# Synthesis of Solvents for Water Desalination: Amines and Ethers

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ONE METHOD currently under investigation for the conversion of saline water into water of low salt content takes advantage of the lower consolute temperature behavior exhibited by certain types of organic solvents when they are mixed with water. Solvents possessing this particular property to a practical degree are essentially restricted to certain types of amines and ethers. The most useful of these classes of compounds are secondary and tertiary aliphatic amines and aliphatic ethers in which there is a significant degree of branching adjacent to the nitrogen or oxygen atoms. The synthesis and properties of certain amines which may be useful for this application are described here.

For a solvent to be an ideal substance for water desalination, certain properties are important: The solvents should have a lower consolute temperature behavior when mixed with water. The solubility of water in the organic phase should be high at, or somewhat above, ambient temperatures and should decrease to a very small value over a relatively small temperature range. The organic solvent should have a very low solubility in the water phase at somewhat elevated temperatures. Because ions such as magnesium are precipitated as the hydroxide at approximately pH 10 or higher and because such precipitates cause difficulties in bringing about clean phase separation and make solvent recovery from the raffinate difficult, the saturated aqueous solution of such solvents should possess a pH lower than 10. To cause rapid phase separation, the density of the organic solvent should be as far as possible from the density of water, and the solvents should have reasonable volatility. The compounds should have good stability to oxidation and hydrolysis.

Most of the amines had such properties. The one property in which the amines were inherently deficient was that of the pH of the saturated aqueous solution. All attempts to reduce the basicity of the amines below that at which magnesium hydroxide is precipitated caused a simultaneous loss of most of the other desirable properties. The utility of these solvents for the desalination of water is discussed in reports to the Office of Saline Water of the U. S. Department of Interior (*13, 21, 22*).

Most of the amines described here have been reported earlier; however, for our purpose it was necessary to produce these compounds in a high state of purity and as such, a number of our physical constants did not agree well with the earlier values. At least one derivative of each amine was prepared; in a number of instances no derivatives had been described for these compounds.

An exasperating discrepancy was encountered during our study of N,N-dimethylallylamine. We first prepared this compound from allylamine, formaldehyde, and formic acid by the Leuckart reaction. Table I shows that our boiling point and refractive index corresponded with the majority of the previous literature reports, but the picrate salt, melting sharply at 117–117.5°, melted 9° higher than the highest previously reported value and approximately 20° higher than three of the earlier values.

Since this amine appears not to have been prepared previously by the Leuckart reaction but rather by the reaction between dimethylamine and allyl bromide, we duplicated this synthesis. The tertiary amine recovered from this reaction had properties identical with the Leuckart product and produced the picrate salt melting at 118°. In a further attempt to identify the Leuckart product, a portion was reduced catalytically over platinum on carbon. The basic product was shown to be dimethylamine by conversion to the picrate salt. Reduction of N,N-dimethylallylamine over Adams' platinum oxide resulted in the production of a small amount of dimethylamine along with a large quantity of N,N-dimethyl-*n*-propylamine. A similar reduction in the presence of excess HCl produced only N,N-dimethyl-*n*-propylamine. Thus, it appears that the reductive cleavage of an allyl group from a nitrogen atom may be controlled by the type of catalyst employed and by the presence or absence of acid. The recovery of N,N-dimethyl-*n*-propylamine from these reductions provided additional proof that our starting material was N,N-dimethylallylamine.

Finally, the amine from the allyl bromide-dimethylamine reaction was converted into the hydrobromide salt and then brominated. The crystalline product had the same melting point as has been reported (*28, 31*) for N,N-dimethyl-2,3-dibromopropylamine hydrobromide. This provides conclusive proof of the structure of this amine, even though the discrepancy involving the melting point of the picrate salt remains.

Another anomaly involved certain of the Leuckart reactions which gave unexpected byproducts. In the reactions involving formic acid and formaldehyde and either allylamine or isopropylamine, a considerable quantity of tri-

Table I. Reported Properties of N,N-Dimethylallylamine

| | Ref. | B.P., ° C. | $n_D$ | Picrate Salt M.P., ° C. |
|---|---|---|---|---|
| From Leuckart reaction, this article | . . . | 63.0-63.5 (755 mm.) | 1.3977 (25°) | 117-117.5 |
| From allyl bromide-dimethylamine, this paper | . . . | 63-64 (755 mm.) | 1.3980 (25°) | 118 |
| Indzhikyan, others | (*23*) | 48-50 | . . . | 91-2; 108 |
| Bailey and Nicholas | (*1*) | 64 (752 mm.) | 1.3977 (25°) | 95-6 |
| Cromwell and Hassner | (*11*) | 61 (726 mm.) | . . . | 94-6 |
| Lukes and Trojanek | (*28*) | 63-4 | . . . | . . . |
| Cope and Towle | (*10*) | 64 | 1.3981 (25°) | . . . |
| Weston, others | (*40*) | 61-4 | 1.3998 (20°) | . . . |
| von Braun | (*39*) | . . . | . . . | 100 |
| Knorr and Roth | (*26*) | 64-66 (753 mm.) | . . . | 95 |

methylamine was identified as a byproduct. In the isopropylamine reaction a 6% yield of trimethylamine was recovered. This may be a general behavior in certain Leuckart reactions involving formaldehyde and formic acid because similar low boiling amine products were noted in the reactions involving *n*-propylamine and isobutylamine. No such byproduct was detected in the diethylamine, formic acid, formaldehyde reaction.

