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Long-Chain Stereomeric 2-Alkyl-4-methoxycarbonyl-1,3-dioxolanes in Glycerol Acetal Synthesis[1]

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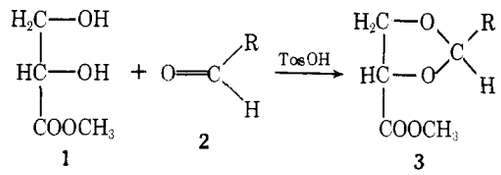
The prostaglandin-like, smooth muscle contracting effect of lipophilic glycerol acetal phosphates, the physiologically active principle of "Darmstoff" described by Vogt[2] and others,[3] has stimulated interest in an efficient synthesis of isomeric long-chain cyclic glycerol acetals. Current procedures of glycerol acetal synthesis are based on the condensation of glycerol and aldehyde[4,5] and favor formation of the isomeric 1,3-dioxanes;[5] the lesser amounts of *cis*- and *trans*-1,3-dioxolanes formed are separable, as acetates only, by tedious multiple gas chromatographic (GC) fractionation.[5]

In the present note we describe a convenient preparative method for the specific synthesis of pure *cis*- and pure *trans*-2-alkyl-4-hydroxymethyl-1,3-dioxolanes. 1,3-Dioxane formation is avoided through use of methyl glycerate as the three-carbon backbone. More important, the stereomeric glycerate acetals are separable by adsorption chromatography due to their significantly different polarities dependent upon the orientation of the methoxycarbonyl function relative to the long-chain substituted ring system. Subsequent conversion of the individual glycerate acetals to glycerol acetals by $LiAlH_4$ hydrogenolysis is quantitative.

Results and Discussion

Acid-catalyzed condensation of methyl glycerate (**1**) with hexadecanal (**2a**),[6] or *cis*-9-octadecenal (**2b**),[6] afforded a mixture of geometrical isomers of methyl glycerate cyclic acetals **3** (Scheme I) which were readily separated by thin-layer

Scheme I



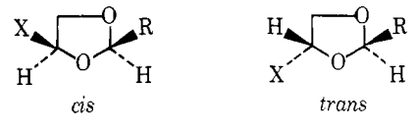
1 2 3

a, R = pentadecyl ($C_{15}H_{31}$)
b, R = *cis*-8-heptadecenyl ($C_{17}H_{33}$)

chromatography (TLC)[7] (developing solvent, hexane–diethyl ether, 75:25, v/v). Both the smaller (~40%), more polar (R_f 0.54) fraction, and the larger (~60%), less polar (R_f 0.64) fraction of **3a** (or **3b**) showed mass spectral fragmentation profiles consistent with the long-chain acetal structure **3** with characteristic ions M^+, $[M - H]^+$, $[M - alkyl]^+$, and $[M - alkyl\ CO]^+$ (ref 8). Their infrared spectra showed characteristic carbonyl splittings ($\Delta\nu$ ~22 cm^{-1}) probably due to coupling between the carbonyl stretching mode and ring vibrations.[9]

When the glycerate acetal fractions of **3a** were reduced with $LiAlH_4$,[10] the more polar isomer (R_f 0.54) gave *cis*-2-pentadecyl-4-hydroxymethyl-1,3-dioxolane (*cis*-**4a**), the less polar isomer (R_f 0.64) yielded *trans*-2-pentadecyl-4-hydroxymethyl-1,3-dioxolane (*trans*-**4a**). *cis*- and *trans*-**4a** were identified, after acetylation with Ac_2O/pyridine,[5] by comparison with authentic 2-pentadecyl-4-acetoxymethyl-1,3-dioxolanes *cis*- and *trans*-**5a** of known configuration prepared via an alternate route (Scheme II)[5]

