give a mixture of its higher homologs and triethylaluminum under distillation conditions, so its isolation by usual purification methods was difficult. Nevertheless, the analytical data (*Anal.* Calcd for $C_8H_{20}OAl_2$: Al, 29.0; C_2H_5:Al, 2.0. Found: Al, 26.5; C_2H_5: Al, 1.9) approximate the expected values. Product II is quite similar in chemical properties and in distillation behavior to the reaction product of triethylaluminum and water in a molar ratio of 1:0.5.

$$\mathrm{Et_3Al + LiOH \longrightarrow \underset{I}{Et_2AlOLi} + EtH} \tag{1}$$

$$\mathrm{\underset{I}{Et_2AlOLi} + Et_2AlCl \longrightarrow \underset{II}{Et_2AlOAlEt_2} + LiCl} \tag{2}$$

The 5,6-benzoquinolinate (IV) of bis(diethylaluminum) oxide was obtained in crystalline state (90% yield) when the 5,6-benzoquinolinate (III) of diethylaluminum chloride was used at room temperature instead of diethylaluminum chloride. Compound III was recrystallized from *n*-hexane, colorless needles, mp 43°. *Anal.* Calcd for $C_{17}H_{19}NClAl$: Al, 9.0. Found: Al, 9.1. Product IV was recrystallized from *n*-hexane, pale yellow needles, mp 75° dec. The structure of IV was confirmed by analysis (*Anal.* Calcd for $C_{21}H_{29}ONAl_2$: Al, 14.80; C_2H_5:Al, 2.0. Found: Al, 14.82; C_2H_5:Al, 1.9), cryoscopic molecular weight determination (benzene) (*Anal.* Calcd for $C_{21}H_{29}ONAl_2$: mol wt, 365. Found: mol wt, 531.4 (5.272 moles $l.^{-1}$), 475.3 (2.636 moles $l.^{-1}$), 380.4 (1.318 moles $l.^{-1}$), and 350 (extrapolated value to zero concentration)), and nmr spectra [$\delta_{C_6D_6}$ (ppm):[8] 1.69 (12.16 methyl H, triplet), 0.77 (8.00 methylene H, quartet), and 6.83–9.17 (8.91 ring H, multiplet)]. The equivalency of four ethyl groups observed by nmr study corresponds to a rapid migration of a donor between two aluminum atoms in solution. The isolation of compound IV is of value as an evidence for the actual existence of $Et_2AlOAlEt_2$ and for its acceptor property for coordination.

$$\mathrm{\underset{I}{Et_2AlOLi} + \underset{III}{[Et_2AlCl]\cdot[5,6\text{-}benzoquinoline]} \longrightarrow \underset{IV}{[Et_2AlOAlEt_2].[5,6\text{-}benzoquinoline]} + LiCl} \tag{3}$$

N,N-Bis(ethylzinc)-*t*-butylamine (EtZnN(*t*-Bu)ZnEt, V) was obtained in about 35% yield by allowing 2 moles of diethylzinc and 1 mole of *t*-butylamine in toluene to react at 80° for 10 hr,[9] giving, recrystallized from *n*-heptane, colorless needles, mp 67–69°. The structure of V was confirmed by analysis (*Anal.* Calcd for $C_8H_{19}NZn_2$: Zn, 50.4; C_2H_5:Zn, 1.00. Found: Zn, 51.7; C_2H_5:Zn, 0.84), cryoscopic molecular weight determination (benzene) (*Anal.* Calcd for $C_8H_{19}NZn_2$: mol wt, 260. Found: mol wt, 264 (0.624 mole $l.^{-1}$), 260 (0.312 mole $l.^{-1}$)), and nmr spectra [$\delta_{C_6H_6}$ (ppm):[8] 1.50 (5.75 methyl H, triplet), 0.53 (4.00 methylene H, quartet), and 1.32 (9.30 *t*-butyl H, singlet)].

$$\mathrm{2Et_2Zn + \mathit{t}\text{-}BuNH_2 \longrightarrow \underset{V}{EtZnN(\mathit{t}\text{-}Bu)ZnEt} + 2EtH} \tag{4}$$

Preliminary results of the polymerization of propylene oxide by using compounds I–V are summarized in Table I. Acetone-insoluble fractions of the polymer are confirmed to be isotactic crystalline polyethers by their infrared spectra and X-ray diffraction patterns. From this table it appears that the compounds IV and V are crystalline stereospecific catalysts and that the Zn–N–Zn compound V has a stereoregulating power far higher than that reported earlier. In addition, these compounds have well-defined structures, are soluble in hydrocarbon solvents, and therefore act as homogeneous catalysts. All these properties make these catalysts particularly suitable for mechanism studies.[10,11] Details of the polymerization mechanism concerned with the real active species are now in progress.

