Acetal Derivatives of Methyl 9(10)-Formylstearate: Plasticizers for PVC[1]

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ABSTRACT

Several acetals and an enol ether were prepared from methyl 9(10)-formylstearate and characterized with respect to their thermal, spectroscopic and chromatographic properties. These low-melting (below -80 C) compounds were generally compatible as secondary poly(vinyl chloride) plasticizers and imparted low-temperature properties that were intermediate between those obtained with dioctyl phthalate and dioctyl sebacate.

INTRODUCTION

Esters of C_{19} dicarboxylic acids reportedly are efficient, low-temperature plasticizers for poly(vinyl chloride) (PVC) (1-3). The C_{19} dibasic acids can be made from oleic and carbon monoxide either by carboxylation in the presence of a strong acid catalyst (Koch reaction) or by hydroformylation in the presence of cobalt carbonyl (oxo reaction) followed by oxidation of the formylstearic acid product. The products from either method are usually referred to as 9(10)-carboxystearic acid but, in fact, are mixtures having a wide distribution of positional isomers (4,5). Now a new, selective hydroformylation procedure places the formyl group exculsively in the 9 and 10 positions (6). The selectivity of this new process arises from use of a rhodium catalyst in the presence of triphenylphosphine.

In view of the excellent low-temperature properties and stabilization imparted to PVC by certain ester-acetal derivatives of azelaaldehydic acid (7,8), we wished to evaluate corresponding derivatives of 9(10)-formylstearic acid. If this application were successful, use of the formylstearic acid from the oxo process would obviate conversion to the diacid. Further it would be desirable to compare the properties of the more homogeneous mixture of 9,10-isomers with those of the mixture obtained by conventional methods. This paper reports preparation of, and plasticizer evaluations for, ester acetals and ethers depicted in Figure 1. Although the dimethyl acetal II (4-6) and spiroacetal VI (9) have been previously reported, they have not been characterized in detail. None of the compounds have been previously evaluated as PVC plasticizers.

EXPERIMENTAL PROCEDURE

Materials

Methyl 9(10)-formylstearate (I) prepared as in Reference 6 had a purity of 88% or better. Urea adduct formation was effective in removing stearate and oleate. Methyl azelaaldehydate (MAZ) and its pentaerythritol acetal (MAZPA) were prepared as previously reported (10). Technical grade 3-chloro-1,2-propanediol and 2-ethylhexyl alcohol were fractionally distilled; $KHSO_4$ was fused and ground; all other chemicals were used as purchased.

Analytical Methods

Thin layer chromatography (TLC) with commercially precoated plates (Brinkmann, Silica Gel F-254) or with laboratory-prepared plates (Brinkmann Silica Gel G) was carried out as previously described (4). Gas liquid chromatography (GLC) of the acetals was performed in an F&M Model 810 instrument with a glass-lined injection port, stainless steel fittings and 6 ft x 1/8 in. stainless steel columns packed with 3% JXR on Gas Chrom Q (100-120 mesh); temperature programing, 150-240 C at 4 C/min; helium flow, 50 ml/min; injection port temperature, 275 C; detector, 300 C. Analyses of acetals required scrupulously cleaned columns, which were reserved specifically for acetal determinations. GLC with a 25% DEGS column was carried out as outlined earlier (4), and also NMR and mass spectrometry. IR spectra were recorded from CCl_4 solutions (ca. 6%) or neat liquid with either a Beckman IR8 or a Perkin-Elmer Model 337 grating spectrophotometer. Refractive index was measured with a Bausch & Lomb Abbe refractometer. Thermal analyses were made with a DuPont 900 and 950 Thermoanalyzer System. Conditions for determining melting point endotherms were: macrosample size, heating rate 5 C/min from ca. -120 C to ca. 30 C, sensitivity 0.2 and SiC reference. Conditions for TGA were: 10 C/min heating rate, 50 C/in. of chart, 5 mg sample size and 30 cc/min N_2 flow.

Methyl 9(10)-Dimethoxymethylstearate (II)

Method A: A solution of 100 g aldehyde I (ca. 92% by GLC) in 142 ml CH_3OH and 170 ml 2,2-dimethoxypropane to which was added 1.5 g $KHSO_4$ was refluxed under N_2 for 1.5 hr. After the reaction mixture had cooled, insoluble catalyst was filtered out. Filtrate was concentrated, diluted with CH_2Cl_2 and washed with 5% bicarbonate solution. After the organic phase had been washed three times with water, it was dried ($MgSO_4$). Filtration and removal of solvent left a clear, pale yellow liquid (99.8 g; GLC analysis showed 86.7% II and 4.9% I). Fractional distillation (0.75 x 3.5 in. Vigreux column) of 96.6 g crude acetal afforded three major fractions boiling in the range 155-165 C/0.05 mm. GLC, TLC and IR showed them to be mixtures of dimethyl acetal II and methyl 9(10)-methoxymethylenestearate (III).

