A New Reaction of Epoxy Aldehydes Resulting in the Formation of Epoxy β-Propiolactones

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In the presence of aluminum alkoxides the α-methyl derivatives of glycidaldehyde were shown to yield mainly epoxy β-propiolactones and, as might have been expected, the corresponding diepoxy esters formed in a Tischenko–Claisen reaction. The structure of the resulting diastereomeric epoxy derivatives of β-propiolactone was established and a correlation was found to exist between their yield and the concentration of the catalyst.

The disproportionation reaction of aliphatic aldehydes to esters in the presence of aluminum alkoxides constituted the subject of detailed studies of Tischenko,[1-3] and is known in the literature as the Tischenko–Claisen reaction. Although that reaction takes place generally in the presence of aluminum alkoxides, other catalysts such as boric acid[4] and hydrides of alkali metals may be also used.[5] The mechanism of the reaction has been discussed in numerous publications, an ionic reaction mechanism[6] and a ionic–coordinative mechanism[7] having been postulated.

Studies in this field were initially confined to simple saturated aliphatic aldehydes, such as acetaldehyde, propionaldehyde, isobytyric aldehyde, to some unsaturated aldehydes, e.g., acrolein, and also to aromatic aldehydes.[3]

Reaction of such simple epoxy aldehydes as, e.g., glycidaldehyde and its homologues, carried out in the presence of aluminum isopropoxide had been described by one of us earlier, the disproportionation reaction having been found to yield corresponding diepoxy esters which might subsequently polymerize under suitable reaction conditions. The possibility of the presence of small amounts of epoxy β-propiolactone derivatives was also suggested, but their structure has not been investigated in greater detail.[8]

However, more attention has been paid recently to the syntheses of bifunctional compounds containing a β-lactone ring and various reactive substituents.[9]

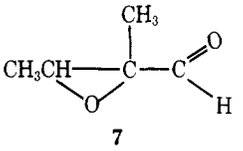
The present work is concerned with the reaction of α-methylepoxy aldehydes carried out in the presence of various aluminum alkoxides, resulting in the formation of epoxy β-propiolactone derivatives. 2-Methyl-2,3-epoxypropanal (**1**) and 2-methyl-2,3-epoxybutanal (**7**) were selected as model compounds.

Results and Discussion

2-methyl-2,3-epoxypropanal (**1**) was found to yield in the presence of aluminum isopropoxide **2a** epoxy derivatives of β-propiolactone **4**, and also a small amount of 2-methyl-2,3-epoxypropyl 2-methyl-2,3-epoxypropionate (**3**).

The formation of epoxy derivatives of β-propiolactone **4** was not found to take place in the presence of all standard Tischenko reaction catalysts. Thus, as earlier reported, in the presence of sodium hydride the corresponding ester **3** was the only reaction product and no β-lactones were formed in that particular case.[10]

However, with epoxy aldehydes having the methyl group in the α position (**1** and **7**) the corresponding derivatives of β-propiolactone were found to be the main products in the presence of aluminum alkoxides.



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This new and hitherto unreported reaction makes possible the synthesis of α-oxirane-substituted β-propiolactone derivatives, difficult to obtain by other synthetic routes.

It is also possible to synthesize exoxy β-propiolactones with various alkoxy substituents (compounds **4**, **5**, and **6**, Scheme I) using different aluminum alkoxides, as described in detail in the Experimental Section.

This reaction proceeds both in neat and in nonpolar solvents. The yield of β-lactones was increased by raising the concentration of aluminum alkoxide catalyst (above 0.1 mol/L). Moreover, the Tischenko reaction leading to the formation of an epoxy ester was found to be negligible at higher concentrations of the catalyst (viz. Table I).

The mixture of diepoxy ester **3** and β-lactones was separated by means of gas chromatographic techniques. Substances with relative retentions of 1.33 and 1.44 (peaks **4a** and **4b** in Figure 1) had the same mass spectra and were also found to give identical infrared spectra with the characteristic stretching vibrations of the β-lactone ring carbonyl group at 1815 cm^{-1}. Results of elementary analysis and determinations of the molecular weight of both compounds were found to be identical in the case of the two substances analyzed (**4a** and **4b**). These results suggest that the two analyzed substances were diastereomers of structure **4**.

The presence of three asymmetric carbon atoms in the compound **4** does in fact make possible the existence of eight enantiomers (Figure 2), which form four pairs of diastereomers.