In this work all impure yields were sacrificed. In general, the most convenient method for producing a compound in a good state of purity was chosen. All compounds gave neutralization equivalents within 1% of the calculated values.

A number of ethers were found to have some of the properties required for a good water desalination solvent. In general when these ethers were mixed with water the resulting phase diagrams were not as good as those produced by some of the better water-amine mixtures. The densities of the ethers were relatively close to that of water, resulting in poorer phase separation and, in general, the volatility of the ethers was lower than desired. The one desirable feature the ethers possessed was the relatively low pH values of the saturated aqueous solutions which did not cause the troublesome precipitation of magnesium hydroxide in waters containing appreciable quantities of magnesium ions.

These ethers were synthesized generally by well recognized procedures. $\alpha,\gamma$-Dialkyl ethers of glycerol were prepared by condensing epichlorohydrin with an alcohol in the presence of either $SnCl_4$ or $BF_3$, converting the resulting chlorohydrin into the glycidol ether and causing this product to react with an additional quantity of alcohol to give the final product. Ethers of propylene glycol were prepared similarly by an acid catalyzed reaction between propylene oxide and an alcohol. Cyclic acetals were produced by the acid catalyzed reaction between a glycol and a carbonyl compound. Amino acetals were prepared by condensing a secondary amine with an alcohol and formaldehyde. Ethers of propylene glycol were shown (*8*) to be mixtures of the primary and secondary ethers when prepared in the manner here employed. No attempts were made to separate these isomers, although the monoether fraction was separated into two fractions in the case of the butyl ether. The product from *n*-propanol and propylene oxide was separated into three major fractions. These were believed to be the mono-*n*-propyl ethers of propylene, dipropylene, and tripropylene glycols. Undoubtedly these fractions were still isomeric mixtures.

As in the case of the amine solvents, these ethers were purified by careful fractional distillation and only those successive fractions having virtually identical physical properties were saved and evaluated as water desalination solvents.

A number of these ethers had either not been reported previously or else had been characterized inadequately.

## EXPERIMENTAL

All melting points are corrected and all boiling points are uncorrected. Elemental analyses were determined by Galbraith Laboratories, Knoxville, Tenn.

Starting materials for both amines and ethers were the purest commercially available grade and were used without further purification. The final products were distilled with special care, generally through a 50-plate, concentric tube distilling column or a 24 by 1-inch column packed with glass helices at a 10 to 1 reflux ratio. Only successive fractions having virtually identical physical constants were saved. This resulted in relatively poor yields in some instances, because yields are reported only for products of highest purity. The molecular refraction (M.R.) was calculated from the Lorenz-Lorentz equation, whereas M.R. summation was derived from the sum of the atomic refractions of the various elements and groups in the molecule.

Typical examples of the syntheses of amines and ethers are given.

**N-Ethyl-*sec*-butylamine (Synthesis 1).** Ethylamine, 100 g. (2.22 moles), was dissolved in 200 ml. absolute ethanol and this solution was mixed with 155 g. (2.15 moles) 2-butanone. This solution was reduced in four equal portions over 1 g. 10% Pt on carbon in a Parr low pressure hydrogenator. The product was filtered, the filtrate added to excess dilute HCl below 20° and the resulting acid solution was concentrated to remove volatile organic compounds. Excess NaOH was added to the concentrated solution, and the amine was distilled from this alkaline solution as the water azeotrope, b.p. approximately 78°. The azeotrope was dried over KOH pellets and was redistilled, see Table II.

**N-Ethyl-*tert*-butylamine (Synthesis 2).** This compound was prepared from 292 g. (4 moles) *tert*-butylamine and 220 g. ethyl bromide by the method of Bortnick and others (*5*) Table II.

**N-Methyl-*n*-amylamine (Synthesis 3).** *n*-Valeryl chloride was prepared by adding 282 g. (2.37 moles) thionyl chloride to 200.4 g. (1.97 mole) *n*-valeric acid, heating the mixture to reflux for 30 minutes and distilling. The distillate boiled at 120–6° and weighed 188.4 g.

To a solution containing 76 g. (2.45 moles) methylamine, 160 g. (1.58 mole) triethylamine and 500 ml. dry toluene at −10° was added 188.4 g. (1.56 mole) *n*-valeryl chloride, dissolved in 100 ml. dry benzene. The solid was removed by filtration and washed well with benzene. The filtrate was extracted with dilute HCl, $NaHCO_3$ solution and finally with water. After drying, the organic solution was distilled. The desired N-methylvaleramide was recovered at 122–3° (11 mm.), $n_{\mathrm{D}}^{25}$ 1.4410, yield 82.6 g. (46.0%). D'Alelio and Reid (*12*) gave $n_{\mathrm{D}}^{2}$ 1.4401 for N-methylvaleramide. From the other information in this article, this appears to be a mistake and $n_{\mathrm{D}}^{25}$ was probably intended.

The N-methylvaleramide was reduced by adding it to 42 g. (1.1 mole) $LiAlH_4$, dissolved in 500 ml. dry ether in a nitrogen atmosphere. The resulting mixture was heated under reflux for 10 hours and allowed to stand for 32 hours. The excess $LiAlH_4$ was destroyed with water and 80 g. NaOH in 200 ml. water was added. A difficult emulsion resulted. After diluting with 1 liter of water, the ether layer was removed and the water was extracted twice with 300-ml. portions of ether. The product was extracted from the ether with dilute HCl and the HCl extracts were concentrated to a small volume. Excess NaOH was added, the liberated amine was extracted with ether, the ether extracts were dried over KOH pellets and were distilled. Careful fractional distillation was necessary to recover the pure amine, Table II.

