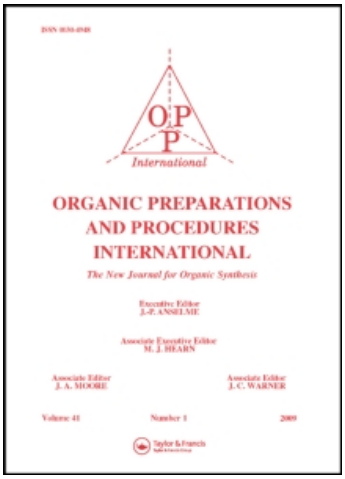

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SYNTHESIS OF 7-OXO ALCOHOLS *via* ENAMINE

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SYNTHESIS OF 7-OXO ALCOHOLS via ENAMINE

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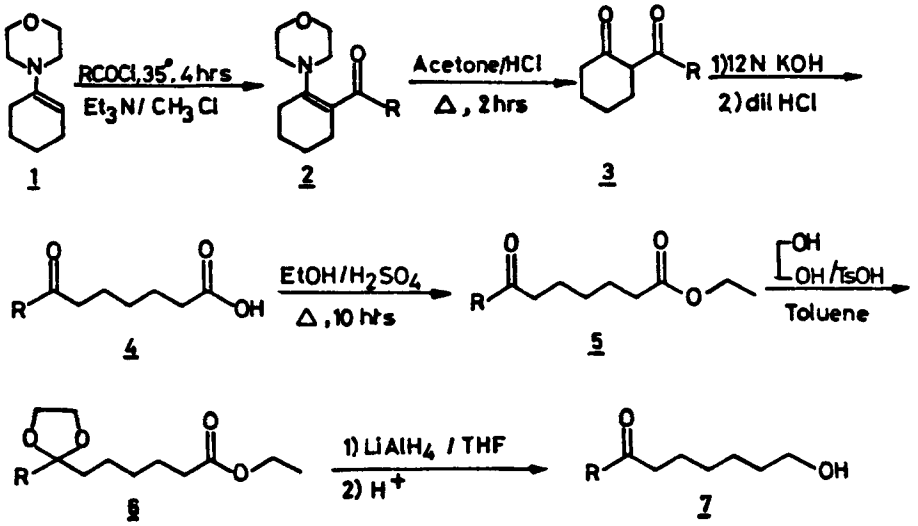
In the course of our investigations on the structural aspects of the polymers based on 7-oxoalkyl acrylates and methacrylates as pour point depressants for petroleum oils, a general route for the synthesis of long chain 7-oxo alcohols was needed. The present paper reports the synthesis of a series of 7-oxo alcohols ranging in carbon number from C_{12}-C_{22} for the first time. The facile acylation of enamines[1] has been exploited for the extension of carbon chain length by six carbon atoms following literature procedures[2-5] to obtain 2-5. Ketalization of 5 with 1,2-ethanediol gave ethyl 7-ketal alkanoate 6 which on reduction with $LiAlH_4$ in dry THF followed by hydrolysis yielded the corresponding 7-oxo alcohol 7.



EXPERIMENTAL SECTION

Melting points were determined on a Buchi 512 melting point apparatus in capillary tubes and are uncorrected. The IR spectra were recorded on a Perkin-Elmer model 283B infrared spectrophometer. PMR spectra were obtained on 90 MHz JEOL-FX-90-Q spectrometer using TMS as the interal standard and $CDCl_3$ as solvent. Mass spectra were recorded on a VG 7070 H Mass spectrometer at 70 eV.