It was expected that each chromatographic peak corresponded to a mixture of two diastereomers, since the physical properties of diastereomers can be influenced by differences in the configuration at the neighboring asymmetric carbon atoms (atoms 2 and 3 in Figure 2). That supposition was confirmed by proton NMR spectra. Ratios of signals due to different alkyl groups were found to be identical in both cases and equal to 1:3:2:12, which indicated the presence of 18 protons in each substance (**4a** and **4b**).

On the other hand, differences due to the influence of cen-

Scheme I

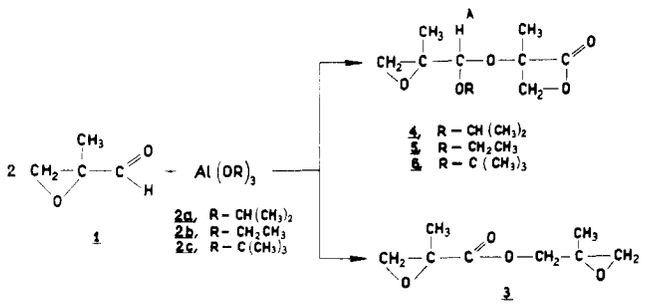

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Table I. Effect of Concentration and Type of Catalyst on the Course of the Reaction of Aldehyde 1

reaction conditions[a]			composition of the reaction products,[b] %		
catalyst system	catalyst concn, mol/L	time, h	3	4a	4b
2a	0.1	120	58	22	20
2a	0.2	120	13	48	39
2a	0.3	120	7	51	42
2a	0.4	120	5	52	43
NaH	0.3	30	100		

[a] Solvent, benzene; reaction temperature, 20 °C; initial concentration of aldehyde 1, 4 mol/L. [b] Determined by gas chromatography, taking the total concentration of compounds 3, 4a, and 4b as 100%.

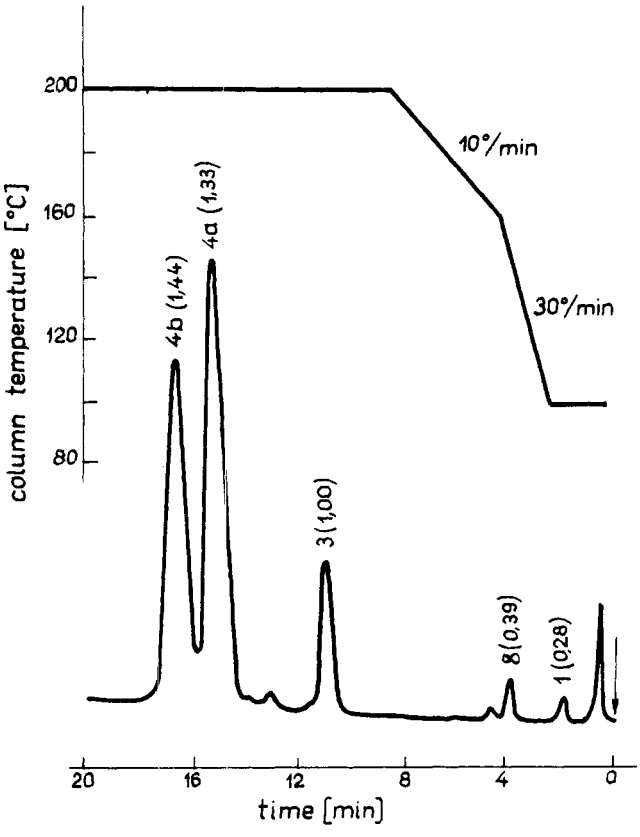


Figure 1. Chromatogram of the oily fraction resulting from the reaction of aldehyde 1 in the presence of alkoxide **2a**: initial aldehyde concentration, 4 mol/L; initial alkoxide concentration, 0.4 mol/L; solvent, benzene; reaction temperature, 20 °C; retention times with respect to 3 are given in the brackets.

ters of asymmetry were to be observed. This effect becomes particularly pronounced in the case of two different signals of the methine group (proton A, Scheme I).

The possibility of two signals of the proton A being due to a spin–spin coupling was excluded by double resonance experiments and recording the ^{1}H NMR spectra at various field frequencies (60 and 100 MHz), as shown in Table II.

The two different signals of the proton A observed in the ^{1}H NMR spectra of each chromatographically separated substance (**4a** and **4b**) may be thus seen to correspond to two methine protons of different diastereomers.

The results indicate clearly that diastereomeric epoxy derivatives of β-propiolactone having the structure **4** are formed in the reaction studied.

The gas chromatogram also shows the presence of unreacted aldehyde 1 and the mixed ester 8, the latter and the corresponding diepoxy ester 3[11] constituting the byproducts of the investigated reaction.

