-D-gulopyranoside.—Methyl α-D-gulopyranoside·$CaCl_2·2H_2O$[1] (6.2 g.) was dissolved in water and the solution deionized by successive passage through columns of Amberlite IR-120[8] and Duolite A-4.[9] The effluent was concentrated *in vacuo* to a sirup which was dried by azeotroping ethanol therefrom. The sirup was then dissolved in 14 ml. of 1% methanolic hydrogen chloride and the solution treated with 2 ml. of freshly distilled benzaldehyde. After 10 days at +5° the crystalline product (1.4 g., 27%) was removed and recrystallized from 5 parts of absolute alcohol. The pure substance melted at 147–148° and rotated in chloroform (*c* 0.90) $[\alpha]^{20}D$ +79.8°.

Anal. Calcd. for $C_{14}H_{18}O_6$: C, 59.56; H, 6.43. Found: C, 59.24; H, 6.31.

A sample (0.6212 g.) of the product described above was oxidized in aqueous solution with sodium metaperiodate. After 23 hr. analysis showed the consumption of 1.08 moles of oxidant per mole of substance taken. In a 4-dm. tube the oxidation mixture rotated +1.63° while a completely parallel oxidation of an equal quantity of the form of methyl 4,6-*O*-benzylidene-α-D-galactopyranoside, which melts at 171° and shows $[\alpha]^{20}D$ +144° (*c* 0.57, $CHCl_3$), gave a rotation of +2.35°.

An attempt to obtain the dibenzoate of the above compound in crystalline form failed.

Methyl 4,6-*O*-Benzylidene-β-D-gulopyranoside.—Methyl β-D-gulopyranoside[10] (300 mg.) was dissolved in 2 ml. of hot methanol, the solution cooled and treated with 1.2 ml. of 1% methanolic hydrogen chloride and 0.17 ml. of freshly distilled benzaldehyde. After 2 days at +5° the solution was concentrated to a crystalline magma which was extracted with water. Extraction of the aqueous extracts with methylene chloride, followed by concentration of the organic solvent gave a crystalline residue which, from 1:1 absolute alcohol–pentane, gave slender rods (27.8 mg., 6.4%) melting at 177–178°. Recrystallization failed to change this value. The pure substance rotated $[\alpha]^{20}D$ −87.8° in chloroform (*c* 1.01).

Anal. Calcd. for $C_{14}H_{18}O_6$: C, 59.56; H, 6.43. Found: C, 59.69; H, 6.57.

A sample of the compound described above was oxidized in aqueous solution with a slight excess of sodium metaperiodate. After 18 hr. at room temperature 1.13 moles of oxidant had been consumed per mole of substance taken.

Methyl 2,3-Di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-gulopyranoside.—Benzoylation of methyl 4,6-*O*-benzylidene-β-D-gulopyranoside with benzoyl chloride and pyridine in the usual manner gave from alcohol lath-shaped needles melting at 141–146°. Recrystallization from 10 parts of absolute ethanol afforded material melting at 155–156° and showing $[\alpha]^{20}D$ −57.3° in chloroform (*c* 0.61).

Anal. Calcd. for $C_{28}H_{26}O_8$: C, 68.56; H, 5.34. Found: C, 68.70; H, 5.61.

Acknowledgment.—We wish to thank Mr. Edward W. Tracy and Mr. John T. Sipes for preparing the D-gulose calcium chloride compound. Drs. Horace S. Isbell and Harriett L. Frush kindly furnished seeds of the anomeric methyl D-gulopyranosides and their tetraacetates. Analytical data were obtained in the Institutes' Microanalytical Laboratory under the direction of Dr. William C. Alford.

NATIONAL INSTITUTE OF ARTHRITIS AND
METABOLIC DISEASES
NATIONAL INSTITUTES OF HEALTH
PUBLIC HEALTH SERVICE
U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
BETHESDA 14, MARYLAND

(8) A product of Rohm & Haas Co., Philadelphia, Pa.

(9) A product of the Chemical Process Co., 901 Spring St., Redwood City, Calif.

(10) This substance, first prepared by Isbell (ref. 1) by boiling α-D-gulose·$CaCl_2·H_2O$ with methanolic hydrogen chloride, was found to be more readily accessible through the following series of reactions: α-D-gulose·$CaCl_2·H_2O$ → D-gulopyranose pentaacetate → tetra-*O*-acetyl-D-gulopyranosyl bromide → methyl β-D-gulopyranoside tetraacetate → methyl β-D-gulopyranoside.

