Anal. Calcd. for $C_{18}H_{12}O_6$: C, 66.7; H, 3.73; 1 MeO—, 9.63; 1 CH_3CO—, 13.3. Found: C, 66.8; H, 3.82; MeO—, 9.59; CH_3CO—, 13.5.

7-O-Benzylcoumestrol. Coumestrol diacetate (3.0 g.) was refluxed with a mixture of benzyl chloride (30.0 ml.), potassium iodide (4.0 g.), anhydrous potassium carbonate (10.0 g.), and dry acetone (160 ml.) for 20 hr. The filtered acetone solution was evaporated to an oil. Warm hexane (100 ml.) was added, the mixture was cooled, and the crystalline precipitate was collected. It was purified by dissolving it in acetone (500 ml.). The filtered solution was concentrated to about 50 ml. and diluted with methanol (50 ml.). The colorless product (2.8 g.; m.p. 203°) was collected and recrystallized twice more from acetone-methanol. 7-*O*-Benzylcoumestrol acetate separated in colorless fluffy needles, m.p. 205°.

Anal. Calcd. for $C_{24}H_{16}O_6$: C, 72.0; H, 4.03; 1 CH_3CO—, 10.8. Found: C, 72.0; H, 4.09; CH_3CO—, 11.1.

A solution of the above acetate (2.6 g.) in acetone (400 ml.) was treated with ethanol (100 ml.), water (20 ml.), and concentrated hydrochloric acid (20 ml.). The mixture was heated on a steam bath for 1 hr., most of the acetone being allowed to evaporate during this period. Crystallization of the product then began. Water (80 ml.) was slowly added and the solid was collected. Recrystallized from acetone-methanol (charcoal), 7-*O*-benzylcoumestrol separated in colorless needles, m.p. 211° (1.8 g.). It dissolved instantly in cold aqueous sodium hydroxide to give a yellow solution.

Anal. Calcd. for $C_{22}H_{14}O_5$: C, 73.7; H, 3.94. Found: C, 73.7; H, 4.02.

Reacetylation of the 7-*O*-benzylcoumestrol gave 7-*O*-benzylcoumestrol acetate, m.p. 205°.

4'-O-Methyl-7-O-benzylcoumestrol. A mixture of the 7-*O*-benzylcoumestrol (1.4 g.), methyl iodide (15.0 ml.), anhydrous potassium carbonate (6.0 g.) and dry acetone (50 ml.) was refluxed for 2.5 hr. The filtered acetone solution was evaporated. The crystalline residue was washed with cold dilute aqueous sodium hydroxide and then recrystallized from acetone-methanol. 4'-*O*-Methyl-7-*O*-benzylcoumestrol was obtained in colorless felted needles, m.p. 187° (1.1 g.).

Anal. Calcd. for $C_{23}H_{16}O_5$: C, 74.2; H, 4.33; 1 MeO—, 8.39. Found:C, 74.2; H, 4.39; MeO—, 8.23.

4'-O-Methylcoumestrol. A solution of the 4'-*O*-methyl-7-*O*-benzylcoumestrol (1.0 g.) in glacial acetic acid (200 ml.) and concentrated hydrochloric acid (100 ml.) was heated on a steam bath for 15 min. Water (500 ml.) was added and the precipitated ether was collected. Recrystallized from acetone, 4'-*O*-methylcoumestrol separated in colorless needles, m.p. 337° (0.55 g.).

Anal. Calcd. for $C_{16}H_{10}O_5$: C, 68.1; H, 3.83; MeO—, 11.0. Found: C, 68.3; H, 3.77; MeO—, 10.7.

The 4'-*O*-methylcoumestrol was acetylated by boiling it with acetic anhydride and sodium acetate for 1 min. 4'-*O*-methylcoumestrol acetate crystallized from acetone-methanol in colorless needles, m.p. 240° (with sintering at 234°).

Anal. Calcd. for $C_{18}H_{12}O_6$: C, 66.7; H, 3.73; 1 MeO—, 9.63; 1 CH_3CO—, 13.3. Found: C, 66.9; H, 3.89; MeO—, 9.58; CH_3CO—, 13.3.

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Some Urethans Derived from 3-Amino-1-propanol[1]

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Previous publications[2,3] have shown that 3-amino-1-propanol and ethylene carbonate are convenient starting materials for preparing the cyclic urethan tetrahydro-2*H*-1,3-oxazin-2-one, now known[4,5] to be convertible to a polyurethan. In the course of a restudy[6] of the preparation and polymerization of this cyclic urethan, several hitherto unreported derivatives of 3-amino-1-propanol were prepared.

