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Design and Synthesis of Novel Hydrolyzable Polysulfides from 2,4-Dimethylene-1,3-dioxolane

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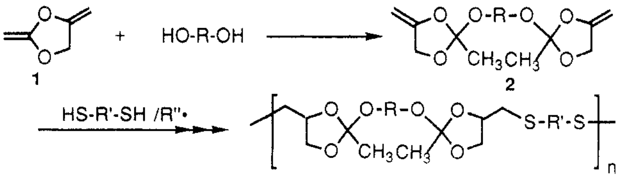
ABSTRACT: New polymers containing ortho ester and thioether moieties in the polymer backbone were synthesized by radical polyadditions using 2,4-dimethylene-1,3-dioxolane (1). Alcohols added to the 2-methylene group of 1 selectively to afford vinyl ethers 3 having an ortho ester structure, especially diols gave divinyl ortho esters 2 for the polyaddition. Thiol added to the vinyl ether 3 in good yield in the presence of azobis(isobutyronitrile) at 60 °C in benzene, and hence the radical polyadditions of dithiols to 2 were carried out under the same conditions to obtain polysulfides bearing ortho ester moieties in the backbone. Ortho ester units in the polymer could easily undergo hydrolysis in water–tetrahydrofuran at 65 °C, and the structure of the compounds obtained was speculated by the hydrolysis of the model compounds 3.

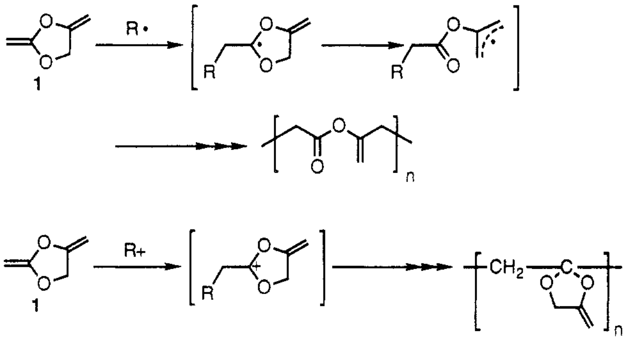
Introduction

The development of polymerization of functional monomers containing specific reactive groups has led to the production of many kinds of functional polymers. For the polymerization of these functional monomers, radical polymerization has been often used, since radical reaction tolerates a wide variety of functional groups and it is not necessary to protect them.

However, it has not been until recently that radical polyaddition developed by Marvel[1] has been utilized for the synthesis of functional polymers containing specific reactive groups. In the previous papers, we have reported the synthesis of functional polysulfides containing spiro ortho carbonate moieties and reactive carbon–carbon double bonds in the polymer backbone by the radical polyadditions of dithiols to 2,7-dimethylene-1,4,6,9-tetraoxaspiro[4.4]nonane[2] and to bis(alkoxyallene)s,[3] respectively; both polymers can undergo cross-linking with Lewis acids. Kobayashi et al.[4] have prepared the polysulfides having carbon–carbon double bonds by the radical additions of dithiols to diynes. Recently, Luo et al.[5] have reported the preparation of polysulfides containing spiro ortho carbonate moieties by the polyadditions using 3,9-dimethylene-1,5,7,11-tetraoxaspiro[5.5]undecane.

In the present article, we describe the synthesis of hydrolyzable polysulfides containing ortho ester moieties from 2,4-dimethylene-1,3-dioxolane (1). We have already found that the 2-methylene group (C═C of the ketene acetal moiety) of 1 is more reactive than the 4-methylene group (C═C of the vinyl ether moiety), since 1 undergoes radical ring-opening polymerization[6] and cationic vinyl polymerization of the 2-methylene group[7] while retaining the 4-methylene group. Further, ketene acetals are well known to react easily with alcohols to produce ortho esters.[8,9] Accordingly, a hydrolyzable polysulfide bearing ortho ester moieties would be synthesized if the 2-methylene group of 1 selectively reacted with diol to afford divinyl ether 2, which was subjected to radical polyaddition of dithiol. In other words, the 2-methylene group of 1 is used for the preparation of monomer 2 and the 4-methylene group is used for the polyaddition with dithiol.





In this paper is described selective addition of alcohols involving diols to 1 affording ortho esters, radical addition of thiols to the ortho esters involving polyaddition, and the study of hydrolysis of the polymer obtained by the polyaddition of dithiols to 2.

