THE REACTION OF TRIETHYLALUMINUM WITH EPOXIDES*

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SUMMARY

Triethylaluminum and 1,1-dialkylethylene oxides yield as major products (after hydrolyses) substituted neopentyl alcohols. Triethylaluminum and propylene oxide react (mole ratio > 1) forming 2-methylbutanol in high (ca. 98%) yield. The products of this reaction are dependent on the mole ratio of reactants. When the ratio (triethylaluminum/propylene oxide) is 0.7, 2-pentanol is the major product. The products of reaction with *cis*- and *trans*-2,3-epoxybutane (mole ratio triethylaluminum/epoxide > 1) were *threo*-3-methyl-2-pentanol and *erythro*-3-methyl-2-pentanol respectively indicating inversion had occurred at the carbon receiving the ethyl group. Mechanisms for these reactions are discussed.

INTRODUCTION

When an organometallic compound is allowed to react with an unsymmetrically substituted epoxide, two alcohols are possible, depending on the direction of the ring opening. If the metal is magnesium, and if addition is not preceded by isomerization of the epoxide to a carbonyl compound, addition of the organic residue occurs at the least substituted carbon. Attack of the organic residue at the most substituted carbon occurs when this carbon is benzylic or allylic[1].

Trialkylalanes are powerful Lewis acids which complex and react with many oxygen-containing compounds[2,†]. We have investigated several aspects of the reactions of triethylaluminum with epoxides. The first stage of the reaction of triethylaluminum with epoxides is considered to involve coordination to form a complex with a dative bond from oxygen to the aluminum atom, similar to that observed with ethers and carbonyl compounds[2]. When triethylaluminum was added to *cis*-2,3-epoxybutane in *o*-dichlorobenzene, the NMR signals of hydrogen attached to carbons bearing the epoxide oxygen were observed to shift downfield by 0.8 ppm as the mole ratio became 1/1. As the proportion of triethylaluminum was increased to 2/1, no further shift was observed. That this shift was not due to irreversible change of the epoxide was determined by GLC analyses.

RESULTS

Reaction of *cis*-2,3-epoxybutane and triethylaluminum (mole ratio triethyl-aluminum/epoxide > 1) at 80° followed by hydrolytic work-up of the reaction gave good yields (75%) of *threo*-3-methyl-2-pentanol. The *erythro* isomer was not detect-able. Similarly, *trans*-2,3-epoxybutane gave *erythro*-3-methyl-2-pentanol. These reactions were accompanied by some reduction of epoxide to 2-butanol.

The reaction of triethylaluminum with propylene oxide yields 2-pentanol and 2-methyl-1-butanol. At mole ratios > 1, 2-methyl-1-butanol is formed in high yield. As the mole ratio is decreased to unity and below the amount of 2-pentanol increases (Table 1).

TABLE 1

REACTION OF TRIETHYLALUMINUM AND PROPYLENE OXIDE

[Triethylaluminum]	Products (%)	
[Propylene Oxide]	2-Pentanol	2-Methyl-1-butanol
0.7	31	18
1.0	24	44
1.5	1	98
2.0	1	98

The reaction of triethylaluminum with 1,2-epoxy-2-methylbutane and 1,2-epoxy-2-methylpentane is much faster than reactions with propylene oxide or 2,3-epoxybutanes. The major products were substituted neopentyl alcohols and, again, are formed by opening of the epoxide ring with attack at the more substituted carbon. In this series, rearrangement of initially formed triethylaluminum epoxide complex to the triethylaluminum–carbonyl complex is observed and becomes increasingly more important as the reaction temperature is increased. Alkylation of this complex gives 4-methyl-3-heptanol and reduction of this and/or the epoxide complex results in formation of 2-methyl-1-pentanol. An additional product believed to be an un-

TABLE 2

REACTION OF TRIETHYLALUMINUM WITH 1,2-EPOXY-2-METHYLPENTANE

| Temp. (°C)	Products (%)[a]			
	2-Methyl-2-ethyl-1-pentanol	4-Methyl-3-heptanol	2-Methyl-1-pentanol	Unknown
−40	78	15	5	3
−32	74	14	8	5
0	70	19	6	5
50	60	21	13	6
100	48	28	15	7

[a] Yields based on epoxide.

saturated 2-methyl-1-pentanol was detected by GLC but not isolated*.