Scheme II



cis *trans*

3, X = MeO–CO–
4, X = HO–CH_2–
5, X = MeCO–O–CH_2–

Configurational assignments for the isomers of glycerate acetal **3** were substantiated by ^1H NMR on the basis of the chemical shifts observed for the H-2 signals in the spectra of **3a–5a** (Table I).[11] The H-2 triplet at δ 4.98 ppm for the *cis*-methoxycarbonyl-1,3-dioxolane **3a** was shifted to 5.08 ppm for the trans-isomer **3a**. Such deshielding by 0.1 ppm was also observed for the *trans*-hydroxymethyl and *trans*-acetoxymethyl isomers **4a** and **5a**.[5,12] These NMR data also demonstrated that configurations were maintained in the process of converting **3a** to **5a**.

The ^1H NMR spectra of the 4-hydroxymethyl and 4-acetoxymethyl-1,3-dioxolanes (**4** and **5**) showed poorly resolved signals near 3.5–4.3 ppm due to H-4,5 and the 4-substituent protons. In contrast, the methoxycarbonyl isomers **3a** (or **3b**) gave characteristic and better resolved H-4,5 signals. The pairs of doublets centered at 4.55 ppm ($J_{4,5}$ = 7.5 Hz, *cis*-**3a**) and 4.58 ppm ($J_{4,5}$ = 7.1 Hz, *trans*-**3a**) were readily assigned to the proton (1 H) at carbon-4 with J values as expected for such 1,3-dioxolane systems.[13] The spectrum of the trans isomer also exhibited well-resolved signals at 4.28 ppm (pair of doublets, 1 H) and 3.86 ppm (pair of doublets, 1 H) for the H-5 protons in positions syn and anti, respectively, relative to the vicinal methoxycarbonyl function. Interference between 2-alkyl and 4-methoxycarbonyl substituents in the cis isomer of **3a** resulted in a less methoxycarbonyl-deshielded syn H-5 and in overlapping multiplets in the 4.29–3.92 ppm region for syn and anti H-5 in *cis*-**3a**.

Proton-decoupled ^{13}C NMR spectra of the glycerate and glycerol cyclic acetals **3–5** revealed distinct spectral differences between cis/trans isomeric pairs, and as a result of different substituents in position 4 (Table II). Assignments of ring and 4-substituent carbons were based on off-resonance proton decoupling and on specific deuteration in position 2 and in the methylene group in position 4 (**4b, 5b**).

Comparison of the carbon chemical shifts in 2-pentadecyl-1,3-dioxolane with those of the unsubstituted 1,3-dioxolane (C-2, 94.3; C-4, 63.8)[15] made it possible to estimate the deshielding increments due to the 2-alkyl group. 2-Alkyl substitution produced a downfield shift of 10.6 ppm for C-2, while the effect of the 4-substituents on C-2 in **3b–5b** was in the order of 0.1–1.9 ppm downfield, with cis substitution leading to larger deshielding than trans. In contrast, introduction of a 2-alkyl substituent into 1,3-dioxolane affected C-4,5 by a small (1.0 ppm) downfield shift only, but methoxycarbonyl (**3**) or acetoxymethyl (**5**) substitution at the 4 position produced a deshielding effect of ~8.9 ppm on C-4, and hydroxymethyl substitution (**4**) an even larger effect of ~11.6 ppm. The C-4 chemical shifts were minimally affected by the dioxolane configuration.

More surprising was the overall effect of the C-4 substitu-

Table I. H-2 NMR Signals in the Spectra of Isomeric 4-Substituted 2-Alkyl-1,3-dioxolanes[a]

	δ, ppm (J, Hz)					
Isomer	3a	Registry no.	4a	Registry no.	5a	Registry no.
cis	4.98 (4.7)	63340-16-9	4.90 (4.5)	30889-28-2	4.90 (4.5)[b]	63340-18-1
trans	5.08 (4.5)	63340-17-0	5.00 (4.5)	30889-31-7	4.98 (4.5)[b]	63340-19-2

[a] Chemical shifts (δ) of the H-2 triplets (1 H) in 2-pentadecyl-1,3-dioxolanes **3a–5a.** The shifts for H-2 in the 2-*cis*-8′-heptadecenyl derivatives **3b–5b** are identical to those of **3a–5a,** respectively. [b] See also ref 5.

