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ADDITION OF DIAZOMETHANE AND SULFUR YLIDES TO THE CARBONYL GROUP IN DERIVATIVES OF KETOSES AND ALDOSES–III

REACTIONS OF 1,2-DIDEOXY-4,5-*O*-ISOPROPYLIDENE-D-*GLYCERO*-3-PENTULOSE

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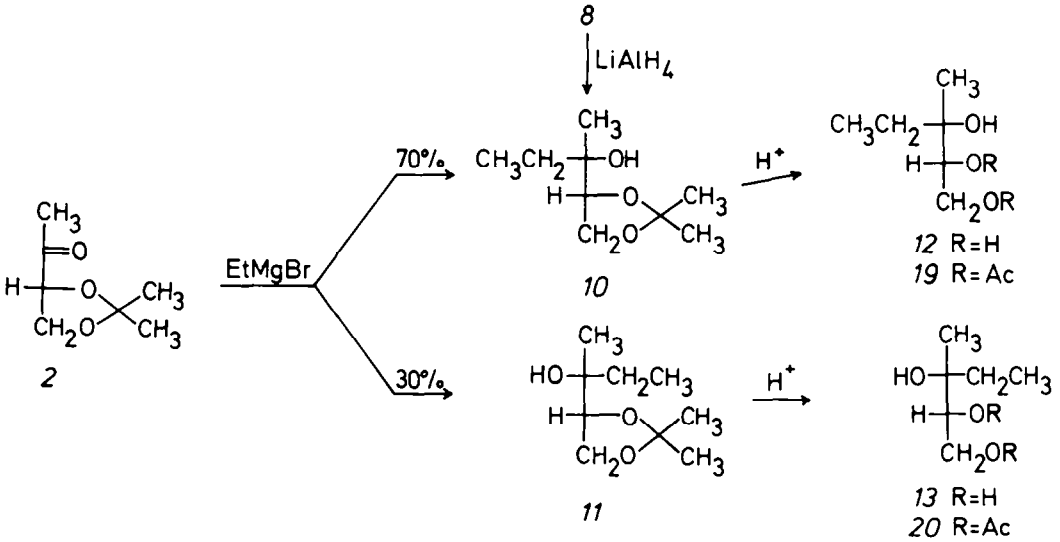
Abstract The reactions of diazomethane and dimethyloxo-sulfonium methylide with 1,2-dideoxy-4,5-*O*-isopropylidene-D-*glycero*-3-pentulose were studied. The sulfur ylide yielded two epimeric epoxides while diazomethane in addition furnished a homologous ketone. The reaction with diazomethane was carried out with varying concentrations of methanol in the reaction medium, and the relative yields of the three products were determined in each case. The results were explained on the basis of a two-step reaction mechanism proposed earlier. Steric effects and complexation between the positive nitrogen and one of the oxygens were inferred to be important.

Recent communications[1,2] reported studies of the reactions of 2,3-*O*-isopropylidene-D-glyceraldehyde (**1**) and 1-deoxy-3,4-*O*-isopropylidene-D-*glycero*-tetrulose (**2**), with diazomethane and sulfur ylides. Such chiral compounds are excellently suited for the study of the stereoselectivity of additions to the carbonyl group. The reaction between dimethyloxosulfonium methylide and **1** yielded epoxides **3** and **4**, while the reaction between dimethyloxosulfonium methylide and **2** yielded epoxides **5** and **6**. The reaction between diazomethane and **1** yielded in addition to **3** and **4**, **2**, which reacted further to **5** and **6** when there was an excess of diazomethane. The reaction between diazomethane and **2** yielded in addition to **5** and **6**, 1,2-dideoxy-4,5-*O*-isopropylidene-D-*glycero*-3-pentulose (**7**), which also reacted further.

For the reaction with diazomethane, a two-step mechanism was proposed upon a basis of experiments with reaction media of varying polarity.[1,2] This mechanism is mainly based on the so called "dipolar model" for steric control of asymmetric induction[3] and explains why the *erythro* epoxides **3** and **5** are dominant. However, it also includes an explanation of why homologation occurs at the cost of the *erythro* epoxide only, in polar medium.