The Stereochemistry of the Reaction of Aluminum Bromide with α-Phenethyl Aryl Ethers

BY HAROLD HART AND RAYMOND J. ELIA

RECEIVED JANUARY 8, 1954

An unusual result was obtained recently by Tarbell and Petropoulos[1] in a study of the action of aluminum bromide on benzyl phenyl ether. In several solvents, a conversion of the ether to *o*-benzylphenol (55%) and phenol (40%) occurred *within five seconds, even at −40°*. This rapid reaction was followed by a slower one, in which *o*-benzylphenol was converted to phenol. In both reactions, the benzyl group also entered into various transformations with the solvent. Because no *p*-benzylphenol was isolated, the authors suggested that the transition state had to be so constructed as to permit an *intramolecular* shift of the benzyl group, as well as cleavage of the ether to form a benzyl carbonium ion.

Having recently prepared several optically active α-phenethyl aryl ethers and established their configurations,[2] and also the configurations of the related α-phenethylphenols,[3] we decided to investigate the stereochemistry of the reaction described by Tarbell.

It was first established that *dl*-α-phenethyl phenyl ether reacted with aluminum bromide in chlorobenzene in a fashion analogous to the rapid reaction of benzyl phenyl ether. The α-phenethylphenols were analyzed by a spectrophotometric procedure[4] and found to be 85% *o*- and 15% *p*-isomer. From *dl*-α-phenethyl 2,6-xylyl ether, however, only the cleavage product was obtained (2,6-xylenol, 94%). Thus, when both *ortho* and *para* positions are available, rearrangement occurs predominantly to the *ortho* carbon, but when this position is blocked, cleavage is the principal result. (−)-α-Phenethyl phenyl ether gave (+)-α-phenethylphenols, predominantly the *ortho* isomer. This result implies retention of configuration.[2,3] The same stereochemical result was obtained with α-phenethyl *p*-tolyl ether, (−)-ether giving (−)-*o*-α-phenethyl-*p*-cresol. Since in this case the product consisted of only one isomer, a calculation of the extent of retention of optical purity was possible. Using rotation established previously,[2,3] we estimate that migration occurred with about 76% retention of optical purity. These stereochemical results are in accord with the proposed intramolecularity of the rearrangement. The reaction may be analogous to S_Ni displacements.

Experimental

General Procedure for the Rearrangement.—The rearrangements were carried out according to the procedure described by Tarbell and Petropoulos[1] for isolating their initial reaction products. Solutions of the ether (about 0.09 mole) and aluminum bromide (about 0.21 mole) in chlorobenzene (total volume about 800–900 ml.) were mixed at room temperature. To the red solution thus formed, there was added, within 10 seconds, 500 ml. of water to quench the reaction. Petroleum ether was added to aid in separating layers. Phenolic products were extracted from the or-

(1) D. S. Tarbell and J. C. Petropoulos, THIS JOURNAL, **74**, 244 (1952).

(2) H. Hart and H. S. Eleuterio, *ibid.*, **76**, 519 (1954).

(3) H. Hart and H. S. Eleuterio, *ibid.*, **76**, 516 (1954).

(4) H. Hart, *Anal. Chem.*, **24**, 1500 (1952).

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	$\alpha^{25}D$ of the ether[a]	% yield of α-phenethyl-phenol	$\alpha^{25}D$ of the alkylphenol[a]
Phenyl	.....	22[b]	....
Phenyl	− 3.30	20[c]	0.30
2,6-Xylyl	.....	0[d]	....
p-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. [e] 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 $C_{17}H_{18}O_3$: C, 75.6; H, 6.7. Found: C, 75.5; H, 6.9.

KEDZIE CHEMICAL LABORATORY
MICHIGAN STATE COLLEGE
EAST LANSING, MICHIGAN

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

BY I. HECHENBLEIKNER

RECEIVED DECEMBER 14, 1953

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 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 nonvolatile residue of 5 g.

Anal. Calcd. for $C_3HN_3Cl_2$: 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.*

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

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

AMERICAN CYANAMID COMPANY
STAMFORD, CONN.

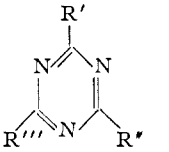
Basic Substituted Triazines

BY BRUCE W. HORROM

RECEIVED FEBRUARY 11, 1954

Many amino and alkoxy triazines have been made by the reaction of cyanuric chloride with amines and alcohols. Only two instances where trisubstituted 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$_2$CH$_2$CH$_2$N⟨morpholino⟩O; R‴ = Cl

II, R′ = R″ = R‴ = —HNCH$_2$CH$_2$CH$_2$N⟨morpholino⟩O

III, R′ = R″ = R‴ = —OCH$_2$CH$_2$CH$_2$—N⟨morpholino⟩O·HCl

IV, R′ = R″ = R‴ = —OCH$_2$CH$_2$N(CH$_3$)$_2$·CH$_3$I

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).