Analogous products were obtained from the reaction of triethylaluminum with 1,2-epoxy-2-methylbutane.

DISCUSSION

The reaction of *cis*- and *trans*-2,3-epoxybutanes and triethylaluminum involves predominant stereospecific backside opening of the epoxide ring. The ethyl groups attached to an aluminum complexed with the reacting epoxide molecule are not in sterically favorable position to attack the epoxide from the opposite side of the ring. This implies that the reaction must be at least bimolecular; that is, attack must be from a molecule of triethylaluminum (free or complexed) not directly complexed with the epoxide undergoing attack.

threo-3-methyl-2-pentanol

erythro-3-methyl-2-pentanol
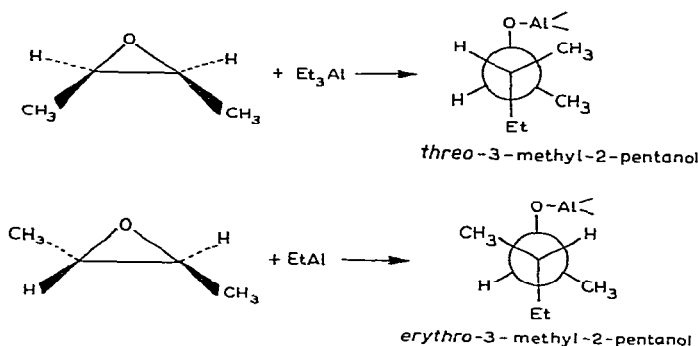
Reaction of triethylaluminum with propylene oxide under conditions that resulted in backside displacement with *cis*- and *trans*-epoxybutanes yields 2-methyl-1-butanol as essentially the only product. A mechanism which accomodates these observations must combine the S_N2 character required to account for the stereochemistry and the S_N1 character to explain the direction of ring opening in propylene oxide. This type of borderline S_N2 mechanism has considerable analogy in epoxide reactions**. Reaction of optically active *trans*-2,3-epoxybutane with methanol catalyzed by sulfuric acid gave active *erythro*-3-methoxy-2-butanol, the product of *trans* addition of methanol[6]. Reaction of 1,2-epoxy-2,4,5-trimethylpentane with alcohols catalyzed by acid or base gave attack at the tertiary or primary carbon respectively[7].

Reduction of epoxides by lithium aluminum hydride or aluminum hydride occurs with inversion of configuration[8]. However, instead of the electrophilic ring opening observed in the reaction of triethylaluminum and propylene oxide in hydrocarbon solvent, reduction of propylene oxide with aluminum hydride in ether results in predominately nucleophilic attack on the less substituted carbon, even with excess hydride[9]. Ether probably reduces the tendency for electrophilic ring opening. Different products were observed in the reaction of trimethylaluminum and styrene

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* Analogy for this is afforded by the reaction of 1,2-epoxycyclododecane and diisobutylaluminum hydride to form (after hydrolysis) 1-hydroxy-2-cyclododecene[+].
** For a brief review see ref. 5.

oxide in ether and hexane. In excess ether the only alcohol isolated was 1-phenyl-2-propanol but in hexane the major product was 2-phenyl-1-propanol. The reaction in ether proceeded via intermediate formation of phenylacetaldehyde[10]. Reaction of trimethylaluminum with 1,2-epoxy-3-phenylpropane in hexane solvent resulted in a quantitative yield of 2-methyl-3-phenyl-1-propanol when the mole ratio of trimethylaluminum/epoxide was two[11].