Results and Discussion

Addition of Alcohols to 1. As the preliminary experiment, the reaction of 1 with 1 equiv of methanol was first carried out in $CDCl_3$. Immediately after addition of methanol to the solution of 1 in $CDCl_3$, the signal of the 2-methylene protons of 1 at 3.39 ppm disappeared completely, and new signals assignable to the methyl and methoxy protons appeared at 1.58 and 3.28 ppm in the ^1H NMR spectrum, respectively. On the other hand, the signals of the 4-methylene protons at 4.00–4.20 and 4.45–4.62 ppm and of 1,3-dioxolane ring protons at 4.62–4.77 ppm of 1 were all slightly shifted upfield. These observations indicate that methanol selectively added to the 2-methylene group (C═C of the ketene acetal moiety) of 1 to afford the ortho ester having a vinyl ether moiety.

Since it was troublesome and caused a decrease of the yield of 1 to separate low-boiling 1 from *tert*-butanyl alcohol and tetrahydrofuran (THF) obtained in a trap at

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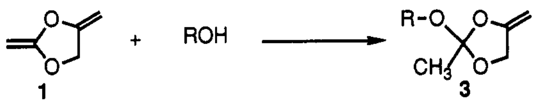
Table 1. Addition of Alcohols to 1[a]



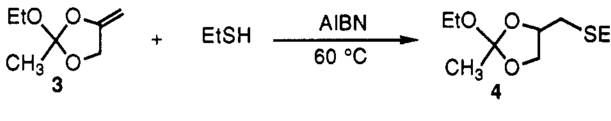
alcohols	equiv of alcohols	time, h	yield of 3, %
CH_3OH[b]	1.0	instantly	100[c]
CH_3CH_2OH	3.0	3	100[c]
$C_6H_5CH_2OH$	1.0	28	85
$HOCH_2CH_2OH$	0.5	85	81
$HOCH_2CH_2CH_2OH$	0.5	40	83

[a] The reaction was carried out in THF at ambient temperature using 1 collected in a trap at −78 °C in vacuo from the reaction flask for the preparation of 1 with potassium *tert*-butoxide in THF. [b] The reaction was carried out in $CDCl_3$ using 1 redistilled after the collection in a trap at −78 °C from the reaction flask in vacuo. [c] ^1H NMR yield.

−78 °C in vacuo from the reaction flask for the preparation of 1 via elimination with potassium *tert*-butoxide in THF,[6] addition of other alcohols to 1 was next carried out using crude 1 obtained with *tert*-butanyl alcohol and THF by the distillation directly from the reaction flask (Table 1). Although it took a longer time, the corresponding ortho esters were obtained in good yields, especially from diols were the intended divinyl ortho esters 2 for the polyaddition of dithiols obtained. The IR and ^1H NMR spectra of the ortho esters are consistent with the corresponding 3. *tert*-Butanyl alcohol in crude 1 did not cause serious problems in the addition of alcohols to 1 because *tert*-butanyl alcohol added to 1 more slowly than alcohols in Table 1.

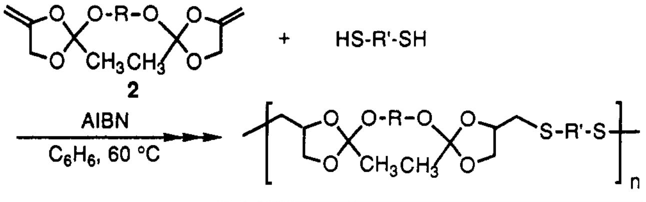
The addition of dithiols to 1 was also attempted instead of diols, but the addition proceeded very slowly and the products were decomposed during distillation.

Addition of Thiols to 2 or 3 with Radical Initiator. Addition of thiols to 3 (R = CH_2CH_3) was first carried out in the presence of azobis(isobutyronitrile) (AIBN) as a radical initiator as a model reaction of the radical polyaddition of dithiols to 2. The reaction of 3 with ethanethiol in bulk at 60 °C afforded the adduct 4 in 57% yield, whereas the reaction with thiophenol did not give the corresponding adduct. Thin-layer chromatography (TLC) of the products showed many spots, and IR spectra of the mixture showed the characteristic absorption of a carbonyl group at 1740 cm^{-1}, implying that many side reactions including ring-opening reactions might occur in the reaction of 3 with thiophenol. An improved 82% yield of the adduct of ethanethiol to 3 could be attained in benzene solution.