The combined fractions (83.1 g) were dissolved in 100 ml of dry CH_3OH and 25 ml of 5% HCl in CH_3OH was added. After this solution had stood 48 hr, complete regeneration of dimethyl acetal II occurred as indicated by TLC. Catalyst was neutralized with bicarbonate and the mixture was concentrated on a rotary evaporator. The cloudy concentrate was dissolved in CH_2Cl_2 and washed several times with water. The organic phase was dried and filtered. Removal of solvent left 77.2 g of clear, colorless liquid (94.5% II; 2.2% I by GLC). NMR ($CDCl_3$) δ3.32 (s,6) for $(C\underline{H}_3O)_2\overset{H}{C}$-, 3.63 (s,3) for $C\underline{H}_3O\text{-}\overset{O}{\overset{\|}{C}}$-, 4.2 (d,1) for $\begin{matrix}-O \\ -O\end{matrix}\!\!>\!C\underline{H}\text{-}\overset{|}{C}H$-; IR ($CCl_4$) 2835 cm^{-1} (acetal overtone or C-H stretch), 1730 (ester C=O), 1240 and 1165 (methyl ester C-O-C), 1190 and 1110 (ester and acetal C-O-C), 1075 and 1052 (acetal C-O-C). Analyses and properties are listed in Table I.

Method B: Aldehyde I (350.4 g, 97%) was dissolved in

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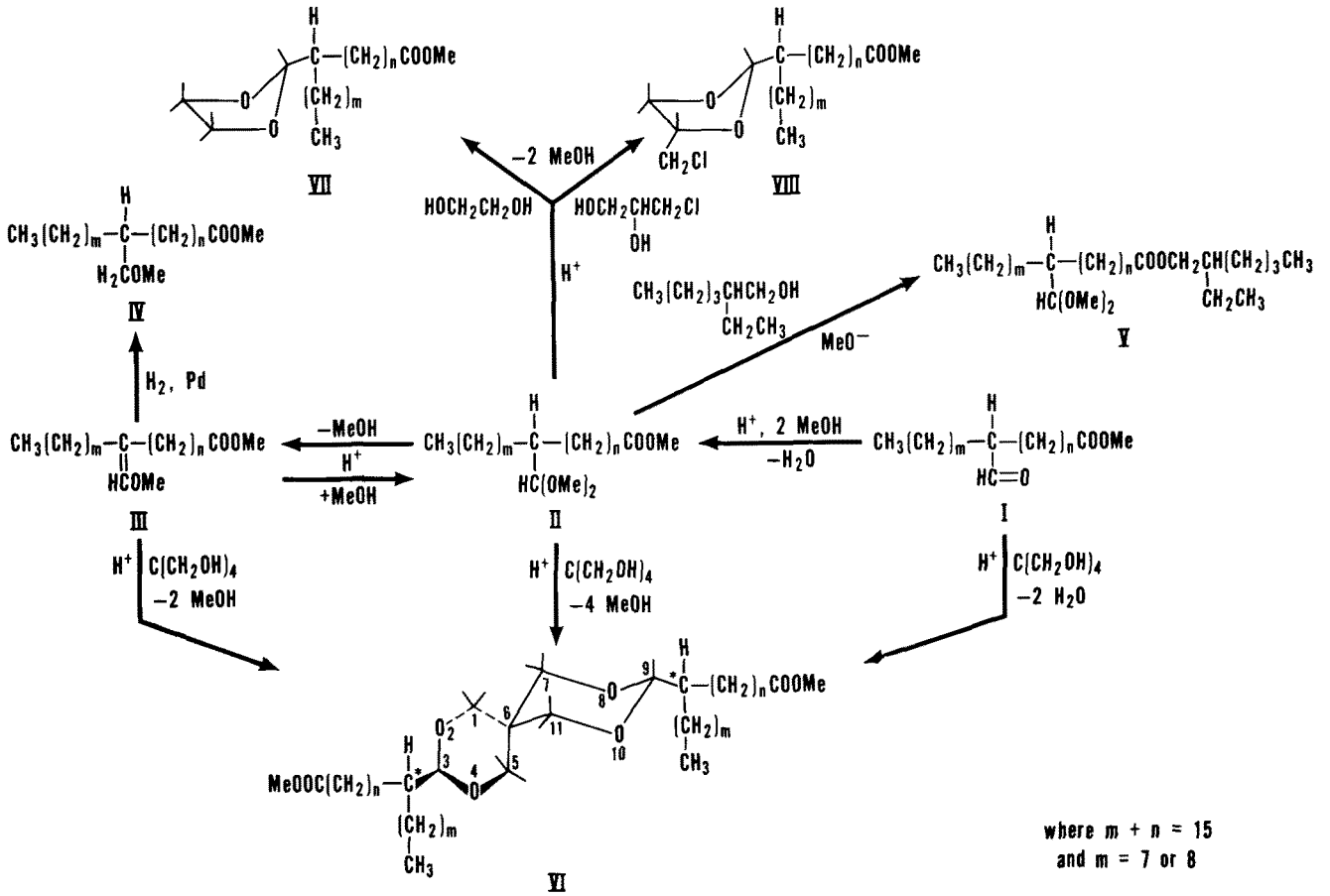

FIG. 1. Ester acetals and ethers from methyl 9(10)-formylstearate. I = methyl 9(10)-formylstearate (6); II = methyl 9(10)-dimethoxymethylstearate; III = methyl 9(10)-methoxymethylenestearate; IV = methyl 9(10)-methoxymethylstearate; V = 2-ethylhexyl 9(10)-dimethoxymethylstearate; VI = 3,9-bis[8-carbomethoxy-(1-*n*-nonyl)octyl]- and 3,9-bis[9-carbomethoxy-(1-*n*-octyl)nonyl]-2,4,8,10-tetraoxaspiro[5.5]-undecane; VII = methyl 9(10)-(1,3-dioxolan-2-yl)stearate; and VIII = methyl 9(10)-(4-chloromethyl-1,3-dioxolan-2-yl)stearate.