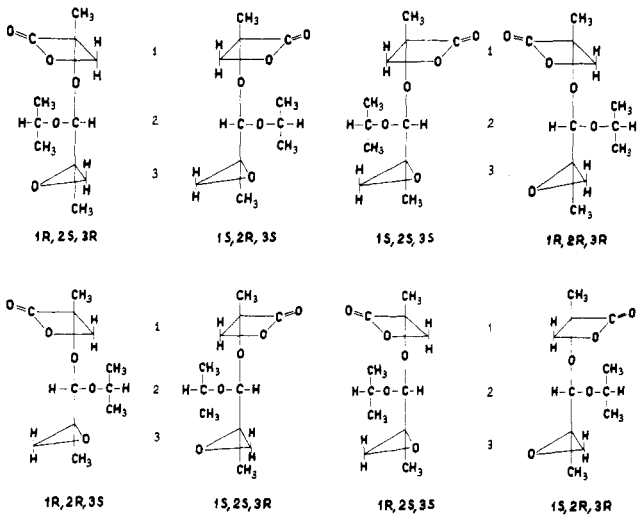
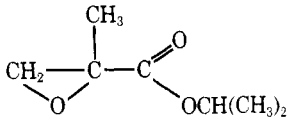


Figure 2. Structures of the possible enantiomers of β-lactone **4**.

Table II. Differences in the Chemical Shifts of the Methine Group Protons of the Diastereomeric Pairs of the Compound 4

compd	chemical shifts[a] of proton A, δ	differences in chemical shifts of proton A, Hz 100 MHz	60 MHz
4a	5.27; 5.30	3.5	1.8
4b	4.97; 5.01	4.5	2.7

[a] Taken at 100 MHz from 5% solution in CCl_4.



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Conclusions

The hitherto unreported reaction of α-methylepoxy aldehydes in the presence of aluminum alkoxides was found to yield diastereomeric epoxy derivatives of β-propiolactone. This reaction was found to take place only in the case of epoxy aldehydes with an electron donor substituent at the α carbon atom. The reaction yield was found to increase considerably with increase of the concentration of aluminum alkoxide and reach 80% of the theoretical value.

The epoxy β-propiolactone derivatives obtained have not been described till now and the investigated reaction makes possible the further studies of the chemistry of these bifunctional compounds.

Experimental Section

Gas chromatographic separations were made on the Varian 2800 gas chromatograph equipped with a preparative unit and an electronic integrator. The quantitative and qualitative GC analyses were carried out in the following conditions: a 2 mm i.d. glass column 2 m long packed with Carbowax 20 M TA 10% on Chromosorb W DMSC; injector temperature 225 °C; detector temperature 250°C. The column temperature variation during the analysis is given in Figure 1; the carrier gas is argon at a flow rate of 25 mL/min. A flame-ionization detector (FID) is used.

The preparative separations were run on a 7 mm i.d. glass column 3 m long packed with Carbowax 20 M 20% on Chromosorb W 30–60 mesh.

The IR spectra were recorded on a UR-120 Carl Zeiss Jena spectrophotometer.

The ^1H NMR spectra were recorded on the Vairan XL-100 and JEOL JNM-C-60 spectrometers, using Me_4Si as an internal standard.

The GC–MS analyses were done on a Varian MAT 711 mass spectrometer at 70 eV and at the ion source temperature of 200 °C.

Reagents. 2-Methyl-2,3-epoxypropanal (1) was obtained from methacrolein and hydrogen peroxide by the modified Payne's method.[12] 2-Methyl-2,3-epoxybutanal (7) was synthsized by the modified Payne's method.[13] Aluminum isopropoxide **2a** (POCh, Poland) was distilled twice under reduced pressure in an atmosphere of dry nitrogen, the fraction boiling at bp 146–148 °C (12 mm Hg) being collected. Aluminium ethoxide **2b** (Ferak, DDR) was crystallized from benzene. Aluminum *tert*-butoxide[14] **2c** was purified by recrystallization from benzene after extraction with ether. Benzene was dried by conventional techniques.