TABLE 1. Analytical and Spectral Data of Ethyl 7-Oxo Alkanoates 5

Cmpd	R	Yield (%)	mp. (°C)	IR($CHCl_3$) (cm^{-1})	MS (m/z)	PMR($CDCl_3$) (ppm)
5a	$-(CH_2)_4CH_3$	96	26	3000,2930 2855,1720 1710,1460 1375,1180 1120,720	242(M^+),197, 196 166,140,129,125 114,112,97,86 73,71,69,57,55 43.41	0.88(t, 3H, CH_3) 1.10-1.25(t, 3H, CH_3) 1.30-1.72(m, 12H, CH_2) 2.2-2.3(t, 6H, $COCH_2$) 3.99-4.23(q, 2H, OCH_2)
5b	$-(CH_2)_6CH_3$	96	32	3000,2935 2855,1720 1710,1460 1370,1190- 1110, 720	270(M^+),225,224 194,142,140,129 125,114,112,97 73,71,69,55,43 41	0.88(t, 3H, CH_3) 1.12-1.26(t, 3H, CH_3) 1.35-1.70(m,16H, CH_2) 2.21-2.34(t, 6H, $COCH_2$) 3.95-4.24(q, 2H, OCH_2)
5c	$-(CH_2)_8CH_3$	95	38	3000,2930 2855,1720 1710,1460 1375,1180- 1100,720	298(M^+),253,252 222,170,140,129 127,125,112,97 73,71,69,57,55 43.41	0.88(t, 3H, CH_3) 1.1-1.24(t, 3H, CH_3) 1.34-1.7(m, 20H, CH_2) 2.21-2.4(t, 6H, $COCH_2$) 3.99-4.27(q, 2H, OCH_2)
5d	$-(CH_2)_{10}CH_3$	94	42	3000,2930 2855,1720 1710,1465 1375,1175- 1100,720	326(M^+),281,280 250,198,183,155 140,129,125,112 97,73,71,69,57 55,43,41	0.88(t, 3H, CH_3) 1.12-1.26(t, 3H, CH_3) 1.34-1.74(m, 24H, CH_2) 2.2-2.4(t, 6H,$COCH_2$) 4.0-4.24(q, 2H, OCH_2)
5e	$-(CH_2)_{12}CH_3$	92	49	3000,2925 2855,1720 1710,1465 1370,1170- 1100,720	354(M^+),309,308 278,250,226,211 183,140,129,125 112,97,73,71,69 57,55,43,41	0.88(t, 3H, CH_3) 1.12-1.2(t, 3H, CH_3) 1.36-1.74(m, 28H, CH_2) 2.3-2.4(t, 6H, $COCH_2$) 3.99-4.24(q, 2H, OCH_2)
5f	$-(CH_2)_{14}CH_3$	90	56	3000,2930 2855,1720 1705,1460 1375,1180- 1100,720	382(M^+),337,336 306,254,239,211 186,171,140,129 125,112,97,73,71 69,57,55,43,41	0.88(t, 3H, CH_3) 1.1-1.2(t, 3H, CH_3) 1.35-1.75(m, 32H, CH_2) 2.34-2.42(t, 6H, $COCH_2$) 3.97-4.25(q, 2H, OCH_2)

Ethyl 7- Ketal Alkanoates (6).- A mixture of ethyl 7-oxo alkanoate 5 (10 mmol), prepared by a published procedure,[5] and 1,2-ethanediol (2.5 ml, 44 mmol) in 40 ml of dry toluene was heated under reflux overnight using a Dean-Stark trap. The reaction mixture was extracted with toluene and the organic layer was separated and washed first with water, then with 5% aqueous sodium bicarbonate and twice with saturated brine solution. After drying over sodium sulphate, the solvent was removed in vacuo to yield 90-95% of the 7-ketal alkanoate 6. The analytical and spectral data of these compounds are recorded in Table 2.