From these results of the model reactions, the polyadditions of 2 were carried out in benzene using alkanedithiols. Thus, equimolar 2 and alkanedithiols were heated at 60 °C in the presence of 4 mol % of AIBN in benzene for 48 h. The polymers were purified by dissolution in chloroform, followed by precipitation with hexane. The results are summarized in Table 2. The polymers obtained in Table 2 were clear viscous liquids. The yields and molecular weights of the polymers were almost unchanged irrespective of the R′ of dithiols in the polyaddition of **2a** derived from 1 and ethylene glycol, whereas the yields and molecular weights were dependent on the R′ of dithiols in the polyaddition of **2b** derived from 1 and 1,3-propanediol, and an improved yield and molecular weight could be attained by using 1,4-butanedithiol.

Table 2. Radical Polyaddition of Dithiols to 2[a]



R in 2	R′ in dithiols	yield, %[b]	$\bar{M}_n$[c]
$-(CH_2)_2-$, **2a**	$-(CH_2)_2-$	89	4200
	$-(CH_2)_3-$	88	4700
	$-(CH_2)_4-$	86	4800
$-(CH_2)_3-$, **2b**	$-(CH_2)_2-$	68	3400
	$-(CH_2)_3-$	57	3400
	$-(CH_2)_4-$	90	7200

[a] The polyaddition was carried out with 4 mol % of AIBN in benzene at 60 °C for 48 h. [b] Polymer insoluble in hexane. [c] Number-average molecular weight $\bar{M}_n$ estimated by means of GPC with solvent THF (based on polystyrene standard).

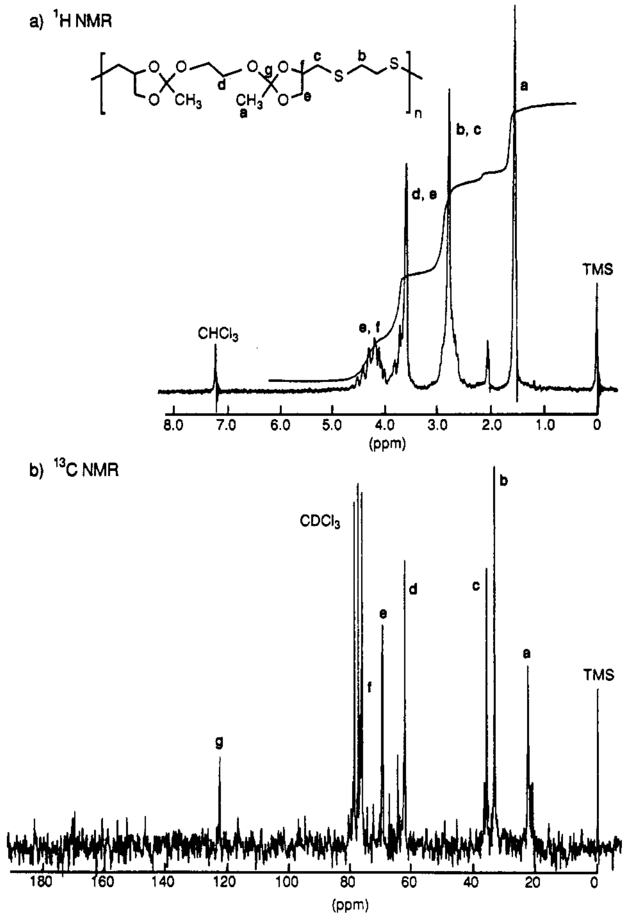
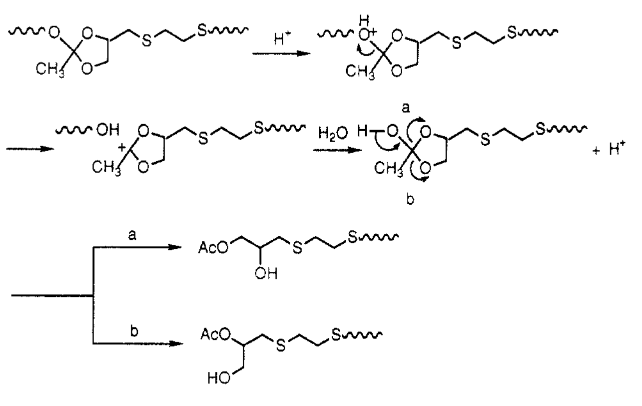


Figure 1. (a) 60-MHz ^1H NMR and (b) 50-MHz ^{13}C NMR spectra of the polymer from **2a** and ethanedithiol in $CDCl_3$ at 27 °C.