**N,N-Dimethylallylamine (Synthesis 4).** A mixture of 202 g. (6.12 moles) paraformaldehyde (approximately 91%) and 497 g. (9.5 moles) formic acid (88%) was mixed and maintained below 35° while 171 g. (3.0 moles) allylamine was added. In the reaction involving *tert*-butylamine, *sym*-trioxane would not substitute for paraformaldehyde. The mixture was then warmed to about 50° where a mild exothermic reaction began with the evolution of $CO_2$. The mixture was held at 50° to 55° with occasional cooling until excessive heat evolution ceased. It was then heated to reflux for 45 minutes, cooled, excess 50% NaOH was added with cooling and the liberated amine was recovered by distillation as the amine-water azeotrope (b.p. 58–60°). The azeotrope was dried over KOH pellets and distilled from Na, see Table II.

During the recovery of the product as the amine-water azeotrope, a low boiling byproduct was collected in a dry ice condenser. A picrate salt of this byproduct separated from alcohol as long yellow needles, m.p. 226–226.5°. An

Table II. Amines. RR′R″N

| R | R′ | R″ | Synthesis | B.P., ° C. | $n_{D}^{25}$ | $d_{4}^{25}$ | M.R. Calcd. | M.R. Summation | Picrate M.P., ° C. | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|
| Et | *sec*-Bu | H | 1 | 98.8(755 mm.)[a] | 1.3999[b] | 0.7336[c] | 33.63 | 33.66 | . . .[d] | 79.0 |
| Me | *n*-Amyl | H | 3 | 114–119(755 mm.)[e] | 1.4073[f] | 0.7412[f] | 33.63 | 33.66 | 122–123[e, g] | 41.8 |
| Et | iso-Pr | H | 1 | 71–72(750 mm.)[h] | 1.3866 | 0.7095 | 28.89 | 29.04 | . . .[i] | 72.8 |
| Et | *n*-Pr | H | 1 | 82–84(757 mm.)[h, j] | 1.3934 | 0.7192 | 28.95 | 29.04 | . . .[k] | 24.6 |
| Et | *tert*-Bu | H | 2 | 86–87(754 mm.)[l] | 1.3943 | 0.7196 | 33.66 | 33.66 | 147.5–148.5[m] | 76.1 |
| Me | Me | *tert*-Bu | 4 | 88–90.5(756 mm.)[n] | 1.4028 | 0.7374 | 33.48 | 34.01 | 290 (dec.)[o] | 77.2 |
| Me | 1,3-DiMeBu | H | 1 | 112–122.5(755 mm.)[p, q] | 1.4136[c] | 0.7459[c] | 38.31 | 38.28 | 99–99.5[r] | 70.0-71.1 |
| Me | Me | *sec*-Bu | 4 | 91–94.5(756 mm.)[s] | 1.4010 | 0.7329 | 33.55 | 34.01 | 197.5–198[t] | 62.2 |
| Me | Et | Et | 4 | 66–66.5(752 mm.)[u] | 1.3873 | 0.7004 | 29.31 | 29.39 | 188–189[v] | 83.4 |
| Me | Me | allyl | 4 | 63–63.5(758 mm.)[w] | 1.3977[w] | 0.7122 | 28.86 | 28.92 | 117–117.5[w, x] | 47.6 |
| Me | Me | allyl | 5 | 63–64(756 mm.)[w] | 1.3980 | . . . | . . . | . . . | 118[w] | 43.3 |
| Me | Me | *n*-Pr | 4 | 64.5–66(753 mm.)[y] | 1.3845 | 0.6962 | 29.31 | 29.39 | 111–112[w] | 53.3 |
| Me | Me | iso-Pr | 4 | 65.5–67(756 mm.)[z] | 1.3890 | 0.7098 | 29.04 | 29.39 | 252 (dec.)[aa] | 67.9 |
| Me | Me | iso-Bu | 4 | 81–82.5(756 mm.)[ab] | 1.3898 | 0.7039 | 34.06 | 34.01 | 129–130[ab] | 59.0 |

