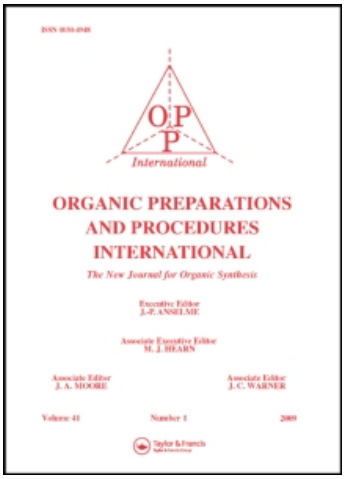

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SYNTHESIS OF FUNCTIONALIZED ACRYLATES

Michele Curci[a]; Jean-Luc Mieloszynski[a]; Daniel Paquer[a]
[a] Laboratoire de Chimie Organique, Université de Metz Ile du Saulcy, Metz, FRANCE

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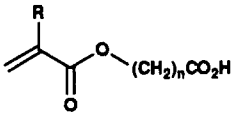
SYNTHESIS OF FUNCTIONALIZED ACRYLATES

Michele Curci, Jean-Luc Mieloszynski and Daniel Paquer*

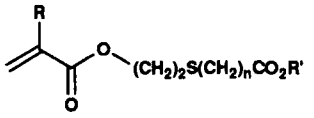
Laboratoire de Chimie Organique, Université de Metz
Ile du Saulcy, 57045 Metz, FRANCE

Only a few methods designed to generate acrylic monomers containing a carboxylic acid function have been described. Such monomers are obtained by reaction of hydroxyalkyl acrylate with cyclic anhydrides[1] or by enzymatic hydrolysis of esters.[2] The presence of a carboxyl function in acrylic monomers provides metal-adhesive properties to the resultant polymers.[3] This paper describes two different methods to introduce a carboxylic acid function in the side-chain of acrylic monomers of general structures **A** and **B**.



A

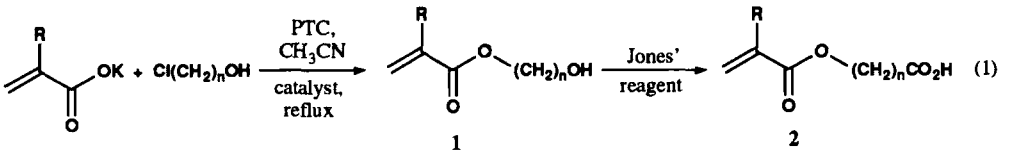
R = H, Me



B

R = H, Me; R' = H, *t*-Bu

Compounds of structure **A** were obtained by oxidation of the corresponding hydroxy compounds (**1**), easily prepared with phase-transfer catalyzed alkylation by reaction of potassium methacrylate with chloroalcohols. Of the many agents able to convert primary alcohols to carboxylic acids,[4,5] potassium permanganate, chromic acid and nitric acid are the most important. However, these reagents were tested without success as were more selective ones, able to give aldehydes (PCC, $H_2O_2/RuCl_3$, $DMSO/P_2O_5$, HNO_3). Only Jones' reagent[6] provided the desired acids (**2**) in good yields (Eq. 1).



(1)

1

1a: R = Me; *n* = 3; 72%
1b: R = Me; n = 6; 70%

2

2a: R = Me; n = 2; 43%
2b: R = Me; n = 3; 54%
2e: R = Me; n = 6; 69%
2f: R = H; n = 2; 41%

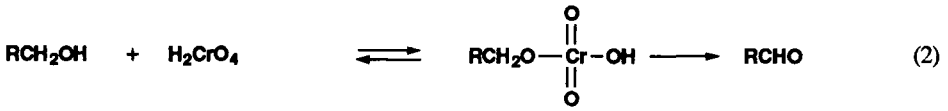
The oxidation of hydroxyalkyl acrylates with chromic anhydride-sulfuric acid (Jones' reagent) was examined under a variety of conditions (Table). With 1 or 1.5 equivalents of CrO_3 (entries 3-6),

the oxidation is incomplete, while with two-fold excess of chromic oxide, it leads to the formation of an undesired ester by-product (entries 7 and 8).[5]

TABLE. Oxidation of Hydroxyalkyl Acrylates by Jones' Reagent

Entry	n	R	Equiv. of CrO_3	Reaction time (hrs)	Alcohol (%)	Acid (%)	By-product (%)
1	2	Me	1	4	51	49	0
2	2	Me	1	20	47	53	0
3	2	Me	1.5	20	45	55	0
4	2	H	1.5	20	35	65	0
5	3	Me	1.5	20	32	68	0
6	6	Me	1.5	4	26	74	0
7	2	Me	3	20	0	91	9
8	2	H	3	20	0	84	16

Moreover, it must be noted that the yield of acid increases with the number of methylene groups in the chain. This observation can be rationalized from the mechanism of oxidation. The first step is an equilibrium between the alcohol and H_2CrO_4. The more nucleophilic the alcohol is, the more is the equilibrium shifted to the right (Eq. 2).