CH_3OH (500 ml) and 5% HCl in CH_3OH (100 ml), together with a little Drierite. The mixture was swirled occasionally and allowed to stand under N_2 for 4 days. The solution was filtered, neutralized and worked up as in Method A. A clear colorless liquid resulted (374 g) which exhibited the same properties as the product from Method A.

Methyl 9(10)-Methoxymethylenestearate (III)

$KHSO_4$ (0.7 g) was added to 200 g of dimethyl acetal II (ca. 92% II and 6.2% I by GLC) in a round-bottomed flask with sidearms to which were fitted a N_2 capillary and a thermometer. A variable-take-off distillation head was attached. After the apparatus was evacuated with a water aspirator, the mixture was heated quickly to 70 C, then gradually to 100 C in the first hour and to 145 C in the next hour. In this interval the trap collected 18 g of clear liquid. Heating was continued at 145-150 C for another 3.5 hr, but only 0.2 g of additional liquid was collected in the trap. Pot liquid was decanted from the catalyst into a separatory funnel; residual catalyst and the flask were rinsed with ether. Crude products were combined and washed with 1% bicarbonate and phase separation was facilitated by adding saturated NaCl.

The organic phase was washed with water and dried ($MgSO_4$). After removal of drying agent and solvent, a clear yellow liquid was obtained (180.3 g). Fractional distillation (0.75 x 2.5 in. Vigreux column) afforded a main fraction (150 g) distilling at 146-150 C/0.004 mm as a clear colorless liquid analyzing 94.8% as enol ether III and 3.5% as aldehyde I. NMR ($CDCl_3$) δ1.92 (m,4) for $-C\underline{H}_2-\overset{H}{\underset{|}{C}}=\overset{-C-}{\underset{|}{C}}-C\underline{H}_2-$, 3.48 (s,3) for $C\underline{H}_3-O-\overset{H}{\underset{|}{C}}=C-$, 3.63 (s,3) for $C\underline{H}_3O-\overset{O}{\underset{\|}{C}}-$, 5.71 (s,1) for $\rangle C=C\underline{H}-O-$, IR ($CCl_4$) 1730 cm^{-1} (ester C=O), 1663 ($\rangle C=C\langle$), 1192 and 1160 (methyl ester C-O-C), 1130 and 1095 (ester and ether C-O-C); mass spectrum (70 eV) m/e (relative intensity) 29(7), 41(18), 43(11), 55(25), 59(7), 67(11), 71(12), 81(15), 85(100), 95(12), 97(5), 109(6) and 340(11). These mass spectral data are abbreviated and selected according to the scheme of Hertz et al. (11). Other analyses are shown in Table I.

Methyl 9(10)-Methoxymethylstearate (IV)

A solution of enol ether III (10 g, 94.8%) in 50 ml hexane containing several drops of glacial HOAc was added to 0.2 g 10% Pd/C in a 300 ml rocker autoclave. The autoclave was sealed, flushed with N_2, filled with H_2 to 600 psi and heated to 150 C; pressure was adjusted from 890 to 970 psi. An initial uptake of H_2 was indicated during heating. Once the operating temperature of 150 C was reached, the pressure remained steady for 3 hr. The autoclave was then opened and the reaction mixture filtered, washed and transferred with CH_2Cl_2. After removal of solvent, 9.9 g of a clear, nearly colorless liquid was left. GLC on a DEGS column (97.1% IV, 2.4% stearate and 0.4% I) showed essentially complete hydrogenation, which was confirmed by IR and NMR. NMR ($CDCl_3$) δ3.22 (d,2) for $-\overset{H}{\underset{|}{C}}H-C\underline{H}_2-O-$, 3.28 (s,3) for $C\underline{H}_3O-CH_2-$, 3.64 (s,3) for $C\underline{H}_3O-\overset{O}{\underset{\|}{C}}-$; IR ($CCl_4$) 1730 cm^{-1} (ester C=O), 1240, 1190 and 1165 (methyl ester C-O-C), 1105 (ester or ether C-O-C). Mass spectrometry showed a weak (0.56) molecular ion peak at m/e 342 and a base peak at m/e 55. Relatively intense (>10) peaks were observed with m/e <170 but only several with m/e >170, specifically 278(38), 310(22) and