Table II. ^{13}C Chemical Shifts in the Spectra of Isomeric 2-Alkyl-1,3-dioxolanes[a]

	δ (ppm)						
Carbon No.	4-Methoxycarbonyl		4-Hydroxymethyl		4-Acetoxymethyl		2-Pentadecyl-1,3-dioxolane[b,j]
	cis-3b[g]	*trans*-3b[g]	*cis*-4b[h]	*trans*-4b[h]	*cis*-5b[i]	*trans*-5b[i]	
2	106.8	106.3	105.3	105.1	105.6	105.0	104.9
4	73.7	73.7	76.4	76.3	73.7	73.5	64.8
5	68.5	68.0	66.5	66.8	67.1	67.2	64.8
C=O[c]	171.3	171.8			170.6	170.6	
CH_3[d]	52.2	52.2			20.7	20.7	
CH_2[e]			63.5	62.9	64.8	64.3	
1′[f]	33.8	33.5	34.0	34.4	34.0	34.0	34.1
2′[f]	24.0	23.8	24.0	24.0	23.9	23.9	24.1

[a] Proton-decoupled spectra of 2-*cis*-8′-heptadecenyl 4-substituted 1,3-dioxolanes **3b–5b** and of 2-pentadecyl-1,3-dioxolane at 20 MHz; the respective data for the pentadecyl acetals **3a–5a** were identical; chemical shifts (δ) in parts per million downfield from Me_4Si; solvent $CDCl_3$. [b] Prepared from ethanediol and hexadecanal essentially as described for **3a.** [c] Methyl ester C=O in **3b,** acetyl C=O in **5b.** [d] Methyl ester CH_3 in **3b,** acetyl CH_3 in **5b.** [e] Hydroxymethyl CH_2 in **4b,** acetoxymethyl CH_2 in **5b.** [f] *1′* and *2′* refer to the first and second methylene groups of the long side chain. Additional aliphatic signals occur at δ 29.4–29.7 (methylene envelope), 14.1 (ω CH_3), 22.7 (ω-1 CH_2), and 32.0 (ω-2 CH_2), with olefinic signals at 129.9 (C-8′, C-9′), 27.3 (C-7′, C-10′) and at 29.8 (C-6′, C-11′).[14] [g] Registry no.: *cis*-**3b,** 63340-20-5; *trans*-**3b,** 63392-99-4. [h] Registry no.: *cis*-**4b,** 63340-21-6; *trans*-**4b,** 63393-00-0. [i] Registry no.: *cis*-**5b,** 63340-22-7; *trans*-**5b,** 63393-01-1. [j] Registry no.: 4360-57-0.

ents on the adjacent C-5 methylene ^{13}C shifts. While all 4-substituents in both isomers caused deshielding, the methoxycarbonyl function showed the strongest effect (3.2–3.7 ppm). Deshielding of the CH_2 carbon in the 4-hydroxymethyl group (**4b**) upon acetylation (**5b**) resulted in a downfield shift by 1.3–1.4 ppm as expected for primary acetates.[15]

We had hoped that the significant polarity differences observed in chromatography between *cis*- and *trans*-4-methoxycarbonyl-1,3-dioxolanes **3** would be reflected in the carbonyl chemical shifts due to a different degree of C=O polarization in cis and trans isomers. However, such polarization would mostly affect the electron density at the carbonyl oxygen, while the simultaneous net electron-density change at the carbonyl carbon could well be compensated by resonance participation of methoxy electrons. In fact, such phenomena have previously been measured in other carbonyl-substituted ring systems where a change in ^{17}O chemical shifts by 20 ppm was accompanied by a ^{13}C shift of a mere 0.4 ppm in the same carbonyl group.[16]