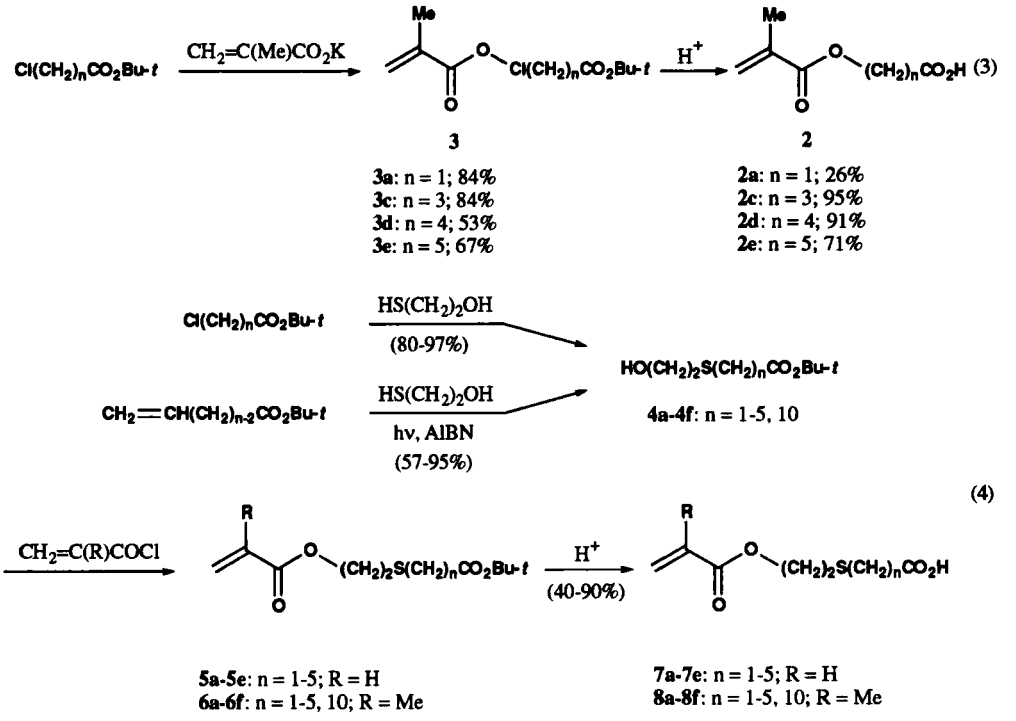


(2)

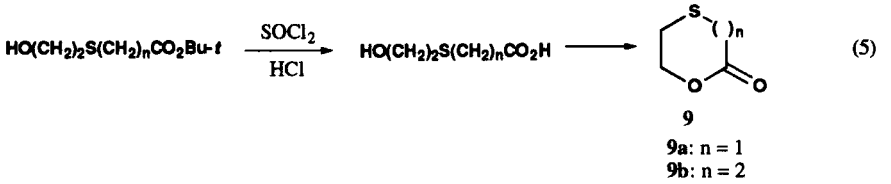
The electron-withdrawing methacrylyl group exerts a field effect on the hydroxyl function, through the methylene units; this effect which decreases by a factor of 2.7 for each methylene unit,[7] explains the relative decrease of the nucleophilicity of the hydroxy group of hydroxyethyl methacrylate, compared with those of hydroxyhexyl methacrylate.

It was then decided to develop a more general sequence to afford the desired monomers **A** and **B** involving conversion of an ester located in the side-chain into an acid as illustrated in Eq. 3 and 4. *t*-Butyl esters were selected because they are stable in basic *media* and are easily hydrolyzed under acidic conditions. Although this sequence is longer than the one previously described, it involves very simple reactions (Eq. 3). The required haloester were prepared from haloalcohols by oxidation followed by esterification with *t*-BuOH in the presence of N,N'-dicyclohexylcarbodiimide.[8]

This procedure was extended to the preparation of compounds **B**.[9] The required alcohols were obtained in good yields by reaction of mercaptoethanol either with a halo- or an ethylenic ester. The hydroxy compounds were then either condensed directly with methacryloyl chloride or first chlorinated with thionyl chloride and then condensed with potassium methacrylate by use of phase-transfer catalysis.[10]



However, chlorination step of **4a-4f** required the addition of a base such as pyridine or Et_3N to avoid the formation of thialactones. These cyclic compounds are usually formed by heating a hydroxyacid.[11] In the present case, the hydrochloric acid generated during the reaction leads to the thialactone by elimination of the *t*-butyl group (Eq. 5). This side-reaction has been observed mainly



(5)

when n = 1 and n = 2 to afford 1,4-oxathian-2-one (**9a**, 75%) and 1,5-oxathiepan-2-one (**9b**, 12%). When the number of methylene unit increases, this side-reaction is evidently not observed. High dilution can also be used in order to prevent the cyclization.