We have now undertaken a study of reactions with 1,2-dideoxy-4,5-*O*-isopropylidene-D-*glycero*-3-pentulose (**7**). The reaction of **7** with dimethyloxosulfonium methylide yielded a mixture of the two epoxides **8** and **9**, which was separated on a silica gel column. ^{13}C NMR and glc showed that the epimeric epoxides were formed in a ratio of 55:45. The



Scheme 1.

resonances due to the two C-1 carbons at δ 48.6 and 49.0 were particularly useful for determining this ratio. The latter peak was the larger and since **7** is related to **1** and **2**, it probably belongs to the *erythro*-epoxide (**8**). This assumption was confirmed as follows:

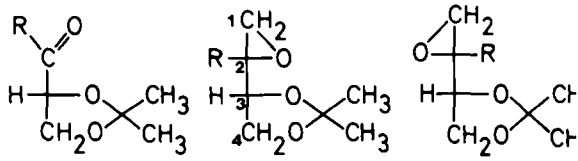
Reaction between **2** and ethylmagnesium bromide yielded a mixture of two epimeric alcohols **10** and **11** in a ratio of 70:30. This mixture was separated on a silica gel column. The dominant alcohol (**10**) was identical with the alcohol obtained by the reduction of **8** with LAH (Scheme 1). The ratio 70:30 was exactly the same as the one obtained when **1** reacted with MeMgBr, and in this case the alcohol with the *erythro* configuration was dominant.[1]

At this stage it should be noted that the term *erythro* here and in the following refers to the quaternary Me group as C-1. This includes that the Et group in **8** and **9** is considered to be substituting H-2. Although not strictly correct this convention makes it more simple to see how the reactions described here are related to another.

The conclusive evidence for the stereochemistry of the alcohols **10** and **11** follows from synthesis of the triols **12** and **13** as given in Scheme 2.

obtained on hydrolysis of **10**. A similar *trans* hydroxylation showed the connection between **18** and **11** *via* the triol **13**. The triol **12** and **13** gave the diacetates **19** and **20**, respectively, which were also characterized.

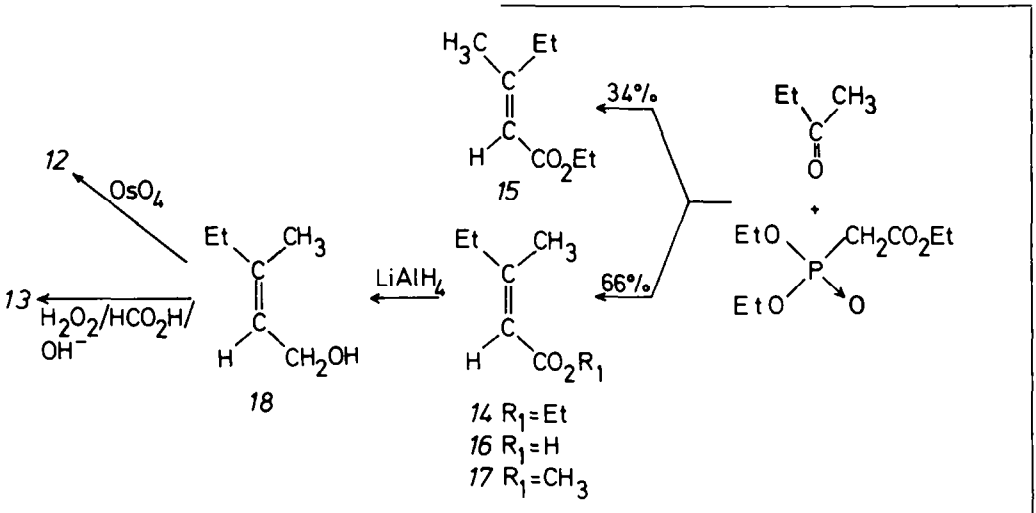
The reaction of **7** with diazomethane was performed in diethyl ether solutions containing 0, 10, 20 and 30% methanol. The relative yields of the epimeric epoxides **8** and **9** and the homologous ketone **21** after four days



