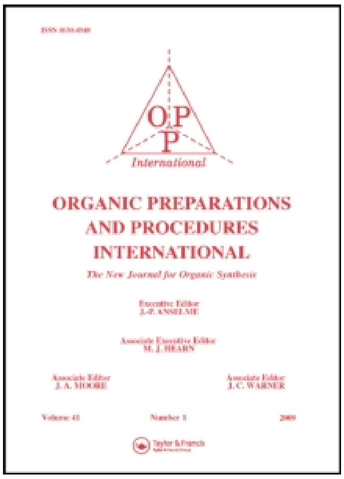

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DEOXYGENATION OF EPOXIDES WITH ALUMINUM

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Anal. Calcd for $C_{11}H_{10}N_2O_4$: C, 56.41; H, 4.30; N, 11.96

Found: C, 56.52; H, 4.60; N, 12.04

5-Carbomethoxy-6-hydroxy-2-methyl-7-oxo-isoxazolo[2,3-a]pyrimidine (4).- A mixture of 3-amino-5-methylisoxazole (98 mg), 1b (260 mg) and methanol (4 ml) was heated under reflux for 4 hrs. The solvent was evaporated and the oily residue crystallized upon cooling. Crystallization from 1-propanol yielded the product (85 mg, 40% yield), mp. 164-166°.

^{1}H NMR ($CDCl_3$): δ 2.20 (s, 3H, Me), 3.85 (s, 3H, COOMe), 5.65 (s, 1H, H-3), 6.80 (bs, 1H, OH).

Anal. Calcd for $C_8H_8N_2O_5$: C, 45.29; H, 3.80; N, 13.21

Found : C, 45.42; H, 4.02; N, 13.48

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DEOXYGENATION OF EPOXIDES WITH ALUMINUM

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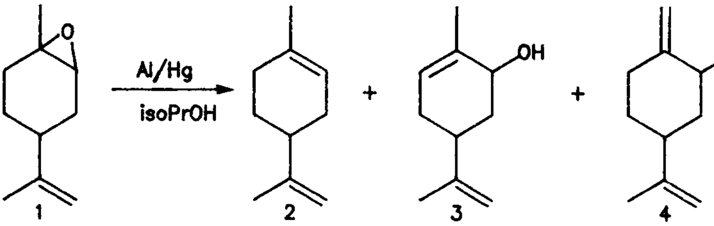
Amalgamated aluminum dissolves readily in isopropanol to give aluminum isopropylate and hydrogen. It was thought that this economical and easy-to-handle system might be capable of reducing epoxides to alcohols and provide a useful alternate to expensive reagents such as lithium aluminum hydride. When applied to limonene epoxide (1), instead of the desired β-terpineol (5), there was obtained a mixture of allylic alcohols (3 and 4) by alkoxide-catalyzed rearrangement[1] and, surprisingly, a significant amount of a hydrocarbon which was identified by its GC retention time on two different columns and by GC/MS as limonene (2)!



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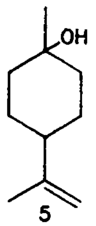

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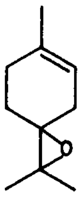
This discovery is interesting in light of a recent comment by Shields and Schuster[2] that "facile epoxide deoxygenation is a sought-after synthetic process". Two reviews describe a variety of reagents which are useful for this purpose.[3,4] Some, such as samarium diiodide[5] now commercially available, are rather exotic and new ones continue to be described.[6-9] The present finding represents a potentially useful alternative employing a comparatively simple and inexpensive system.

By modifying the reaction conditions such as by dilution of the system with toluene or by use of a less reactive alcohol, e. g. t-butanol, the competing side-reaction to allylic alcohols, catalyzed by aluminum alkoxides,[1] can be minimized and respectable yields of olefins are obtained. The function of the alcohols, without which no reaction occurs, appears to be that of continuous regeneration of an active aluminum surface which can then react not only with more alcohol, but also with other oxygenated species such as the epoxide from which it removes oxygen to yield the olefin. The product composition may therefore depend on the relative amounts of alcohol and epoxide and on the relative ease with which the epoxide is deoxygenated by the activated metal surface or rearranged by the dissolved alkoxide.