In a final step, esters are converted to the acid by hydrolysis in high efficiency. The reaction is performed by shaking the ester with formic acid. No hydrolysis of the acrylic ester function was observed.

EXPERIMENTAL SECTION

All methacrylates were stabilized with hydroquinone monomethylether. *t*-Butyl chloroalkyl acetates were prepared from the chloroalcohols.[8] ^1H and ^{13}C NMR spectra were recorded on Jeol PMX 60 and Brucker AM-400 spectrometers, respectively.

Compounds 1a and 1b.- A solution of potassium methacrylate (1.5 g, 12 mmol), chloroalcohol (10 mmol), hydroquinone monomethylether (100 ppm), tricaprylylmethylammonium chloride (Aliquat® 336, 5% by weight) and 30 mL of CH_3CN was refluxed for 24 hrs. After cooling, the mixture was filtered and extracted with CH_2C1_2. The organic phase was washed (water), dried ($MgSO_4$) and concentrated. The residue was purified by distillation under reduced pressure.

Compound 1a: 72%, colorless oil, n_D^{20} 1.4500, bp 90° (1 Torr). ^1H NMR (CCl_4): δ 6.0 (m, 1H), 5.4 (m, 1H), 4.2 (t, 2H), 3.6 (t, 2H), 1.8 (m, 2H), 1.9 (s, 3H), 3.0 (1s, 1H). ^{13}C NMR ($CDCl_3$): δ 167.4, 135.9, 125.2, 61.6, 59.6, 24.0, 17.9.

Anal. Calcd for C7H1203: C, 58.32; H, 8.39. Found: C, 58.26; H, 8.52

Compound 1b: 70%, colorless oil, n_D^{20} 1.4551, bp 119° (1 Torr). ^1H NMR (CCl_4): δ 6.0 (m, 1H), 5.45 (m, 1H), 4.0 (t, 2H), 3.5 (t, 2H), 1.45 (m, 8H), 1.9 (s, 3H), 2.9 (1s, 1H). ^{13}C NMR ($CDCl_3$): δ 167.1,136.1,124.8, 64.3, 62.2, 32.3, 28.2, 25.4, 25.1, 17.9.

Anal. Calcd for C10H1803: C, 64.49; H, 9.74. Found: C, 64.63; H, 9.57

General Procedure of Oxidation of 1 to 2 (Compounds 2a-2f).- To a stirred solution of hydroxyalkyl methacrylate (100 mmol) in acetone (100 mL) cooled to 20°, Jones' reagent[12] (150 mmol) was added slowly and stirring was continued for 10 hrs. Acetone was decanted and the residue was extracted into Et_2O. The organic phase was dried on $MgSO_4$ and evaporated *in vacuo*. The residue was basified with aqueous Na_2CO_3, washed with Et_2O and acidified with HCl. It was then extracted with EtOAc, washed (water), dried ($MgSO_4$), and concentrated to provide compounds **2a** to **2f**. These liquids could not be distilled, but were purified by filtration through silica gel.

Compound 2a: 43%, white solid, mp. 62°, ^1H NMR (CCl_4): δ 6.2 (m, 1H), 5.6 (m, 1H), 4.7 (s, 2H), 9.5 (is, 1H), 2.0 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 173.5, 166.6, 135.2, 127.0, 60.4, 18.0.

Anal. Calcd for $C_6H_8O_4$: C, 50.01; H, 5.59. Found: C, 50.26; H, 5.39

Compound 2b: 54%, colorless oil, n_D^{20} 1.4495, ^1H NMR (CCl_4): δ 6.1 (m, 1H), 5.6 (m, 1H), 4.5 (t, 2H), 2.4 (t, 2H), 9.5 (1s, 1H), 1.95 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 176.4, 167.1, 135.9, 125.9, 59.7, 33.6, 18.1.

Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 53.32; H, 6.06

Compound 2e: 69%, colorless oil, n_D^{20} 1.4485, ^1H NMR (CCl_4): δ 6.0 (m, 1H), 5.3 (m, 1H), 4.1 (m, 2H), 2.3 (m, 2H), 1.6 (m, 6H), 9.0 (1s, 1H), 2.0 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 179.5, 167.5, 136.4, 125.2, 64.4, 33.8, 28.2, 25.4, 24.2, 18.1.

