SCISSION OF OXIRANES BY ACID ANHYDRIDES TO UNSATURATED ALCOHOL ESTERS

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The reactions of some 1-R-3-methyl-2,3-epoxybutanes with acetic and propionic anhydrides takes place at 140-160°C, regioselectively, with the formation of β-metallyl alcohol esters.

1-Halo-3-methyl-2,3-epoxybutanes Ia, b, in the presence of acids or by simple heating, are isomerized to α-substituted β-metallyl alcohols [1, 2]. In analogous conditions, alkene oxides form carbonyl compounds instead of alcohols [3, p. 374]. The unusual behavior of oxiranes Ia, b is explained by the presence of an electron-accepting substituent (halogen), which hinders the deprotonation of the intermediate carbonium cation from the methine position.

In this connection, we showed that when substituting a phenoxy group for the halogen (the phenoxy group occupies a position between alkyl groups and halogens by its induction constant [4, p. 84]), the regioselectivity of the deprotonation of the intermediate carbanion cation A changes towards the expected direction: 4-phenoxy-2,3-epoxybutane If gives a mixture of butanone IV and hydroxybutene V isomers in a ratio of 30:70.

We confirmed additionally the effect of the electron acceptance of the substituent on the regioselectivity also while investigating the dehydrochlorination of 2-acetoxy- and 2-hydroxybutanes VIa, b with DMFA by the method described in [5]. The former yielded only the acetate IIh, while the latter produced a mixture of ketone IV and alcohol V (70:30 according to PMR and GLC data). Ketone IV was produced by inverse synthesis from 2-methyl-4-phenoxy-2,3-epoxybutane and sodium phenolate.

This reaction as well as the acid-catalyzed isomerization of epoxides, constitute examples of acid catalyzed elimination via an intermediate carbonium cation [6, 7], therefore it is quite logical that the intermediate carbonium cation A with a more electronegative substituent produces an ester, while the basic compound VIb produces a carbonyl compound.

Starting with such premises about the isomerization mechanism of compounds Ia, b, f similar transformations could have been expected also for oxides, containing instead of a halomethyl or phenoxymethyl other, more electron-accepting groups, such as acetoxyl, carbalkoxy, etc. We investigated the behavior of the available acetyloxirane Ic. We found, however, that in the conditions described in [1] this compound reacted differently forming preferentially 4-methyl-2,3-pentanedione [8]. This can be explained by the fact that in the presence of a carbonyl group, the expected carbonium cation is not produced because of the preferential protonation at the carbonyl and not at the oxirane oxygen atom.

Based on the above considerations, we used acetic anhydride instead of the acid as the electrophilic reagent. The anhydride has a higher tendency to attack the epoxy group than the carbonyl oxygen [3]. Moreover, it was expected that during the generation of the carbanion cation, its deprotonation from the neighboring methine position would be hindered as compared to the basic non-acetylated analogs (obtained when reacting oxiranes with proton acids) because of the presence of the acetoxy group. This supposition is supported by data in [9], according to which certain 2,3-diacetoxy-2-methyl-4-pentanones were observed to split to metallyl alcohol acetates, although with low yields (13-41%).

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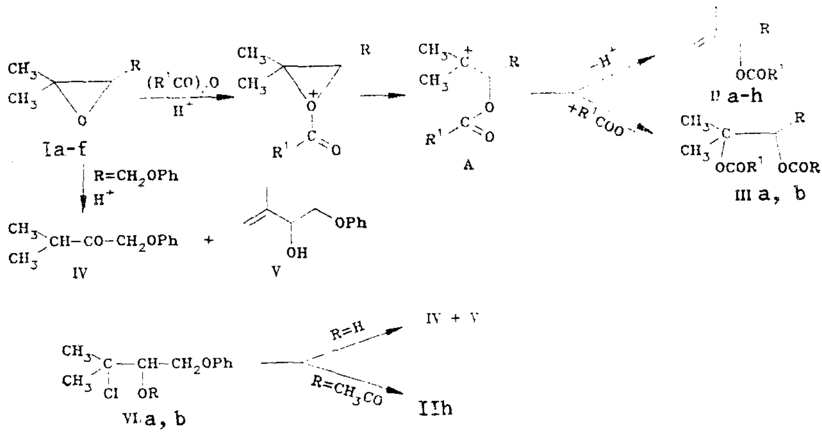
In fact, as was expected, the reaction between oxiranes Ia-f and acetic anhydride produced with high yields the metallyl alcohol acetates IIa-d, g, h.



