(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

LESLIE G. HUMBER[1]

Received May 1, 1959

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).

sodium salt was then obtained by precipitation with alkali.

For the preparation of sodium perbutyrate, perbutyric acid was prepared from butyric acid and 90% hydrogen peroxide[6] and the salt was prepared as in the case of sodium peracetate.

The salts so obtained were found to contain one atom of active oxygen which could be analyzed iodometrically.

In the analysis of the active oxygen content, it was found that on treating with acidified potassium iodide solution, in neither case was liberation of iodine instantaneous; thus in the case of sodium peracetate, iodine liberation was complete only after 30 min. at room temperature and in the absence of light while sodium perbutyrate required 75 min. under the same conditions.

Sodium peracetate decomposes at 55° leaving a residue which contains no active oxygen. On standing at room temperature for 3 days in a moist atmosphere, a sample of sodium peracetate lost all of its active oxygen content and when a sample was stored *in vacuo* at room temperature, the active oxygen content had decreased by 66% after 24 hr. and by 93% after 7 days.

EXPERIMENTAL

Note: The use of a safety shield is recommended in carrying out the following reactions.

Sodium Peracetate. A saturated solution of sodium carbonate was added with constant stirring to "Becco" peracetic acid[3] (50 ml.) at 8–10° until a *p*H of 8.0 was obtained as indicated by a *p*H meter. The resulting mixture was extracted with ether (5 × 50 ml.) and the extracts dried over magnesium sulfate. Analysis of an aliquot showed that the combined extracts contained 5.94 g., of peracetic acid. To the ethereal solution was added at 0°, sodium hydroxide (3.13 g.) dissolved in water (5 ml.) and 95% ethanol (70 ml.), causing an immediate precipitate. It was allowed to stand for 15 min. The salt was separated by filtration, washed with ethanol, then with ether and dried *in vacuo* at room temperature.

The sodium peracetate was analyzed for active oxygen iodometrically and for sodium gravimetrically as the sulfate.[7] Found: active O, 16.42; Na, 24.31% CH_3CO_3Na requires: active O, 16.32; Na, 23.46%.

Sodium perbutyrate. To an aqueous solution of perbutyric acid at 0° was added a saturated solution of sodium carbonate until a *p*H of 8.0 was obtained as indicated by a *p*H meter. To the pure peracid (2.7 gm.) in ethyl acetate was added at 0°, sodium hydroxide (1.05 gm.) dissolved in 95% alcohol. On standing at 0° for 2 hr., sodium perbutyrate precipitated. It was filtered off, washed and dried *in vacuo* at room temperature and analyzed for active oxygen iodometrically. Found: active O, 12.80% $C_4H_7O_3Na$ requires: active O, 12.68%.

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(6) J. D'Ans and W. Frey, *Ber.*, **45**, 1845 (1912).

(7) A similar preparation of several grams of dry sodium peracetate exploded violently, while sitting in a flask at room temperature. Caution is recommended in handling this compound.

A New Technique in Preparing 2,4-Dinitrophenylhydrazones. III. Two Examples of Hitherto Unobtainable Simple Derivatives: Diacetone Alcohol and Methyl Vinyl Ketone

HENRY J. SHINE

Received May 4, 1959

Recently[1] the convenient use of diglyme (dimethylether of diethylene glycol) solutions of 2,4-dinitrophenylhydrazine for preparing 2,4-dinitrophenylhydrazones was described. It was suggested at that time that the new technique might be usable for preparing 2,4-dinitrophenylhydrazones of sensitive compounds. This suggestion has now been found to be valid, and in view of the interest that has been shown in the earlier publication[1a] we are prompted to illustrate the further usefulness of the new technique with two examples. We have been able to prepare for the first time the true derivative of diacetone alcohol and the derivative of methyl vinyl ketone.

Diacetone alcohol. The 2,4-dinitrophenylhydrazone, melting point 203°, that is everywhere listed as the derivative of diacetone alcohol, is really the derivative of mesityl oxide. The conventional methods of preparation[1a] of the 2,4-dinitrophenylhydrazone cause the acid-catalyzed dehydration of the ketol to mesityl oxide.

If a solution of diacetone alcohol in a diglyme solution of 2,4-dinitrophenylhydrazine is acidified with acetic acid, however, the orange derivative, I, formed is that of diacetone alcohol and has a melting point of 157–159°. If, instead of acetic acid, hydrochloric acid is used, or if I is dissolved in ethanol and acidified with hydrochloric acid, the dark red derivative of mesityl oxide is obtained.

Methyl Vinyl Ketone. The only report of the reaction of 2,4-dinitrophenylhydrazine with this simple ketone is that of I. N. Nazarov and coworkers.[2] These authors report a compound with a melting point of 217°, the carbon analysis of which was 2.3% low for the expected derivative. They do not appear to have accepted their derivative as authentic. We have prepared the authentic derivative of this ketone; it has a melting point of 139.5–140.5°. It was prepared first in these laboratories by the diglyme technique using hydrochloric acid for catalysis. If attempts were made to prepare this derivative by conventional methods, using ethanol as solvent, the derivative was not obtained, but one of the products obtained was the derivative of 4-ethoxybutanone-2, melting point 92–93°. If methanol were used as a solvent, the derivative of 4-methoxybutanone-2 was obtained,

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(1) (a) H. J. Shine, *J. Org. Chem.*, **24**, 252 (1959); (b) H. J. Shine, *J. Chem. Ed.*, **36**, 575 (1959).

(2) I. N. Nazarov, L. A. Kazitsyna and I. I. Zaretskaya, *Zhur. Obshchei Khim.*, **27**, 606 (1957).