[a] B.p. 97–8° (741 mm.), $d_{0}^{20}$ 0.7358 (2). [b] Value at 20° was 1.4032. [c] Value determined at 20° rather than 25° C. [d] Formed very $H_2O$- and alcohol-soluble picrate with low m.p. Phenylthiourea derivative, m.p. 106.5–107°, white needles from cyclohexane. *Anal.* Calcd. for $C_{13}H_{20}N_2S$: N, 11.85. Found: N, 11.68, 11.80. [e] B.p. 116–18°, $d_{4}^{15}$ 0.738, m.p. of picrate 119–120° (*27*). [f] Values determined at 26.5° C. [g] Small yellow needles from dilute alcohol. [h] B.p. 76° for ethylisopropylamine (*6*). B.p. 81–3°, $n_{D}^{25}$ 1.3936 for ethylisopropylamine and b.p. 69.5–71°, $n_{D}^{25}$ 1.3861 for ethyl-*n*-propylamine (*9*). First constants relate to the last amine and vice versa. [i] Picrate liquid at room temperature. Phenylthiourea derivative, m.p. 132–33°, white needles from benzene and little ethanol. *Anal.* Calcd. for $C_{12}H_{18}N_2S$: N, 12.60. Found: N, 12.28, 12.38. [j] B.p. 77–80° (738 mm.), $n_{D}^{20}$ 1.3966, $d_{4}^{20}$ 0.7318 (7). [k] A crude picrate melted at 57–9°; no suitable solvent was found for recrystallization. An α-naphthylthiourea derivative had m.p. 126.5° from alcohol; m.p. 122–23° (*6*). [l] B.p. 76–9°, $n_{D}^{25}$ 1.3941 (5). We found the amine-$H_2O$ azeotrope to boil at 76–8°. Private communication from Dr. Bortnick confirmed that their reported b.p. was an error. [m] Yellow needles from $C_6H_6$. *Anal.* Calcd. for $C_{12}H_{18}N_4O_7$; N; 16.96. Found: N, 16,67, 16.54. [n] B.p. 89–90°, $n_{D}^{25}$ 1.4020, $d_{25}^{25}$ 0.7372 (*5*). [o] Yellow needles from $H_2O$. *Anal.* Calcd. for $C_{12}H_{18}N_4O_7$; N, 16.96. Found: N, 16.74, 16.82. The methyl *p*-toluenesulfonate derivative hygroscopic plates from ethyl acetate–methanol, m.p. 200° (dec.). M.p. 184–7° (*35*). [p] A sample of this compound was also prepared from $C^{14}$-labeled methylamine. [q] B.p. 122–24° (*25*). [r] Orange needles from $C_6H_6$. *Anal.* Calcd. for $C_{13}H_{20}N_4O_7$: N, 16.27. Found N, 16.08, 16.14. The phenylthiourea derivative was white needles from $C_6H_6$, m.p. 113°. *Anal.* Calcd. for $C_{14}H_{22}N_2S$: N, 11.19. Found: N, 11.25, 11.32. The HCl salt had m.p. 136–38°. M.p. 130–32° (*25*). [s] B.p. 93–93.5°, $n_{D}^{25}$ 1.4000, $d_{4}^{25}$ 0.7340 (*9*). [t] Yellow plates from alcohol. M.p. 192–93° (*37*). [u] B.p. 63° (728 mm.), $n_{D}^{25}$ 1.3879, $d_{4}^{23}$ 0.703 (*41*). [v] M.p. 185–86° (*3*). [w] See Table I. [x] Yellow needles from alcohol. *Anal.* Calcd. for $C_{11}H_{14}N_4O_7$: C, 42.03; H, 4.49; N, 17.83. Found: C, 41.96 42.40; H, 4.50; 4.52; N, 17.97, 17.92. [y] B.p. 65–6°, picrate m.p. 108–9° (*18*). [z] B.p. 65.5–65.7° (740 mm.), $n_{D}^{25}$ 1.3874, $d_{4}^{25}$ 0.7106 (*35*). [aa] Yellow leaflets from alcohol. *Anal.* Calcd. for $C_{11}H_{16}N_4O_7$: N, 17.72. Found: N, 17.48, 17.69. [ab] B.p. 80–1° and m.p. 124° for the picrate (*18*).

authentic sample of trimethylamine picrate was prepared from pure trimethylamine and was recovered as long yellow needles, m.p. 226–226.5°. A mixture of these two salts gave the same melting behavior, indicating that the low boiling impurity was trimethylamine. Similar low boiling impurities were detected in the Leuckart reactions involving *n*-propylamine and isobutylamine. The low boiling impurity from the isopropylamine reaction was collected in dilute HCl, liberated from the HCl with NaOH and collected in alcoholic picric acid. The resulting yellow needles melted at 223°, 226° after recrystallization from $H_2O$ and this m.p. was not depressed by the presence of an equal amount of trimethylamine picrate.

Since the picrate salt of our N,N-dimethylallylamine did not show the melting behavior that has been reported previously for this compound (see Table I), it seemed necessary to provide additional evidence for the identity of this amine. Therefore, a quantity of the amine, dissolved in alcohol, was reduced catalytically over 10% Pt on carbon in a low pressure Parr hydrogenator. The reduction product was treated with a slight excess of picric acid, the alcohol was removed on a steam bath and the residue was dissolved in hot ethyl acetate. Chilling this solution produced yellow flat plates, m.p. 160–1°. This was unexpected since the melting point of N,N-dimethyl-*n*-propylamine picrate had been found to be 111°. Authentic dimethylamine picrate was prepared and found to separate from alcohol or ethyl acetate as yellow plates which looked entirely different from the unknown picrate salt. However, the authentic dimethylamine picrate melted at 160–1°, and this melting point was not changed when the two picrate salts were mixed in equal quantities. Thus, this reaction of N,N-dimethylallylamine was shown to produce dimethylamine as the only product detected.

**N,N-Dimethylallylamine (Synthesis 5).** This was a repetition of the method of Cromwell and Hassner (*11*). This product had physical constants virtually identical with those of the Leuckart product, see Table II.

A quantity of this amine was reduced in an alcohol solution over Adams' platinum oxide. The amine product was converted into the picrate salt, which was fractionally crystallized from alcohol and from ethyl acetate to give a 75% yield of N,N-dimethyl-*n*-propylamine picrate, m.p. 110.5–111.5°, and a 17.5% yield of dimethylamine picrate, m.p. 160–1°.

When a portion of N,N-dimethylallylamine was reduced over platinum oxide in the presence of a slight excess of HCl, a 75% yield of recrystallizated N,N-dimethyl-*n*-propylamine picrate, m.p. 111–12° from ethyl acetate, was recovered, and there was no evidence of any other product. When this picrate was caused to melt and then resolidify, at times it remelted at the same temperature and at other times it remelted at 104°. This lower melting point seemed to correspond to a metastable form of this compound.

A picrate salt from this preparation of N,N-dimethylallylamine, m.p. 118°, when mixed with the picrate salt from the allylamine Leuckart reaction showed no depression of the melting point, indicating that the two compounds were identical.

