SYNTHESIS AND SOME REACTIONS OF ISOPROPENYLOXIRANE

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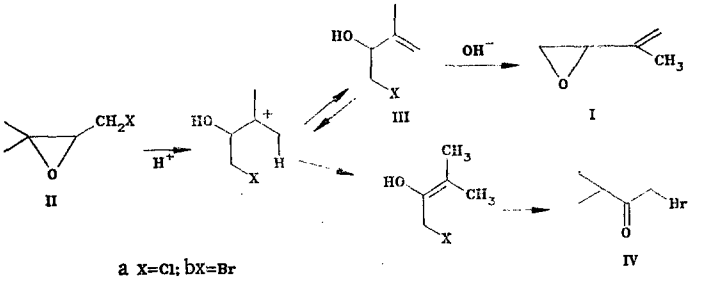
A convenient method for the synthesis of isopropenyloxirane by dehydrohalogenation of halohydrins obtained by isomerization of 1-halo-3-methyl-2,3-epoxybutanes was developed. The reactions of isopropenyloxirane with alcohols, water, secondary amines, hydrogen halides, dichlorocarbene, acetic acid anhydrides, and Grignard reagents were studied.

The existing methods for the preparation of isopropenyloxirane (I) are based on the use of trimethylsulfonium iodide [1], phenylthiomethyllithium [2], ylids [3], and some other reagents [4, 5] and are not sufficiently convenient for the preparation of oxirane I.

Meanwhile, increased interest in oxirane I has been manifested in recent years, since it, owing to the peculiarities of its structure, along with 2-methyl-2-vinyloxirane, may serve as a convenient synthone for the introduction of an isoprenoid C_5 fragment into various molecules, including those of natural origin [2, 6].

In this respect, we have obtained interesting data in the course of a study of some aspects of the chemistry of 1-halo-3-methyl-2,3-epoxybutanes II. Taking into account the concepts of the p effect of the neighboring group [7], we were able to isomerize 1-halo-3-methyl-2,3-epoxybutanes (II) to 3-hydroxy-4-halo-2-methyl-1-butenes (III) by the action of p-toluenesulfonic acid. As in many other cases [7], the intermediate carbonium ion generated by opening of the oxide ring of II under the influence of an acid is deprotonated primarily in nonconformity with the Zaitsev (Saytzeff) rule to give unsaturated halohydrins III; halomethyl isopropyl ketones are formed only as side products. When the time of contact with the catalyst is increased, III are converted completely and in high yields to halomethyl ketones IV [8], whereas under the influence of a base they are converted to isopropenyloxirane (I) in 74-79% yields [9].



a X=Cl; b X=Br

Having at our disposal an accessible method for the preparation of oxirane I, we subjected it to a systematic study of its chemical properties.

We demonstrated that oxirane I, like methylvinyloxirane [10], in an alkaline medium reacts with alcohols to give a mixture of alcohol esters in which the compound with an allylic alcohol function (Va) preponderates. This ratio increases on passing from methanol to ethanol and isopropyl alcohol [44:56, 18:82, and 7:93, respectively, gas-liquid chromatography (GLC)]. In the presence of acidic catalysts the addition of alcohols leads exclusively to homoallylic alcohols Vb-d, derivatives of which are also formed in the reaction of oxirane I with water, acetyl chloride, and acetic anhydride (Ve-g, Table 1). The reaction of oxirane I with acetone in the presence of catalytic amounts of $BF_3 \cdot OEt_2$ gives 2,2-dimethyl-4-isopropenyl-1,3-

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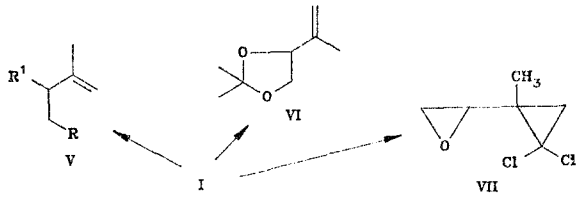
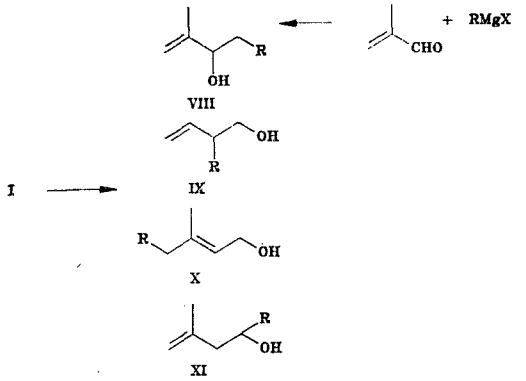


