EXPERIMENTAL

*α-Trifluoromethylbenzyl alcohols.* α,α,α-Trifluoroacetophenones were prepared by the procedure of Levine,[1] using the Grignard reagent from 1.0 mole of aryl bromide and 0.40 mole of trifluoroacetic acid. Hydrogenation of α,α,α-trifluoroacetophenone at 25 lbs. pressure using platinum oxide catalyst afforded α-trifluoromethylbenzyl alcohol in 48% yield. A better yield was obtained by sodium borohydride reduction in aqueous dioxane, so this procedure was used to prepare all of the substituted alcohols.

*α-Chloro-α-trifluoromethyltoluenes.* The α-trifluoromethylbenzyl alcohols (0.28 mole) were stirred at 150° for 2–3 hr. with 0.29 mole of pyridine and 0.29 mole of thionyl chloride. The reaction mixtures were poured into water, washed with dilute sulfuric acid, water, dilute sodium bicarbonate, and again with water, dried, and distilled.

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## Carbamates and Dimethanesulfonates of Some New Glycols[1]

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The inhibitory effect of Myleran, 1,4-butanediol dimethanesulfonate[2] and urethane on the development of various tumors has been noted previously.[3] The availability of a series of previously unknown glycols has prompted our preparation of their dimethanesulfonates and dicarbamates as part of a program on cancer chemotherapy. The glycols were made available through the generosity of the Tennessee Eastman Company. Typical procedures for the preparation of the two types of compounds are given in the experimental section. Data for the preparation and characterization of all samples are given in Tables I and II. Dimethanesulfonates were obtained for all the glycols. Dicarbamates were obtained from most but not all. Available test data from the evaluation of these compounds in tumor retardation studies using Sarcome 180 has thus far disclosed no significant activity in any.[4]

EXPERIMENTAL[5]

*Cyclohexane-1,4-dimethanol dimethanesulfonate.* A solution of 2.8 g. (0.02 mole) of cyclohexane-1,4-dimethanol in 10 ml. of pyridine was cooled to 5–10°. Methanesulfonyl chloride, 5.7 g. (0.05 mole), was added dropwise with stirring. The reaction mixture was poured onto dilute hydrochloric acid and the precipitated product was collected, washed, dried, and recrystallized from benzene-petroleum ether to give 3.3 g. (56%) of the dimethanesulfonate, m.p. 162–163°.

*Cyclohexane-1,4-diol dicarbamate.* A solution of 2.3 g. (0.02 mole) of cyclohexane-1,4-diol in 25 ml. of dry acetone was added dropwise to a solution of 5 g. (0.05 mole) of phosgene in 35 ml. of dry acetone at −10°. The solution was warmed to 10° for 30–60 min., cooled to −20°, and treated with 100 ml. of concentrated ammonium hydroxide. The

TABLE I
GLYCOL DIMETHANESULFONATES

| Glycol | M.P. (°C.) | Yield (%) | Solvent[a] | Analysis: Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found |
|---|---|---|---|---|---|---|---|
| Cyclohexane-1,2-diol | 136 | 76 | AW | 35.29 | 35.34 | 5.88 | 6.00 |
| Cyclohexane-1,4-diol | 148 | 45 | AW | 35.29 | 35.36 | 5.88 | 6.14 |
| Cyclopentane-1,1-dimethanol | 91 | 81 | AW | 37.76 | 37.86 | 6.29 | 6.37 |
| Cyclohexane-1,1-dimethanol | 54 | 66 | MW | 40.00 | 39.92 | 6.67 | 6.51 |
| Cyclohexane-1,4-dimethanol | 163 | 56 | BP | 40.00 | 39.92 | 6.67 | 6.68 |
| 3-Cyclohexene-1,1-dimethanol | 87 | 100 | AW | 40.27 | 40.30 | 6.04 | 5.97 |
| Norcamphane-2,2-dimethanol | 112 | 80 | AW | 42.31 | 42.24 | 6.41 | 6.71 |
| Norcamphane-2,3-dimethanol | 115 | 36 | MW | 42.31 | 42.27 | 6.41 | 6.46 |
| Norcamphane-2,5-dimethanol | 136 | 49 | MW | 42.31 | 42.40 | 6.41 | 6.46 |
| 2,2′-(1,5-Naphthylenedioxy)-diethanol | 189 | 90 | N | 47.52 | 47.81 | 4.95 | 5.20 |
| Perhydro-1,4-naphthalenediol | 152 | 30 | MW | 44.17 | 44.02 | 6.75 | 6.78 |
| 2,2′-(2,5-Dichloro-*p*-phenylenedioxy)diethanol | 160 | 83 | AW | 34.04 | 34.15 | 3.78 | 3.76 |
| 2,2′-(2,5-Di-*t*-butyl-*p*-phenylenedioxy)diethanol | 175 | 92 | AW | 51.50 | 51.58 | 7.30 | 7.50 |
| 2,2′-(4,4′-Sulfonyldiphenoxy)-diethanol | 134 | 87 | AW | 43.72 | 43.68 | 4.45 | 4.46 |
| 5-Hydroxymethyl-β,β-5-trimethyl-2-*m*-dioxaneethanol | 86 | 90 | MW | 40.00 | 39.92 | 6.67 | 6.72 |
| β,β,β′,β′-Tetramethyl-2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diethanol | 184 | 84 | AW | 44.35 | 44.45 | 6.96 | 7.16 |

[a] Solvent for recrystallization: B, benzene; P, petroleum ether; A, acetone; W, water; M, methanol; N, nitromethane.

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(2) This compound is indexed by *Chemical Abstracts* under methanesulfonic acid, tetramethylene ester.