The reaction of epoxides with alkylalanes is similar in product formation and stereochemistry to the known examples of acid catalyzed opening of epoxides. In the present case (I) considerable breaking of the oxygen–secondary carbon bond must occur as bond formation with the attacking group proceeds*. This is a reasonable

(I)
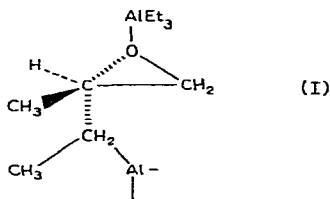
expectation since the alane is a very weak nucleophile. Thus, if toluene is the reaction solvent, attack of the alane–epoxide complex by toluene occurs in preference to attack by triethylaluminum[13]. Although we have not determined the stereochemistry of opening of the propylene oxide in the present case, one would expect to obtain inversion, since analogous opening of 2,3-epoxybutanes occurs with inversion. Alkylation of benzene with optically active propylene oxide catalyzed by $AlCl_3$ involves inversion at the central carbon atom[14].

The reaction of triethylaluminum and propylene oxide in mole ratios of unity or below proceeds through two distinct mechanistic paths, the importance of which depends on the ratio of the alane to the epoxide. A similar situation has been observed by Ashby et al. in the reaction of trimethylaluminum and benzophenone[12]. The reaction of triethylaluminum and propylene oxide may involve the steps described in eqns. (1)–(4).

(1)

(2)

(3)

(4)
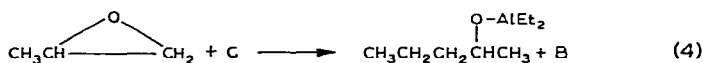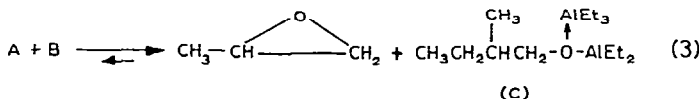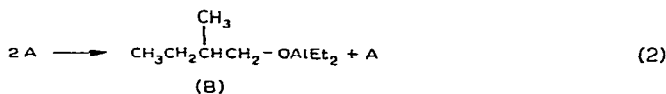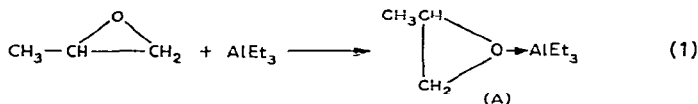
* A cyclic transition state containing two molecules of triethylaluminum may be involved similar to that proposed by Ashby et al.[12] for the reaction of benzophenone and trimethylaluminum.

Relative amounts of 2-methyl-1-butanol and 2-pentanol produced are consistent with this mechanism. Thus a triethylaluminum/epoxide ratio of unity yields a mixture of 2-methyl-1-butanol and 2-pentanol richer in the former in the early stages of the reaction. Such a situation could arise if the initially formed alane–epoxide complex undergoes attack on the central carbon [transition state (I)]. It is reasonable to expect product (B) to draw triethylaluminum away from the alane–epoxide complex*. The latter stages of reaction would then involve uncomplexed epoxide and the alane–B complex. This should lead to attack on the least hindered carbon of the epoxide. Thus the relative amount of 2-pentanol should increase as the reaction proceeds, as indeed it does (Fig. 1).
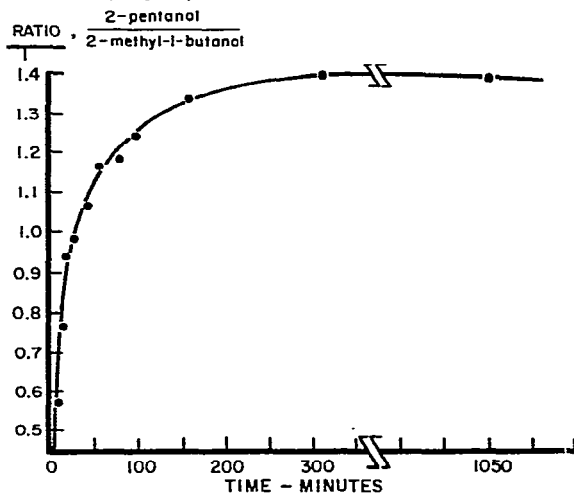

Fig. 1. The reaction of propylene oxide with triethylaluminum (mole ratio AlEt$_3$/propylene oxide 0.95; temperature 80°).