The immediate product from the reaction of 3-amino-1-propanol with ethylene carbonate at a temperature below 50° is a viscous liquid, identified by Delaby and coworkers[3] as 2-(hydroxyethyl)-*N*-3'-(hydroxypropyl)-urethan (I). The yield of this product, not given by previous workers,[2,3] was shown to be practically quantitative by conversion to the dicarbanilate (VI). Heating the viscous liquid gives the cyclic urethan (II).

Another route to the cyclic urethan involved *N*-3-hydroxypropyl-*N'*-phenylurea (III), which was obtained by the reaction of 3-amino-1-propanol with phenyl isocyanate under mild conditions. The urea (III) was converted to the urethan (II) by applying Weickmann's method of ring closure.[7] The structure of the urea (III) was indicated by its amide carbonyl absorption at 1625 cm.$^{-1}$ and at 1541–1600 cm.$^{-1}$ with the absence of absorption characteristic of the urethan carbonyl. By treatment of the urea (III) with phenyl isocyanate in the presence of triethylamine, a quantitative yield of the 3-phenylurethan (VII) was obtained. This compound showed urethan carbonyl absorption at 1653 cm.$^{-1}$ in addition to the amide absorption bands of compound (III).

The cyclic urethan (II) gave a γ-phenylallophanate, (V), when treated with phenyl isocyanate during heating.

In agreement with recent work[4,5] and contrary to our previous statement,[2] the cyclic urethan (II) polymerized on heating, to give the polyurethan

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[1] From the M.S. thesis of R. E. Read, University of Delaware, 1957.

[2] E. Dyer and H. Scott, *J. Am. Chem. Soc.*, **79**, 672 (1957).

[3] R. Delaby, R. Damiens, and G. d'Huyteza, *Compt. rend.*, **239**, 674 (1954).

[4] E. K. Drechsel, U. S. Patent **2,701,246**, Feb. 1, 1955; *Chem. Abstr.*, **50**, 2686 (1956); and U. S. Patent **2,744,897**, May 8, 1956; *Chem. Abstr.*, **51**, 498 (1957).

[5] H. K. Hall, Jr., and A. K. Schneider, *J. Am. Chem. Soc.*, **80**, 6409 (1958).

[6] The authors were then unaware of the work in ref. (4) and (5).

[7] A. Weickmann, Ger. Patent **858,402**, Dec. 8, 1952; *Chem. Abstr.*, **47**, 11255 (1953).

(IV). Barium oxide speeded the reaction. By heating I in such a way as to cause elimination of ethylene glycol, II or IV or mixtures of II and IV could be obtained, depending on the conditions. Pyrolysis of the polyurethan gave the cyclic urethan (in 9% yield), carbon dioxide, and water-soluble degradation products.

EXPERIMENTAL

2-Hydroxyethyl-N-3′-hydroxypropylurethan (I) *and its dicarbanilate* (VI). To 3.52 g. (0.040 mol.) of ethylene carbonate[8] (b.p. 79° at 0.2 mm.) was added 3.00 g. (0.040 mol.) of 3-amino-1-propanol[9] (b.p. 54–56° at 1 mm.) with cooling to keep the temperature below 50°. To 6.21 g. (0.040 mol.) of the presumed 2-hydroxyethyl-*N*-3′-hydroxypropylurethan (I) was added 9.00 g. (0.065 mol.) of distilled phenyl isocyanate and the mixture warmed gently. The product, isolated by solution in boiling methanol and precipitation with water, consisted of 15.0 g. (a 98.6% yield) of solid, m.p. 116–118°. The infrared spectrum of the compound in KBr showed strong infrared absorption bands at 1700 cm.$^{-1}$ (C=O) and at 3333 cm.$^{-1}$ (N—H) characteristic of linear urethans.[10]

Anal. Calcd. for $C_{20}H_{23}N_3O_6$: C, 59.83; H, 5.73; N, 10.52. Found: C, 60.50; H, 5.78; N, 10.32.

N-3-Hydroxypropyl-N′-phenylurea (III). Treatment of 5.00 g. (0.067 mol.) of 3-amino-1-propanol with 14.40 g. (0.121 mol.) of phenyl isocyanate in 40 ml. of dry xylene at room temperature gave a 98% yield of III, m.p. 108–110°. After recrystallization from chloroform–petroleum ether, the compound melted at 110–111°.

Anal. Calcd. for $C_{10}H_{14}N_2O_2$: C, 61.89; H, 7.20; N, 14.43. Found: C, 62.00; H, 7.30; N, 14.32.

3-Phenylurethan of N-3-hydroxypropyl-N′-phenylurea (VII). By refluxing an ether solution of 0.400 g. (0.002 mol.) of III, 7.50 g. (0.063 mol.) of phenyl isocyanate, and three drops of triethylamine, a 99% yield of VII was obtained, m.p. 148–150°. After recrystallization from chloroform the substance melted at 149–150°.