Synthesis of α-Methyl-α-(1-isopropoxy-2-methyl-2,3-epoxypropyloxy)-β-propiolactone (4). A 14.2-g (0.165 mol) sample of 1 distilled over CaH_2 in an atmosphere of dry nitrogen [fraction boiling at bp 58 °C (100 mm Hg), 99.6% GC] was added to a solution containing 4.1 g (0.02 mol) of **2a** in 30 mL of dry benzene. The course of the reaction was followed by GC, samples being taken directly from the reaction flask via a silicone rubber gasket. The reaction was conducted for 200 h at the temperature of 20 °C. The post-reaction mixture was then added dropwise into 300 mL of vigorously stirred *n*-heptane, and then filtered off. The filtrate was flashed to yield 8 mL of a yellow oil. The oil was then rectified and a fraction boiling at bp 120–135 °C (5 mm Hg) collected. That fraction was subsequently separated using preparative gas chromatography (PGC) and peaks were collected having the following relative retentions: **4a,** *R* 1.33 and **4b,** *R* 1.44.

Peak **4a:** IR capillary cell ν_{max} 2980, 2940, 2880, 1815, 1460, 1380, 1340, 1290, 1200, 1150, 1100, 995 cm^{-1}; mass spectroscopy *m/e* 230 (M^+), 200 ($M^+ - CH_2O$); epoxide number, theoretical 0.43, found 0.41; molecular weight for $C_{11}H_{18}O_5$, calcd 230, found by the cryoscopic method 229; ^1H NMR (CCl_4) δ 1.12 [d, 6, *J* = 3.5 Hz, $OCH(CH_3)_2$], 1.33 (s, 3, $CH_2OC^*CH_3$), 1.34 [s, 3, $CH_3C^*C(O)OCH_2$], 2.56, 2.75 and 2.57, 2.76 (dd and dd, 2, *J* = 5.0 Hz, $CH_2OC^*CH_3$), 3.52, 3.57 [dd, 2, *J* = 5.0 Hz, $CH_3C^*C(O)OCH_2$], 3.56 [m, 1, *J* = 3.5 Hz, $OCH(CH_3)_2$], 5.27 and 5.30 (s and s, 1 C*H). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.5; H, 7.8. Found: C, 57.5; H, 7.9.

Peak **4b:** IR capillary cell ν_{max} 2980, 2880, 1815, 1460, 1380, 1340, 1290, 1200, 1150, 1100, 995 cm^{-1}; mass spectroscopy *m/e* 230 (M^+), 200 ($M^+ - CH_2O$); epoxide number, theoretical 0.43, found 0.42; molecular weight for $C_{11}H_{18}O_5$, calcd 230, found by the cryoscopic method 232; ^1H NMR (CCl_4) δ 1.09 [d, 6, *J* = 3.5 Hz, $OCH(CH_3)_2$], 1.24 and 1.27 (s and s, 3, $CH_2OC^*CH_3$), 1.32 [s, 3, $CH_3C^*C(O)OCH_2$], 2.53, 2.71 and 2.54, 2.72 (dd and dd, 2, *J* = 5.0 Hz, $CH_2OC^*CH_3$), 3.44, 3.46 [ss, 2 $CH_3C^*C(O)OCH_2$], 3.54 [m, 1, *J* = 3.5 Hz, $OCH(CH_3)_2$], 4.97 and 5.01 (s and s, 1 C*H). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.5; H, 7.8. Found: C. 57.4; H, 7.9.

Synthesis of α-Methyl-α-(1-ethoxy-2-methyl-2,3-epoxypropyloxy)-β-propiolactone (5). A 14.2 g (0, 165 mol) sample of 1 was added in the atmosphere of dry nitrogen to a solution containing 4.1 g (0.025 mol) of **2b** in 30 mL of dry benzene. The reaction was conducted for 300 h at the temperature of 20 °C. The oil fraction was separated from the post-reaction mixture as described above. The oil was then rectified and a fraction boiling at bp 120–140 °C (5 mmHg) was collected. That fraction was subsequently separated using PGC and peaks were collected having the following relative retentions.

Peak **5a:** *R* 1.38; IR capillary cell ν_{max} 2960, 2900, 1815, 1450, 1420, 1390, 1330, 1290, 1250, 1200, 1160, 1120, 995 cm^{-1}; mass spectroscopy *m/e* 216 (M^+), 186 ($M^+ - CH_2O$); epoxide number, theoretical 0.46, found 0.45; ^1H NMR (CCl_4) δ 1.17 (t, 3, *J* = 7.0 Hz, OCH_2CH_3), 1.34 (s, 3, $CH_2OC^*CH_3$), 1.35 [s, 3 $CH_3C^*C(O)OCH_2$], 2.57, 2.77 (dd, 2, *J* = 5.0 Hz, $CH_2OC^*CH_3$), 3.50, 3.57 [dd, 2, *J* = 10.0 Hz, $CH_3C^*C(O)OCH_2$], 3.48 (q, 2, *J* = 7.0 Hz, OCH_2CH_3), 5.27 and 5.29 (s and s, 1 C*H). Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.6; H, 7.4. Found: C, 55.6; H, 7.4.