The reaction of triethylaluminum with 1,1-dialkylethylene oxides proceeds much faster (a few minutes, room temperature) than the reaction with propylene oxide (several hours, 80°). The major product again, results from attack at the more substituted carbon. The transition state for this opening probably involves more carbonium ion character at the more highly substituted carbon than the reaction with propylene oxide. The stereochemistry of attack on carbon with 1,1-dialkyl-ethylene oxides was not determined.

EXPERIMENTAL

Chemicals

Propylene oxide was obtained from Matheson, Coleman and Bell, Cincinnati, Ohio, and distilled over calcium hydride prior to use.

The epoxybutanes were prepared by epoxidation of *cis*- and *trans*-2-butenes with *m*-chloroperbenzoic acid in dibutyl ether solution, b.p. 56–58° [16].

1,2-Epoxy-2-methylbutane was prepared from the olefin and peracetic acid containing 5% sodium acetate, b.p. 79.5–79.6° (lit.[17] 81–82°).

Triethylaluminum was used as obtained from Texas Alkyls, Houston, Texas.

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* Complex B may be a mixed alkoxy-alkyl bridged dimer similar to that reported by Ashby *et al.*[15].

Reaction of cis- and trans-2,3-epoxybutane with triethylaluminum

To a 15 ml of 1 M triethylaluminum in *o*-dichlorobenzene was added 1.1 g *cis*-2-butene epoxide and 1.10 g tetradecane as an internal standard. After 30 h at 80° the reaction was hydrolyzed with 20% NaOH, the organic layer was decanted, dried and analyzed by GLC*. The two components were 2-butanol (6%) and *threo*-3-methyl-2-pentanol (93%). The latter component was identified by comparison with sample prepared from ethyllithium and *cis*-2,3-epoxybutane. This was different than *erythro*-3-methyl-2-pentanol prepared by the reaction of ethyllithium and *trans*-2,3-epoxybutane. These latter two reactions are described below. The reaction was repeated with *trans*-2,3-epoxybutane. A high yield of *erythro*-3-methyl-2-pentanol was obtained along with a small amount of 2-butanol.

Reaction of cis and trans-2,3-epoxybutanes with ethyllithium

A suspension of 1.4 g lithium metal in 50 ml of dry ether containing 10.8 g of ethyl bromide, was stirred for several hours at 0°. After this time the reaction solution was divided into two equivalent portions. To one portion was added 2.0 g (excess) *cis*-2,3-epoxybutane. This reaction was stirred for 1 h at room temperature, then poured onto water. The ether layer was decanted, dried over $MgSO_4$, and analyzed by GLC. Two components were evident, *cis*-2,3-epoxybutane and an alcohol which was identical to the least polar component (*i.e.*, that compound having the shorter GLC retention time) of a mixture of *erythro*- and *threo*-3-methyl-2-pentanols obtained from Beacon Chemical Industries, Inc., Cambridge, Massachusetts. This alcohol was assumed to be *threo*-3-methyl-2-pentanol by analogy with the stereospecific *trans* cleavage of 1,2-epoxycyclohexane with propyl- and butyllithium[18].

The reaction of ethyllithium with *trans*-2,3-epoxybutane epoxide gave, in the same manner, an alcohol identical to the most polar component of the "Beacon" mixture. This was assigned the *erythro* configuration.

Reaction of cis-2,3-epoxybutane with triethylaluminum in benzene and toluene

To 20 ml of a 1.0 M solution of triethylaluminum in benzene was added 0.74 g *cis*-2,3-epoxybutane (a weighed amount of tetradecane was added as an internal standard). The reaction was heated at 80° for two days, then hydrolyzed with aqueous base. The organic phase was decanted, dried over $MgSO_4$ and analyzed by GLC. The only products observed were 2-butanol (28%) and *threo*-3-methyl-2-pentanol (70%). No alkylation of the aromatic solvent was observed.

The above reaction was repeated using toluene as a solvent. No alkylation of toluene occurred and only 2-butanol (28%) and *threo*-3-methyl-2-pentanol (71%) were evident.

