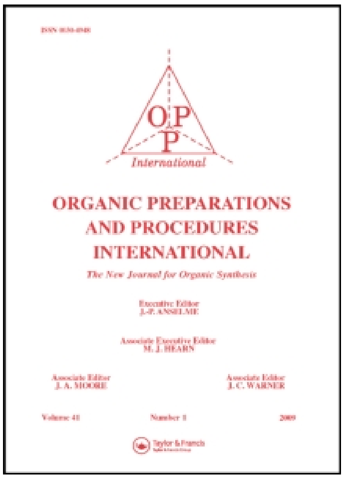

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3-(2-HYDROXYETHYL) TETRAHYDROFURAN. CYCUZATIONS IN LITHIUM ALUMINUM HYDRIDE REDUCTIONS

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3-(2-HYDROXYETHYL)TETRAHYDROFURAN. CYCLIZATIONS IN LITHIUM ALUMINUM HYDRIDE REDUCTIONS

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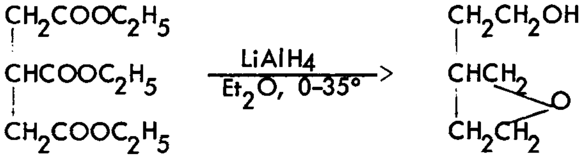
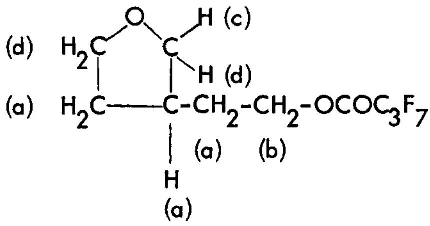
Although it is known that in the reduction of several polyfunctional compounds by lithium aluminum hydride cyclic ethers and amines can be formed, the occurrence is rare and the yields have not been reported.[1] We have found that the reduction of triethyl propane-1,2,3-tricarboxylate (triethyl tricarballylate) gives 3-(2-hydroxyethyl)tetrahydrofuran in 38% yield.


I

The proton n.m.r. spectrum had a multiplet representing 5 protons between 1.10 and 2.56 p.p.m. relative to tetramethylsilane (T.M.S.), a multiplet between 3.15 and 4.02 p.p.m. representing 6 protons, and a singlet at 4.33 p.p.m. representing one proton. The line at 4.33 p.p.m. was shifted to 4.75 p.p.m. by the addition of HCl so is due to a hydroxyl. The group between 3.15 and 4.02 p.p.m. was separated by making the perfluorobutyrate ester which shifted the triplet for the two protons adjacent to the hydroxyl to 4.42 p.p.m. (b) leaving a doublet split into a doublet at 3.36 p.p.m. (c) representing one proton and a multiplet between 3.62 and 4.08 p.p.m. representing three protons (d). The multiplet between 1.10 and 2.56 p.p.m. could not be fully assigned but the fact that it was a complex of fairly sharp lines adds credence to the presence of a cyclic structure in which the environment of each proton is slightly different rather than an open-chain structure in which geminal protons see an averaged environment. It represents the five protons (a). This pattern, particularly the triplet at 4.42 (b) and the doublet of doublets at 3.36 (c), is consistent with I and eliminates a pyran structure.



The mass spectra of the alcohol and the ester also bore out the tetrahydrofuran ring structure since the cleavage pattern indicated a side chain loss to a furan ring rather than a pyran ring and the ester fragments included a pattern involving a two-carbon chain before branching rather than just one carbon.

Reduction of triethyl tricarballylate by lithium aluminum hydride has been reported[2] as giving 1,2,3-trimethylolpropane but without details; the product had properties consistent with that structure. On reduction in ether both at reflux temperature and at -5 to 0°, we obtained only the cyclized product.

It appears that in order for cyclization to occur a compound must have three positions at which aluminum salts can form, either through reduction or by reaction with an active hydrogen. All known examples have had this characteristic. For example, diethyl glutamate was reduced to 2-hydroxymethyl pyrrole[3], 4-cyano-4-ethoxycarbonyl tetradecanonitrile to 3-aminomethyl-3-decylpiperidine[4], and diethyl-3-methyl-3-(ethoxycarbonylmethyl)glutarate to 4-methyl-4-(2-hydroxyethyl)tetrahydropyran[5]. Reduction of a series of 2-alkylsuccinic esters, even those where the 2-alkyl group is branched, gave only the diols on reduction.[6]

EXPERIMENTAL

Boiling points are uncorrected. The NMR spectra were obtained using a Varian model A-60, 60 megacycle spectrometer (Varian Associates, Palo Alto, Calif.). Tetramethylsilane was an internal standard and $CDCl_3$ was the solvent.

Reduction of Triethyl Propane-1,2,3-tricarboxylate. - A solution of 24 g (0.092 mole) of triethyl propane-1,2,3-tricarboxylate in 40 ml of anhydrous ether was added to 8 g (0.22 mole) of $LiAlH_4$ in 250 ml of anhydrous ether at such a rate that the temperature remained at -5 to 0°. The mixture was stirred for 0.5 hour and the excess $LiAlH_4$ destroyed by the addition of ethyl acetate. Water, 50 ml, was added and the pH adjusted to 9.0 with 50% NaOH. Addition of 500 ml of acetone precipitated 31 g of salts which were removed by filtration. Distillation of the filtrate gave 4 g (0.035 mole), 38%, of 3-(2-hydroxyethyl)tetrahydrofuran, bp 80° (0.3 mm), n_D^{20} 1.4585.

Anal. Calcd for $C_6H_{12}O_2$: C, 62.04; H, 10.41. Found: C, 61.79; H, 10.44.

Another reduction in refluxing ether gave the same alcohol. No product was obtained corresponding to the properties of 1,2,3-trimethylolpropane, reported to boil at 162° (0.5 mm), n_D^{20} 1.4800.[2]

Esterification. - A mixture of 14 g (0.12 mole) of 3-(2-hydroxyethyl)-tetrahydrofuran and 84 g (0.39 mole) of heptafluorobutyric acid was refluxed in 150 g of $CHCl_3$ for 31.5 hours during which time water was separated in the distillation head. Distillation gave 32 g (0.15 mole) of heptafluorobutyric acid and 50 g of liquid boiling between 84 and 94° (0.1 mm).

A portion was washed with 5% sodium bicarbonate to remove complexed perfluorobutyric acid and the ester distilled, bp 68.9° (1.2 mm), n_D^{20} 1.3671. The infrared, n.m.r., and mass spectra confirmed the structure of the ester.

Anal. Calcd for $C_{10}H_{11}F_7O_3$: C, 38.47; H, 3.55; F, 42.60. Found: C, 38.58, 38.29; H, 3.29, 3.26; F, 42.81, 42.95.

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REFERENCES

1. N. G. Gaylord, "Reductions with Complex Metal Hydrides", Interscience Publishers, Inc., New York, N. Y., 1956, pp. 416-17.
2. P. D. Faurote, C. M. Henderson, C. M. Murphy, J. G. O'Rear, and H. Ravner, Ind. Eng. Chem., 48, 445-54 (1956).
3. P. Karrer and P. Portmann, Helv. Chim. Acta, 31, 2088 (1948).
4. V. C. Barry, J. G. Belton, R. M. Ketty, and D. Twomey, Nature, 166, 303 (1950).
5. R. Lukes and M. Ferles, unpublished results reported in J. Rudinger, M. Ferles, and M. Protiva, Chem. Listy, 45, 355 (1951).
6. C. G. Overberger and C. W. Roberts, J. Am. Chem. Soc., 71, 3618 (1949).

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