V a R=OC_3H_7-*i*; b–e, *l*, m R=OH; f, g R=OAc; h R=$N(CH_3)_2$; i R=$N(C_2H_5)_2$; j R=$N(CH_2)_4O$; k R=$N(CH_2)_5$; a, e, h–k R^1=OH; b R^1=OCH_3; c R^1=OC_2H_5; d R^1=OC_3H_7-*i*; f, *l* R^1=Cl; g R^1=OAc; m R^1=Br

dioxolane (VI) (Table 1). Dichlorocarbene, generated under interphase-catalysis conditions, affects only the double bond to give (2,2-dichloro-1-methyl)cyclopropyloxirane (VII) (Table 1).

Opening of the oxide ring occurs with secondary amines upon heating to 70°C (in a sealed ampul for lower amines), and amino alcohols Vh-k are formed in good yields (Table 1). The reaction of bromohydrin III with secondary amines leads to the same amines. The addition of hydrogen chloride, as in the hydrogenation reaction, leads only to homoallylic alcohols Vl, m.

Oxirane I also reacts with a Grignard reagent. According to a single report [2], this reagent, in the presence of 5% Cu(I)I in tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) (20:1 ratio of the latter two solvents), reacts with oxirane I to give only a carbinol of the X type in 95% yield. Our more detailed studies of the reaction of oxide I with the Grignard reagent showed that one almost always observes the formation of a mixture of alcohols VIII-X, the ratio of which changes over a broad range, depending on the experimental conditions and the character of the radical in the organomagnesium compounds.



VIII—X a R=C_2H_5; b R=*i*-C_3H_7; c R=*i*-C_5H_{11}; d R=C_6H_5; e R=$C_6H_5C{\equiv}C$

Thus, under normal reaction conditions (Table 2), one observes primarily (R = C_2H_5, iso-C_3H_7, iso-C_5H_{11}) or almost exclusively (R = Ph, C≡C–Ph) the formation of carbinols IX, which were identified from the presence in their PMR spectra of characteristic peaks from the protons of the isopropenyl fragment (Table 2), as well as from splitting of the signal of the primary hydroxy proton into a triplet in DMSO [11]. Carbinols of the XI type, which could be formed after prior isomerization of oxide I to give an unsaturated aldehyde, as was observed in the case of another isopropene oxide [12], were not detected in our experiments.

The addition of 5% Cu(I)I to the reaction mixture changes the direction of attack by the Grignard reagent and leads primarily (when R = C_2H_5, iso-C_3H_7, iso-C_5H_{11}) to alcohols of the X type. However, in the case of phenyl- and phenylethynylmagnesium bromides the effect of Cu(I)I is barely noticeable (Table 2). A similar pattern is also observed in the case of an equimolar ratio of the Grignard reagent and Cu(I)I: Alcohols X are formed exclusively in the form of cis-trans isomers with preponderance of the trans isomer (assignment in analogy with [2], PMR) only in the a and c cases. However, when ether is replaced by THF in the presence of 5% Cu(I)I, one observes the formation of alcohols VIII; these products (VIIIa-c; for VIIId,e see Table 2) are the dominant ones. The structure of VIII was proved by alternative synthesis from α-methylacrolein and the corresponding Grignard reagent (for VIIIa,b) with subsequent identification of the samples by gas-liquid chromatography (GLC) and PMR spectroscopy.