TABLE I

Analytical and Physical Properties of Formylstearate Derivatives

Compound (see Fig. 1)	Empirical formula	Purity, % by GLC[a]	Physical properties			Molecular weight		Carbon, %		Hydrogen, %		Substituent X, %		
			n_D^{20}	bp (C/mm)	mp (C)[b]	Calculated	Found	Calculated	Found	Calculated	Found	X	Calculated	Found
Dimethyl acetal II	$C_{22}H_{44}O_4$	>94	1.4496	Decomposed	-88	372	---	70.91	70.23	11.90	12.00	CH_3O-	24.96	23.99
Enol ether III	$C_{21}H_{40}O_3$	95	1.4574	146-150/0.004	-89	340	374	74.05	73.89	11.84	12.08	CH_3O-	18.21	17.56
		96	1.4568		-95		[340][c]							
Methyl ether IV	$C_{21}H_{42}O_3$	97	1.4489	164/0.08	-13	342	[342][c]	73.61	73.36	12.36	12.33	---	---	---
Ethylhexyl ester V	$C_{29}H_{58}O_4$	98	1.4526	188-91/0.005	-90	471		73.98	74.41	12.42	12.75	---	---	---
Butyl ester dimethyl acetal	$C_{25}H_{50}O_4$	>98	1.4494	162-4/0.003	-93	415	---	72.41	72.51	12.15	12.18	---	---	---
Spiroacetal VI	$C_{45}H_{84}O_8$	---	1.4712	---	<100	753	777	71.76	71.54	11.24	11.36	---	---	---
			1.4706	---										
Cyclic acetal VII	$C_{22}H_{42}O_4$	95	1.4575	163-6/0.005	-86	370	---	71.31	71.69	11.43	11.59	---	---	---
Chloroacetal VIII	$C_{23}H_{43}O_4Cl$	95	1.4640	Undistilled	-84	419	439	65.92	67.18	10.34	10.71	Cl	8.46	8.26

[a]Gas liquid chromatography (GLC) analyses of all compounds except methyl ether IV were performed on a 6 ft x 1/8 in. column of 3% JXR (see Experimental Procedure); GLC analysis of IV was performed on a 6 ft x 1/8 in. column of 25% DEGS (see Experimental Procedure).

[b]Melting points determined by differential thermal analysis (see Experimental Procedure).

[c]Values determined by mass spectrometry; other values, by vapor pressure osmometry.

311(13). Other analyses are given in Table I.

2-Ethylhexyl 9(10)-Dimethoxymethylstearate (V)

Dimethyl acetal II (109.2 g, 93%), 2-ethylhexyl alcohol (427 g) and $NaOCH_3$ (0.2 g) were added to a round-bottomed, three-necked flask fitted with a N_2 capillary and a thermometer. A distillation head with a drying tube was connected to the flask. The solution was stirred magnetically as it was heated to 95-100 C for 11 hr, but only a few drops of methanol distilled. The pot temperature was decreased to 50 C and the flask evacuated cautiously to 15 mm. The temperature was then raised to 70 C and held for another 1.5 hr. Glacial HOAc (0.25 ml) was added and most of the alcohol (380 g) was distilled (85-87 C/15 mm) with the pot temperature below 95 C. Clear, nearly colorless residue was diluted with CH_2Cl_2 and an equal volume of water was added; the mixture was shaken and allowed to separate. Because the mixture was slightly basic, another 0.25 ml of acid was added and again the mixture was shaken. The organic layer was separated and washed with water. After having been dried ($MgSO_4$) and filtered, the solution was passed through 100 g of alumina (Fisher Sci., A-540) in a medium porosity filter tube. The alumina was washed once with CH_2Cl_2. Removal of solvent left a slightly hazy liquid (128.1 g) which was clarified by refiltration through a bed of Celite. GLC analysis gave: 93% ethylhexyl ester V and 6% dimethyl acetal II; TLC showed two minor, highly polar impurities. Distillation (without a column) of 68.5 g crude product (n_D^{20} 1.4521) provided the following main fractions: (a) 172-186 C/0.005 mm; n_D^{20} 1.4524; 33.8 g (68.5% V, 30% II); and (b) 185-190 C/0.005 mm; n_D^{20} 1.4527; 30.1 g (99% V). Fraction b proved to be pure by IR and TLC. Analyses in Table I are for another distilled fraction of equivalent purity by GLC. NMR ($CDCl_3$) δ3.32 (s,6) for -CH($OC\underline{H}_3$)$_2$, 3.97 (d,2) for $\diagdown$CH$\underline{H}_2$-O-, 4.12 (d,1) for $\diagdown$CH$\underline{H}$(O-)(O-); IR (CCl_4) 2827 cm^{-1} (acetal overtone or C-H stretch), 1735 (ester C=O), 1238 (ester C-O-C), 1190, 1170 and 1110 (acetal and ester C-O-C), 1075 and 1051 (acetal C-O-C).

Butyl 9(10)-Dimethoxymethylstearate

The butyl ester dimethyl acetal was prepared by base-catalyzed transesterification of dimethyl acetal II with butanol as for ethylhexyl ester V. Analyses are given in Table I. NMR ($CDCl_3$) δ3.32 (s) for -CH($OC\underline{H}_3$)$_2$, 3.94-4.18 (m) for $\diagdown$CH$\underline{H}$(O-)(O-) and -$CH_2C\underline{H}_2$O-C(=O)-; IR (neat liquid) 1735 cm^{-1} (ester C=O), 1240 (ester C-O-C), 1175, 1115 (acetal and ester C-O-C), 1075, 1055 and 965 (acetal C-O-C).