Ia R=CH$_2$Cl; b R=CH$_2$Br; c R=COCH$_3$; d R=COC$_2$H$_5$; e R=CH$_2$O-i-Pr; f R=CH$_2$OPh. IIa, e R=CH$_2$Cl; b R=CH$_2$Br; c R=COCH$_3$; d, f R=COC$_2$H$_5$; g R=CH$_2$O-i-Pr; h R=CH$_2$OPh; a-d, h R^1=CH$_3$; e, f R^1=C$_2$H$_5$; g R^1=COCH$_3$. IIIa R=COCH$_3$; b R=COC$_2$H$_5$; a, b R^1=CH$_3$. VIa R=COCH$_3$; b R=H.

At ~140°C the process is completed in 15-30 min (controlled by PMR data). At lower temperatures, apparently as a result of a stabilization of particles formed by the attachment of anions, the corresponding diesters of glycols IIIa, b were also formed [9, 10]. The formation scheme of monoacetates via intermediate diacetates is excluded because during the thermal decomposition of the latter (as known from the example of oxiranes Ic, d [9, 10]), isomeric vinyl acetates are also formed together with allyl alcohol acetates.

It was established that propionic anhydride participated in the reaction just as successfully (temperature ~160°C), converting oxiranes Ia, d to esters IId, f. It must be noted that bromomethyloxirane Ib formed 3-acetoxybutene IIb, which under the reaction conditions underwent a cascade homoallyl anionotropy [11], and the metallyl chloride oxide gave a mixture of three monoacetates, 3-acetoxy-2-chloromethyl-1-propene, 3-acetoxy-2-methyl-1-chloro-1-propene, and 1-acetoxy-2-methyl-3-chloro-1-propene in a ratio 45:19:36 (based on PMR data).

EXPERIMENTAL

The PMR spectra were recorded with a Perkin-Elmer R-12B instrument (60 MHz) in CCl$_4$ and with HMDS as the internal standard. The chromatography was conducted with a LKhM-8MD instrument (with a katharometer) using 1 and 3 m columns with SE-30 (or 15% APL) on Chromaton N-AW-HMDS and 5% OV-17 on Chromaton N-Super. The carrier gas (helium) flow rate was 40-60 ml/min and the temperature, 120-200°C.

The characteristics of the synthesized compounds are presented in Table 1. The elemental analysis data for C, H, and Halogen agreed with the calculated data.

Reaction of 1-R-2,3-Epoxybutanes Ia-f with Acetic and Propionic Anhydrides. To a mixture of 10.2 g (100 mmole) acetic anhydride and 0.19 g (1 mmole) p-toluenesulfonic acid at 140°C we added quickly 10 mmole of oxirane I. The mixture was then heated at the boil. The reaction was monitored by PMR following the signals of the methyl groups of oxirane at 1.20-1.30 ppm and the signals of compounds II at 1.70-1.78 ppm. After 15-30 min the reaction mixture was distilled.

The reaction with propionic anhydride was carried out analogously at 160°C.

Reaction of 2-Methyl-3-chloro-1,2-epoxypropane with Acetic Anhydride. In an analogous manner, we obtained from 10.7 g (100 mmole) or 2-methyl-1-chloro-2,3-epoxypropane and 10.2 g (10 mmole) of acetic anhydride (8 h at 125°C), 10.7 g (72%) of a mixture of 3-acetoxy-2-chloromethyl-1-propene, 3-acetoxy-2-methyl-1-chloro-1-propene, and 1-acetoxy-2-methyl-3-chloro-1-propene; ratio, 45:19:36; bp 75-87°C at 12 mm Hg column. The ratio of the isomers was determined from the integral intensity of signals of CH$_2$-, ClCH-, and AcOCH- at 5.30, 5.93, and 6.15 ppm.