TABLE 2. Analytical and Spectra Data of Ethyl 7-Ketal Alkanoates 6

Cmpd	R	Yield (%)	mp. (°C)	IR($CHCl_3$) (cm^{-1})	MS (m/z)	PMR($CDCl_3$) (ppm)
6a	$-(CH_2)_4CH_3$	94	27	2930,2855, 1720,1710, 1460,1375, 1260,1150, 1060,790-720	286(M^+),287, 242,241,215, 205,143,186, 171,140,129, 125,101,99, 73,55,43	0.88(t, 3H, CH_3) 1.12-1.2(t, 3H, CH_3) 1.3-1.57(m, 8H, CH_2) 2.20-2.54(m,12H,$(CH_2)_2C$-$(CH_2)_2$, $CO(CH_2)_2$) 3.85(s, 4H, OCH_2CH_2O) 4.07-4.20(q, 2H, OCH_2)
6b	$-(CH_2)_6CH_3$	94	32	2925,2855, 1720,1710, 1460,1375, 1260,1160- 1040,790- 720	314(M^+),315, 270,269,235, 215,186,171, 140,129,125, 101,99,73, 45,43	0.88(t, 3H, CH_3) 1.1-1.2(t, 3H, CH_3) 1.36-1.56(m, 10H, CH_2) 2.20-2.56(m,12H,$(CH_2)_2C$- $(CH_2)_2$, $CO(CH_2)_2$) 3.85(s, 4H, OCH_2CH_2O) 4.07-4.18(q, 2H, OCH_2)
6c	$-(CH_2)_8CH_3$	92	37	2930,2850, 1730,1720, 1460,1375, 1265,1150- 1040,790- 720	342(M^+),343, 298,297,253, 215,199,186, 171,140,129, 125,101,99 73,55,43	0.88(t, 3H, CH_3) 1.1-1.2(t, 3H, CH_3) 1.3-1.57(m, 14H, CH_2) 2.20-2.56(m,12H,$(CH_2)_2C$- $(CH_2)_2$, $CO(CH_2)_2$) 3.85(s, 4H, OCH_2CH_2O) 4.07-4.20(q, 2H, OCH_2)
6d	$-(CH_2)_{10}CH_3$	93	41	2925,2855, 1730,1710, 1465,1375, 1265,1150- 1050,800- 720	370(M^+),326, 325,281,227, 215,186,171, 140,129,125, 101,99,73, 55,43	0.88(t, 3H, CH_3) 1.1-1.2(t, 3H, CH_3) 1.3-1.58(m,18H, CH_2) 2.21-2.55(m, 12H, $(CH_2)_2C$- $(CH_2)_2$, $CO(CH_2)_2$) 3.85(s, 4H, OCH_2CH_2O) 4.06-4.19(q, 2H, OCH_2)
6e	$-(CH_2)_{12}CH_3$	92	48	2930,2855, 1730,1710, 1465,1370, 1260,1150- 1040,800- 720	398(M^+),399, 354,353,311, 255,215,186, 171,140,129, 125,101,99, 73,55,43,	0.88(t, 3H, CH_3) 1.1-1.2(t, 3H, CH_3) 1.3-1.57(m, 22H, CH_2) 2.20-2.54(m, 12H$(CH_2)_2C$- $(CH_2)_2$, $CO(CH_2)_2$) 3.85(s, 4H, OCH_2CH_2O) 4.07-4.20(q, 2H,OCH_2)
6f	$-(CH_2)_{14}CH_3$	90	56	2925,2855, 1730,1710, 1465,1375, 1260,1150- 1050,800- 720	426(M^+),427, 382,381,337, 283,254,239, 215,186,171, 140,129,125, 101,99,73, 55,43	0.88(t, 3H, CH_3) 1.1-1.2(t, 3H,CH_3) 1.3-1.5(m, 26H, CH_2) 2.20-2.6(m, 12H,$(CH_2)_2C$- $(CH_2)_2$, $CO(CH_2)_2$) 3.85(s, 4H, OCH_2CH_2O) 4.07-4.19(q, 2H, OCH_2)

7-Oxo Alcohol (7).- Ethyl 7-ketal alkanoate 6 (10 mmol) in dry THF (15 ml) was added dropwise in 15 minutes to a well stirred solution of $LiAlH_4$ (1 g, 24 mmol) in dry THF (25 ml) so as to maintain gentle reflux. When the addition was complete, the reaction mixture was heated at reflux for 4-5 hrs. At the end reaction, the mixture was cooled in an ice bath and ethyl acetate (10 ml) was added slowly to consume the excess hydride after which water (20 ml) and 6N HCl (10 ml) were added to dissolve the aluminium salts and to hydrolyze the ketal group (deketalization).[6-8] Extraction with ether followed by recrystallization from hexane or benzene yielded 7-oxo alcohol 7 (Table 3).

TABLE 3. Analytical Data of 7-Oxo Alcohols 7

Cmpd	R	Yield (%)	Crystallizing solvent	mp. (°C)	Molecular formula
7a	$-(CH_2)_4CH_3$	80	Hexane	40	$C_{12}H_{24}O_2$
7b	$-(CH_2)_6CH_3$	79	Hexane	59	$C_{14}H_{28}O_2$
7c	$-(CH_2)_8CH_3$	78	Hexane-benzene	61	$C_{16}H_{32}O_2$
7d	$-(CH_2)_{10}CH_3$	76	Hexane-benzene	67	$C_{18}H_{36}O_2$
7e	$-(CH_2)_{12}CH_3$	74	Benzene	73	$C_{20}H_{40}O_2$
7f	$-(CH_2)_{14}CH_3$	72	Benzene	81	$C_{22}H_{44}O_2$

7-Oxododecan-1-ol (7a).- IR ($CHCl_3$): 3500-3260, 2935, 2860, 1705, 1460, 1410,1375,1045; PMR ($CDCl_3$): d 0.88 (t, 3H, CH_3), 0.95-1.65 (m, 14H, CH_2), 2.08 (s, 1H, exchangeable with D_2O), 2.15-2.45 (t, 4H, CH_2COCH_2) 3.55-3.65 (t, 2H,CH_2O), MS (m/z): 200 (M^+), 201 (M+1) (100), 202 (M+2) 183, 144, 126, 111, 99, 83, 71, 58, 55, 43, 41, 31.