TABLE 1. Characteristics of Va-m, VI, and VII

Compound (lit.)	bp (mp), °C (mm)	n_D^{20}	d_4^{20}	PMR spectrum, δ, ppm	Found, %			Empirical formula	Calc., %			Yield, %
					C	H	N(Hal)		C	H	N(Hal)	
Va	67—68 (11)	1,4355	0,8961	1,71 (3H, d, J=1 Hz, CH_3); 3,11 (1H, br, OH); 1,05 [6H, d, J=7 Hz, $(CH_3)_2$]; 3,24—3,70 (3H, m, CH_2O); 3,94—4,28 (1H, m CH); 4,98 and 4,83 (2H, m, J=1 Hz, $=CH_2$)	66,5	11,0	—	$C_8H_{16}O_2$	66,7	11,1	—	47
Vb	151—153 (654)	1,4380	0,9314	1,69 (3H, t, J=1 Hz, CH_3); 3,31 (3H, s, OCH_3); 3,38—3,79 (4H, m, $CH+CH_2+OH$); 5,06 (2H, m, J=1 Hz)	62,0	10,5	—	$C_6H_{12}O_2$	62,1	10,4	—	75
Vc	64—67 (14)	1,4345	0,9105	1,67 (3H, dd, J=1 Hz, CH_3); 3,20 (1H, s, OH); 1,17 (3H, t, J=7 Hz, CH_3CH_2); 3,20—3,86 [5H, m, $(CH_2)_2O+CH$]; 4,88 (2H, m, J=1,2 Hz)	64,5	10,4	—	$C_7H_{14}O_2$	64,6	10,7	—	36
Vd	72—75 (15)	1,4329	0,8951	1,68 (3H, d, J=1 Hz, CH_3); 3,09 (1H, br, OH); 1,12 [6H, d, J=7 Hz, $(CH_3)_2$]; 3,39—3,96 (4H, m, $2CHO+CH_2OH$); 4,96 (2H, br, $=CH_2$)	66,5	11,0	—	$C_8H_{16}O_2$	66,7	11,1	—	35
Ve [13]	68—70 (2)	1,4655	1,0284	1,54 (3H, dd, J=1 Hz, CH_3); 3,32—3,44 (2H, m, CH_2); 3,85—4,08 (1H, m, CH); 4,75 and 4,87 (2H, m, J=1,2 Hz, $=CH_2$)	58,5	9,6	—	$C_5H_{10}O_2$	58,8	9,8	—	47
Vf [14]	70—73 (13)	1,4560	1,0936	1,84 (3H, t, J=1 Hz, CH_3); 3,60 (1H, s, OH); 4,49 (1H, t, J=6,2 Hz, CH_3); 3,79 (2H, d, J=6,2 Hz, CH_2); 5,21 and 5,10 (2H, m J=1 Hz, $=CH_2$)	51,6	7,1	(21,5)	$C_7H_{11}ClO_2$	51,7	6,8	(21,9)	68
Vg [15]	98—100 (13)	1,4370	1,0472	1,82 (3H, d, J=1 Hz CH_3); 2,02 and 2,06 (6H, s, $COCH_3$); 5,41 (1H, m, J=7,5 Hz CH); 4,12—4,27 (2H, m, CH_2); 5,09 (2H, m, J=1 Hz, $=CH_2$)	57,9	7,9	—	$C_9H_{14}O_4$	58,1	7,5	—	40
Vh	58—60 (13)	1,4470	0,8795	1,69 (3H, dd, J=1 Hz, CH_3); 2,27 [6H, s, $(CH_3)_2$]; 2,29 (2H, d CH_2N); 3,85 (1H, s, OH); 4,03 (1H, m, CH); 4,96 and 4,79 (2H, m, J=1 Hz, $=CH_2$)	64,9	11,4	10,5	$C_7H_{15}NO$	65,1	11,6	10,9	89 (80)[a]
Vi	82—83 (14)	1,4468	0,8658	1,67 (3H, d, J=1 Hz, CH_3); 3,55 (1H, br, OH); 4,09 (1H, t, J=7 Hz, CH); 3,54—3,75 [4H, m, $(CH_2)_2O$]; 2,75—2,99 [6H, m, $(CH_2)_3N$]; 4,85 and 5,01 (2H, m, J=1,5 Hz, $=CH_2$)	68,7	12,0	8,6	$C_9H_{19}NO$	68,8	12,1	8,9	82 (78)