TABLE 1. Characteristics of Compounds IIa-h and IV, V, and VIa, b

Compound	Elemental formula	bp, °C (mm Hg column)	n_D^{20}	d_4^{20}	PMR spectrum, δ, ppm	Yield, %
IIa	$C_7H_{11}ClO_2$	69 . . . 71 (11)	1,4470	1,0766	1,78 (3H, dd, $J=1$ Hz, CH_3); 2,10 (3H, s, $CH_3C{=}O$); 3,63 (2H, d, $J=6,6$ Hz, CH_2Cl); 5,01 . . . 5,19 (2H, m, $=CH_2$); 5,32 (1H, t, $J=6,6$ Hz, CH—OAc)	68
IIb	$C_7H_{11}BrO_2$	81 . . . 82 (11)	1,4680	1,3152	1,70 (3H, dd, $J=1,0$ Hz, CH_3); 2,02 (3H, s, $CH_3C{=}O$); 3,45 (2H, d, $J=6,6$ Hz, CH_2Br); 5,04 (2H, m, $=CH_2$); 5,37 (1H, t, $J=6,6$ Hz, CH—OAc)	80
IIc	$C_8H_{12}O_3$	78 . . . 81 (10)	1,4375	1,0069	1,71 (3H, dd, $J=1$ Hz, CH_3); 2,11 (6H, s, $CH_3C{=}O$); 5,19and5,31 (2H, two m $=CH_2$); 5,41 (1H, s, CH)	60
IId	$C_9H_{14}O_4$	91 . . . 92 (11)	1,4295	1,0242	1,20 (3H, t, $J=7,1$ Hz, $CH_3—CH_2$); 1,77 (3H, dd, $J=1$ Hz, $CH_3C{=}$); 2,09 (3H, s, $CH_3C{=}O$); 4,15 (2H, q, $J=7,1$ Hz, OCH_2CH_3); 5,03 and5,11 (2H, two m, $=CH_2$); 5,22 (1H, s, CH—OAc)	72
IIe	$C_8H_{13}ClO_2$	80 . . . 82 (12)	1,4460	1,0397	1,12 (3H, t, $J=7,3$ Hz, CH_3CH_2); 1,78 (3H, dd, $J=1$ Hz, CH_3); 2,30 (2H, q, $J=7,3$ Hz, $CH_2—CH_3$); 3,52 (2H, d, $J=6,1$ Hz, CH_2Cl); 4,88 . . . 5,03 (2H, m, $=CH_2$); 5,23 (3H, br.t, $J=6,1$ Hz, CH)	68
IIf	$C_{10}H_{16}O_4$	101 . . . 102 (12)	1,4330	1,0099	0,95 . . . 1,31 (6H, m, two $CH_3—CH_2$); 1,75 (3H, dd, $J=1$ Hz, CH_3); 2,34 (2H, q, $J=7,5$ Hz, CH_2CO); 4,12 (2H, q, $J=7,5$ Hz, $CH_2—OC{=}O$); 4,94 . . . 5,13 (2H, m, $=CH_2$); 5,20 (1H, br.s, CH)	65
IIg	$C_{10}H_{16}O_3$	81 . . . 83 (13)	1,4260	0.9347	1,11 (6H, d $J=6,5$ Hz, $(CH_8)_2—CH$); 1,75 (3H, dd, $J=1$ Hz, CH_3); 1,98 (3H, s, CH_3CO); 3,45 (2H, d, $J=6,5$ Hz, CH_2O); 3,33 . . . 3,75 (1H, m, $(CH_3)_2CH$); 4,86 and4,92 (2H, two m $=CH_2$); 5,22 (1H, br.t, $J=6,5$ Hz, CH—OAc)	67
IIh	$C_{13}H_{16}O_3$	128 . . . 131 (3)	1,5075	0,9069	1,75 (3H, dd, $J=1$ Hz, $=CCH_3$); 1,99 (3H, s, $CH_3C{=}O$); 3,94 (2H, d $J=6,0$ Hz, CH_2); 4,90 and4,93 (2H, two m, $=CH_2$); 5,36 (1H, t, $J=6,0$ Hz, CH—OAc); 6,61 . . . 7,06 (5H, m, C_6H_5)	75
IV	$C_{11}H_{14}O_2$	90 . . . 92 (3)	1,5075	1,0355	1,08 [6H, d, $J=6,6$ Hz, $(CH_3)_2$]; 2,98 (1H, m, CH); 4,50 (2H, s, CH_2O); 6,86 . . . 7,30 (5H, m, C_6H_6)	71
V		117 . . . 119 (4)	1,5272	1,0474	1,69 (3H, dd, $J=1$ Hz, CH_3); 2,98 (1H, br.s, OH); 3,82and4,31 (2HandH, A_2B, $J_{AB}=4,7$ Hz, $CHCH_2OPh$); 4,86and5,08 (2H, two m, $=CH_2$); 6,72 . . . 7,38 (5H, m, C_6H_5)	
VIa	$C_{13}H_{17}ClO_3$	142 . . . 146 (3)	1,5050	1,1340	1,51 (3H, s, CH_3); 1,58 (3H, s, CH_3); 1,98 (3H, s, CH_3CO); 4,09 . . . 4,43 (2H, m, CH_2); 5,18 . . . 5,34 (1H, m, CH); 6,73 . . . 7,31 (5H, m, C_6H_5)	74
VIb	$C_{11}H_{15}ClO$	126 . . . 128 (14)	1,5250	1,1835	1,66 (3H, s, CH_3); 1,70 (3H, s, CH_3); 3,03 (1H, s, OH); 3,82, 4.25 (2HandH, A_2B, $J_{AB}=8,0$ Hz, CH_2CH_2OPh); 6,73 . . . 7,23 (5H, m, C_6H_5)	83