Table I. Polymerization of Propylene Oxide[a]

Catalyst	Rate of polymerization	Polymer Yield, %	Polymer Acetone-insoluble fraction, %[b]	Polymer [η]
I	....	0	..	....
II	Very high[c]	95	40	2.1[d]
III	....	0	..	....
IV	Low	79	45	2.6[d]
V	Low	39	81	8.3[e]

[a] Polymerization conditions: temperature, 30°; time, 7 days; solvent, toluene; catalyst, 3 mole % of monomer. [b] Fractionation was done at room temperature. [c] Spontaneous exothermic reaction. [d] 0.1–0.30 g/100 ml of benzene at 25.0 ± 0.1°. [e] 0.1–0.25 g/100 ml of benzene at 25.0 ± 0.1°.

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(8) Chemical shifts (δ values) are internally standardized to benzene (7.37 ppm).

(9) This reaction is the extension of that of the aluminum analogs to the zinc compound; see H. Tani and N. Oguni, *J. Polymer Sci.*, **B3**, 123 (1965).

(10) In view of the facile disproportionation of II, it may be questioned if the actual active species is II or not.

(11) The disproportionation

$$\mathrm{\underset{IV}{2[Et_2AlOAlEt_2]\cdot[5,6\text{-}benzoquinoline]} \rightleftharpoons \underset{II}{Et_2AlOAlEt_2} + \underset{VI}{[Et_2AlOAlEt_2]\cdot 2[5,6\text{-}benzoquinoline]}}$$

may be assumed to exist in the polymerization system, but, in view of catalytic activity of VI (extremely low) and of II (very high), it is reasonable to conclude that the results reported in Table I may be mainly due to IV.

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Intramolecular, Long-Range Oxidations at Saturated Carbon Centers

Sir:

The past 7 years have witnessed the development of powerful new methods of organochemical synthesis by the utilization of intramolecular, free-radical decompositions of certain alcohol derivatives. Lead tetraacetate oxidation of alcohols,[1] photolysis of nitrites,[2] and thermolysis or photolysis of hypohalites[3]

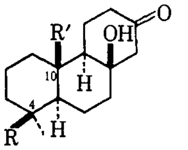
(1) (a) G. Cainelli, M. L. Mihailović, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **42**, 1124 (1959), and subsequent papers; (b) see review by K. Heusler and J. Kalvoda, *Angew. Chem.*, **76**, 518 (1964).

(2) (a) D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. Pechet, *J. Am. Chem. Soc.*, **82**, 2640 (1960), and subsequent publications; (b) see review by M. Akhtar, *Advan. Photochem.*, **2**, 263 (1964).

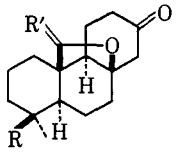
(3) (a) C. Meystre, K. Heusler, J. Kalvoda, P. Wieland, G. Anner, and A. Wettstein, *Experientia*, **17**, 475 (1961), and subsequent papers; (b) see also ref 1b and 2b.

have permitted functionalization of saturated hydrocarbon centers (especially methyl groups) in close proximity to the original hydroxy functions. We now wish to report application of one of the methods of alcohol oxidation for the functionalization of methyl groups some distance from the hydroxyl sites.