Vj	89—91 [61—62] (2)			1,70 (3H, dd, J=1 Hz, CH_3); 2,75—2,99 [6H, m, $(CH_2)_3N$]; 3,31 (1H, br, OH); 3,53—3,75 [4H, m, $(CH_2)_2O$]; 4,09 (1H, t, J=7 Hz CH); 4,85 and 5,01 (2H, m, J=1,5 Hz $=CH_2$)	63,5	9,4	7,9	$C_9H_{17}NO_2$	63,2	9,9	8,2	80 (81)
Vk	107—109 (12)	1,4789	0,9436	1,66 (3H, dd, J=1 Hz, CH_3); 1,38 [6H, m, $(CH_2)_3$]; 2,16—2,61 [6H, m, $(CH_2)_3N$]; 3,50 (1H, s, OH), 4,01 (1H, t, J=7 Hz, CH); 4,76 and 4,90 (2H, m, J=1,2 Hz, $=CH_2$)	70,9	11,1	8,1	$C_{10}H_{19}NO$	71,0	11,2	8,3	81 (75)
Vl	66—68 (13)	1,4730	1,0938	1,84 (3H, t, J=1 Hz, CH_3); 3,60 (1H, s, OH); 4,49 (1H, t, J=6,2 Hz, CH); 3,79 (2H, d, J=6,2 Hz CH_2); 5,21 and 5,10 (2H, m J=1 Hz, $=CH_2$)	49,5	7,3	(29,1)	C_5H_9ClO	49,8	7,5	(29,5)	60
Vm	74—76 (10)	1,5112	1,4417	1,88 (3H, br, CH_3); 3,50 (1H, s, OH); 3,75 (2H, d, J=8 Hz, CH_2); 4,56 (1H, t, J=8 Hz. CH); 5,04 and 5,20 (2H, m, J=1 Hz, $=CH_2$)	36,2	5,3	(48,3)	C_5H_9BrO	36,4	5,5	(48,5)	58, 62[b]
VI	137—140 (654)	1,4280	0,9166	1,70 (3H, t, J=1 Hz $=CCH_3$); 1,31 and 1,36 (6H, s, CH_3); 3,65 (1H[c], t, J=8,0 Hz, from CH_2) and 4,05 (1H[c], dd J=8,0 Hz and 6,6 Hz, from CH_2); 4,50 (1H, m, CH); 4,90 and 5,07 (2H, m, J=1 Hz, $=CH_2$)	67,4	9,7	—	$C_8H_{14}O_2$	67,6	9,9	—	70
VII	77—78 (13)	1,4820	1,2762	1,34 (3H, s, CH_3); 1,10 and 1,50 (2H, H_A[d], H, J_{AB}=7 Hz, CH_2); 2,85—2,39 (2H, m, CH_2O); 3,09 (1H, m, CH)	43,3	4,6	42,2	$C_6H_8Cl_2O$	43,1	4,8	42,5	66

[a] Obtained from bromohydrin Vm.
[b] The gaseous HBr.
[c] An ABX system.
[d] An ABC system.