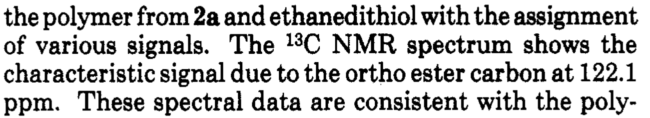
In the IR spectra of the polymers, two characteristic absorptions of vinyl ether moieties of 2 at 1690 and 1290 cm^{-1} completely disappeared, whereas absorption attributable to an ortho ester moiety at 1050 cm^{-1} was observed similarly to 2. In the ^1H NMR spectra of the polymers, the signals of the *exo*-methylene groups of 2 at 3.68–3.90 and 4.15–4.37 ppm disappeared, and the signal assignable to the methylene protons on a carbon atom of a sulfide linkage at 2.36–3.17 ppm and the signal assignable to the methine proton on a carbon atom adjacent to an oxygen atom at 3.95–4.67 ppm were observed, indicating that the *exo*-methylene groups of 2 were changed to sulfide linkages by the addition of thiols to the *exo*-methylene groups. Figure 1 shows the ^1H and ^{13}C NMR spectra of

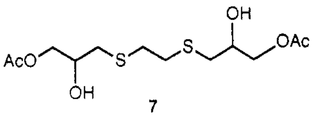
Scheme 1



the polymer from **2a** and ethanedithiol with the assignment of various signals. The ^{13}C NMR spectrum shows the characteristic signal due to the ortho ester carbon at 122.1 ppm. These spectral data are consistent with the polysulfides containing ortho ester structures as shown in the equation.

Hydrolysis of Polysulfide. Since the polysulfides obtained have hydrolyzable ortho ester moieties, their hydrolysis is expected to take place smoothly. The polysulfide derived from **2a** and ethanedithiol was heated in THF containing water for 4 h to afford low molecular weight organic compounds. The ^1H NMR of the products showed no signals of the polysulfide, and their IR showed the characteristic absorption of a hydroxy group at 3440 cm^{-1} and of a carbonyl group at 1735 cm^{-1}, implying that the hydroysis took place. However, TLC showed several spots and then the structure of the products could not be determined completely. Accordingly, as a model reaction for the hydrolysis of the polymer, the hydrolysis of **4** was carried out under the same conditions. After purification by column chromatography on silica gel, two kinds of hydroxy acetates **5** and **6** were mainly obtained in 58 and 29% yield, respectively. Consequently, in the hydrolysis of the polysulfide, hydroxy acetates **7–9** were considered to be formed, and **7** was probably a main product. The production of **7–9** can be explained by assuming the involvement of elimination of the diol promoted by protonation on the oxygen of the diol component in the polysulfide and decomposition of a hemiacetal-type intermediate as shown in Scheme 1.

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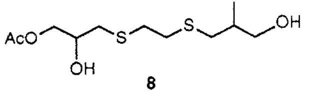
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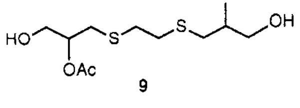
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Experimental Section

Measurements. ^1H NMR spectra were obtained on a JEOL PMX-60, and ^{13}C NMR spectra were obtained on a JEOL FX-200. FTIR spectra were recorded on a JASCO FT/IR-3. The average molecular weights of polymers were measured with a TOYO SODA CCP-8000 GPC unit using TSK-Gel columns (eluent: THF, calibration: polystyrene standards).

Materials. 2,4-Dimethylene-1,3-dioxolane (**1**) was prepared according to our previous paper.[6] Alcohols and diols were distilled over a small portion of sodium. Thiols and dithiols were distilled just before use. AIBN was used as received. Benzene and THF was distilled over sodium.

Addition of Methanol to 1 in NMR Tube. Into a solution of purified **1** (0.026 g, 0.3 mmol) in $CDCl_3$ (0.6 mL) was added methanol (0.008 g, 0.3 mmol), and the adduct **3** was confirmed by direct measurement with ^1H NMR: ^1H NMR ($CDCl_3$) δ 4.64–4.43 (m, 2H), 4.43–4.25 (m, 1H), 3.97–3.79 (m, 1H), 3.28 (s, 3H), 1.58 (s, 3H).