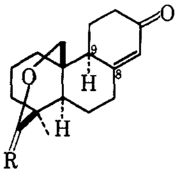
As part of our continuing study of oxidation of diterpenic alcohols[4] the ketol degradation product (Ia) of manool[5] was exposed to hypoiodite oxidation. Treating Ia with lead tetraacetate and iodine in cyclohexane or benzene solution yielded the expected[3] ketooxide IIa [32%; mp 88–90°; infrared (Nujol): 5.84 μ (C=O, s); nmr ($CDCl_3$): one-proton doublets at δ 3.52, 4.19 (J = 9.0 cps, oxymethylene), six-proton singlet at 0.92 (methyls). *Anal.* Found: C, 77.92; H, 10.06] as well as the iodoketooxide IIb [22%; mp 185° dec; infrared (Nujol): 5.85 μ (C=O, s); nmr ($CDCl_3$): two-proton singlet at δ 3.48 (iodomethylene), one-proton doublets at 3.59, 4.10 (J = 9.0 cps, oxymethylene), three-proton singlet at 1.07 (Me). *Anal.* Found: C, 52.51; H, 6.61]. Rigorous proof of the structure of IIb evolved from the consequences of its treatment with sodium bicarbonate in dimethyl sulfoxide. The products were IIIa [mp 80–81°; infrared (Nujol): 6.00 (C=O, s), 6.20 μ (C=C, m); λ_{max} (EtOH) 239 mμ (ϵ 8300). *Anal.* Found: C, 78.61; H, 9.47], its liquid $\Delta^{8,9}$ isomer [infrared (CCl_4): 5.81 μ (C=O, s). *Anal.* Found: C, 78.51; H, 9.01], and a mixture of hemiacetals from which upon Jones oxidation there could be isolated the enone lactone IIIb [mp 218–220°; infrared (Nujol): 5.81 and 6.01 (C=O, s), 6.20 μ (C=C, m); λ_{max} (EtOH) 239 mμ (ϵ 8250). *Anal.* Found: C, 74.58; H, 7.91]. Lead tetraacetate–iodine oxidation of the ketol degradation product (Ib) of methyl agathate[6] yielded the same lactone (IIIb), the ester IIc [mp 145°; infrared (Nujol): 5.78 μ (C=O, s). *Anal.* Found: C, 70.35; H, 8.38], and the diester IId whose Jones oxidation produced the lactone IIe [mp 178–180°; infrared (Nujol): 5.68 and 5.78 μ (C=O, s). *Anal.* Found: C, 67.48; H, 7.44].



Ia, R = R′ = Me
b, R = CO_2Me; R′ = Me
c, R = CH_2I; R′ = Me
d, R = Me; R′ = CH_2I



IIa, R = Me; R′ = H_2
b, R = CH_2I; R′ = H_2
c, R = CO_2Me; R′ = H_2
d, R = CO_2Me; R′ = HOAc
e, R = CO_2Me; R′ = O



IIIa, R = H_2
b, R = O

Since the unexpected substance IIb constitutes a product of two oxidations of Ia, a search of the primary intermediates, the iodohydrins Ic and/or Id, was undertaken. While no trace of Ic was found even upon reduction of reaction time or of concentration of oxidizing agents, conditions which led to recovery of starting material, the unstable iodide Id [mp 86° dec; infrared (Nujol): 2.95 (OH, s), 5.85 μ (C=O, s); nmr (pyridine): one-proton doublets at δ 3.73, 5.17 (J = 11.0 cps, iodomethylene), three-proton singlets at 0.85, 0.90 (methyls)] could be isolated. Short heating of a pyridine solution of the latter yielded the ketooxide IIa. Lead tetraacetate–iodine oxidation of Id gave the iodo compound IIb (51%). Thus the novel long-range oxidation appears to use Id as a substrate and to consist of two consecutive alkoxy-radical-generated 1,5-hydrogen shifts, the second of which represents one of only few cases of intramolecular hydrogen abstraction from a saturated carbon–hydrogen bond site by a carbon radical.[7,8] While overoxidation in hypohalite reactions has been observed previously,[3] the second oxidation always has taken place on the same carbon center as the first oxidation and has led to iodo- or acetoxytetrahydrofuran products (*e.g.*, Ib → IId). The iodohydrin Id embodies the first structure whose framework permits more than one 1,5-hydrogen shift upon alkoxy radical generation and thus liberates more than one carbon radical site for attack by the iodine scavenger. The exclusivity of iodination of the 4β-methyl group is probably a reflection of the steric congestion at the 10β-iodomethyl location.

A second example of the new "billiard" reaction is the lead tetraacetate–iodine oxidation of friedelan-3β-ol[9] (IV). The major products were Va (41%, mp 221–223°)[10] and Vb [15%; mp 205–206°; m/e 552.2827 (M); nmr ($CDCl_3$): one-proton doublets at δ 3.53, 4.35 (J = 8.5 cps, oxymethylene), three-proton multiplet at 3.72–4.00 (3α-H and iodomethylene). *Anal.* Found: C, 64.97; H, 9.04]. Palladium-induced hydrogenolysis of the iodide Vb yielded Va. Although rigorous proof of the structure of the iodide must still be sought, the hydrogenation result, pmr spectrum of the compound, and a mechanistic interpre-

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(4) The first completed investigation involved the conversion of podocarpic acid into deisopropyldehydroabietic acid: E. Wenkert, J. B-son Bredenberg, and B. L. Mylari, manuscript in preparation (presented by E. W. in a lecture at the Centre National de la Recherche Scientifique, Institut de Chimie des Substances Naturelles, Gif-sur-Yvette, Essone, France, Nov 10, 1964, and in lectures at several Australian universities under the auspices of the Australian Academy of Science, May 1966).