1 R=H *2* R=CH_3 *7* R=CH_2CH_3 *21* R=$CH_2CH_2CH_3$

3 R=H *5* R=CH_3 *8* R=CH_2CH_3

4 R=H *6* R=CH_3 *9* R=CH_2CH_3

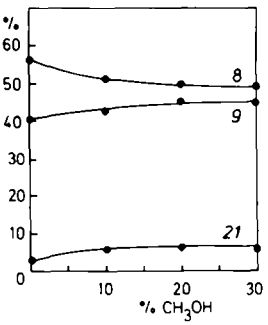


Scheme 2.

A mixture of (*E*)- and (*Z*)-ethyl-3-methyl-2-pentenoate (**14** and **15**) was obtained from a Horner reaction between 2-butanone and ethyl diethylphosphonoacetate.[4] From this mixture which contained the *E* and *Z* isomers in a ratio of 66:34 as seen from glc and ^{13}C NMR, it was possible to isolate chromatographically pure *E*-isomer (**14**). However, we did not succeed in isolating the *Z*-isomer (**15**) in this manner. The ethyl esters are also quite volatile and due to this not simple to free from solvent. A more convenient method of separation included hydrolysis of the mixture of the ethyl esters and from the resulting mixture of acids (*E*)-3-methyl-3-pentenoic acid (**16**) crystallized (m.p. 47°). After re-esterification of this acid with diazomethane, the resulting methyl ester (**17**) was reduced with LAH to yield (*E*)-3-methyl-2-pentenol (**18**). Hydroxylation of **18** with osmium-tetroxide furnished the racemic triol **12** which had identical NMR spectra (^1H, ^{13}C) with the triol as a function of methanol concentration is given in Fig. 1. The trend is the same as in the corresponding figures for 2,3-*O*-isopropylidene-D-glyceraldehyde (**1**)[1] and 1-deoxy-3,4-*O*-isopropylidene-D-*glycero*-tetrulose (**2**).[2] The amount of the *threo*-epoxide (**9**) shows a slight increase with increasing methanol concentration, while the *erythro* epoxide (**8**) is decreasing. This decrease is connected with a corresponding increase in the yield of the ketone **21**.

We have proposed earlier[1] that this connection is due to the formation of **8** and **21** from a common "*erythro*"-intermediate. The *threo* epoxide is formed from the 2-epimeric "*threo*"- intermediate (C-1 being the carbon of the $CH_2N_2^+$ group).

The effect of substituting the aldehyde proton in **1** by Me (**2**) and Et (**7**) on the yields of epoxides and ketones may be seen from Table 1. The decrease in stereoselectivity in the diazomethane reaction as seen from the first column on going from the aldehyde (**1**) to



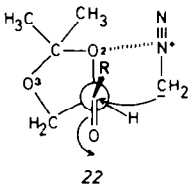


Fig. 1 The relative yields of **8**, **9** and **21** when **7** reacted with diazomethane with various concentration of methanol in diethylether.

the ketones (**2** and **7**) is mainly due to the fact that the rotational barrier around the C-1–C-2 bond is greater in aldehydes than in ketones.[5] Hence a conformation **22** (R=H) in which the CO group and O 2 are antiperiplanar, should be favoured and lead to greater dominance of the isomer with the *erythro* configuration. The difference in the stereoselectivity between the two ketones may be due to steric reasons. The intermediate (**22**, R=Et) formed in the epoxidation of the ethyl ketone **7** is sterically more hindered than the one (**22**, R=Me) formed from the methyl ketone **2**.