TABLE 2. Characteristics of VIII-X

Compound [lit.]	bp, °C (mm)	n_D^{20}	d_4^{20}	PMR spectrum, δ, ppm	Found, % C	Found, % H	Empirical formula	Calc., % C	Calc., % H	VIII : IX : X ratio (overall yield, %) starting substances: RMgBr—ether	Cu(I)I, 5%,—ether	Cu(I)I—RMgBr, 1 : 1,—ether	Cu(I)I, 5%,—IIt
VIIIa	55—57 (11)	1,4390	0,8471	1,66 (2H, s, $=CCH_3$); 1,38 [4H, m, $(CH_2)_2$]; 0,89 (3H, m, CH_3); 3,56 (1H, s, OH); 3,96 (1H, t, J = =6 Hz, CH); 4,84 and 4,74 (2H, m, J=1 Hz $=CH_2$)	73,6	12,3	$C_7H_{14}O$	73,7	12,3	0 : 80 : 20 (75)	0 : 8 : 92 (60)	0 : 0 : 100 (64)	75 : 3 : 22 (70)
IXa [16]	58—61 (10)	1,4435	0,8536	1,63 (3H, s, $=CCH_3$); 3,49 [2H, s, CH_2 (OH)]; 0,82 (3H, t, J=6,5 Hz, CH_2CH_3); 1,22—1,53 (2H, m, CH_2CH_3); 1,95—2,23 (1H, m, CH); 3,37 (1H, s, OH); 4,83 and 4,76 (2H, m, J=1 Hz $=CH_2$)	73,4	12,1							
Xa [17]	77—79 (15)	1,4512	0,8736	1,62 and 1,68 (E : Z=73 : 27, 3H, br.d, J=1,2 Hz, CH_3); 0,88 (3H, t, J=6,5 Hz, CH_3); 1,31 (2H, m, CH_2); 1,99 (2H, m, $CH_2C=$); 3,75 (1H, br, OH); 4,02 [2H, d, J=7,2 Hz, CH_2(OH)]; 5,35 (1H, t, J=6,6 Hz, =CH)	73,5	12,4							
VIIIb	65—67 (12)	1,4385	0,8385	1,68 (3H, dd, J=1 Hz, $=CCH_3$); 0,89 [6H, d, J= =6,5 Hz, $(CH_3)_2$]; 1,21—1,93 (3H, m, CH+CH_2); 3,35 (1H, br, OH); 4,05 [1H, t, J=6,8 Hz, CH(OH)]; 4,76 and 4,90 (2H, m, J=1,2 Hz, $=CH_2$)	74,8	12,3							
IXb	64—67 (8)	1,4450	0,8493	1,68 (3H, dd J=1 Hz, $=CCH_3$); 0,89 [6H, m, $(CH_3)_2$]; 1,52—2,08 [2H, m, CH+CH$(CH_3)_2$]; 2,86 (1H, br, OH); 3,54—3,63 (2H, m, CH_2); 4,78 and 4,89 (2H, m, J=1 Hz, $=CH_2$)	75,1	12,3	$C_8H_{16}O$	75,0	12,5	0 : 53 : 47 (74)	0 : 6 : 94 (50)	Resinified	87 : 0 : 13 (66)
Xb [18]	76—79 (8)	1,4505	0,8473	1,59 (3H, s, CH_3); 0,86 [6H, d, J=6,2 Hz, $(CH_3)_2$]; 1,64—1,88 [3H, m, CH_2+CH$(CH_3)_2$]; 4,08 (1H, s, OH); 4,04 (2H, d, J=6 Hz, CH_2); 5,34 (1H, m, =CH)	74,9	12,4							
VIIIc	91—92 (12)	1,4473	0,8429	1,68 (3H, dd, J=1 Hz, $=CCH_3$); 0,87 [6H, d, J= =6,7 Hz, $(CH_3)_2$]; 3,17 (1H, br, OH); 4,01 [1H, m, CH(OH)]; 1,07—1,47 [7H, m, $(CH_3)_2$+CH]; 4,81 and 4,92 (2H, m, J=1 Hz, $=CH_2$)	76,9	12,7							
IXc	68—71 (2)	1,4475	0,8446	1,65 (3H, d, J=1 Hz, $=CCH_3$); 0,86 [6H, d, J= =6,2 Hz, $(CH_3)_2$]; 1,18—1,45 [5H, m, $(CH_2)_2$CH]; 1,75 (1H, m, CH— allyl); 2,85 (1H, m, OH); 3,35 (2H, d, J=7,3 Hz, CH_2OH); 4,75 and 4,48 (2H, m, J=1 Hz, $=CH_2$)	76,9	12,8	$C_{10}H_{20}O$	76,9	12,8	0 : 84 : 16 (82)	0 : 10 : 90 (75)	0 : 0 : 100 (40)	64 : 2 : 34 (82)
Xc [19]	80—81 (2)	1,4550	0,8627	1,64 and 1,73 (E : Z=65 : 35, 3H, dd, J=1 Hz, $=CCH_3$); 0,89 [6H, d, J=6 Hz, $(CH_3)_2$]; 1,22—1,51 [5H, m, CH$(CH_2)_2$]; 1,82—2,10 (2H, m, CH_3OH); 3,82 (1H, br, OH); 4,06 (2H, d, J=6,6 Hz, CH_2OH); 5,41 (1H, t, J=7 Hz, =CH)	76,8	12,4							
IXd	91—94 (2)	1,5400	1,0142	1,56 (3H, d, J=1 Hz, $=CCH_3$); 2,93 (1H, br, OH); 3,21—3,51 (1H, br, CH); 3,66—3,96 (2H, m, CH_2); 4,88 (2H, m, J=1 Hz, $=CH_2$); 7,23 (5H, s, C_6H_5)	81,4	8,4							
Xd [20]	112—115 (3)	1,5410	1,0046	1,53 and 1,60 (E : Z=74 : 26, 3H, dd, J=1 Hz, CH_3); 3,24 (1H, s, OH); 4,08 (2H, d, J=7,2 Hz CH_2OH); 5,49 (1H, t, J=7 Hz, =CH); 7,16 (5H, s, C_6H_5)	81,6	8,7	$C_{11}H_{14}O$	81,5	8,6	0 : 100 : 0 (85)	0 : 59 : 41 (72)	0 : 30 : 70 (85)	0 : 90 : 10 (80)
IXe	123—125 (2)	1,5660	1,0197	1,81 (3H, dd, J=1 Hz, CH_3); 3,14 (1H, br, OH); 3,71 (2H, d, J=6,5 Hz, CH_2); 3,25—3,46 (1H, m, CH); 4,90 and 5,30 (2H, m, J=1 Hz, $=CH_2$); 7,25 (2H, m, C_6H_5)	83,9	7,4	$C_{13}H_{14}O$	83,9	7,5	0 : 100 : 0 (89)	0 : 84 : 16 (84)	0 : 65 : 35[a] (39)	0 : 59 : 41 (93)