Experimental Section

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian CFT-20 pulse Fourier transform instrument equipped for ^{13}C (20 MHz) and proton (79.54 MHz) observation. Spectra were measured with 4K data points at a spectral width of 1000 (^1H) or 4000 Hz (^{13}C) at ambient probe temperatures of 35 ± 1 and 39 ± 1 °C, respectively. $CDCl_3$ served as solvent and for locking purposes, unless noted otherwise. Chemical shifts (δ) are given in parts per million (ppm) downfield from Me_4Si (δ 0.0); coupling constants (*J*) are expressed in Hz. Mass spectra (MS) were recorded on a Hitachi Perkin-Elmer single-focusing instrument, RMU-6D, at a 70-eV ionization potential (source temperature, 230 °C; inlet temperature, 190 °C; direct inlet), or on an LKB-9000 spectrometer under comparable conditions. Relative ion intensities are given in parentheses. Infrared spectra were taken with a Perkin-Elmer Model 21 spectrophotometer on CS_2 and C_2Cl_4 solutions, or on liquid films. Melting points were determined on a Kofler hot stage and are corrected. Elemental analyses were carried out by M-H-W Laboratories, Garden City, Mich.

Methyl Glycerate (1). Calcium salt of glyceric acid (hydrate, Aldrich), 14.3 g (0.1 mol), 100 mL of dry MeOH, and 50 mL of 14% (w/v) methanolic BF_3 were stirred under N_2 at reflux temperature for 45 min. After cooling to room temperature, 450 mL of dry Et_2O and 6.0 g of NaF were added, and the mixture was stirred for 30 min. The precipitate was filtered on a sintered glass funnel and washed with 200 mL of Et_2O–MeOH, 3:1 (v/v), and the solvent was removed under reduced pressure. Distillation (bp 67–69 °C, 0.1 mm; lit.[17] 123–125 °C, 10 mm) yielded 7.6 g of methyl glycerate (**1**) (63%): R_f in TLC (developing solvent, $CHCl_3$–MeOH, 60:40, v/v) 0.76; ^1H NMR (MeOH-d_4) δ 3.75 (s, 3 H, CH_3), 3.76 (d, J = 4.5 Hz, CH_2), 4.23 (t, J = 4.3 Hz, 1 H, CH); ^{13}C NMR (MeOH-d_4) δ 52.4 (CH_3), 65.0 (CH_2), 73.3 (CH), 174.5 (C=O); assignments were verified by off-resonance proton decoupling.

2-Alkyl-4-methoxycarbonyl-1,3-dioxolanes (3) were synthesized by condensation of **1** with long-chain aldehyde **2.**[6] A representative procedure is given for the preparation of **3a.**

2-Pentadecyl-4-methoxycarbonyl-1,3-dioxolanes (3a). Hexadecanal (**2a**)[6] (2.40 g, 10 mmol), 1.44 g (12 mmol) of methyl glycerate (**1**), 0.5 g of *p*-toluenesulfonic acid, and 200 mL of benzene were placed in a three-necked flask equipped with water separation head, reflux condenser, inlet and outlet for dry nitrogen, and magnetic stirrer. The reaction mixture was kept at reflux temperature for 2 h, while the water formed was continuously removed by azeotropic distillation; then most of the benzene was distilled off. After cooling, ice-cold 2% aqueous K_2CO_3 was added, and the products were extracted with three 150-mL portions of Et_2O. The organic phase was washed with two 50-mL portions of water, dried (Na_2SO_4), and concentrated in vacuo, yielding 3.05 g (89%) of **3a,** consisting of 41.3% of *cis*-**3a** and 58.7% of *trans*-**3a,** as determined by densitometry[18] of a thin-layer chromatogram.[7] Although stabile, the isomers were not separable by gas chromatography on EGSS-X, OV-1, DEGS or SILAR 10-C.

