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ENTRY INTO THE ALLENE OXIDE-CYCLOPROPANONE SYSTEM VIA VINYLSILANES.
II. ISOLATION AND CHARACTERISATION OF 1-t-BUTYLALLENE OXIDE[1].

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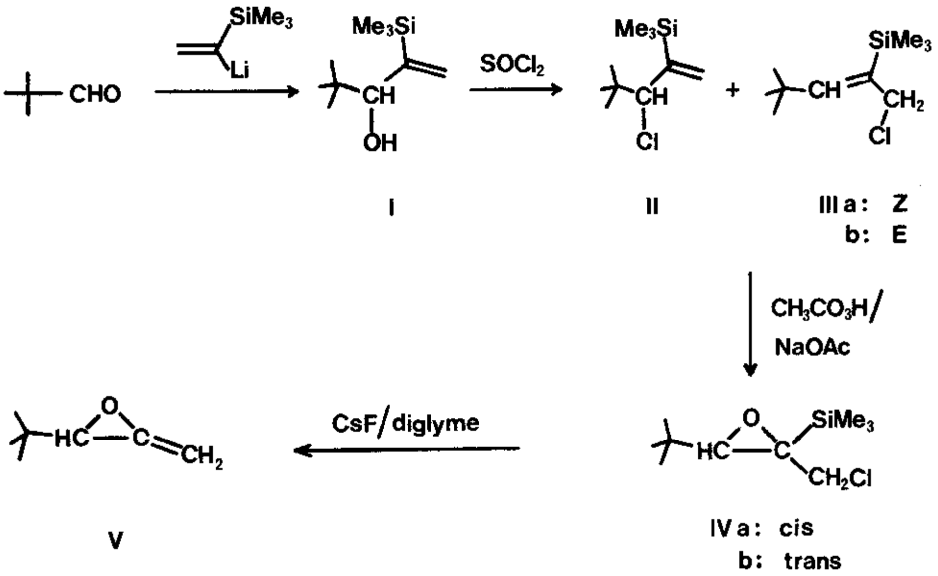
The allene oxide-cyclopropanone isomerization problem has elicited much current interest[2-7]. There are two aspects to the problem; one is the relative stability of the two structures and the other is the mechanism of the isomerization process - whether the zwitterionic oxyallyl is involved as intermediate or not. Experimentally, it is known that 1,3-di-t-butylallene oxide isomerizes to the corresponding cyclopropanone upon heating, thus establishing the cyclopropanone form to be more stable than allene oxide for that particular case.[8] On the other hand, 1,1,3-tri-t-butylallene oxide[9,10] has been found not to isomerize to the cyclopropanone. The cause for the stability of the allene oxide could have been either kinetic or thermodynamic in nature.

One difficulty associated with the study of the chemistry of allene oxides is the ease with which the epoxide structure is opened under acidic conditions during peracid oxidation of allenes. Recently, we suggested that allene oxides can be generated from vinylsilanes under neutral conditions.[1] In this and the following communications, we wish to report on the isolation of 1-t-butylallene oxide, a reactive monosubstituted allene oxide, and the effect of substituent on the allene oxide-cyclopropanone isomerization process.

The synthesis of 1-t-butylallene oxide (V) has been achieved according to scheme 1. Reaction of pivalaldehyde (75 mmole) with an equivalent of α-trimethylsilylvinyl lithium[11] at -78° in ether afforded in 79% yield the alcohol I: b.p. 69-71°/5 mm; pmr (CCl_4); 0.15 (s, 9H), 0.90 (s, 9H), 1.85 (broad, 1H), 3.90 (s, 1H) and 5.6 (AB, J = 3 Hz, 2H) ppm.



Scheme 1

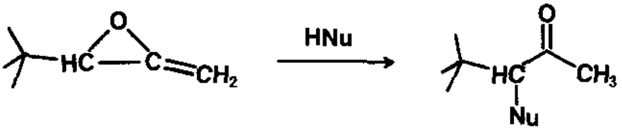
A solution of I (50 mmole) in ether (40 ml) was treated with 20% excess of thionyl chloride in ether (20 ml) at 25° for 1½ hr. The product, b.p. 90-97°/14 mm, obtained in quantitative yield, was a mixture of isomeric chlorides II, IIIa and IIIb in the ratio of 13:52:35 by pmr[12]. The structures of the isomeric chlorides were assigned on the basis of the chemical shifts and splitting of the vinyl hydrogens in the pmr spectrum by comparison with compounds of similar structures[11].