A quantity of N,N-dimethylallylamine from this synthesis was converted into the hydrobromide salt, this salt was dissolved in dioxane and excess bromine was added. After removing the solvent, the pale yellow solid was recrystallized from alcohol, giving white needles, m.p.

187.5–188.5° (dec.). Earlier workers (*28, 31*) have reported that the hydrobromide salt of N,N-dimethyl-2,3-dibromopropylamine melts at 188–9°. This and the previous data appear to confirm the structure of our N,N-dimethylallylamine products.

**N-Isopropylmorpholine (Synthesis 6).** Isopropyl *p*-toluenesulfonate was prepared in 55.3% yield (*14*). To 287 g. (3.3 moles) morpholine, heated to 90°, 236 g. (1.1 mole) isopropyl *p*-toluenesulfonate was added dropwise at a rate to maintain the reaction temperature at 95–105° without external heating. After the addition of 60 g. NaOH in 60 ml. $H_2O$, the amine was recovered by steam distillation. Ether extraction of the amine before steam distillation failed, probably because of the solublizing action of the sodium *p*-toluenesulfonate. Excess HCl was added to the distillate, the solution was concentrated to a volume of 50 ml., excess NaOH was added and the solution was extracted with three 100-ml. portions of ether. The extracts were dried over KOH pellets and $CaH_2$ and were distilled (Table III).

**N-Methylpyrrole (Synthesis 7).** Same as the method for preparing pyrrole (*29*). From the methylamine salt of mucic acid (from 1 kg. mucic acid) and 625 ml. glycerol, there was recovered an N-methylpyrrole-$H_2O$ azeotrope, b.p. 84–5°. After this was dried over KOH pellets, the pure product was distilled (Table III).

**N-*n*-Butoxymethylmorpholine (Synthesis 8).** This was a modification of a previously described procedure (*36*). To a mixture of 222 g. (3 moles) *n*-butanol and 45 g. (1.37 mole) paraformaldehyde (91%) was added 130.5 g. (1.5 mole) morpholine until the exothermic reaction caused the temperature to rise to 60°, and then the amine was added at a rate to maintain this temperature. After the addition, the clear solution was stirred for one hour longer and 53 g. $Na_2CO_3$ was added. The mixture was stirred and cooled to 10°, it was filtered and the filtrate was distilled, see Table III.

**Alkyl Glycidyl Ethers.** A mixture of 1,472 g. (32 moles) absolute ethanol and 24 ml. $BF_3$-etherate (50%) was heated to boiling. Epichlorohydrin (740 g., 8 moles) was added slowly at a rate to maintain a steady reflux without supplying external heat. After boiling for 30 additional minutes, 24 g. $NaHCO_3$ was added, the excess ethanol was removed by distillation, the cooled residue was filtered and the filtrate was heated to 80° (25 mm.) in order to remove remaining ethanol. The residue was composed of 1,079 g. (97.3%) crude 1-chloro-3-ethoxy-2-propanol. To this crude residue was added a cold solution of 342 g. (10% excess) NaOH in 1,213 ml. $H_2O$ while the mixture was stirred vigorously with a Hershberg stirrer for 2 hours and while maintaining a temperature of 30°. This epoxidation procedure was essentially that described in a private communication from the Shell Development Co. The two phases were separated, the water layer was extracted twice with ether, the combined organic extracts were dried over $Na_2SO_4$ and distilled. There was recovered 666.5 g. ethyl glycidyl ether, b.p. 83.5–85° (75 mm.), corresponding to an 81.6% yield from epichlorohydrin. This compound has been prepared in 46% yield and reported (*15*) to have b.p. 61° (65 mm.).

Essentially the same procedure was used for the preparation of methyl glycidyl ether except that the crude chlorohydrin was stirred with the 22% NaOH solution for only 25 minutes at 30°. Reaction appeared to be very rapid. From 6 moles epichlorohydrin there was recovered a 60.7% yield of methyl glycidyl ether, b.p. 110–11° (754 mm.), $n_D^{25}$ 1.4022. Flores-Gallardo and Pollard (*15*) gave b.p. 53.5–53.7° (85 mm.) and a yield of 46.4% from epichlorohydrin. There was evidence that for this compound a reaction time of less than 25 minutes would produce a greater yield. Longer reaction times appeared to cause hydrolysis of the epoxide group. For instance, a reaction time of 30 minutes reduced the yield to 43.3%.

For the production of 1,3-dimethylbutyl glycidyl ether, 4-methyl-2-pentanol was condensed with epichlorohydrin at 80–90°. The resulting 1-(1,3-dimethylbutoxy)-3-chloro-2-propanol was recovered in 80.7% yield, b.p. 47–50° (0.5 mm.), $n_D^{25}$ 1.4435, $d_4^{25}$ 0.9965, M.R. (calcd.) 51.97, M.R. (summation) 51.80. *Anal.* Calcd. for $C_9H_{19}ClO_2$: C, 55.52; H, 9.84. Found: C, 55.14, 55.37; H, 9.93, 10.21.

The above chlorohydrin was stirred with 22% NaOH solution at 30° for 2.5 hours. Distillation of the product caused the recovery of 37% of the chlorohydrin. Therefore, this was stirred with additional NaOH solution for 9.5 hours at 30°, resulting in an over-all yield of 87.5% of the corresponding epoxide, b.p. 92–5° (28 mm.), $n_D^{25}$ 1.4207, $d_4^{25}$ 0.8860, M.R. (calcd.) 45.25, M.R. (summation) 44.85. *Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.32; H, 14.44. Found: C, 68.24, 68.18; H, 14.49, 14.60.