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.99; H, 8.05. Found: C, 59.62; H, 8.17

Compound 2f: 41%, colorless oil, n_D^{20} 1.4478, ^1H NMR (CCl_4): δ 6.1-6.7 (m, 2H), 5.66.0 (m, 1H), 4.7 (s, 2H), 9.0 (1s, 1H).

Anal. Calcd for $C_5H_6O_4$: C, 46.16; H, 4.65. Found: C, 46.37; H, 4.39

Compounds 3a-3e.- A solution of potassium methacrylate (18.6 g, 150 mmol), *t*-butyl chloroalkylacetate (100 mmol), hydroquinone monomethylether (100 ppm), aliquat (5% by weight) and 100 mL of CH_3CN was refluxed for 24 hrs. After cooling, the mixture was filtered and extracted with CH_2Cl_2. The organic phase was washed (water), dried ($MgSO_4$) and concentrated. The residue was purified by

distillation under reduced pressure.

Compound 3a: 84%, colorless oil, n_D^{20} 1.4405, bp 60° (3.0 Torr).^{1}H NMR (CCl_4): 5 6.2 (m, 1H), 5.6 (m, 1H), 4.5 (s, 2H), 2.0 (m, 3H), 1.5 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 173.8, 166.7, 135.5, 126.3, 82.1, 61.2, 27.9, 18.0.

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.99; H, 8.05. Found: C, 59.75; H, 8.26

Compound 3c: 84%, colorless oil, n_D^{20} 1.4386, bp 95° (1.0 Torr). ^{1}H NMR (CCl_4): δ 6.0 (m, 1H), 5.5 (m, 1H), 4.2 (s, 2H), 2.2 (m, 2H), 2.0 (m, 3H), 1.9 (m, 2H), 1.5 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 172.0, 167.1,136.3, 125.2, 80.3, 63.6, 31.9, 28.0, 24.1, 18.1.

Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 63.41; H, 8.74

Compound 3d: 53%, colorless oil, n_D^{20} 1.4380, bp 106° (0.75 Torr). ^{1}H NMR (CCl_4): δ 6.0 (m, 1H), 5.5 (m, 1H), 4.2 (m, 2H), 2.2 (m, 2H), 2.0 (m, 3H), 1.7 (m, 4H), 1.5 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 172.5, 167.2, 136.7, 125.0, 80.0, 64.1, 34.9, 28.0 (2 C), 21.6, 18.1.

Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.67; H, 9.38

Compound 3e: 67%, colorless oil, n_D^{20} 1.4408, bp 106° (0.35 Torr). ^{1}H NMR (CCl_4): δ 6.0 (m, 1H), 5.5 (m, 1H), 4.2 (m, 2H), 2.2 (m, 2H), 1.9 (m, 3H), 1.7 (m, 6H), 1.4 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 172.7, 167.3, 136.4, 125.0, 79.9, 64.1, 35.3, 28.3, 28.0, 25.4, 24.6,18.1.

Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.58; H, 9.46. Found: C, 65.31; H, 9.67

Compounds 4a, 4c-4e.- A solution of KOH (5.6 g, 100 mmol) in EtOH at was treated with 2-mercaptoethanol (7.8 g, 100 mmol). The mixture was stirred for 30 min and cooled to room temperature. Then, the *t*-butyl chloroalkylacetate (100 mmol) was added dropwise and the solution was refluxed 4 hrs. It was filtered, extracted with $CHCl_3$, washed (water), dried ($MgSO_4$) and concentrated.

Compound 4a: 90%, colorless oil, n_D^{20} 1.4710, ^{1}H NMR (CCl_4): δ 3.8 (t, 2H), 3.2 (s, 2H), 2.8 (t, 2H), 2.7 (s, 1H), 1.7 (s, 9H).

Anal. Calcd for $C_8H_{16}O_3S$: C, 49.97; H, 8.38; S, 16.67. Found: C, 49.74; H, 8.49; S, 16.53

Compound 4c: 97%, colorless oil, n_D^{20} 1.4719, ^{1}H NMR (CCl_4): δ 3.6 (t, 2H), 2.5 (m, 4H), 2.5 (s, 1H), 2.3 (m, 2H), 1.8 (m, 2H), 1.4 (s, 9H).

Anal. Calcd for $C_{10}H_{20}O_3S$: C, 54.51; H, 9.15; S, 15.85. Found: C, 54.39; H, 9.28; S, 15.72

Compound 4d: 97%, colorless oil, n_D^{20} 1.4708, ^{1}H NMR (CCl_4): δ 3.6 (m, 2H), 2.6 (m, 4H), 2.5 (s, 1H), 2.3 (m, 2H), 1.6 (m, 4H), 1.4 (s, 9H).

