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OXIDATION OF ORGANIC COMPOUNDS WITH CERIUM(IV). IX. FORMATION OF 2-METHYLTETRAHYDROFURAN BY OXIDATION OF 1-PENTANOL (1)

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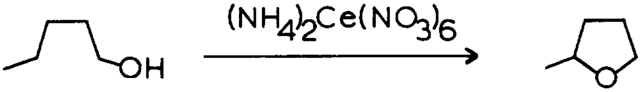
Although benzyl alcohols (2,3) and cyclopropanemethanol (4) are converted to the corresponding aldehydes in nearly quantitative yield by the oxidation with ceric ammonium nitrate (CAN), we have found that many other alcohols undergo a cleavage reaction when oxidized with CAN (1,5). In this communication we wish to report that the CAN oxidation of a typical primary aliphatic alcohol, 1-pentanol, gives the corresponding tetrahydrofuran as the major neutral product and only traces of the corresponding aldehyde. Tetrahydrofuran formation is thus the third type of reaction that alcohols undergo when oxidized with CAN.



A quantity of 5 mmoles of 1-pentanol (obtained from Mallinckrodt) was dissolved in 40 ml of aqueous 0.5 M CAN solution (‡). The deep red solution

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‡The reaction can be carried out in aqueous acetic acid and aqueous acetonitrile solutions. These solvents may be more useful for higher molecular weight alcohols.

was heated on a steam bath for 30 min. After 5 min of heating, the solution turned colorless and cloudy. After an additional 25 min of heating (‡‡), the clear solution was allowed to cool and 1.5 mmoles of the internal standard, 3-pentanone, was added. The solution was extracted with 40 ml of ether. The ether solution was washed with 20 ml of 2 N sodium hydroxide solution, dried ($MgSO_4$), and analyzed by glpc. Yields were determined by making use of relative extraction ratios and thermal conductivities which were determined by the method that was previously described (3). The identity of the 2-methyltetrahydrofuran was confirmed by glpc peak enhancement with an authentic sample (obtained from Matheson, Coleman and Bell) on three different columns.*** Further confirmation of the production of 2-methyltetrahydrofuran was obtained from the nmr spectrum of the products. A reaction mixture to which no internal standard had been added was extracted with 5 ml of carbontetrachloride instead of ether. The carbontetrachloride solution was washed with sodium hydroxide and dried. An nmr spectrum of the solution clearly showed the presence of the doublet of the methyl group of 2-methyltetrahydrofuran at 1.12 δ (J=6 cps). The spectrum was consistent with that of a mixture of 2-methyltetrahydrofuran and 1-pentanol.

In Table I are presented yields of 2-methyltetrahydrofuran and recovered 1-pentanol obtained from the CAN oxidation of 1-pentanol in water at 90° for 30 min. It is seen that based on the amount of alcohol used, 20% 2-methyltetrahydrofuran is produced. Since only traces of other neutral products were observed by glpc, products other than the tetrahydrofuran must be acidic or very water soluble.

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‡‡Shorter reaction times resulted in lower yields of 2-methyltetrahydrofuran. Possibly the tetrahydrofuran is freed from a metal complex as the reaction mixture turns from cloudy to clear.

***The columns used were 4' x 1/4" packed with 20% carbowax 20 M on chromosorb P (60/80 mesh), 5' x 1/4" packed with UCON HB-2000 (polar) chromosorb P (60/80 mesh), and 5' x 1/4" packed with 20% SF-96 silicone fluid on chromosorb W (60/80 mesh). The columns were used at 110°.

Table I. Yields of 2-Methyltetrahydrofuran (MTHF) and Recovered Alcohol from the Oxidation of 1-Pentanol (PenOH) with Ceric Ammonium Nitrate (CAN) in Water at 90°.

Concentration of CAN, M	Concentration of PenOH, M	Yield of MTHF, %[a]	Amount of Recovered PenOH, %[a]	Yield of MTHF based on PenOH used, %[a]
0.25	0.125	11.5 ± 0.2	42.5 ± 1.3	20.0 ± 0.8
.5	.125	15.2 ± 0.1	18.8 ± 0.6	18.7 ± 0.3

[a] Yields are based on three runs; the mean deviation is given.

Lead tetraacetate (LTA) is the only other metal oxidant that has been reported to oxidize primary alcohols to tetrahydrofurans (6). The yield of 2-methyltetrahydrofuran from the oxidation of 1-pentanol by CAN is comparable to that obtained from the oxidation by LTA (7, 8). Partch (7) reported that oxidation of 1-pentanol by LTA in 50:50 heptane-acetic mixture gave 31% 2-methyltetrahydrofuran and Mihailovic *et al.* (8) reported that the same oxidation in benzene gave 37-43%* of 2-methyltetrahydrofuran. Thus tetrahydrofuran formation may be quite high in the oxidation of more rigid alcohols by cerium(IV) as it is with lead(IV) (9).

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*Partch (7) reported that only 25% of the tetrahydrofuran was obtained when the reaction was carried out in benzene.

REFERENCES

1. Paper VIII. W. S. Trahanovsky, P. J. Flash, and L. M. Smith, J. Am. Chem. Soc., in press.
2. W. S. Trahanovsky and L. B. Young, J. Chem. Soc., 1965, 5777.
3. W. S. Trahanovsky, L. B. Young, and G. L. Brown, J. Org. Chem., 32, 3865 (1967).
4. L. B. Young and W. S. Trahanovsky, ibid., 32, 2349 (1967).
5. P. M. Nave and W. S. Trahanovsky, J. Am. Chem. Soc., 90, 4755 (1968).
6. K. Heusler and J. Kalvoda, Angew. Chem. Intern. Ed. Engl., 3, 525 (1964).
7. R. E. Partch, J. Org. Chem., 30, 2498 (1965).
8. M. Lj. Mihailovic, J. Bosnjak, Z. Maksimovic, Z. Cekovic, and Lf. Lorenc, Tetrahedron, 21, 955 (1966).
9. K. B. Wiberg, Ed., "Oxidation in Organic Chemistry," Academic Press, New York, N. Y., 1965, pp. 321-326.