Routes to Spiroacetal VI

This product is a mixture of 3,9-bis[8-carbomethoxy-(1-*n*-nonyl)octyl]-2,4,8,10-tetraoxaspiro-[5.5]-undecane and 3,9-bis[9-carbomethoxy-(1-*n*-octyl)nonyl]-2,4,8,10-tetraoxaspiro-[5.5]-undecane which was prepared by the following procedures.

Direct acetalation: Essentially the procedure of Leech and Rose (9) was followed. Reaction of aldehyde I (53.2 g, 94%) with pentaerythritol (10.1 g) in 90 ml of dioxane, catalyzed with 0.02 ml of H_2SO_4, yielded a viscous, light amber liquid (58.4 g). Although TLC of this liquid showed neither aldehyde I nor dimethyl acetal II present, TLC did indicate acid or alcohol impurities. Accordingly 10 g of the slightly hazy liquid was dissolved in 25 ml CH_2Cl_2, shaken with K_2CO_3 and passed through a column of alumina (15 g) on a layer of Celite filter-aid. Removal of solvent

gave a clear liquid that according to TLC contained only trace impurities and was identified as spiroacetal VI. Molecular weight and analyses are given in Table I. NMR ($CDCl_3$) δ3.64 (s,6) for $C\underline{H}_3O\text{-}\overset{O}{\overset{\|}{C}}\text{-}$, 4.34 (d,2, J<2) for -ĊH-C$\underline{H}$(O-)(O-), 4.54 (m,2, $^4J{\sim}2$, $^2J{\sim}6$) for ring protons 5e, 11e (see Fig. 1 and Discussion); IR (CCl_4) 1730 cm^{-1} (ester C=O), 1235 and 1160 (methyl ester C-O-C), 1190 and 1120 (ester and acetal C-O-C), 1085, 1040 and 1023 (acetal C-O-C).

Transacetalation: The method of Pryde et al. (10) was modified slightly. A mixture of dimethyl acetal II (5.25 g, 92%), pentaerythritol (1.25 g) and $KHSO_4$ (0.1 g) was heated at 125-140 C for 4 hr; 10 ml of toluene was then added. Slow distillation was carried out for 3 hr without permitting the vapor temperature to exceed 100 C and the pot temperature, 143 C. Pot temperature was adjusted to 125 C and a water aspirator vacuum was applied for 1 hr. The reaction mixture was cooled, diluted with C_6H_6 and filtered. Filtrate was washed with dilute bicarbonate solution and then with water and dried ($MgSO_4$). Filtration and removal of solvent yielded an amber but clear, viscous liquid (5.08 g) identified as spiroacetal VI by IR, NMR and TLC.

Enol ether: A mixture of pentaerythritol (12.2 g), dioxane (108 ml), enol ether III (55.5 g, 94.8%) and concentrated H_2SO_4 (0.02 ml) was heated at 90 C with N_2 bubbling for 1 hr. The mixture converted to a clear, yellow solution in the first hour, and slow distillation occurred below 70 C. In the next 1.5 hr, pot temperature was increased slowly to 109 C; vapor temperature increased to 98 C and then declined as distillation ceased. After the solution had cooled, pressure was reduced with a water-aspirator vacuum, and pot temperature was held at 50-60 C for 30 min as distillation occurred at 35-42 C. The pot liquid was cooled and diluted with CH_2Cl_2. NaOAc (0.11 g) was added to the solution with stirring for 30 min and the solution was filtered and concentrated on a rotary evaporator. The concentrate was diluted with 60 ml of CH_2Cl_2. After 4 g of activated charcoal was added, the mixture was stirred, filtered and passed through a column of alumina (30 g). The column was washed once with 50 ml of CH_2Cl_2. Removal of solvent from the effluent left 56.2 g of pale yellow viscous liquid (see analyses in Table I). IR, NMR and TLC were consistent for spiroacetal VI. A second fraction (5.8 g) of lower purity was obtained by washing the alumina column with 60 ml acetone.

Methyl 9(10)-(1,3-Dioxolan-2-yl)stearate (VII)

A mixture of dimethyl acetal II (139 g, 90%), ethylene glycol (21.7 g) and $KHSO_4$ (0.25 g) was heated to 90-100 C at 50 ± 5 mm Hg for 9 hr. The distillate (22 g) was collected in a dry-ice trap. The decanted pot liquid was transferred with ether, washed with dilute bicarbonate and water, dried and filtered. After solvent was removed, a clear colorless liquid (135 g, 91% VII by GLC; n_D^{20} 1.4573) was left. Distillation (without a column) of 72.4 g gave 55.9 g of liquid identified as cyclic acetal VII (see analyses in Table I). NMR ($CDCl_3$) δ3.63 (s,3) for $C\underline{H}_3O\text{-}\overset{O}{\overset{\|}{C}}\text{-}$, 3.87 (m,4) for -OC$\underline{H}_2$-C$\underline{H}_2$-O-, 4.75 (d,1, J~4) for >CHC$\underline{H}$(O-)(O-); IR (CCl_4) 1735 cm^{-1} (ester C=O), 1240 and 1165 (methyl ester C-O-C), 1192 and 1105 (ester and acetal C-O-C), 1120 and 1035 (acetal C-O-C).