**1-Ethoxy-3-isopropoxy-2-propanol (Synthesis 9).** Ethyl glycidyl ether was condensed with isopropanol in the same manner as ethanol was condensed with epichlorohydrin (Table IV).

**1,3-(2-Butoxy)-2-propanol (Synthesis 10).** Essentially, the procedure of Henze and Rogers (*19*) was employed (Table IV).

**1-(1,3-Dimethylbutoxy)-2,3-propanediol (Synthesis 11).** A mixture of 158 g. (1 mole) 1,3-dimethylbutyl glycidyl ether and 180 g. 0.2% $H_2SO_4$ in water was heated at 95–100° with vigorous stirring for 11.5 hours, the mixture was neutralized with NaOH, the upper layer was separated, the water layer was extracted once with ether, the combined organic layers were dried over $Na_2SO_4$ and distilled (Table IV).

**Methyl *tert*-butyl ether (Synthesis 12).** Prepared by the method of Norris and Rigby (*30*) (Table V).

**2,2-Dimethyl-1,3-dioxolane (Synthesis 13).** A mixture of 124 g. (2 moles) ethylene glycol, 174 g. (3 moles) acetone, 2 g. *p*-toluenesulfonic acid and 100 ml. methylene dichloride was placed in a distilling flask to which was attached an efficient fractionating column. The top of the column was fitted with a modified Stark and Dean tube, topped by a reflux condenser. The mixture was heated to boiling, causing the water-methylene dichloride azeotrope to condense in the Stark and Dean tube, the methylene dichloride was returned to the reaction flask and the water was removed periodically. The theoretical quantity of water (36 ml.) was recovered after 19 hours. The product was recovered by distilling the material remaining in the reaction flask (Table V).

**Ethers of Propylene Glycol (Synthesis 14).** To each mole of alcohol was added 3 ml. $BF_3$-etherate (50%) and the propylene oxide was added with cooling at a temperature of 40–65°. After standing over night, 1 g. $NaHCO_3$ was added for each 1 ml. $BF_3$-etherate used, the mixture was heated to 100° with stirring, cooled, and filtered. Distillation of the filtrate allowed the recovery of the ethers (Table V).

**1-Methoxy-3-(1,3-dimethylbutylamino)-2-propanol (Synthesis 15).** A mixture of 505 g. (5 moles) 1,3-dimethylbutylamine and 36 g. $H_2O$ was heated to boiling. Methyl glycidyl ether (88 g., 1 mole) was added at a rate to produce slow boiling, refluxing was continued for 1 hour more and the mixture was distilled (Table V).

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Table III. Miscellaneous Amines

| Amine | Synthesis | B.P., ° C. | $n_D^{25}$ | $d_D^{25}$ | M.R. Calcd. | M.R. Summation | Picrate M.P., ° C. | Yield, % |
|---|---|---|---|---|---|---|---|---|
| N-Butylmorpholine | 4 | 82–86(31 mm.)<br>180–181(756 mm.)[a] | 1.4434 | 0.8877 | 42.80 | 42.69 | 129.5–130[b] | 49.3 |
| N-Isopropylmorpholine | 6 | 153-157(748 mm.)[d] | 1.4448 | 0.9112 | 37.72 | 38.07 | 191–191.5[e] | 85.5 |
| N-Methylpyrrole | 7 | 110.5–112(754 mm.) | 1.4861[f] | 0.9037[f] | 25.71 | 26.26[g] | ... | 17.6 |
| N-*n*-Butoxymethylmorpholine | 8 | 116–117.5(31 mm.)[h] | 1.4433 | 0.9392 | 49.17 | 48.95 | ... | 89.0 |
| N-*n*-Propoxymethylmorpholine | 8 | 100–102(30 mm.)[i] | 1.4416 | 0.9523 | 44.20 | 44.33 | ... | 77.1 |

[a] B.p. 178–81° (*24*). [b] Yellow dendritic crystals from alcohol. *Anal.* Calcd. for $C_{14}H_{20}N_4O_8$: N, 15.09. Found N, 14.60, 14.71. [c] When 5 moles morpholine and 1.5 mole triisopropyl phosphite were heated under reflux for 1 hour, only the starting materials were recovered. [d] *Anal.* Calcd. for $C_7H_{15}NO$: C, 65.07; H, 11.70. Found: C, 64.89, 65.02; H, 11.93, 11.75. [e] Needles from alcohol. *Anal.* Calcd. for $C_{13}H_{18}N_4O_8$: N, 15.64. Found: N, 15.25, 15.49. [f] Values $n_D^{17}$ 1.48985 and $d_4^{15}$ 0.9145 (*34*). [g] Value includes no exhaltation value for conjugated double bonds. [h] *Anal.* Calcd. for $C_9H_{19}NO_2$: C, 62.39; H, 11.05 Found: 62.04, 62.42; H, 11.09, 11.34. [i] *Anal.* Calcd. for $C_8H_{17}NO_2$: C, 60.35; H, 10.76. Found: C, 60.44, 60.80; H, 10.99, 11.20.