There is a marked difference in the tendency of ketone formation in the reactions of **1**, **2** and **7**. This tendency as seen from the second column in Table 1, is probably due to a decrease in the ease of migration in the order H > Me > Et. Such a migration is necessary for the formation of a ketone from the intermediate instead of an epoxide. Finally the two last columns compare the stereoselectivity in the addition of diazomethane and dimethyloxosulfonium methylide to **1**, **2** and **7**. The *erythro:threo* ratio was in all three cases greatest in the diazomethane reaction. We have previously[1] suggested an electrostatic interaction between the positive nitrogen and one of the ring oxygens as depicted in **22**. This interaction, which will increase the stereoselectivity, seems not to have any parallel in the sulfur ylide reaction.

EXPERIMENTAL

General methods such as conditions for chromatography and spectroscopy and procedures for the preparation of diazomethane and sulfur ylides have been given earlier.[1] NMR spectra of the water soluble compounds were recorded in D_2O solns with MeOH as internal reference, ^1H ν_{CH_3} = 3.40 and ^{13}C ν_{CH_3} = 49.33 ppm.

1,2-*Dideoxy*-4,5-O-*isopropylidene*-D-glycero-3-*pentulose* (**7**). To a soln of **1** (2.7 g, 0.02 mol) in Et_2O (10 ml) was added at 0° EtMgBr (prepared from 1.2 g Mg and 5.5 g EtBr) in anhyd Et_2O (15 ml). The mixture was stirred for 2 hr at room temp, neutralized with a sat NH_4Cl soln, the water layer extracted with Et_2O (2 × 50 ml), the combined extracts washed with water dried over Na_2SO_4 and concentrated to yield a mixture of 1,2-dideoxy-4,5-*O*-isopropylidene-D-*ribo* and D-*arabino*-pentitol (2 g) in the ratio 80:20. To this mixture (4 g, 0.025 mol) in EtOH-free $CHCl_3$ (80 ml) and water (80 ml) were added anhyd K_2CO_3 (1.0 g, 7.2 mmol), potassium meta periodate (10.7 g, 0.04 mol) and RuO_2 (10.23 g, 1.4 mmol). The reaction was followed on tlc (30% acetone in hexane). When all the starting material had reacted i-PrOH was added the reaction mixture filtered, the water layer extracted with $CHCl_3$ (3 × 50 ml), the combined extracts washed with water, dried over Na_2SO_4 and concentrated to give oily **7** (3.25 g, 75.6%). $[\alpha]_D$ = +52.2° (*c* = 0.92, $CHCl_3$). ^1H NMR, δ ppm: 1.06 (*t*, 3 H) and 2.64 (q, 2 H), ethyl group, 1.40 and 1.49 (both *s*, isopropylidene group), ABC-system: ν_A = 3.98, ν_B = 4.19 and ν_C = 4.41 (H-3, 2 H-4). ^{13}C NMR, ppm: 25.0, 26.0 and 110.8 (isopropylidene group), 7.0 (C-1), 31.9 (C-2), 66.6 (C-5), 80.1 (C-4) and 211.5 (C-3). MS: *m/e* 158 (2%, M^+) obs 158.0936, calc. for $C_8H_{14}O_3$ 158.0939. *m/e* 143 (6%, M-15). *m/e* 101 (63%, $C_5H_9O_2^+$). *m/e* 57 (23%, $C_3H_5O^+$). *m/e* 43 (100%, $C_2H_3O^+$)

Reaction between **7** *and dimethyloxosulfonium methylide.* To a vigorously stirred mixture of dimethylsulfoxide (7 ml) and dimethyloxosulfonium methylide, prepared from trimethyloxosulfonium iodide (0.66 g, 3 mmol) and NaH (0.15 g, 3 mmol) **7** (0.39 g, 2.46 mmol) in dimethylsulfoxide (5 ml) was added at room temp and under N_2. After stirring for 4 hr ice water (100 ml) was added and the mixture was extracted with Et_2O (3 × 5 ml). The combined extracts were washed with water (2 × 50 ml), dried over Na_2SO_4 and concentrated to yield a mixture of the epimeric epoxides **8** and **9** (0.2 g, 39.3%). Glc showed a ratio of 55:45 which was confirmed by ^{13}C NMR.