(5) E. Wenkert, J. R. Mahajan, M. Nussim, and F. Schenker, *Can J. Chem.*, **44**, 2575 (1966), and references cited therein.

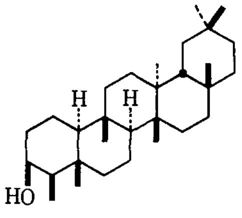
(6) J. Haeuser, R. Lombard, F. Lederer, and G. Ourisson, *Tetrahedron*, **12**, 205 (1960).

(7) M. Fisch and G. Ourisson, *Chem. Commun.*, 407 (1965); J. G. Traynham and T. M. Couvillon, *J. Am. Chem. Soc.*, **87**, 5806 (1965); E. I. Heiba and R. M. Dessau, *ibid.*, **88**, 1589 (1966).

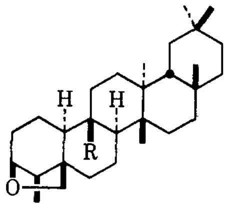
(8) Although the isolation of Id suggested that the ketooxide IIa was not a direct product of the hypoiodite reaction but was formed on reaction work-up, its intermediacy along the reaction path toward IIb could not be fully discounted. As a consequence IIa was exposed to a lead tetraacetate–iodine oxidation. However, only starting material was recovered.

(9) E. J. Corey and J. J. Ursprung, *J. Am. Chem. Soc.*, **78**, 5041 (1956).

(10) While the melting point differed from that (208–211°) previously reported for this substance [J. L. Courtney and W. Stern, *Tetrahedron Letters*, 1607 (1965)], infrared and pmr spectral comparisons with an authentic sample kindly supplied by Drs. Courtney and Stern proved their identity.



IV



Va, R = Me
b, R = CH_2I

tation of its formation support Vb as the most likely structure.[11,12]

The availability of substances of structure type IIIb opens an easy route to the highly oxygenated diterpenic constituents of *Sciadopitys verticillata*[13] and diterpene alkaloids. The transformation products of friedanol can be of aid in the determination of the structures of the friedelanic triterpenes of *Siphonodon australe* Benth.[14,15]

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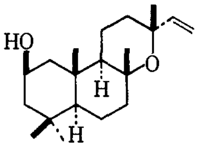
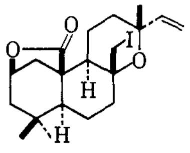
[11] Whereas in principle the friedanol skeleton should permit three 1,5-hydrogen shifts to take place, no products of overoxidation of established constitution derived from such changes have been isolated. However, two of the minor products, $C_{30}H_{48}O$ [mp 341–343°; no C=O (infrared), no C=C (infrared, pmr)] and $C_{30}H_{48}O_2$ [mp 284–285°; no C=O, C=C (infrared)], may be such representatives.

[12] Both transformations Ia → IIb and IV → Vb illustrate V-shaped chemical billiard shots. The consequence of a linear shot is portrayed by ii (mp 162–164° dec), one of the products of lead tetraacetate–iodine oxidation (followed by Jones oxidation) of 2β-hydroxymanoyl oxide (i).



i



ii

[13] M. Sumimoto, *Tetrahedron*, **19**, 643 (1963); C. Kaneko, T. Tsuchiya, and M. Ishikawa, *Chem. Pharm. Bull.* (Tokyo), **11**, 271 (1963).

[14] Reference cited in footnote 10.

[15] The authors are indebted to the National Science Foundation for support of this work, to Drs. C. Djerassi, O. E. Edwards, M. Fétizon, and P. Grant for samples of compounds used in this work, and to Dr. W. Hargrove for mass spectral determinations.