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl_4 and D_2O were obtained with a Perkin-Elmer R-12 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The purity of the synthesized products was determined by means of GLC with an LKhM-8MD chromatograph with a catharometer with columns with lengths of 2 and 3 m packed with 10% PEG-20M on AW-HMDS Inerton and 5% SE-30 on N-AW-HMDS Chromaton; the carrier-gas (helium) flow rate was 40-60 ml/min, and the temperature was 120-230°C.

The characteristics of compounds V-VII are presented in Table 1, and the characteristics of VIII-X are presented in Table 2.

Isopropenyloxirane (I). A 16.8-g (0.3 mole) sample of KOH was placed in a flask equipped with a stirrer and a descending condenser, and 16.5 g (0.1 mole) of halohydride IIIb was added slowly dropwise. A temperature of 80°C was maintained due to the exothermic reaction, after which the mixture was heated for another 30 min until the evolution of oxide I ceased. The oxide was removed by distillation, dried with $MgSO_4$, and fractionated to give 6.7 g (80%) of oxide I with bp 80-82°C (650 mm) [9]. The yield from halohydrin IIIa was 70%.

Reaction of Oxide I with Grignard Reagents. A) A 4.2-g (0.05 mole) sample of oxide I in 30 ml of ether was added to a Grignard reagent obtained from 2.4 g (0.1 mole) of magnesium and 0.1 mole of the halide in 100 ml of absolute ether, after which the mixture was heated at 35°C for 1 h. It was then cooled to 0°C and decomposed with a saturated solution of ammonium chloride. The resulting mixture was allowed to stand for another 3 h, after which the ether solution was decanted to separate it from the precipitate and fractionated *in vacuo* (Table 2).

B) The Grignard reagent similarly obtained from 0.1 mole of magnesium was cooled to −70 to −80°C, 19.1 g (0.1 mole) of Cu(I)I was added, and the mixture was stirred for 30 min. The temperature was then raised to 0°C, and 4.2 g (0.05 mole) of oxide I was added slowly dropwise. The resulting mixture was then allowed to stand overnight, after which it was poured over ice. The aqueous mixture was stirred, ammonium chloride was added, and the organic layer was separated. The aqueous layer was extracted with ether, and the ether extracts were combined, dried with $MgSO_4$, and distilled (Table 2).

C) The experiment was carried out as in method B with the exception that the temperature was −20°C, and 5% Cu(I)I was used (Table 2).

D) The experiment was carried out as in method C, but the reaction was carried out in absolute THF (Table 2).

2-Methyl-4-dialkylamino-1-buten-3-ols (Vh-k). A) A mixture of 6.3 g (0.075 mole) of oxide I and 0.075 mole of a secondary amine in 20 ml of benzene was stirred at 75°C for 20 h, after which it was fractionated *in vacuo* to give amino alcohols Vj, k.

B) A mixture of 4.7 g (0.056 mole) of oxide I, and 0.07 mole of the amine was heated in an ampul (bath temperature 80°C) for 30 h, after which it was fractionated *in vacuo* to give Vh,i. IR spectrum: 3430 (OH) and 3080 cm^{-1} (=CH_2).

C) An 8.2-g (0.05 mole) sample of 4-bromo-2-methyl-1-buten-3-ol Vm was added dropwise to a mixture of 0.01 mole of the amine and 30 ml of benzene, and the mixture was stirred at 75°C for 10 h. It was then filtered to remove the precipitated salt and washed with ether. Fractionation gave amino alcohols identical to Vh-k. IR spectrum: 3442 (OH), 3080 (=CH_2), and 1648 cm^{-1} (C=C).

Reaction of Oxide I with Alcohols. A) A mixture of 4.2 g (0.05 mole) of oxide I, 0.1 mole of alcohol, and 0.2 g of p-toluenesulfonic acid was refluxed for 1-2 h, after which fractionation *in vacuo* gave Vb-d.