Methyl 9(10)-(4-Chloromethyl-1,3-dioxolan-2-yl)stearate (VIII)

Chloroacetal VIII was prepared from 3-chloro-1,2-propanediol in essentially the same manner as described for cyclic acetal VII except that the product was not distilled. Analyses for the undistilled product are given in Table I. GLC indicated two major, partially resolved peaks of about equal area (combined area 93.6% of total) which may be due to the *cis* and *trans* ring isomers. NMR ($CDCl_3$) δ3.24-3.82 (m, ca. 2 plus methyl ester protons) probably -C$\underline{H}_2$Cl, 3.90 (d ?, ca. 1, J 4?) for -ĊH-C$\underline{H}_2$O, 4.04-4.40 (m, ca. 2) for (-O-CH$_2$)(Cl-CH$_2$)>C$\underline{H}$-O-, 4.86 (d-s-d, ca. 1, J 3, J 11) for *cis* and *trans* -ĊH-C$\underline{H}$(O-)(O-); IR (CCl_4) 1730 cm^{-1} (ester C=O), 1240 and 1163 (methyl ester C-O-C), 1189 and 1100 (ester and acetal C-O-C), 1112-1087 and 1020-1010 (acetal C-O-C).

TABLE II

Chromatographic Data

Compound[a]	Gas liquid chromatography: relative retention times[b]	Thin layer chromatography: R_f values[c]	
		Point	Range
Methyl stearate	1.00	9.3	9.1-9.5
Aldehyde I	1.43	6.9 7.4	6.6-7.1 (9-) 7.1-7.7 (10-)
Dimethyl acetal II	1.58	6.5	5.8-6.9
Enol ether III	1.39[d]	8.8	8.5-9.0
Methyl ether IV	1.40[d]	8.2	7.5-8.5
Ethylhexyl ester V	2.47	8.5	8.0-9.0
Enol ether of V	2.30	9.5	9.4-9.7
Butyl ester	1.99	7.8	6.8-8.3
Spiroacetal VI	---	4.0	2.5-4.5
Cyclic acetal VII	1.81	5.5	4.5-6.0
Chloroacetal VIII	22.09^6 2.11^3 [e]	7.3	6.3-7.7
Methyl carboxystearate	---	0.9	0-1.1

[a]Compounds I-VIII (see Fig. 1 and Experimental Procedure).

[b]Retention time for methyl stearate: 11.1 ± 0.2 min (3% JXR packing; see Experimental Procedure).

[c]R_f values determined on a laboratory plate of Silica Gel G (see Experimental Procedure).

[d]Enol ether III and methyl ether IV were resolved by a 25% DEGS column (see Experimental Procedure) but not by a 3% JXR column.

[e]Two partially resolved peaks thought to be the *cis* and *trans* isomers.

RESULTS AND DISCUSSION

Acetals II and VI (see Fig. 1) were prepared by direct acetalation of aldehyde I and also by acid-catalyzed addition of methanol or pentaerythritol, respectively, to the enol ether III. Spiroacetal VI was also prepared by transacetalation (10) of dimethyl acetal II as were also the cyclic acetals VII and VIII from the corresponding glycol. Enol ether III was obtained by acid-catalyzed cracking (12) of dimethyl acetal II. Hydrogenation of enol ether III gave methyl ether IV, but moderate pressure and elevated temperatures were necessary to hydrogenate completely with Pd/C catalyst. The 2-ethylhexyl ester V was prepared from dimethyl acetal II by the selective alcoholysis procedure of Pryde et al. (12,13) who showed that transesterification occurs exclusively when alcoholysis is done on ω-dialkoxy esters.

Spiroacetal VI was purified by adsorption chromatography. Because all compounds in Figure 1 had low melting points, except perhaps methyl ether IV and aldehyde I, and high boiling points (see Table I), crystallization was not convenient and fractional distillation of acetals II and VI was not practical because the compound either tended to degrade or boiled too high. Unlike acyclic acetals, the cyclic

TABLE III

Chemical Shifts and Coupling Constants[a]

Proton assignments	TMAPA (15)[b] (In C_6H_6-CCl_4, ca. 1:1)	MAZPA (10)[b] (In $CDCl_3$)	Spiroacetal VI (In $CDCl_3$)
1-ax	2.95	3.29 (d)	3.25
1-eq	3.26	3.56	3.54
3-ax	3.84	4.42 (t)	4.34 (d?)
5-ax	3.24	3.49	3.45
5-eq	4.50	4.54	4.54
7-ax	2.95	3.29 (d)	3.25
7-eq	3.26	3.56	3.54
9-ax	3.84	4.42 (t)	4.34 (d?)
11-ax	3.24	3.49	3.45
11-eq	4.50	4.54	4.54
^2J 1-ax, 1 eq	11.00	11.5	5.5
^2J 5-ax, 5 eq	11.00	11.5	5.5
^2J 7-ax, 7 eq	11.00	11.5	5.5
^2J 7-ax, 7 eq	11.00	11.5	5.5
^4J 1-eq, 5 eq	2.50	ca. 2.5	ca. 2
^4J 7-eq, 11 eq	2.50	ca. 2.5	ca. 2
^4J 5-ax, 11 ax	ca. 1.90	<2	<1

[a]Chemical shifts in ppm downfield from tetramethylsilane. Coupling constants are indicated by J (15) and are in Hz.