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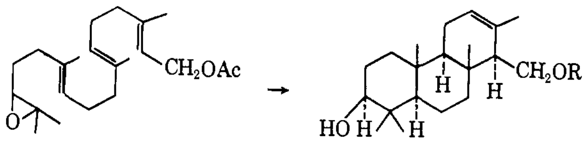
Laboratory Cyclization of Geranylgeranyl Acetate Terminal Epoxide

Sir:

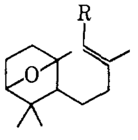
With the demonstration that squalene 2,3-oxide is converted enzymatically in good yield to lanosterol and cholesterol,[1] the study of simpler terpene terminal epoxides[2] gains added interest and importance, especially in the sense that they are implicated as biological precursors of other 3-hydroxylated polycyclic systems. In this publication we describe the terminal epoxide of geranylgeranyl acetate (I) and its reactivity under nonenzymic conditions, including formation of a 3-hydroxylated tricyclic terpenoid (II, R = Ac) featuring six asymmetric centers specifically oriented in the relationship characteristic of the natural product series.[3]



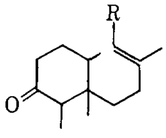
I II

trans,trans,trans-Geranylgeraniol was obtained from *trans,trans*-farnesol by modification of the Ruzicka procedure.[4] N-Bromosuccinimide oxidation of geranylgeranyl acetate in aqueous tetrahydrofuran[5] provided the terminal bromohydrin, which on treatment with potassium carbonate in methanol gave the terminal epoxide of the free alcohol (over-all yield 45%).

Conversion to the oily acetate (I) was followed by cyclization, carried out by exposure to 0.2 molar equiv of stannic chloride in benzene for 5 min at *ca.* 0°. After routine work-up and chromatography of the resulting mixture on silica gel, various entities were isolated, including a hydrocarbon fraction (~5%), cyclic ether III (~5%), monocyclic ketone IV (~27%), and a mixture consisting (by nmr) of acyclic terminal chlorohydrin (~27%) and tricyclic diol monoacetate (~10%). Isolation and purification of the latter was facilitated by conversion of crude fractions to *p*-nitrobenzoate, which was subjected to preparative tlc on silver nitrate–silica gel. Saponification of the chromatographed diol diester provided tricyclic diol II (R = H), the mass spectrum of which was entirely consistent with the assigned structure.

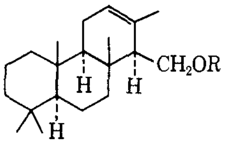


III



IV

Reliable chemical evidence for the molecular and stereochemical nature of the tricyclic substance II was obtained by conversion to a transformation product (V) also derivable in a rational manner from the naturally occurring manool (VI). The synthetic monoester was oxidized by Jones reagent to the corresponding keto acetate, which was subjected to the ethylene dithioketalization–Raney nickel hydrogenolysis se-



V

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[1] (a) E. J. Corey and W. E. Russey, *J. Am. Chem. Soc.*, **88**, 4750 (1966); E. E. van Tamelen, J. D. Willett, R. B. Clayton, and K. E. Lord, *ibid.*, **88**, 4752 (1966).

[2] E. E. van Tamelen, A. Storni, E. J. Hessler, and M. Schwartz, *ibid.*, **85**, 3295 (1963); E. E. van Tamelen, M. Schwartz, E. J. Hessler, and A. Storni, *Chem. Commun.*, 409 (1966); E. E. van Tamelen and R. M. Coates, *ibid.*, 413 (1966).

[3] Nonoxidative conversion of acyclic polyenes to tricyclic substances in the natural product category have been reported by (a) A. Eschenmoser, "Biosynthesis of Terpenes and Sterols," Ciba Foundation Lectures, G. E. W. Wolstenholme and M. O'Conner, Ed., J. and A. Churchill, Ltd., London, 1959, p 224, (b) W. S. Johnson, N. P. Jensen, and J. Hooz, *J. Am. Chem. Soc.*, **88**, 3859 (1966); W. S. Johnson and R. B. Kinnel, *ibid.*, **88**, 3861 (1966).

[4] L. Ruzicka and G. Firmenich, *Helv. Chim. Acta*, **22**, 392 (1939). In our hands, formation of ethyl geranylgeranate (50:50 *cis-trans* α,β-unsaturated ester mixture, by vpc) was carried out by addition of ethoxyacetylene to farnesylacetone, followed by hydrolysis with dilute sulfuric acid (over-all yield >95%). After enrichment (≥90% by vpc) of the all-*trans* isomer by chromatographic means, geranylgeraniol was prepared by lithium aluminum hydride reduction.

[5] E. E. van Tamelen and T. J. Curphey, *Tetrahedron Letters*, 121 (1962).