TABLE II

GLYCOL DICARBAMATES

| Glycol | M.P. (°C.) | Yield (%) | Solvent[a] | Analysis Nitrogen Calcd. | Found |
|---|---|---|---|---|---|
| Cyclohexane-1,4-diol | 265 | 50 | N | 13.86 | 13.81 |
| Cyclopentane-1,1-dimethanol | 155 | 33 | CP | 12.96 | 12.99 |
| Norcamphane-2,3-dimethanol | 157 | 54 | CP | 11.56 | 11.36 |
| Norcamphane-2,5-dimethanol | 223 | 45 | WM | 11.56 | 11.22 |
| 2,2′-(1,5-Naphthylenedioxy)diethanol | 265 | 54 | N | 8.38 | 8.29 |
| 2,2′-(2,5-Dichloro-*p*-phenylenedioxy)diethanol | 236 | 94 | H | 7.93 | 7.67 |
| 2,2′-(2,5-Di-*t*-butyl-*p*-phenylenedioxy)diethanol | 178 | 25 | CP | 7.07 | 6.80 |
| 2,2′-(4,4′-Sulfonyldiphenoxy)diethanol | 227 | 25 | N | 6.60 | 6.89 |
| 5-Hydroxymethyl-β,β,5-trimethyl-2-*m*-dioxane-ethanol | 196 | 33 | AW | 9.69 | 9.33 |
| β,β,β′,β′-Tetramethyl-2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diethanol | 241 | 82 | AW | 7.18 | 7.02 |
| 2,2-Dimethyl-1,5-pentanediol | 155 | 97 | WM | 12.84 | 12.69 |

[a] Solvent for recrystallization: H, acetic acid; N, nitromethane; A, acetone; W, water; C, chloroform; P, petroleum ether M, methanol.

reaction mixture was then warmed to room temperature and poured onto ice to precipitate the product. Recrystallization from nitromethane gave 2.0 g. (50%) of the dicarbamate, m.p. 265°.

*Cyclopentane-1,1-dimethanol dicarbamate.* This compound was prepared by an adaptation of the method previously described.[6] A solution of 2.6 g. (0.02 mole) of cyclopentane-1,1-dimethanol in 25 ml. of chloroform and 5 ml. of pyridine was added to a solution of 5 g. (0.05 mole) of phosgene in 40 ml. of toluene at 0–5°. After warming to room temperature for about 10 hr. the solution was cooled to −78° and treated with liquid ammonia. The mixture was warmed to room temperature. The precipitate was collected and recrystallized from chloroform-petroleum ether to give 1.1 g. (33%) of the dicarbamate, m.p. 154–155°.

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(3) C. C. Stock in J. P. Greenstein and A. Haddow, *Advances in Cancer Chemotherapy*, Vol. II, pp. 446, 459, Academic Press, New York, 1954.

(4) The authors are indebted to Drs. C. C. Stock and D. A. Clarke of the Sloan-Kettering Institute for conducting these tests.

(5) Analyses by Micro Tech Laboratories, Skokie, Ill. All melting points are corrected.

(6) B. Ludwig and E. Piech, *J. Am. Chem. Soc.*, **73**, 5779 (1951).

## Preparation and Polymerization of Vinyl Azide

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Vinyl azide, which has been previously described,[1] has been prepared by an improved process. This process is suited for the laboratory preparation of vinyl azide if proper precautions for handling this highly sensitive material are observed. On one occasion a sample in a distilling flask with a ground glass joint detonated when the joint was rotated. Vinyl azide should be handled as a highly sensitive material which is easily detonated. Statements in the literature[1a,2a] that this material is "surprisingly stable" should be regarded as misleading and erroneous.

Some preliminary polymerization studies with vinyl azide have established that a white, apparently infusible solid polymeric product can be obtained by bulk polymerization with peroxide or azo bis initiators. The polymer is highly combustible. Above 70° the azide decomposes with the formation of hydrazoic acid. It has been established that no triazole is present in the higher boiling liquids during the polymerization.

### EXPERIMENTAL

*β-Chloroethyl azide.* One hundred grams of β-chloroethyl *p*-toluenesulfonate was refluxed with a slight excess of sodium azide in the minimum amount of methanol-water mixture necessary to give a homogeneous solution. This solution was prepared by adding methanol to the ester and a half-saturated aqueous solution of sodium azide until a homogeneous solution was obtained. After 24 hr. refluxing the reaction mixture was diluted with water and extracted with ether. The washed and dried ether solution was distilled to give 57–65% yields of β-chloroethyl azide, b.p. *ca.* 45°/25 mm.

*Vinyl azide.* To a hot solution of 100 g. potassium hydroxide in 400 ml. of water and 500 ml. of ethylene glycol was added 52.5 g. of β-chloroethyl azide dropwise. The vinyl azide distilled from the reaction mixture as formed. A short period of reflux after the completion of the addition completed the reaction. The water-vinyl azide mixture in the receiver was freed of water by freezing and decantation. The vinyl azide, b.p. 30°, does not freeze even at −80°. It is obtained in yield of about 20 g. (*ca.* 60%). This amount is probably larger than should be handled by ordinary laboratory procedures, since this amount can cause very severe damage on detonation. Ethanol may be used instead of ethylene glycol, but the separation of pure vinyl azide from the aqueous-alcohol distillate is then much more difficult.

*Vinyl azide polymerization.* All polymerizations were run in nitrogen-filled screw cap vials.

(1) M. O. Forster and S. H. Newman, *J. Chem. Soc.* (*a*) **97**, 2570 (1910); (*b*) **99**, 1278 (1911).

(2) C. E. Schildknecht, *Vinyl and Related Polymers*, John Wiley and Sons, 1952, (*a*) p. 80, (*b*) p. 397.