[b]TMAPA is the pentaerythritol acetal of trimethyl acetaldehyde and MAZPA is that of methyl azelaaldehydate.

acetals, such as spiroacetal VI, are very stable (12,14). In later preparations, acetals II and VI were generated as needed from enol ether III, which had been fractionally distilled and was expected to keep better than dimethyl acetal II.

Chromatography

There is some controversy as to whether dimethyl acetals of higher aldehydes can be distilled and chromatographed without alteration (5,12,14), and the tendency for these acetals to convert to enol ethers or aldehydes has been well-documented, particularly during GLC (12,14). When dimethyl acetal II was distilled, partial conversion to enol ether III was observed, yet several samples of ethylhexyl ester V were distilled without evidence of any conversion. However ethylhexyl ester V showed significant conversion to its enol ether during GLC even under optimum conditions. Unlike the dimethyl acetals, the five- and six-membered cyclic acetals are reported to be quite stable (12,14). Thus cyclic acetal VII distilled without alteration, and both cyclic acetal VII and chloroacetal VIII were sufficiently stable to GLC conditions.

GLC was used to estimate the purities of the dimethyl acetals, as well as the cyclic acetals other than spiroacetal VI. Special precautions were taken (see Experimental) and the possible formation of impurities caused by GLC were ruled out by TLC, IR and NMR. Unless these precautions are taken, conversion of dimethyl acetal to enol ether on the column, as described previously, complicates GLC analysis. Table II presents retention data from TLC and GLC of compounds listed in Figure 1. This table compares the effectiveness of these two chromatographic methods in resolving and characterizing these compounds and possible impurities.

Nuclear Magnetic Resonance

NMR of major functional groups are listed with each compound in the Experimental Procedure section. In addition, observed resonances common to the stearyl moiety were: terminal methyl, δ0.87(t); chain methylenes, 1.26(m); ester β-methylenes, 1.60(m); and ester α-methylenes, 2.28(t). The methyl proton resonances at δ3.48(s), 3.32(s) and 3.63(s) associated, respectively, with the enol ether, dimethyl acetal, or methyl ester groups were particularly useful for confirming or refuting any GLC analyses that suggested such impurities. The enol ether resonance at δ5.71(s); the acetal, at 4.12(d); and the aldehyde, at 9.54 (d, J~3) were equally valuable.

NMR data for pentaerythritol acetals (PA) of: aldehyde I, MAZ and trimethyl acetaldehyde (TMA) are compared in Table III. The resonance pattern for the spiroacetal ring protons has been established previously for the spectrum of TMAPA (15); the spiro ring effect makes the 5e and 11e protons (see conformation of spiroacetal VI in Fig. 1) nonequivalent and shifts these resonances downfield nearer to the acetal protons 3a and 9a. Long range coupling (^4J) was also observed. Chemical shifts and coupling constants found for the spiro ring protons are compared for these three spiroacetals in Table III.

The spectrum of MAZPA seems consistent with that found by Anderson (15) for TMAPA with respect to the

TABLE IV

Thermogravimetry of Spiroacetal VI (Fig. 1) Versus Several MAZ Acetals

Compound[a]	T_i (C)[b]	T_{10} (C)[b]	Rate (mg/C) x 10^2[c]
Spiroacetal VI	163	263	-4.0
MAZPA	183	243	-8.0
MAZGA	117	162	-7.8

[a]MAZPA (10) is the pentaerythritol acetal of methyl azelaaldehydeate (MAZ); MAZGA (18), the glycerol acetal of MAZ.

[b]T_i is the temperature for initial weight loss; T_{10}, at 10% weight loss.

[c]The rates of weight losses (slopes) were measured only in the linear regions of the thermogravimetric curves.

TABLE V

Mechanical Properties (20) of PVC Sheets Containing 32% Plasticizer (50:50)

Ester[a]	Torsional stiffness temperature, C		Compatibility, Δ	Tensile strength, psi	Elongation, %	100% Modulus, psi	Migration weight loss, %	Volatility weight loss, %
	T_f[b]	T_4[b]						
Control (DOP)	-29	1	30	2830	355	1190	4.3	2.3
Control (DOS)	-57	-7	50	2355	295	1045	19.3	1.6
Control (DOP/DOS)	-43	-5	38	2790	290	1150	12.2	1.5
Aldehyde I[c]	-46	-16	30	2550	360	1110	10.5	5.2
Aldehydes[c,d]	-40	-10	30	2690	210	1355	6.9	3.1
Dimethyl acetal II	-38	0	38	2655	350	1155	8.8	2.1
Dimethyl acetals[d]	-41	0	41	2670	355	1060	9.0	2.3
Enol ether III	-45	1	46	2400	290	1070	11.3	2.8
Enol ethers[d]	-45	3	48	2705	410	1110	11.3	3.1
Ethylhexyl V (Distilled)	-43	13	56	2690	355	1235	9.4	2.2
Ethylhexyl V[c] (Undistilled)	-47	10	57	2340	275	1075	13.0	3.7
Butyl	-40	4	44	2540	310	1230	10.0	1.2
Cyclic acetal VII	-39	1	40	2740	345	1130	8.4	2.1
Chloroacetal VIII	-36	8	44	2775	245	1250	8.1	1.4

[a]DOP and DOS are, respectively, di-2-ethylhexyl phthalate and di-2-ethylhexyl sebacate.