To a solution of the mixed chlorides (30 mmole) in methylene chloride (45 ml) was added a mixture of 40% peracetic acid in acetic acid (8.0 g) and sodium acetate (0.51 g). The reaction mixture was refluxed for one day. On work up, the mixture gave 4.83 g of epoxides IVa and b, b.p. 87-90°/9 mm, in a ratio of 62:38 by pmr.[13] The unrearranged chloride II was not epoxidised under the reaction conditions.

The epoxides, IVa and b, (0.44 g) were stirred at room temperature with a slight excess of cesium fluoride (0.35 g) in diglyme (6 ml). A slow stream of dried nitrogen was bubbled into the reaction mixture so as to carry over the volatile products into a cold trap at -78°. After one day, a colorless liquid was collected in the cold trap and identified to be 1-t-butylallene oxide (V). The pmr (CCl_4) spectrum of V showed peaks at

0.99 (s, 9H), 3.25 (s, 1H) and 4.15 (AB, J = 4 Hz, 2H). The structure of V was further confirmed by its Cmr spectrum which showed peaks at 25.94 (CH_3-), 31.89 (tBu-C), 68.01 (CH-), 70.52 (CH_2-), and 144.32 (-C=) ppm. The mass spectrum of V showed the molecular ion at m/e 112 and the appropriate fragments. The ir spectrum of V (CCl_4) showed absorptions at 1840 (m), 1815 (s) and 1780 (m) cm^{-1}. The yield of the isolated V was greater than 55%.

1-t-Butylallene oxide was stable at 25° for about 1.5 hr but polymerisation was observed *after 3 hr at room temperature. No sign of isomerisation* of V to t-butylcyclopropanone could be detected either on heating or on treatment with boron trifluoride. In either case, polymer was obtained. The polymer showed carbonyl absorption in the ir and pmr signals below 2 ppm. The polymer appears not to have the polycyclopropanone structure.[14] 1-t-Butylallene oxide undergoes reaction with nucleophiles to give addition products (VIa-c) in good yields (Table).



V

VI a Nu: OH
b SC_2H_5
c $O\underset{\overset{\|}{O}}{C}CCl_3$

Table: Spectroscopic data and yields of Compounds VI

Nu	Yield	nmr δ ($CDCl_3$)	IR cm^{-1}
OH	68[a]	1.0(s,9H) 2.2(s,3H) 2.8(br,1H) 3.85(s,1H)	3400, 1710
SC_2H_5	74%[b]	1.05(s,9H), 1.2(t,J=7Hz,3H), 2.25(s,3H) 2.45(q,J=7Hz,2H), 3.05(s,1H)	1700
$O\underset{\overset{\|}{O}}{C}CCl_3$	78%[a]	1.05(s,9H) 2.2(s,3H) 4.75(s,1H)	1720,1780

a. GLPC yield

b. isolated yield from TLC.

The present results demonstrate that allene oxides can indeed be generated easily from vinylsilanes. Furthermore, this synthesis permits the generation of isomeric allene oxides in a specified manner, the significance of which will be reported in the next communication.

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References and Footnotes

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12. Pmr of the isomeric chlorides in CCl_4 showed: II: 0.20 (s, 9H), 1.05 (s, 9H), 4.3 (s, 1H), 5.8 (AB, 2H). IIIa: 0.30 (s, 9H), 1.15 (s, 9H), 4.05 (s, 2H), 6.35 (s, 1H); IIIb: 0.15 (s, 9H), 1.20 (s, 9H), 4.25 (s, 2H) and 5.75 (s, 1H).
13. Pmr of the isomer epoxides in CCl_4 showed: IVa: 0.35 (s, 9H), 1.05 (s, 9H), 2.5 (s, 1H), 3.25 (AB, J_{AB} = 10 Hz, $\Delta\nu_{AB}$ = 71 Hz, 2H). IVb = 0.15 (s, 9H), 1.1 (s, 9H), 2.5 (s, 1H), 3.7 (AB, J_{AB} = 11 Hz, $\Delta\nu_{AB}$ = 13 Hz, 2H).
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