Reaction between **7** *and diazomethane.* To freshly prepared solns of **7** in Et_2O with varying amounts of MeOH (0, 10, 20 and 30% of the total volume of the mixture) were added Et_2O solns of diazomethane (molar ratio diazomethane: **3** = 4:1). The mixtures were left in the dark at room temp and the reaction followed by glc for 4 days at intervals beginning immediately after the reaction was initiated. ^{13}C NMR spectra were also recorded from time to time as a double control.

1,2 *Anhydro*-2-C-*ethyl*-3,4-O-*isopropylidene*-D-*erythritol* (**8**). The epimeric mixture (0.5 g) from the reaction between **7** and dimethyloxosulfonium methylide was separated on a silica gel column (1 kg/cm² pressure, 8% acetone in hexane). Pure and identical (glc) fractions (20 ml) from 3 runs were

Table 1. The relative yields of epoxides and ketones when *1*, *2* and *7* react with diazomethane in diethyl ether solutions and dimethyloxosulfonium methylide (DMOSM)

	Diazomethane			DMOSM
Compound	erythro:threo intermediate	ketone:epoxides	erythro:threo epoxides	erythro:threo epoxides
1 R = H	95:5	43:57	91:9	70:30
2 R = CH_3	74:26	5:95	73:27	65:35
7 R = CH_2CH_3	61:39	3:97	60:40	55:45

combined and concentrated to yield oily **8** (0.39 g). $[\alpha]_D$ = +17.0° (*c* = 0.99, $CHCl_3$). ^1H NMR, δ ppm: 0.92 (*t*, 3 H), 1.67 and 1.85 (2 H, Et group), 1.44 and 1.37 (both *s*, isopropylidene group), 2.70 (*s*, 2 H-1), ABC system ν_A = 3.78, ν_B = 4.00 and ν_X = 4.14 (H-3, 2 H-4). ^{13}C NMR: 8.19 and 23.25 (Et group), 25.2, 26.1 and 109.6 (isopropylidene group), 48.98 (C-1), 59.26 (C-2), 65.75 (C-4) and 76.56 (C-3). MS: *m/e* 172 (absent, M^+), *m/e* 157 (21%, M-15), obs. 157.0860, calc. for $C_8H_{13}O_3$ 157.0861, *m/e* 101 (17%), $C_5H_9O_2^+$), *m/e* 72 (14.5%, $C_4H_8O^+$), *m/e* 43 (100%, $C_2H_3O^+$).

The NMR data for the epimeric epoxide **9** was extracted from spectra of a mixture: ^1H NMR, δ ppm: The main differences were 1.36 and 1.39 for the isopropylidene group and that the two chemical shift equivalent H-1 protons of **8** resonated as an AB system at 2.67 and 2.82. ^{13}C NMR: 8.29 and 24.12 (ethyl group), 25.5, 26.1 and 109.6 (isopropylidene group), 48.64 (C-1), 59.07 (C-2), 65.65 (C-4) and 76.37 (C-3).