Anal. Calcd for $C_{11}H_{22}O_3S$: C, 56.37; H, 9.46; S, 13.68. Found: C, 56.25; H, 9.57; S, 13.79

Compound 4e: 90%, colorless oil, n_D^{20} 1.4656, ^{1}H NMR (CCl_4): δ 3.6 (m, 2H), 2.6 (m, 4H), 2.5 (s, 1H), 2.2 (m, 2H), 1.5 (m, 6H), 1.45 (s, 9H).

Anal. Calcd for $C_{12}H_{24}O_3S$: C, 58.01; H, 9.76; S, 12.90. Found: C, 58.14; H, 9.88; S, 12.76

Compound 4b and 4f.- A solution of *t*-butylacrylate or *t*-butyl undecylenoate (100 mmol) with azobisisobutyronitrile (0.4 g) in cyclohexane was irradiated with UVA (λ = 350 nm). 2-Mercaptoethanol (9 g, 115 mmol) was added and the irradiation was continued for 30 min. After cooling, the reaction mixture was washed with 1N NaOH, water, dried ($MgSO_4$) and concentrated to afford compounds 4b and 4f.

Compound 4b: 95%, colorless oil, n_D^{20} 1.4652, ^{1}H NMR (CCl_4): δ 3.7 (t, 2H), 2.7 (m, 6H), 2.7 (s, 1H), 1.5 (s, 9H).

Anal. Calcd for $C_9H_{18}O_3S$: C, 53.43; H, 8.97; S, 15.85. Found: C, 53.39; H, 8.84; S, 15.92

Compound 4f: 57%, colorless oil, n_D^{20} 1.4619, ^{1}H NMR (CCl_4): δ 3.6 (m, 2H), 2.6 (m, 4H), 2.5 (s, 1H), 2.2 (m, 2H), 1.45 (m, 16H), 1.4 (s, 9H).

Anal. Calcd for $C_{17}H_{34}O_3S$: C, 64.10; H, 10.76; S, 10.06. Found: C, 64.25; H, 10.58; S, 10.22

Compound 5a-5e and 6a-6f.- To a solution of **4a-4f** (100 mmol), triethylamine (100 mmol), hydroquinone monomethylether (800 ppm) in $CHCl_3$ (20 mL) cooled to 0°, was added acryloyl chloride (or methacryloyl chloride) (110 mmol) in $CHCl_3$ (20 mL). The mixture was stirred at room temperature for 24 hrs. Then H_2SO_4 (6N, 100 mL) was added and the reaction mixture was extracted with Et_2O. The ethereal extract was washed with $KHCO_3$ (10%), with water, dried ($MgSO_4$) and concentrated. The products were purified by distillation under reduced pressure or chromatography on a silica gel column with hexane-diethyl ether (85:15) as eluent.

Compound 5a: 55%, colorless oil, n_D^{20} 1.4708, bp 110° (7.7 Torr). ^{1}H NMR (CCl_4): δ 6.3 (m, 1H), 6.1 (m, 1H), 5.8 (m, 1H), 4.3 (t, 2H), 3.1 (s, 2H), 2.9 (t, 2H), 1.5 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 169.3, 166.0, 131.0, 128.2, 81.7, 63.1, 34.9, 30.8, 27.9.

Anal. Calcd for $C_{11}H_{18}O_4S$: C, 53.64; H, 7.36; S, 13.01. Found: C, 53.55; H, 7.49; S, 13.18

Compound 5b: 88%, colorless oil, n_D^{20} 1.4705, bp 120° (3.8 Torr). ^{1}H NMR (CCl_4): δ 6.3 (m, 1H), 6.1 (m, 1H), 5.8 (m, 1H), 4.3 (t, 2H), 2.4-2.9 (m, 6H), 1.4 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 170.9, 165.7, 130.9, 128.1, 80.0, 63.6, 36.0, 30.5, 28.0, 27.4.

Anal. Calcd for $C_{12}H_{20}O_4S$: C, 55.36; H, 7.74; S, 12.31. Found: C, 55.57; H, 7.62; S, 12.52

Compound 5c: 60%, colorless oil, n_D^{20} 1.4710, ^{1}H NMR (CCl_4): δ 6.3 (m, 1H), 6.1 (m, 1H), 5.8 (m, 1H), 4.2 (t, 2H), 2.2-2.8 (m, 6H), 1.6 (m, 2H), 1.4 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 171.2, 165.7, 130.9, 128.1, 80.0, 63.6, 32.6, 31.6, 30.4, 28.0, 24.4.