B) From 1.2 g of sodium and 25-30 ml of alcohol we obtained the alkoxide, to which we added 4.2 g (0.05 mole) of oxide I and heated the mixture to the boiling point for 15-18 h. The excess alcohol was removed by distillation, 15 ml of water was added, and the aqueous mixture was extracted with ether. The extract was dried over $MgSO_4$ and fractionated *in vacuo* to give only alcohol Va in pure form. IR spectrum: 3460 (OH), 3078 (=CH_2), and 1652 cm^{-1} (C=C).

2,2-Dimethyl-5-isopropenyl-1,3-dioxolane (VI). A 6.3-g (0.075 mole) sample of oxide I was added dropwise with stirring to a mixture of 20 ml of acetone and a drop of $BF_3 \cdot OEt_2$. After the exothermic reaction was complete, the mixture was stirred for another 6 h, neutralized with Na_2CO_3, and fractionated. IR spectrum: 1652 (C=C) and 3082 cm^{-1} (=CH_2).

3-Chloro-4-acetoxy-2-methyl-1-butene (Vf). A 6.3-g (0.075 mole) sample of oxide I was added dropwise with stirring at −10°C to a mixture of 6.9 g (0.08 mole) of acetyl chloride, 45 ml of methylene chloride, and 0.3 ml of $SnCl_4$, after which the mixture was stirred for 1 h and allowed to stand overnight. A 1-ml sample of triethylamine was added, and the mixture was filtered to remove the precipitated salt and fractionated. IR spectrum: 3082 (=CH_2), 1447 (C=O), and 1650 cm^{-1} (C=C).

3,4-Diacetoxy-2-methyl-1-butene (Vg). A 6.3-g (0.075 mole) sample of oxide I was added dropwise at 20°C to 10.2 g (0.1 mole) of acetic anhydride in the presence of 0.3 g of p-toluenesulfonic acid, after which the mixture was stirred at 40-50°C for 8-10 h and then neutralized with sodium carbonate. It was then filtered, and the filtrate was fractionated. IR spectrum: 1747 (C=O), 1652 (C=C), and 3100 cm^{-1} (=CH_2).

(2,2-Dichloro-1-methyl-1-cyclopropyl)oxirane (VII). A 0.1-mole sample of chloroform was added with stirring, while maintaining the temperature of the reaction mixture at 30-35°C, to a mixture of 4.2 g (0.05 mole) of oxide I, 24 ml of a 50% solution of NaOH, and catalytic amounts of triethylbenzylammonium chloride (TEBAC), after which the mixture was stirred for 2 h, cooled, and extracted with ether. The ether extract was dried with $MgSO_4$ and fractionated to give VII.

3-Chloro-2-methyl-1-buten-4-ol (VI). A 22-g sample of the $HCl \cdot OEt_2$ complex was added dropwise at 0°C to 15.1 g (0.18 mole) of oxide I, after which the mixture was stirred for another 2 h. The ether was removed by distillation, and the residue was fractionated *in vacuo*. IR spectrum: 3300-3452 (OH), 1652 (C=C), and 3086 cm^{-1} (=CH_2).

2-Methyl-3,4-dihydroxy-1-butene (Ve). A 6 g (0.071 mole) sample of oxide I was added dropwise to 15 ml of 5% sulfuric acid, after which the mixture was stirred at 40°C for 10 h. It was then neutralized with sodium carbonate and fractionated *in vacuo*. IR spectrum: 3320-3500 (OH), 3080 (=CH_2), and 1652 cm^{-1} (C=C).

3-Bromo-2-methyl-1-buten-4-ol (Vm). A) A mixture of 8.4 g (0.1 mole) of oxide I, 20.3 g (0.12 mole) of 48% hydrobromic acid, 11.9 g (0.1 mole) of KBr, and 20 ml of benzene was stirred at 0°C for 2 h, after which it was decanted, and the decantate was neutralized with sodium carbonate, dried with $MgSO_4$, and fractionated *in vacuo* to give Vm.

B) A mixture of 8.4 g (0.1 mole) of oxide I and 30 ml of CCl_4 was cooled to 0°C, and gaseous hydrobromic acid (obtained from 0.33 mmole of PBr_3 and 3 ml of 48% hydrobromic acid) was passed through the mixture. It was then stirred at 16°C for 1 h and fractionated to give Vm.

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