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 72.0; H, 12.0. Found: C, 72.12; H, 12.10

7-Oxotetradecan-1-ol (7b).- IR ($CHCl_3$): 3500-3210, 2930, 2855, 1705, 1465, 1410, 1375, 1130,; PMR ($CDCl_3$): d 0.88 (t, 3H, CH_3), 0.98-1.65 (m, 18H, CH_2), 2.1 (s, 1H, OH, exchangeable with D_2O), 2.16-2.47 (t, 4H, CH_2COCH_2), 3.55-3.69 (t, 2H, CH_2O); MS (m/z): 228 (M^+), 229 (M+1), 230 (M+2), 211, 157, 144, 126, 111, 83, 71, 58, 57, 55 (100), 43, 41, 31.

Anal. Calcd. for $C_{14}H_{28}O_2$: C, 73.68; H, 12.28. Found: C, 73.71; H, 12.31

7-Oxohexadecan-1-ol (7c).- IR ($CHCl_3$): 3580-3220, 2935, 2860, 1705, 1465, 1410, 1375,1120; PMR ($CDCl_3$): δ 0.88 (t, 3H, CH_3), 0.98-1.65 (m, 22H, CH_2), 2.10 (s, 1H, OH, exchangeable with D_2O), 2.16-2.46 (t, 4H, CH_2COCH_2), 3.55-3.65 (t, 2H, CH_2O); MS (m/z): 256 (M^+), 257 (M+1), 258 (M+2), 239, 170, 155, 144, 127, 126, 111, 83, 71, 58, 55, (100), 43, 41, 31.

Anal. Calcd. for $C_{16}H_{32}O_2$: C,75.0; H, 12.5. Found: C,75.2; H, 12.61

7-Oxooctadedcan-1-ol (7d).- IR ($CHCl_3$): 3550-3200, 2935, 2840, 1705, 1450, 1410, 1160, 1090; PMR ($CDCl_3$): δ 0.88 (t, 3H, CH_3). 0.1-1.65 (m, 26H, CH_2), 2.09 (s, 1H, OH, exchangeable with D_2O), 2.16-2.47 (t, 4H, CH_2COCH_2), 3.55-3.64 (t, 2H, CH_2O); MS (m/z): 284 (M^+), 285, (M+1), 286 (M+2), 267, 227, 198, 157, 144, 126, 111, 83, 71, 58, 55 (100), 43, 41, 31.

Anal. Calcd. for $C_{18}H_{36}O_2$: C, 76.05; H, 12.67. Found: C, 76.16; H, 12.72

7-Oxoeicosan-1-o1 (7e).- IR ($CHCl_3$): 3600-3200, 2930, 2835, 1705, 1460, 1410, 1150-1095; PMR ($CDCl_3$): δ 0.88 (t, 3H, CH_3), 0.98-1.62 (m, 30H, CH_2), 2.08 (s, 1H, OH, Exchangeable with

D_2O), 2.16-2.49 (t, 4H, CH_2COCH_2), 3.55-3.6 (t, 2H, CH_2O); MS (m/z): 312 (M^+), 313 (M+1), 314, (M+2), 295, 239, 226, 211, 157, 144, 126, 111, 83, 71, 58, 55, (100), 43, 41, 31.

Anal. Calcd. for $C_{20}H_{40}O_2$: C, 76.92; H, 12.82. Found: C, 76.98, H, 12.91

7-Oxodocosan-1-ol (7f).- IR ($CHCl_3$): 3620-3100, 2930, 2855, 1705, 1460, 1405, 1150-1090; PMR ($CDCl_3$): δ 0.88 (t, 3H, CH_3), 0.99-1.65 (m, 34H, CH_2), 2.1 (s, 1H, OH exchangeable with D_2O), 2.16-2.47 (t, 4H, CH_2COCH_2), 3.55-3.63 (t, 2H,CH_2O); MS (m/z): 340 (M^+), 341 (M+1), 342 (M+2), 323, 254, 239, 170, 157, 144, 126, 83, 71, 58, 55 (100), 43,41, 31.

Anal. Calcd. for $C_{22}H_{44}O_2$: C, 77.64; H, 12.94. Found: C, 77.81; H, 12.99

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