Anal. Calcd for $C_{13}H_{22}O_4S$: C, 56.91; H, 8.08; S, 11.68. Found: C, 56.76; H, 8.23; S, 11.43

Compound 5d: 45%, colorless oil, n_D^{20} 1.4708, ^{1}H NMR (CCl_4): δ 6.3 (m, 1H), 6.1 (m, 1H), 5.8 (m, 1H), 4.2 (m, 2H), 2.2-2.8 (m, 6H), 1.6 (m, 4H), 1.4 (s, 9H). ^{13}C NMR ($CDCl_3$) 172.5, 165.7, 130.8, 128.2, 80.0, 63.6, 34.9, 31.9, 30.4, 29.0, 28.0, 24.1.

Anal. Calcd for $C_{14}H_{24}O_4S$: C, 58.30; H, 8.38; S, 11.12. Found: C, 58.45; H, 8.50; S, 11.04

Compound 5e: 55%, colorless oil, n_D^{20} 1.4702, ^{1}H NMR (CCl_4): δ 6.3 (m, 1H), 6.1 (m, 1H), 5.8 (m, 1H), 4.2 (m, 2H), 2.0-2.8 (m, 6H), 1.6 (m, 6H), 1.4 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 172.7, 165.7, 130.8, 128.2, 79.8, 63.6, 35.3, 32.1, 30.4, 29.2 (2 C), 28.0, 24.5.

Anal. Calcd for $C_{15}H_{26}O_4S$: C, 59.57; H, 8.66; S, 10.60. Found: C, 59.74; H, 8.47; S, 10.42

Compound 6a: 55%, colorless oil, n_D^{20} 1.4691, ^{1}H NMR (CCl_4): δ 6.0 (m, 1H), 5.5 (m, 1H), 4.55 (t, 2H), 3.1 (s, 2H), 2.8 (t, 2H), 1.9 (m, 3H) 1.5 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 170.7, 166.9, 136.0, 125.7, 80.1, 63.4, 33.3, 31.0, 28.0, 18.0.

Anal. Calcd for $C_{12}H_{20}O_4S$: C, 55.36; H, 7.74; S, 12.31. Found: C, 55.23; H, 7.88; S, 12.42

Compound 6b: 88%, colorless oil, n_D^{20} 1.4694, bp 1400C (0.75 Torr). ^{1}H NMR (CCl_4): δ 6.1 (m, 1H),

5.5 (m, 1H), 4.3 (t, 2H), 2.7 (t, 4H), 2.6 (t, 2H), 1.9 (m, 3H) 1.5 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 170.8, 166.9, 136.1,125.6, 80.6, 63.8, 36.0, 30.5, 28.0, 27.4, 18.1.

Anal. Calcd for $C_{13}H_{22}O_4S$: C, 56.91; H, 8.08; S, 11.68. Found: C, 56.84; H, 8.31; S, 11.37

Compound 6c: 71%, colorless oil, n_D^{20} 1.4692, ^{1}H NMR (CCl_4): δ 6.1 (m, 1H), 5.5 (m, 1H), 4.2 (t, 2H), 2.2-2.8 (m, 6H), 1.6 (m, 2H), 1.9 (m, 3H) 1.45 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 172.2, 167.0, 136.1,125.6, 80.2, 63.7, 34.2, 31.6, 31.0, 28.0, 24.9, 18.1.

Anal. Calcd for $C_{14}H_{24}O_4S$: C, 58.30; H, 8.38; S, 11.12. Found: C, 58.59; H, 8.24; S, 11.09

Compound 6d: 58%, colorless oil, n_D^{20} 1.4712, ^{1}H NMR (CCl_4): δ 6.1 (m, 1H), 5.5 (m, 1H), 4.25 (t, 2H), 2.1-2.8 (m, 6H), 1.6 (m, 4H), 1.9 (m, 3H) 1.4 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 172.5, 167.0, 136.1,125.5, 80.0, 63.7, 34.9, 31.9, 30.4, 29.0, 28.0, 24.1, 18.1.

Anal. Calcd for $C_{15}H_{26}O_4S$: C, 59.57; H, 8.66; S, 10.60. Found: C, 59.41; H, 8.78; S, 10.54

Compound 6e: 55%, colorless oil, n_D^{20} 1.4719, ^{1}H NMR (CCl_4): δ 6.1 (m, 1H), 5.5 (m, 1H), 4.15 (m, 2H), 2.1-2.8 (m, 6H), 1.5 (m, 6H), 1.9 (m, 3H) 1.4 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 172.8, 167.0, 136.1, 125.5, 79.8, 63.8, 35.3, 32.1, 30.4, 29.3 (2 C), 28.0, 24.6, 18.1.