2-(*cis*-8′-Heptadecenyl)-4-methoxycarbonyl-1,3-dioxolanes (3b). Condensation of 2.66 g (10 mmol) of *cis*-9-octadecenal (**2b**)[6] and 1.44 g (12 mmol) of **1,** as described for **3a,** produced 3.34 g (91%) of **3b.**

The geometrical isomers of **3a** and of **3b** were separated by preparative TLC[7] (developing solvent, hexane–Et_2O, 75:25, v/v) to yield pure *cis*- and *trans*-**3a,** and *cis*- and *trans*-**3b** (R_f of *cis*-**3a** and *cis*-**3b** 0.54; R_f of *trans*-**3a** and *trans*-**3b** 0.64).

***cis*-3a:** yield 0.61 g (20%, based on **2a**); mp 34–34.5 °C; IR (CS_2,

C_2Cl_4)[19] 1756 (s), 1729 (s), 1407, 1281 (m), 1199 (s), 1177, 1136 (s), 1123 (sh), 1092 (s), 995 (sh), 956, 865; MS *m/e* 342 (<1, M^+), 341 (1), 131 (100, $M - C_{15}H_{31}$), 103 (10, $M - C_{15}H_{31}CO$), 43 (49). Anal. Calcd for $C_{20}H_{38}O_4$: C, 70.13; H, 11.18; O, 18.69. Found: C, 69.97; H, 11.37; O, 18.51.

***trans*-3a:** yield 1.39 g (46%, based on **2a**); mp 30–30.5 °C; IR (CS_2, C_2Cl_4)[19] 1748 (s), 1726 (s), 1410, 1335, 1279 (m), 1199 (s), 1135 (s), 1120 (sh), 1094 (s), 1045 (m), 990, 947, 860; MS *m/e* 342 (<1), 341 (1), 131 (100), 103 (6), 43 (12). Anal. Found: C, 70.16; H, 11.17; O, 18.67.

***cis*-3b:** yield, 1.04 g (31%, based on **2b**); liquid at 0 °C; IR (liquid film)[19] 2940 (m), 1748 (s), 1723 (s), 1640, 1403 (m), 1340 (m), 1284 (m), 1202 (s), 1180 (sh), 1135 (s), 1092 (s), 1058 (m), 1028 (m), 960, 933 (m), 865; MS *m/e* 368 (1, M^+), 367 (1), 131 (100, $M - C_{17}H_{33}$), 103 (20, $M - C_{17}H_{33}CO$), 43 (56). Anal. Calcd for $C_{22}H_{40}O_4$: C, 71.70; H, 10.94; O, 17.36. Found: C, 71.74; H, 10.93; O, 17.21.

***trans*-3b:** yield 1.38 g (42%, based on **2b**); liquid at 0 °C; IR (liquid film)[19] 2958 (m), 1752 (s), 1730 (s), 1645, 1412 (m), 1342 (m), 1285 (m), 1205 (s), 1136 (s), 1095 (s), 1045 (m), 1023 (sh), 957 (sh), 938 (m), 867; MS *m/e* 368 (1), 367 (1), 131 (100), 103 (19), 43 (49). Anal. Found: C, 71.66; H, 10.95; O, 17.14.

2-Alkyl-4-hydroxymethyl-1,3-dioxolanes (4) were prepared from the four respective 4-methoxycarbonyl acetals (*cis*- and *trans*-**3a**, and *cis*- and *trans*-**3b**) by reduction in a saturated solution of $LiAlH_4$[5,10] in dry Et_2O (dropwise addition of **3**, reflux for 2 h, decomposition of excess $LiAlH_4$ with moist Et_2O) and extraction from the basic medium followed by TLC[7] purification (R_f 0.56; developing solvent, hexane–Et_2O, 40:60, v/v) produced the stereomeric five-ring glycerol acetals (**4a, 4b**) in essentially quantitative yields.

2-Pentadecyl-4-hydroxymethyl-1,3-dioxolanes (4a). *cis*-4a: mp 41.5–42.5 °C. Anal. Calcd for $C_{19}H_{38}O_3$: C, 72.56; H, 12.18; O, 15.26. Found: C, 72.71; H, 12.25; O, 15.47.