1-*Deoxy*-2-C-*ethyl*-3,4-O-*isopropylidene*-D-*erythritol* (**10**). A soln of **2**[2] (3 g, 0.02 mol) in Et_2O (15 ml) was added dropwise to a soln of EtMgBr (prepared from 1.2 g Mg and 5.5 g EtBr) in Et_2O (25 ml) at 0°. The mixture was stirred for 30 min at room temp, refluxed for 10 min, cooled and poured into a sat NH_4Cl soln, extracted with Et_2O (3 × 50 ml), the combined extracts washed with water, dried over Na_2SO_4 and concentrated to yield a mixture of the oily alcohols **10** and **11** (2.9 g, 83%) in a ratio of 70:30 (glc, ^{13}C NMR). The epimeric mixture (0.6 g) was separated on a silica gel column (1 kg/cm², hexane: EtOAc = 7:1). Pure and identical fractions (20 ml) after 5 runs were combined and evaporated to yield oily **10** (1.31 g). $[\alpha]_D$ = +20.6° (*c* = 1.68, $CHCl_3$). ^1H NMR, δ ppm: 0.94 (*t*, 3 H), 1.49 and 1.59 (2 H) Et group, 1.04 (*s*, 3 H-1), 1.37 and 1.42 (both *s*, isopropylidene group), ABC systeme ν_A = 3.87, ν_B = 3.92 and ν_X = 3.99 (H-3, 2 H-4), 1.99 (broad *s*, OH). ^{13}C NMR: 7.90 and 32.65 (Et group), 20.52 (C-1), 25.40, 26.37 and 109.07 (isopropylidene group), 64.97 (C-4), 71.64 (C-2) and 80.66 (C-3). MS: *m/e* 174 (absent, M^+), *m/e* 159 (10.2%, M-15), obs 159.1021, calc. for $C_8H_{15}O_3$ 159.1021, *m/e* 101 (12.6%, $C_5H_9O_2^+$), *m/e* 73 (65.4%, $C_4H_9O^+$), *m/e* 72 (11.7%, $C_4H_8O^+$), *m/e* 43 (100%, $C_2H_3O^+$).

The ^{13}C NMR data for the epimeric alcohol **11**, which was not purified, were extracted from a spectrum of a mixture: 7.65 and 30.28 (Et group), 23.25 (C-1), 25.44, 26.40 and 109.16 (isopropylidene group), 64.77 (C-4), 71.84 (C-2) and 81.45 (C-3).

Reduction of 1,2-*anhydro*-2-C-*ethyl*-3,4-O-*isopropylidene*-D-*erythritol* (**8**) *with* LAH. LAH (0.083 g, 2.2 mmol) was suspended in anhyd Et_2O (25 ml). After stirring for 10 min, epoxide **8** (0.39 g, 2.27 mmol) in anhyd Et_2O (10 ml) was added. The mixture was refluxed for 16 hr. EtOAc (5 ml) was added, the mixture was filtered and the residue washed with Et_2O. The combined extracts were dried over Na_2SO_4 and concentrated to yield an alcohol (0.24 g, 70%), which was chromatographically (glc) and spectroscopically (^1H and ^{13}C NMR) identical with the alcohol **10** isolated from the reaction between **2** and EtMgBr.

1-*Deoxy*-2-C-*ethyl*-D-*erythritol* (**12**). The alcohol **10** was hydrolyzed with 5% AcOH (10 ml). After 1 hr on steam-bath, water and AcOH was removed by azeotropic distillation with benzene (2 × 50 ml). This yielded **12** as a colourless syrup (0.13 g), $[\alpha]_{578}$ = +18.2° (*c* = 0.41, $CHCl_3$). MS: *m/e* 134 (M^+, absent), *m/e* 119 (M-15), obs 119.1710, calc for $C_5H_{11}O_3$ 119.0708. ^1H NMR, δ ppm: 0.94 (*t*, 3 H), 1.53 and 1.67 (2 H) Et group, 1.16 (*s*, 3 H-1), ABC system: ν_A = 3.56, ν_B = 3.63 and 3.76 (H-3 and 2 H-4). ^{13}C NMR, δ ppm: 7.37 and 30.71 (Et group), 21.16 (C-1), 62.64 (C-4), 74.87 (C-2) and 77.55 (C-3). A mixture of **10** and **11** was hydrolyzed in the same manner and from the resulting mixture of triols **12** and **13** were extracted the NMR data for **13**. ^1H NMR, δ ppm: 0.95 (*t*, 3 H), 1.51 and 1.63 (2 H) Et group, 1.18 (*s*, 3 H-1), ABC system: ν_A = 3.56, ν_B = 3.68 and ν_X = 3.73 (H-3 and 2 H-4). ^{13}C NMR, δ ppm: 7.17 and 30.57 (Et group), 21.30 (C-1), 62.59 (C-4), 74.82 (C-2), 77.55 (C-3). These data were confirmed by the synthesis of racemic **12** and **13** from **18**.