Reaction of propylene oxide with triethylaluminum

Propylene oxide was added to 1 M triethylaluminum in tetradecane (containing a weighed amount of nonane as an internal standard). The reaction was heated at 80° for 48 h, then hydrolyzed with cold 20% aqueous NaOH, the organic layer was decanted, dried, and analyzed by GLC. The products were identified as 2-pentanol

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* Gas chromatographic analyses were carried out on a 6' × 3/16" 3% FFAP on 80/100 mesh, DMCS Chrom G column temperature programmed from 50–200° at 9°/min and a 5' × 3/16" 20% Carbowax 20 M on 80/100 mesh Chromosorb W programmed at the same rate.

and 2-methyl-1-butanol by comparison with authentic samples obtained from Beacon Chemical Industries, Inc., Cambridge, Massachusetts, and Eastman Kodak Chemical, Rochester, New York, respectively. Results are given in Table 1. Results of a similar experiment, mole ratio 0.95, and in which samples were analyzed during the reaction are presented in Fig. 1.

Reaction of propylene oxide with triethylaluminum in benzene

To 20 ml of 1.0 M solution of triethylaluminum in benzene was added 1.16 g propylene oxide (containing decane as an internal standard). The reaction was heated at 65° for 3 h, poured into cold aqueous NaOH. The organic layer was decanted, dried over MgSO$_4$ and analyzed by GLC. Four components which were evident: 2-methyl-1-butanol (14%), 2-phenyl-2-propanol (3%), 1-phenyl-2-propanol (< 1%) and 2-phenyl-1-propanol (22%). The 2-phenyl-2-propanol was identified by comparison with a sample obtained from Aldrich Chemical Company, Milwaukee, Wisconsin. The 1-phenyl-2-propanol was identified by comparison with a sample prepared by the reaction of phenyllithium and propylene epoxide[19]. The 2-phenyl-1-propanol was identified by comparison with a sample obtained by reduction of 1-phenyl-2-propanone as described below.

Preparation of 1-phenyl-2-propanol

A solution of 25 ml of 1-phenyl-2-propanone in 50 ml of cyclohexane was treated with excess diisobutylaluminum hydride. The reaction was stirred for a few hours, then hydrolyzed with cold 20% HCl. The organic phase was decanted, dried over Na$_2$SO$_4$ and distilled under vacuum. The 1-phenyl-2-propanol had b.p. 109° (20 mm) [lit.[20] b.p. 123.5° (12 mm)].

Triethylaluminum and 1,2-epoxy-2-methylpentane

1,2-Epoxy-2-methylpentane (532 g, 5.3 moles) and triethylaluminum (1242 g, 10.9 moles) were allowed to react at 20° for 1 h. The hydrolyzed reaction mixture, analyzed by GLC, contained 430 g (62%) of 2-methyl-2-ethyl-1-pentanol, 91.4 g (13%) of 4-methyl-3-heptanol, and 88.0 g (16%) of six-carbon alcohols. 2-Methyl-2-ethyl-1-pentanol, b.p. 172–173° (lit.[21] b.p. 174–175°) more than 99% pure by gas chromatography was isolated by distillation. Identification was accomplished by comparison (IR, GLC) with an authentic sample*. The NMR spectrum of epoxide-derived alcohol confirmed the assigned structure. (Found: H, 13.72. C$_8$H$_{18}$O calcd.: H, 13.9%.)

4-Methyl-3-heptanol, b.p. 160–161 (lit.[22] 155.4°), and 2-methyl-1-pentanol**, b.p. 144–146°, were also obtained by distillation in 90–95% purity and identified by comparison (IR, GLC) with authentic samples. The octanol used in this comparison, b.p. 156–158°, was prepared from ethylmagnesium bromide and 2-methylpentanol.

To 4.6 ml of triethylaluminum in 10 ml of toluene was added 1.7 g of epoxide in 10 ml of toluene over a ten minute period at the indicated temperature. After 40 min at this temperature, the reaction mixture was hydrolyzed and analyzed by GLC. Yields of the various alcohols (based on epoxide) are reported in Table 2.

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* We thank Mr. C. E. Thompson for a sample of 2-methyl-2-ethyl-1-pentanol, prepared by LiAlH$_4$ reduction of the corresponding acid.
** Samples of 2-methyl-1-butanol and 2-methyl-1-pentanol were purchased from Eastman Chemical Company and the Union Carbide Company, respectively.

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