***trans*-4a:** mp 44.5–45.5 °C. Anal. Found: C, 72.44; H, 12.31; O, 15.32.

2-(*cis*-8′-Heptadecenyl)-4-hydroxymethyl-1,3-dioxolanes (4b). *cis*-4b: liquid at 0 °C. Anal. Calcd for $C_{21}H_{40}O_3$: C, 74.07; H, 11.84; O, 14.09. Found: C, 73.87; H, 11.73; O, 14.28.

***trans*-4b:** liquid at 0 °C. Anal. Found: C, 73.87; H, 11.69; O, 14.44.

2-Alkyl-4-acetoxymethyl-1,3-dioxolanes (5) were prepared from the individual hydroxymethyl acetals 4 by acetylation with 100 parts (v/w) of acetic anhydride in the presence of 10 parts (v/w) of dry pyridine for 2 h at 80 °C.[5] After extraction from the basic medium, the acetates were purified by TLC[7] (R_f 0.46; developing solvent, hexane–Et_2O, 70:30, v/v). All physical characteristics of the pentadecyl derivatives *cis*- and *trans*-**5a** were identical to those reported previously for the respective five-ring glycerol acetal acetates prepared by an alternate route.[5]

2-(*cis*-8′-Heptadecenyl)-4-acetoxymethyl-1,3-dioxolanes (5b). *cis*-5b: liquid at 0 °C; MS *m/e* 382 (1 M^+), 381 (1), 145 (100, $M - C_{17}H_{33}$), 117 (95, $M - C_{17}H_{33}CO$), 43 (74). Anal. Calcd for $C_{23}H_{42}O_4$: C, 72.21; H, 11.06; O, 16.73. Found: C, 71.99; H, 10.86; O, 17.15.

***trans*-5b:** liquid at 0 °C; MS, *m/e* 382 (1, M^+), 381 (2), 145 (100, $M - C_{17}H_{33}$), 117 (82, $M - C_{17}H_{33}CO$), 43 (84). Anal. Found: C, 71.99; H, 11.00; O, 17.00.

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Registry No.—**1,** 615-34-9; **2a,** 629-80-1; **2b,** 2423-10-1; glyceric acid calcium salt hydrate, 6057-35-8; ethanediol, 107-21-1.

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Synthesis of Alkyl-Substituted Benzo[*c*]phenanthrenes and Chrysenes by Photocyclization

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The synthesis of alkyl-substituted polycyclic aromatic hydrocarbons is often necessary to provide samples to aid trace analyses of these compounds in environmental samples. The reported syntheses of monomethylchrysenes and monomethylbenzo[*c*]phenanthrenes, many of which are reported to be carcinogenic,[1] are generally multistep.[2,3]

We report herein on the syntheses of alkyl-substituted benzo[*c*]phenanthrenes and chrysenes by photocyclization[4] of the requisite naphthylstyrenes.[5,6] Since naphthylstyrenes can be readily prepared via the Wittig or Grignard reactions, this procedure appeared to offer a convenient general synthetic route to alkylchrysenes and alkylbenzo[*c*]phenanthrenes.

The six isomeric monomethylbenzo[*c*]phenanthrenes **2a–f** were prepared as outlined in Scheme I, in yields ranging from 66 to 89% (Table I). The spectral properties of these compounds (^1H NMR, UV) correlate well with published data.[7,8]

In addition, ^1H NMR and GLC data indicated the photocyclization products were free of benzo[*c*]phenanthrene and other isomeric methylbenzo[*c*]phenanthrenes. In all preparations, however, we found small amounts (1%) of isomeric methylbenz[*a*]anthracenes produced through cyclization involving the β position of the naphthalene moiety. However, the chromatographic properties of the benzo[*c*]phenanthrenes and the benz[*a*]anthracenes on alumina permit facile sepa-