Table IV. Glycerol Ethers, $ROCH_2CHOHCH_2OR'$

| R | R′ | Synthesis | B.P., ° C. | $n_D^{25}$ | $d_4^{25}$ | M.R. Calcd. | M.R. Summation | Yield, % |
|---|---|---|---|---|---|---|---|---|
| *sec*-Bu | *sec*-Bu | 10 | 81–83(2 mm.)[a] | 1.4262[a] | 0.9034[a] | 57.97 | 57.81 | 13.6 |
| Et | *n*-Pr | 9 | 103–104(23–4 mm.)[b] | 1.4228 | 0.9351[b] | 44.16 | 43.96 | 62.0[c] |
| Me | *n*-Bu | 9 | 106.5–109(20 mm.)[d] | 1.4257 | 0.9399 | 44.19 | 43.96 | 55.0[c] |
| Et | *n*-HexOEt | 9 | 110–118(0.7–0.8 mm.)[e] | 1.4372 | 0.9412 | 69.00 | 68.69 | 74.0[c] |
| Me | iso-Am | 9 | 112–118(22–3 mm.)[f] | 1.4269 | 0.9276 | 48.77 | 48.57 | 65.0[c] |
| Et | *n*-Bu | 9 | 118–120(24 mm.)[g] | 1.4254 | 0.9217 | 48.93 | 48.57 | 63.5[c] |
| Me | *n*-Am | 9 | 127–130(29–30 mm.)[h] | 1.4285 | 0.9287 | 48.87 | 48.57 | 63.9[c] |
| Et | Et | 10 | 95–105(30 mm.)[i] | 1.4193[i] | ... | ... | ... | 64.7 |
| H | 1,3-DiMeBu | 11 | 84(1 mm.)[j] | 1.4416 | 0.9590 | 48.61 | 48.46 | 69.1 |
| Me | 2-Am | 9 | 111–120(29–30 mm.)[k] | 1.4259 | 0.9260 | 48.70 | 48.57 | 74.2[c] |
| Et | iso-Pr | 9 | 99–103(32 mm.)[l] | 1.4192 | 0.9274 | 44.19 | 43.96 | 67.3[c] |
| Me | *tert*-Bu | 9 | 99–101(31.5 mm.)[m] | 1.4213 | 0.9307 | 44.22 | 43.96 | 51.0[c] |

[a] B.p. 95–6 (2 mm.), $d_4^{20}$ 0.9112, $n_D^{20}$ 1.4279 (*19*). We also found $d_4^{20}$ 0.9074 and $n_D^{20}$ 1.4279. [b] B.p. 86.5 (10 mm.) and $d^{20}$ 0.936 (*4*). [c] These are the yields of the last step, the reaction between an alcohol and an alkyl glycidyl ether. The yields of the alkyl glycidyl ethers are reported in the experimental section. [d] *Anal.* Calcd. for $C_8H_{18}O_3$: C, 59.23; H, 11.17. Found: C, 59.03, 58.80; H, 11.34, 11.51. [e] *Anal.* Calcd. for $C_{13}H_{28}O_4$: C, 62.86; H, 11.36. Found: C, 62.49, 62.54; H, 11.47, 11.58. [f] *Anal.* Calcd. for $C_9H_{20}O_3$: C,61.33; H, 11.44. Found: C, 60.96, 61.14; H, 11.10, 11.20. Ref. 16 reported b.p. 104° (11 mm.) and $n_D^{20\text{-}7}$ 1.4272 but did not indicate the source of this material. [g] *Anal.* Calcd. for $C_9H_{20}O_3$: C, 61.33; H, 11.44. Found: C, 61.04, 60.99; H, 11.28, 11.55. Ref. 16 reported b.p 103° (12 mm.) $n_D^{20\text{-}7}$ 1.4240 but did not indicate the source of this material. [h] *Anal.* Calcd. for $C_9H_{20}O_3$: C, 61.33; H, 11.44. Found: C, 61.08, 61.27; H, 11.71, 11.87. Ref. 16 reported b.p. 102° (10 mm.) $n_D^{20\text{-}7}$ 1.4285 but did not indicate the source of this material. [i] B.p. 61.5–62 (2 mm.) and $n_D^{20}$ 1.4200 (*19*). We found $n_D^{20}$ 1.4205. [j] *Anal.* Calcd. for $C_9H_{20}O_3$: C, 61.31; H, 11.43. Found: C, 61.11, 61.05; H, 11.28, 11.29. [k] *Anal.* Calcd. for $C_9H_{20}O_3$: C, 61.31; H, 11.43. Found: C, 61.02, 61.07; H, 11.54, 11.59. [l] *Anal.* Calcd. for $C_8H_{18}O_3$: C, 59.23; H, 11.17. Found: C, 59.26, 59.58; H, 11.10, 11.05. Ref. 20 gave $d_4^{20}$ 0.9291 but no other information. [m] *Anal.* Calcd. for $C_8H_{18}O_3$: C, 59.23; H, 11.17. Found: C, 59.17, 58.95; H, 11.06, 10.94.