1-*Deoxy*-2-C-*ethyl*-3,4-*di*-O-*acetyl*-D-*erythritol* (**19**). To **12** (0.1 g) was added a mixture of pyridin (1 ml) and Ac_2O (1 ml). After 24 hr at room temp, the mixture was concentrated to yield oily **19** (0.11 g) $[\alpha]_D$ = +21.1° (*c* = 1.4, $CHCl_3$). MS: *m/e* 218 (M^+, absent), *m/e* 217 (M-1), obs 217.1080, calc. for $C_{10}H_{17}O_5$ 217.1076, *m/e* 189 (M-29), obs 189.0768, calc. for $C_8H_{13}O_5$ 189.0763. ^1H NMR, δ ppm: 0.93 (*t*, 3 H), 1.53 (*q*, 2 H) Et group, 2.03 and 2.12 (*s*, 3 H each, acetyl Me's), 2.24 (broad *s*, OH), 1.20 (*s*, 3 H-1), ABX system: ν_A = 4.11, ν_B = 4.48 (2 H-4) ν_X = 5.10 (H-3), J_{AB} = 12.0, J_{AX} = 8.6 and J_{BX} = 2.9 Hz. ^{13}C NMR, δ ppm: 7.60 and 31.73 (Et group), 20.08 and 20.81 (acetyl Me's), 22.13 (C-1), 63.04 (C-4), 73.35 (C-2) and 75.79 (C-3).

Racemic **19** was prepared from racemic **12** and shown to have identical NMR spectra with the D-enantiomer.

1-*Deoxy*-2-C-*ethyl*-3,4-O-*acetyl*-D,L-*threitol* (**20**). In a similar manner as for **12** racemic **13** was acetylated to yield oily racemic **20**. MS as for **19**. ^1H NMR, δ ppm: 0.96 (*t*, 3 H), 1.53 (*q*, 2 H) Et group, 2.03 and 2.12 (*s*, 3 H each, acetyl Me's), 2.63 (broad *s*, OH), 1.18 (*s*, 3 H-1), ABX system: ν_A = 4.11, ν_B = 4.52, ν_X = 5.09, assignements and J's as for **19**. ^{13}C NMR, δ ppm: 7.55 and 31.19 (Et group), 20.81 and 20.96 (acetyl Me's), 22.86 (C-1), 63.02 (C-4), 73.40 (C-2) and 75.79 (C-3).

(E)-*Ethyl*-3-*methyl*-2-*pentenoate* (**14**) *and* (Z)-*ethyl*-3-*methyl*-2-*pentonate* (**15**). A mixture of (*E*)- and (*Z*)- **14** and **15** was synthesized from 2-butanone (15 g) and ethyl diethylphosphonoacetate (42 g)[4] The esters were formed in a ratio of: **14**:**15** = 66:34 (glc). A part of this mixture (1 g) was applied to a silica gel column and eluted with hexane under a N_2-pressure of 1 kg/cm². The later fractions contained the dominant *E*-ester **14** (0.3 g). ^1H NMR, δ ppm: 1.09 (*t*, 3 H) and 2.18 (*q*, 2 H) (Et group), 1.29 (*t*, 3 H) and 4.16 (*q*, 2 H) (ethyl ester), 2.18 (*s*, 3 H, CH_3) and 5.68 (*m*, 1 H, olefinic H). From earlier fractions were isolated oily **15** (0.1 g). ^1H NMR, δ ppm: 1.07 (*t*, 3 H) and 2.64 (*q*, 2 H) (ethyl group), 1.27 (*t*, 3 H) and 4.14 (*q*, 2 H) (ethyl ester), 1.87 (*s*, 3 H, CH_3) and 5.64 (*m*, 1 H, olefinic H).