2-Acetoxy-1-phenoxy-3-chloro-2-methylbutane (VIa). To a solution of 3.9 g (50 mmole) of acetyl chloride in 25 ml CH_2Cl_2, we added 5-6 drops of $SnCl_4$. The mixture was cooled to –5°C and 8.7 g (49 mmole) of oxirane If was added dropwise. The mixture was left standing overnight; 1 ml triethylamine was then added. The precipitated salt was filtered out and the filtrate was distilled. IR spectrum: 1590, 1610 (aromatic $C{=}C$); 1752 ($C{=}O$), 3030 cm^{-1} (aromatic CH).

2-Hydroxy-1-phenoxy-3-chloro-2-methylbutane (VIb). A mixture of 12 g oxirane If and 7 g of complex $Et_2O \cdot HCl$, prepared at 0°C, was held 6 h at this temperature and then vacuum distilled. IR spectrum: 1600, 1610 (aromatic $C{=}C$); 3030 (aromatic CH); 3425-3530 cm^{-1} (OH).

Reaction of 2-Hydroxy-1-phenoxy-3-chloro-2-methylbutane (VIb) with DMFA. A mixture of 7.5 g chlorhydrin VIb and 11 ml of DMFA was mixed 9 h at 130°C according to the method described in [5]. 4.5 g (73%) of a mixture of ketone IV and alcohol V (70:30) was obtained by vacuum distillation [PMR, $(CH_3)_2CH$, and CH_3 signals at 1.08 and 1.78 ppm], bp 110-118°C (8 mm Hg column). IR spectrum of the mixture: 1590, 1600 (aromatic $C{=}C$); 1652 ($C{=}C$); 1725 ($C{=}O$); 3030 (aromatic CH); 3090 ($={CH_2}$); 3380-3530 cm^{-1} (OH), PMR spectrum of compounds IV and V (in CCl_4): 1.08 [6 H, d, J = 6.6 Hz, $(CH_3)_2$]; 1.78 (3 H, two d, J = 1 Hz, CH_3); 2.68-2.79 (1 H, m, CH-i-Pr); 3.02 (1 H, t, J = 6.8 Hz, $C\underline{H}{-}OH$); 3.80 (1 H, br. s, OH); 3.92 (2 H, d, J = 6.8 Hz, $C\underline{H}_2{-}CHOH$); 4.49 (2 H, s $C\underline{H}_2OPh$); 4.94, 5.10 (2 H, m, $={CH_2}$); 6.72-7.32 ppm (5 H, m, C_6H_5).

Ketone IV was identified by GLC in comparison to a sample obtained as described below.

1-Phenoxy-3-methyl-2-butanone (IV). To 4.8 g (0.9 mmole) of phenol we added first 2.4 g (60 mmole) of NaOH in 2.4 ml of water, and then, slowly, 8.4 g (0.9 mmole) of 1-bromo-3-methyl-2-butanone. The mixture was heated 10 h at 80°C, cooled, extracted with ether, and distilled. IR spectrum: 1590 (aromatic $C{=}C$); 1730 ($C{=}O$); 3030 cm^{-1} (aromatic CH).

Reaction of 2-Acetoxy-1-phenoxy-3-chloro-2-methylbutane with DMFA. Analogously [5], we obtained from 6.7 g of chloroacetate VIa in 7.5 ml of DMFA, 3.9 g (70%) acetate IIh, which was identical according to GLC data to the sample obtained directly from oxirane If.

3-Hydroxy-2-methyl-4-phenoxy-1-butene (V). A mixture of 8.9 g oxirane If, 0.3 g of p-toluenesulfonic acid in 10 ml of benzene was boiled during 10 h and then distilled. 7.7 g (87%) of a mixture of ketone IV and alcohol V was obtained in a ratio of 30:70; the bp was 95-115°C (4 mm Hg column). 5.5 g of butene V was separated from this mixture by fractional distillation (62%).

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