Table V. Miscellaneous Ethers

| Name | Synthesis | B.P., ° C. | $n_D^{25}$ | $d_4^{25}$ | M.R. Calcd. | M.R. Summation | Yield, % |
|---|---|---|---|---|---|---|---|
| Methyl *tert*-butyl ether | 12 | 55–55.5(754 mm.)[a] | 1.3668[a] | ... | ... | ... | 55.5 |
| 2,2,4,5-Tetramethyl-1,3-dioxolane | 13 | 118–118.8(756 mm.)[b] | 1.4013[b] | 0.8899 | 35.57 | 35.61 | 61.0 |
| 2,2-Dimethyl-1,3-dioxolane | 13 | 91–92.5(756 mm.)[c] | 1.3964[c] | 0.9307[c] | 26.20 | 26.38 | 72.1 |
| Propylene glycol mono-*n*-butyl ether | 14 | 84–86(32 mm.)[e, f] | 1.4166 | 0.8769 | 37.88 | 37.69 | 72.0 |
|  |  | 86–88.5(31–32 mm.)[f, g] | 1.4175 | 0.8808 | 37.79 | 37.69 |  |
| Dipropylene glycol mono-*n*-butyl ether | 14 | 65.5–70(1 mm.)[i] | 1.4260 | 0.9112 | 53.51 | 53.19 | 25.5 |
| Propylene glycol mono-*n*-propyl ether | 14 | 66–72(30 mm.)[k] | 1.4116 | 0.8848 | 33.21 | 33.08 | 16.2 |
| Dipropylene glycol mono-*n*-propyl ether | 14 | 65–70(1 mm.) | 1.4218 | 0.9197 | 48.69 | 48.57 | 24.0 |
| Tripropylene glycol mono-*n*-propyl ether | 14 | 98.5–103(1 mm.) | 1.4295 | 0.9390 | 64.39 | 64.07 | 20.2 |
| 1-Methoxy-3-(1,3-dimethylbutylamino)-2-propanol | 15 | 83–84.5(1 mm.)[l] | 1.4439 | 0.9097 | 55.27 | 55.30 | 83.0 |

[a] B.p. 55.2° (760 mm.), $n_D^{25}$ 1.3667 (*30*). [b] B.p. 117° (744 mm.) and $n_D^{25}$1.4010 (*38*). [c] B.p. 92–92.5°, $n_D^{20}$ 1.4000, $d_4^{20}$ 0.9417 (*32*). [d] Prepared from 8 moles 1-butanol, 2 moles propylene oxide, and 6 ml. $BF_3$-etherate (50%). [e] Believed to be largely 1-*n*-butoxy-2-propanol. [f] For 1-*n*-butoxy-2-propanol, b.p. 74–74.5° (20 mm.), $n_D^{20}$ 1.4170, $d_{15.6}^{20}$ 0.880 and for 2-*n*-butoxy-1-propanol, b.p. 78–78.5° (20 mm.), $n_D^{20}$ 1.4192, $d_{15.6}^{20}$ 0.888 (*8*). [g] Believed to be largely 1-*n*-butoxy-2-propanol. [h] Prepared from 1.5 mole *n*-butanol, 3 moles propylene oxide and 4 ml. $BF_3$-etherate (50%). [i] B.p. 103° (10 mm.), $d_{20}$ 0.9185 and $n_D^{20}$ 1.4278 (*17*). [j] Prepared from 4 moles *n*-propanol, 8 moles propylene oxide and 12 ml. $BF_3$-etherate (50%). [k] B.p. 148.5–149°, $d_4^{20}$ 0.8857–0.8886, $n_D^{20}$ 1.4130 for 1-*n*-propoxy-2-propanol (*33*). [l] *Anal.* Calcd. for $C_{10}H_{23}NO_2$: C, 63.44; H, 12.25; N, 7.40. Found; C, 63.10, 63.35; H, 12.09, 12.18; N, 7.10, 7.27. The picrate, benzoyl, 3,5-dinitrobenxoyl, phenylthiourea and α-naphthylthiourea derivatives were all liquids.

mono-*n*-hexyl ether (hexyl Cellosolve) from Carbide and Carbon Chemical Co., and *sym*-trioxane from Celanese Chemical Co.

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# Metal Complexing by Phosphorus Compounds

## Solubilities of Magnesium Soaps of Linear Carboxylic Acids

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CALCIUM and magnesium are the two common cations contributing to water hardness. These cations participate in a number of undesirable reactions, one of which is soap precipitation. One way to soften the water is to "sequester" the cations with complexing agents, which in most cases are members of the polyphosphate family.

It is well known in the soap industry that water hardness caused by magnesium is more easily sequestered by polyphosphates than that caused by the presence of calcium. Yet, it has been shown recently (*3, 4*) that the formation constants of magnesium polyphosphate complexes are only slightly higher than the corresponding calcium complexes (*1*). Since sequestration against precipitation is dependent on the insolubility of the precipitate as well as the stability of the complex formed, measurement of solubilities of magnesium soaps is of interest and is reported in this paper. In a previous publication, the solubilities of calcium soaps of linear carboxylic acids were reported (*2*).

### EXPERIMENTAL

Purity of the chemicals and the complexometric procedure for determining solubility of precipitates were the same as previously (*2*) described for calcium soaps. Here again, the precipitation of magnesium soap at pH 12 was made to compete against complexing of magnesium by the tripolyphosphate anion.

### RESULTS AND DISCUSSION

Raw data (Table I) show the amount of $0.1M$ $Mg(NO_3)_2$ solution that must be added to a solution containing tripolyphosphate and linear carboxylate anions to reach a point of incipient precipitation. The individual experimental numbers in Table I are averages of two or more runs. When duplicates did not agree within the experimental error (±0.03 ml.), more checks were made to establish the values more precisely.

Since all the experimental data were collected at pH 12, the concentration of acidic complexes is negligible (*3, 4*). At the nephelometric endpoint, the material balance of magnesium is

$$YZ/A = (Mg^{+2}) + (MgP_3O_{10}^{-3}) + (2Mg_2P_3O_{10}^{-1}) \qquad (1)$$

where $A$ is the volume of solution in ml., $Z$ and $Y$ are the molar concentration and ml. of magnesium solution to reach the nephelometric endpoint, respectively, and parenthesis represent concentration. In reference *2*, there are two misprints: Table II shows logs of the formation constants rather than the negative log. Also, Equation 5 in Reference