(E)-3-*Methyl*-2-*pentenoic acid* (**16**). A mixture of (*E*)- and (*Z*)-**14** and **15** (9 g) was hydrolyzed with 1 N NaOH (82 ml). After 24 hr at 90° the mixture was extracted with Et_2O (200 ml). The water layer was acidified with conc HCl and extracted with Et_2O (3 × 150 ml). The combined extracts were washed with water, dried over $MgSO_4$ and concentrated *in vacuo* to yield a mixture of (*Z*) and (*E*) **16**, yield 3 g, cryst from hexane m.p. 46°C lit[4] 46 68°C. ^1H NMR, δ ppm: 1.09 (*t*, 3 H) and 2.20 (*q*, 2 H) (ethyl group), 2.16 (*d*, J = 1.5 Hz, 3 H, Me), 5.69 (*m*, 1 H, olefinic H), 11.5 (broad *s*, OH). ^{13}C NMR, δ ppm: 11.99 and 34.11 (Et group), 19.19 (Me), 114.14 (C-2), 164.80 (C-3) and 172.76 (C-1).

(E)-*Methyl*-3-*methyl*-2-*pentenoate* (**17**). To (*E*)- **16** (1.5 g) in Et_2O (15 ml) was added CH_2N_2 in Et_2O. Excess CH_2N_2 was destroyed by addition of AcOH. The mixture was concentrated *in vacuo* to yield oily **17** (1.6 g). ^1H NMR, δ ppm: 1.07 (*t*, 3 H) and 2.14 (*q*, 2 H) (Et group), 2.16 (*d*, J = 1.5, Me), 3.68 (*s*, OMe), 5.66 (*m*, 1 H, olefinic H). ^{13}C NMR δ ppm: 11.99 and 33.87 (Et group), 18.25 (Me), 50.83 (OMe), 114.1 (C-2), 162.1 (C-3) and 167.7 (C-1).

(E)-3-*Methyl*-1-*pentenol* (**18**). To a soln of LAH (0.73 g) in anhyd Et_2O (25 ml) was added (*E*)- **17** (1.6 g). After 24 hr at room temp the mixture was poured into ice water (6 ml) and 50% NaOH (10 ml) was added. The water layer was extracted with Et_2O (3 × 100 ml). The combined extracts were washed with water, dried over $MgSO_4$ and concentrated *in vacuo* to yield **18** (0.78 g). ^1H NMR, δ ppm: 1.01 (*t*, 3 H) and 2.02 (*q*, 2 H) (Et group), 3.06 (broad *s*, OH), 1.66 (*s*, Me), 4.13 (*d*, J = 6.8 Hz, 2 H, 2 H-1), 5.38 (*m*, H-2). ^{13}C NMR, ppm: 12.38 and 32.26 (C-5 and C-4) (Et group), 16.13 (Me), 59.17 (C-1), 122.43 (C-2) and 140.75 (C-3).

1-*Deoxy*-2-C-*ethyl*-D,L-*erythritol* (**12**). To OsO_4 (1.0 g) in Et_2O (30 ml) was added at room temp (*E*)- **18** (0.78 g) in Et_2O (15 ml). After 20 hr $Na_2S_2O_5$ (1.8 g), water (30 ml) and pyridine (35 ml) was added to the mixture. After further 15 hr, the mixture was filtered through celite and extracted with

$CHCl_3$ (3 × 150 ml). The combined extracts were dried over $MgSO_4$ and evaporated *in vacuo* to yield racemic **12**. (0.4 g) which had identical ^1H NMR and ^{13}C NMR with optically active **12** obtained by hydrolysis of **10**. Acetylation of racemic **12** furnished a diacetate which had identical NMR spectra with **19**.

1-Deoxy-2-C-ethyl-D,L-threitol (**13**). To (*E*)- **18** (0.2 g) was added H_2O_2 (0.5 ml) and HCO_2H (2 ml). After 24 hr at room temp the mixture was concentrated, and NaOH (0.3 g) in water (5 ml) was added. After 1 hr the mixture was neutralized with Amberlite IR 120, filtered and evaporated to yield racemic oily **13** (0.15 g). MS and NMR spectra were identical with the spectra of optically active **13** (*vide supra*).

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