Peak **5b:** *R* 1.47; IR capillary cell ν_{max} 2960, 2900, 1815, 1450, 1420, 1380, 1330, 1290, 1250, 1200, 1160, 1120, 995 cm^{-1}; mass spectroscopy *m/e* 216 (M^+), 186 ($M^+ - CH_2O$); epoxide number, theoretical 0.46, found 0.45; ^1H NMR (CCl_4) δ 1.17 (t, 3, *J* = 7.0 Hz, OCH_2CH_3), 1.31 and 1.33 (s and s, 3 $CH_2OC^*CH_3$), 1.37 [s, 3 $CH_3C^*C(O)OCH_2$], 2.58, 2.76 and 2.59, 2.77 (dd and dd, 2, *J* = 5.0 Hz, $CH_2OC^*CH_3$), 3.51, 3.55 [dd, *J* = 6.0 Hz, $CH_3C^*C(O)OCH_2$], 3.50 (q, 2, *J* = 7.0 Hz, OCH_2CH_3), 5.04 and 5.07 (s and s, 1 C*H). Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.6; H, 7.4. Found: C, 55.6; H, 7.4.

Synthesis of α-Methyl-α-(1-tert-butoxy-2-methyl-2,3-epoxypropyloxy)-β-propiolactone (6). A 14.2-g (0.165 mol) sample of 1 was added in the atmosphere of dry nitrogen to a solution containing 4.9 g (0.02 mol) of **2c** in 30 mL of dry benzene. The reaction was conducted for 120 h at the temperature of 20 °C. The separated oil was then rectified and the fraction boiling at bp 120–135 °C (5 mmHg) was collected. That fraction was subsequently seaprated by PGC and peaks were collected having the following relative retentions.

Peak **6a:** *R* 1.36; IR capillary cell ν_{max} 2980, 2960, 2880, 1815, 1460, 1380, 1330, 1290, 1250, 1190, 1160, 1100, 995 cm^{-1}; mass spectroscopy *m/e,* molecular ion was not detected, 229 ($M^+ - CH_3$), 214 ($M^+ - CH_2O$); epoxide number, theoretical 0.41, found 0.40; molecular weight for $C_{12}H_{20}O_5$ calculated 244, found by cryoscopic method 243; ^1H NMR (CCl_4) δ 1.15 [s, 9, $OC(CH_3)_3$], 1.32 and 1.33 (s and s, 3, $CH_2OC^*CH_3$), 1.34 [s, 3, $CH_3C^*C(O)OCH_2$], 2.54, 2.74 and 2.55, 2.75 (dd and dd, 2, *J* = 5.0 Hz, $CH_2OC^*CH_3$), 3.45, 3.54 [dd, 2, *J* = 9.5 Hz, $CH_3C^*C(O)OCH_2$], 5.24 and 5.29 (s and s, 1 C*H). Anal. Calcd for $C_{12}H_{20}O_5$: C, 59.0; H, 8.2. Found: C, 59.0; H, 8.2.

Peak **6b:** *R* 1.51; IR capillary cell ν_{max} 2980, 2960, 2880, 1815, 1460, 1380, 1330, 1290, 1250, 1190, 1160, 1100, 995 cm^{-1}; mass spectroscopy *m/e,* molecular ion was not detected, 229 ($M^+ - CH_3$), 214 ($M^+ - CH_2O$); epoxide number, theoretical 0.41, found 0.40; molecular weight for $C_{12}H_{20}O_5$ calculated 244, found by the cryoscopic method 245; ^1H NMR (CCl_4) δ 1.17 [s, 9, $OC(CH_3)_3$], 1.29 and 1.32 (s and s, 3 $CH_2OC^*CH_3$), 1.38 [s, 3 $CH_3C^*C(O)OCH_2$], 2.56, 2.75 and 2.57, 2.76 (dd and dd, 2, *J* = 5.0 Hz, $CH_2OC^*CH_3$), 3.49 [s, 2 $CH_3C^*C(O)OCH_2$], 5.00 and 5.04 (s and s, 1 C*H). Anal. Calcd for $C_{12}H_{20}O_5$: C, 59.0; H, 8.2. Found: C, 59.0; H, 8.2.

Registry No.—1, 52788-68-8; **2a,** 555-31-7; **2b,** 555-75-9; **2c,** 556-91-2; **3,** 52788-67-7; **4,** 67872-64-4; **5,** 67872-65-5; **6,** 67872-66-6.

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