Anal. Calcd for $C_{16}H_{28}O_4S$: C, 60.69; H, 8.92; S, 10.13. Found: C, 60.81; H, 8.85; S, 10.22

Compound 6f: 50%, colorless oil, n_D^{20} 1.4721, ^{1}H NMR (CCl_4): δ 6.1 (m, 1H), 5.5 (m, 1H), 4.2 (m, 2H), 2.1-2.8 (m, 6H), 1.5 (m, 16H), 1.95 (m, 3H) 1.35 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 172.8, 167.0, 136.1, 125.5, 79.8, 63.7, 24.5-35.4 (numerous signals), 28.0,18.1.

Anal. Calcd for $C_{21}H_{38}O_4S$: C, 65.24; H, 9.90; S, 8.29. Found: C, 65.39; H, 9.76; S, 8.41

Compounds 2a-2e, 7a-7e and 8a-8f.-The *t*-butyl ester (40 mmol) was dissolved in 20 mL of formic acid and stirred for 24 hrs. Excess acid was evaporated under reduced pressure. The residue was treated with $NaHCO_3$ (10%), washed with EtOAc and acidified with HCl. The product was finally extracted with EtOAc, washed (water), dried ($MgSO_4$) and concentrated.

Compound 2a: 26%.

Compound 2e: 71%.

Compound 2c: 95%, colorless oil, n_D^{20} 1.4520, ^{1}H NMR (CCl_4): δ 6.0 (m, 1H), 5.6 (m, 1H), 4.2 (s, 2H), 2.5 (m, 2H), 2.0 (m, 2H), 9.6 (1s, 1H), 1.9 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 178.5, 167.3, 125.5, 136.1, 63.5, 30.5, 23.7, 18.1.

Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 55.64; H, 6.71

Compound 2d: 91%, colorless oil, n_D^{20} 1.4535, ^{1}H NMR (CCl_4): δ 6.0 (m, 1H), 5.5 (m, 1H), 4.1 (m, 2H), 2.3 (m, 2H), 1.6 (m, 4H), 11.5 (1s, 1H), 1.9 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 179.3, 167.0, 125.3, 136.3, 64.1, 33.4, 27.9, 21.2, 18.1.

Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.37; H, 7.48

Compound 7a: 80%, yellow oil, n_D^{20} 1.4970, ^{1}H NMR (CCl_4): δ 6.3 (m, 1H), 6.1 (m, 1H), 5.8 (m, 1H), 4.3 (t, 2H), 3.3 (s, 2H), 2.9 (t, 2H), 11.0 (1s, 1H). ^{13}C NMR ($CDCl_3$): δ 175.7, 166.0, 131.3, 127.9, 63.0, 33.3, 31.0.

Anal. Calcd for C7H10O_4S: C, 44.20; H, 5.30; S, 16.86. Found: C, 44.47; H, 4.49; S, 16.91

Compound 7b: 70%, yellow oil, n_D^{20} 1.4965, ^{1}H NMR (CCl_4): δ 6.3 (m, 1H), 6.1 (m, 1H), 5.8 (m,

1H), 4.3 (t, 2H), 2.8 (m, 6H), 10.9 (1s, 1H). ^{13}C NMR ($CDCl_3$): δ 177.3, 165.9, 131.1, 128.0, 63.5, 34.5, 30.5, 26.8.

Anal. Calcd for $C_8H_{12}O_4S$: C, 47.05; H, 5.92; S, 15.70. Found: C, 47.32; H, 5.82; S, 15.51

Compound 7c: 69%, yellow oil, n_D^{20} 1.4928, ^1H NMR (CCl_4): δ 6.3 (m, 1H), 6.1 (m, 1H), 5.8 (m, 1H), 4.3 (t, 2H), 2.2-2.9 (m, 6H), 1.6 (m, 2H), 10.5 (1s, 1H). ^{13}C NMR ($CDCl_3$): δ 178.8, 166.0, 131.1,128.1, 63.6, 32.6, 31.4, 30.2, 24.4.

Anal. Calcd for $C_9H_{14}O_4S$: C, 49.52; H, 6.46; S, 14.70. Found: C, 49.21; H, 6.77; S, 14.63

Compound 7d: 83%, yellow oil, n_D^{20} 1.4919, ^1H NMR (CCl_4): δ 6.3 (m, 1H), 6.1 (m, 1H), 5.8 (m, 1H), 4.3 (m, 2H), 2.3-2.8 (m, 6H), 1.7 (m, 4H), 11.2 (1s, 1H). ^{13}C NMR ($CDCl_3$): δ 179.2, 167.2, 130.9, 128.1, 63.6, 33.3, 31.8, 30.3, 28.8, 23.6.