Using the preferred toluene dilution modification, five epoxides (1, 6-9) were refluxed with an equal weight of isopropanol, a trace of mercuric chloride and some aluminum foil. In every case, the deoxygenated product was the same olefin from which the epoxide was made. Yields were estimated by GC analysis using the toluene as internal standard (Table 1).



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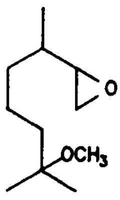

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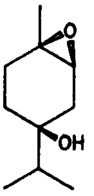

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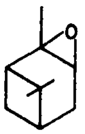

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TABLE 1. Deoxygenation of Various Epoxides

Epoxide	Product	Reflux(hrs)	Conversion (%)	Yield (%)
1	Limonene	3	99	80
6	Terpinolene	3	98	88
8	Terpinen-4-ol	2	100	86
7	MeO-Citronellene	2[a]	99	90
9	α-Pinene	1[a]	100	68

a) Plus 17 hrs at room temperature.

In two preparative-scale experiments on the epoxides of D- and L-limonene, the estimated limonene yield was confirmed and, polarimetry showed retention of optical activity and sign (Table 2). Thus the double bond had been regenerated in its original position with respect to the chiral center at C4.

TABLE 2. Limonene Yield and Specific Rotation

Starting Material	Yield(mole%)	Specific Rotation
D-Limonene epoxide	82	+98.6°
L-Limonene epoxide	87	-101.9°

EXPERIMENTAL SECTION

The monoepoxides (1, 6, 9) of limonene, terpinolene (1 and 6) and of α-pinene were purchased from Viking Chemical Co. and Aldrich and used as received. Methoxycitronellene and terpinen-4-ol were epoxidized to 7 and 8 with 3-chloroperoxybenzoic acid in methylene chloride[10] and t-butylhydroperoxide in toluene with a vanadium catalyst[11] respectively. The crude epoxides were used without further purification. "Reynolds Wrap" heavy-duty aluminum foil was used throughout. The identity of the products was determined by GC retention times compared with reference standards and /or by GC/MS analysis.

Small Scale Screening Procedure.- The epoxide (5 g), toluene (20 g), isopropanol (5 g), aluminum foil (2 g) and mercuric chloride (0.1 g) in a 100 ml RB flask fitted with a condenser and magnetic stirrer was heated at reflux under nitrogen with provision for escape of hydrogen from the reaction flask. Samples taken hourly, were shaken with water and extracted into methylene chloride for analysis on a 12' x 0.25" glass column packed with Carbowax 20 M and temperature programmed at 80° for 10 min., then at 10°/min. to 210°. Yield estimates were made by comparing the product analysis at complete conversion with that of a solution of 4.5 g of the pure product olefin in 20 g of toluene.

Preparative-scale Procedure.- A 1 l. Morton flask was charged with toluene (200 g), D-limonene epoxide (50 g, 96.3% purity; 0.317 mole, specific rotation +60°), mercuric chloride (1 g), isopropanol (50 g) and aluminum foil (20 g). The foil was cut into pieces and rolled into small balls. The mixture was mechanically stirred under nitrogen and heated to reflux and monitored hourly by GC analysis. When reaction was complete (2 hrs), the stirred mixture was allowed to cool overnight, and then decanted from unreacted aluminum and vacuum-filtered to remove some fine dark solid. Toluene was used as rinse liquid. The filtrate was distilled at atmospheric pressure through a 10-plate Oldershaw column to recover toluene (244 g), then limonene (30.1 g) of 99% purity , bp. 170-172° and a further 5.5 g of limonene, bp. 53°/26mmHg, of 99.4% purity was obtained. The total recovered was 35.3 g (82%). The neat product in a 10 dm tube had a rotation of +98.6° (sodium lamp).

The procedure was repeated using 50 g of L-limonene epoxide (97.9% purity, 0.322 mole, specific rotation -64.4°). The reaction took 6 hrs to be complete. Distillation of the filtered product solution gave 31.7 g of L-limonene of 99.6% purity having a specific rotation of -101.9°. A further 8.9 g of product of 73% purity was obtained from the distillation residue (69 g) after treatment with 5% aqueous sulfuric acid to dissolve out the aluminum isopropylate. The total yield of limonene was 38.1 g (87%) .

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