[b]T_f, the flex temperature at which the apparent modulus of elasticity becomes 135,000 psi; T_4, the temperature at which the stiffness of 10,000 psi occurs.

[c]Exudate after 1 week.

[d]Derived from methyl formylstearate which contained only 63% as the 9(10)-substituted isomers according to mass spectrometry (4).

spiro ring protons, except that these absorptions are shifted slightly downfield and the upfield side of the 5e,11e absorptions practically overlaps the downfield side of the 3a,9a absorptions. Also, the downfield side of the 1e,7e absorptions are partially overlapped by the strong singlet of the methyl ester protons (δ3.64). Results of decoupling experiments confirm these proposed assignments for the ring proton resonances.

The NMR spectrum of spiroacetal VI seems consistent with the proposed structure and conformation in Figure 1. The coupling constant between the protons (3a,9a) attached to carbons bearing two oxygens and their adjacent methinyl group is much smaller than that found in MAZPA; this smaller coupling is easily rationalized in terms of a difference in rotamer populations about the starred bonds (Fig. 1). The long range coupling constant (^4J) of 2 Hz suggests that the six-membered rings are predominantly in chair conformations. Addition of two asymmetric centers in going from MAZPA to spiroacetal VI does not complicate the spectrum appreciably because of the similarity of the several racemates presumably present in equal amounts. Other differences in the spectrum of spiroacetal VI were the terminal methyl resonance at δ0.87(t) and reduction in methylene absorption between 1.40 and 1.75. Results of decoupling experiments confirmed the proposed assignments for the resonances.

Except for the NMR spectrum of cyclic acetal VIII, interpretations for spectra of the remaining compounds seemed consistent with the structures given in Figure 1. As expected, chloroacetal VIII showed a complicated pattern with overlapping multiplets that made interpretation difficult because of the large number of possible isomers.

Mass Spectrometry

Mass spectrometry of diester derivatives of aldehyde I can serve for estimating the isomeric composition of the branched hydroformylation products according to fragmentation pattern (4). However molecular ion peaks are weak and often absent. Mass spectrometry of both enol ether III and methyl ether IV gave distinguishable molecular ion peaks, and enol ether III gave an intense peak. A typical fragmentation pattern for normal aliphatic methyl esters was obvious in the spectrum of methyl ether IV but was not in that of enol ether III. Although Manni et al. (16) have shown that mass spectrometry of β-substituted alkenyl ethers is valuable for the structural elucidation of β-substituted aldehydes, our parent aldehyde I is of a different class and produced, as expected, an α,α-disubstituted enol ether, which displayed a different fragmentation pattern. Fragmentation patterns for both ethers III and IV (Fig. 1) were unexpected and were unlike the patterns observed for monofunctional, acyclic ethers and esters. However recent mass spectrometry investigations (17) indicate that acyclic, difunctional compounds can be expected to give unique fragmentation patterns resulting from direct interaction of the two groups.

Thermal Properties

According to differential thermal analysis all derivatives, except methyl ether IV and parent aldehyde I, had melting points below -80 C (Table I). Aldehyde I showed two large endotherms at -8.4 C and +9.9 C. The thermal stability of spiroacetal VI was compared with that of MAZPA (10) and of MAZGA [the glycerol acetal of MAZ (18,19)] by means of thermogravimetry (Table IV). The rate of weight loss increased rapidly with the two MAZ acetals and became linear within 25 C after the initial 10% weight loss (T_{10}). Spiroacetal VI showed initially a moderately convex curve and a significantly lower overall rate. A linear rate was not displayed by spiroacetal VI until after a 25% weight loss (ca. 355 C) was recorded and then the rate was only half as much as that for the two MAZ acetals.

Plasticizer Evaluation

When added in 50:50 mixture with dioctyl phthalate to a total plasticizer level of 32%, all compounds of Figure 1 except spiroacetal VI were compatible with PVC. However all the compounds were incompatible at a plasticizer level of 32% in the absence of dioctyl phthalate. Both aldehyde I and methyl formylstearates, having 37% substitution in other than the 9(10)-position, had the highest degree of compatibility according to the compatibility number indicated in Table V (20). Both formylstearate compounds produced heavy exudate after 1 week. This exudate may result from oxidation of formylstearate to carboxystearate, which would be incompatible because of the free carboxyl

group. The ethylhexyl and butyl ester dimethyl acetals were not as compatible as the corresponding methyl ester. Dimethyl acetal II and the other acetal esters were intermediate between dioctyl phthalate alone and dioctyl sebacate alone.

All the compatible compounds effectively lowered the flex temperature (T_f) of the PVC sheets compared to those plasticized with dioctyl phthalate alone. The T_f, however, did not attain as low a value as that for PVC plasticized with dioctyl sebacate alone. Similarly, for most of the other properties listed in Table V, the values produced by the 50:50 mixtures were intermediate between those for the two control plasticizers when present alone.

In general, dimethyl acetal II and cyclic acetal VII should serve as secondary plasticizers that would enhance low-temperature properties of plasticized PVC.

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