Anal. Calcd. for $C_{17}H_{19}N_3O_3$: C, 65.18; H, 6.07; N, 13.47. Found: C, 64.90; H, 5.97; N, 13.16.

Tetrahydro-2H-1,3-oxazin-2-one (II).[2–5] Heating for 3 hr. under nitrogen at 0.5–1.0 mm. the viscous I from 0.298 mol. of 3-amino-1-propanol and 0.299 mol. of ethylene carbonate, and then distilling, gave ethylene glycol and a 74% yield of II.

Compound II was also obtained in 76% yield by treating 20.0 g. (0.268 mol.) of 3-amino-1-propanol with 12.0 g. (0.103 mol.) of phenyl isocyanate during cooling, heating the mixture in the presence of 0.5 g. of potassium carbonate at 160° for 3 hr., and distilling at 0.4 mm. under nitrogen. Fractions contained aniline (0.077 mol.) identified through the phenyl thiourea,[11] and II (0.077 mol.).

γ-Phenylallophanate of tetrahydro-2H-1,3-oxazin-2-one (V). A mixture of 1.26 g. (0.012 mol.) of II and 11.9 g. (0.100 mol.) of phenyl isocyanate was heated at 125° for 15 hr. After removal of excess isocyanate by distillation under reduced pressure, the resulting solid weighed 1 g., m.p. 118–120° (38% yield). After washing with ether and recrystallizing from chloroform-ligroin, the compound melted at 120–122° and depressed the melting point of VI; λ_{max}^{KBr} 1695, 1640, 1594, 1550–1525 cm.$^{-1}$

Anal. Calcd. for $C_{11}H_{13}N_2O_3$: C, 59.71; H, 5.88; N, 12.73. Found: C, 60.15; H, 5.53; N, 12.71.

Polyurethan (IV). Extended heating of II, especially in the presence of barium oxide, caused partial conversion to a low polymer. Unchanged monomer was removed by its solubility in acetone. The polymer melted at 125–131° and showed typical absorption[2] for a polyurethan.

Anal. Calcd. for $(C_4H_7NO)_n$: N, 13.87. Found: N, 13.87; mol. wt. (ebullioscopic), 1500; $[\eta]$, 0.0659 (in dimethyl formamide at 25°).

The polyurethan was also prepared directly from I. When I was heated under nitrogen at 145° for 14 hr. at about 1 mm., ethylene glycol was distilled and the pot residue contained a 23% yield of polyurethan. Extending the initial heating to 29 hr. gave 30% of the cyclic urethan and 31% of the polyurethan. But advancing the heating to 107 hr. at 140–170° gave only degradation products.

When a sample of the polyurethan was heated for 14 hr. at 160–180° at 1 mm., a 9.3% yield of II and an equivalent amount of carbon dioxide were formed, together with unidentified, water-soluble substances.

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(8) Kindly supplied by Jefferson Chemical Company.

(9) Kindly supplied by American Cyanamid Company.

(10) H. K. Hall, Jr., and R. Zbinden, *J. Am. Chem. Soc.*, **80**, 6428 (1958).

(11) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, Fourth Ed., J. Wiley and Sons, Inc., New York, 1956, p. 288.

Preparation of Anhydrous Sodium Peracetate and Sodium Perbutyrate

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Kolesnikov[2] has described the isolation of anhydrous sodium performate by trituration of green barley leaves with sodium phosphate.

In the present investigation, it has been our purpose to develop a more general method for the preparation of anhydrous metal salts of aliphatic percarboxylic acids. Thus, the two salts, sodium peracetate and sodium perbutyrate, have been prepared.

For this purpose, we first required a solution of peracetic acid in an inert solvent as free as possible from acetic acid, as even small amounts of acetic acid will contaminate the final product with sodium acetate.

A convenient method for obtaining such a solution was found using commercially available peracetic acid[3] which contains 39% of acetic acid and 1% of sulphuric acid as impurities.

As peracetic acid is very weakly acidic, having a *p*K of 8.2,[4] it was possible by neutralization to a *p*H of 8.0 followed by extraction to obtain almost pure peracetic acid in an inert solvent.[5] The

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(1) Present address: Ayerst, McKenna & Harrison, Ltd. Montreal, Canada.

(2) P. A. Kolesnikov, *Chem. Abstr.*, 4730 (1949); *Doklady. Akad. Nauk. S.S.S.R.*, **64**, 99 (1949).

(3) Becco Chemical Division of FMC, Buffalo, New York.

(4) A. J. Everett and G. J. Minkoff, *Trans. Farad. Soc.*, 49, 410 (1953).

(5) Subsequent to the completion of this work, another method has been described for obtaining solutions of peracetic acid in inert solvents. B. Phillips, F. C. Frostick, and P. S. Starcher; *J. Am. Chem. Soc.*, **79**, 5982 (1957).