Anal. Calcd for $C_{10}H_{16}O4S$: C, 51.71; H, 6.94; S, 13.80. Found: C, 51.43; H, 6.68; S, 14.05

Compound 7e: 74%, yellow oil, $n^2{}_D{}^0$ 1.4910, ^1H NMR (CCl_4): δ 6.3 (m, 1H), 6.1 (m, 1H), 5.8 (m, 1H), 4.3 (m, 2H), 2.2-2.9 (m, 6H), 1.7 (m, 6H), 10.7 (1s, 1H). ^{13}C NMR ($CDCl_3$): δ 179.5, 165.9, 131.0, 128.2, 63.7, 33.8, 32.1, 30.4, 29.2, 28.1, 24.1.

Anal. Calcd for $C_{11}H_{18}O_4S$: C, 53.64; H, 7.37; S, 13.01. Found: C, 53.36; H, 7.12; S, 13.28

Compound 8a: 70%, yellow oil, n_D^{20} 1.4883, ^1H NMR (CCl_4): δ 6.1 (m, 1H), 5.5 (m, 1H), 4.4 (t, 2H), 3.3 (s, 2H), 2.95 (t, 2H), 9.6 (1s, 1H) 2.0 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 175.6, 167.2, 135.9, 126.0, 63.2, 33.3, 31.0, 18.0.

Anal. Calcd for $C_8H_{12}O_4S$: C, 47.05; H, 5.92; S, 15.70. Found: C, 47.32; H, 5.82; S, 15.51

Compound 8b: 70%, yellow oil, n_D^{20} 1.4990, ^1H NMR (CCl_4): δ 6.1 (m, 1H), 5.5 (m, 1H), 4.3 (t, 2H), 2.5-3.0 (m, 6H), 10.6 (1s, 1H) 2.0 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 177.4, 167.2, 136.0, 125.8, 63.7, 34.6, 30.6, 28.8, 18.0.

Anal. Calcd for $C_9H_{14}O_4S$: C, 49.53; H, 6.46; S, 14.69. Found: C, 49.29; H, 6.72; S, 14.41

Compound 8c: 86%, yellow oil, n_D^{20} 1.4885, ^1H NMR (CCl_4): δ 6.1 (m, 1H), 5.5 (m, 1H), 4.25 (t, 2H), 2.5-3.0 (m, 6H), 1.6 (m, 2H), 10.0 (1s, 1H) 2.0 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 178.8, 167.2, 136.0, 125.7, 63.7, 32.5, 31.6, 30.2, 24.4, 18.1.

Anal. Calcd for $C_{10}H_{16}O_4S$: C, 51.70; H, 6.94; S, 13.80. Found: C, 51.47; H, 6.74; S, 14.08

Compound 8d: 85%, yellow oil, n_D^{20} 1.4884, ^1H NMR (CCl_4): δ 6.1 (m, 1H), 5.5 (m, 1H), 4.25 (t, 2H), 2.5-3.0 (m, 6H), 1.6 (m, 4H), 10.0 (1s, 1H) 2.0 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 179.2, 167.2, 136.1,125.7, 63.8, 33.4, 31.9, 30.4, 28.9, 23.7, 18.1.

Anal. Calcd for $C_{11}H_{18}O_4S$: C, 53.64; H, 7.37; S, 13.01. Found: C, 53.79; H, 7.58; S, 12.88

Compound 8e: 75%, yellow oil, n_D^{20} 1.4886, ^1H NMR (CCl_4): δ 6.1 (m, 1H), 5.5 (m, 1H), 4.25 (t, 2H), 2.5-3.0 (m, 6H), 1.6 (m, 6H), 9.8 (1s, 1H) 2.0 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 179.6, 167.1,136.1,125.7, 63.9, 33.8, 32.0, 30.4, 29.2, 28.0, 24.1, 18.1.

Anal. Calcd for $C_{12}H_{20}O_4S$: C, 55.36; H, 7.74; S, 12.32. Found: C, 55.09; H, 7.46; S, 12.57

Compound 8f: 40%, yellow oil, n_D^{20} 1.4898, ^1H NMR (CCl_4): δ 6.1 (m, 1H), 5.5 (m, 1H), 4.2 (t, 2H), 2.5-3.0 (m, 6H), 1.4-2.0 (m, 16H), 9.6 (1s, 1H) 1.9 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 179.6, 167.1, 136.1, 125.7, 63.9, 24.1-33.9 (numerous signals), 18.1.

Anal. Calcd for $C_{17}H_{30}O_4S$: C, 61.78; H, 9.15; S, 9.70. Found: C, 61.84; H, 9.10; S, 9.68

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12. H_2SO_4 (13 mL) was added very slowly to a solution of CrO_3 (15 g, 150 mmol) in H_2O (35 mL) at room temoerature.

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