Addition of Alcohols to 1. General Procedure. Into a solution of **1** in THF containing *tert*-butanyl alcohol, which was directly obtained in a trap at −78 °C in vacuo from the reaction flask for the preparation of **1**[6]), equimolar alcohols (0.5 equiv of diols) were added and stirred at ambient temperature. When the reaction proceeded very slowly, a few drops of acetic acid was also added to the reaction mixture. After appropriate time the reaction mixture was concentrated in vacuo and then distilled under reduced pressure. In the case of addition of benzyl alcohol to **1**, purification by column chromatography on silica gel (Wakogel C-200 deactivated by triethylamine, eluent: hexane: ethyl acetate = 15:1) was carried out instead of distillation. **2-Ethoxy-2-methyl-4-methylene-1,3-dioxolane**: bp 72 °C/110 torr; IR (neat) 1690, 1290, 1050 cm^{-1}; ^1H NMR (CCl_4) δ 4.57–4.35 (m, 2H), 4.28–4.10 (m, 1H), 3.77–3.62 (m, 1H), 3.47 (q, J = 7.0 Hz, 2H), 1.49 (s, 3H), 1.15 (t, J = 7.0 Hz, 3H). **2-(Benzyloxy)-2-methyl-4-methylene-1,3-dioxolane**: R_f = 0.39 (hexane:ethyl acetate = 15:1); IR (neat) 1690, 1290, 1050 cm^{-1}; ^1H NMR (CCl_4) δ 7.15 (s, 5H), 4.62–4.35 (m, 4H), 4.35–4.17 (m, 1H), 3.85–3.68 (m, 1H), 1.40 (s, 3H). **Bis[(2-methyl-4-methylene-1,3-dioxolan-2-yl)oxy]ethane (2a)**: bp 77 °C/0.1 torr; IR (neat) 1690, 1290, 1050 cm^{-1}; ^1H NMR (CCl_4) δ 4.65–4.42 (m, 4H), 4.37–4.19 (m, 2H), 3.90–3.72 (m, 2H), 3.57 (s, 4H), 1.55 (s, 6H). **1,3-Bis[(2-methyl-4-methylene-1,3-dioxolan-2-yl)oxy]propane (2b)**: bp 79 °C/0.05 torr; IR (neat) 1690, 1290, 1050 cm^{-1}; ^1H NMR (CCl_4) δ 4.59–4.38 (m, 4H), 4.33–4.15 (m, 2H), 3.85–3.68 (m, 2H), 3.50 (t, J = 6.0 Hz, 4H), 1.73 (quin, J = 6.0 Hz, 2H), 1.50 (s, 6H).

Radical Addition of Ethanethiol to 3 (R = CH_2CH_3). A mixture of **3** (R = CH_2CH_3) (0.140 g, 1.0 mmol), ethanethiol (0.059 g, 1.0 mmol), AIBN (3.8 mg, 0.02 mmol), and benzene (0.427 g) was placed into a glass tube. It was degassed three times by the standard freeze-thaw method under nitrogen, and then the tube was sealed in vacuo. The mixture was stirred for 48 h at 60 °C. The tube was opened and the mixture was concentrated in vacuo to afford the adduct **4** (0.165 g; 82% yield): IR (neat) 1050 cm^{-1}; ^1H NMR (CCl_4) δ 4.51–3.90 (m, 2H), 3.90–3.26 (m, 3H), 3.00–2.35 (m, 2H), 2.55 (q, J = 7.0 Hz, 2H), 1.43 and 1.40 (2s, 3H), 1.25 (t, J = 7.0 Hz, 3H), 1.12 (t, J = 7.0 Hz, 3H).

Radical Polyaddition of Dithiols to 2. A mixture of **2** (1.0 mmol), alkanedithiol (1.0 mmol), AIBN (6.6 mg, 0.04 mmol), and benzene (200 wt % to **2** and alkanedithiol) was placed into a polymerization tube. It was degassed three times by the standard freeze-thaw method under nitrogen, and then the tube was sealed in vacuo. The mixture was stirred for 48 h at 60 °C. The tube was opened and the viscous solution was diluted by chloroform, followed by precipitation with hexane to give polymer as a viscous liquid. **Polymer from 2a and ethanedithiol**: IR (neat) 2940, 1380, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.67–3.95 (m, 4H), 3.95–3.21 (m, 6H), 3.21–2.37 (m, 8H), 1.55 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 122.1, 76.1, 69.2, 62.0, 35.5, 33.0, 22.3.

Polymer from 2a and 1,3-propanedithiol: IR (neat) 2940, 1380, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.60–3.96 (m, 4H), 3.96–3.58 (m, 6H), 2.92–2.47 (m, 8H), 2.00–1.40 (m, 8H). **Polymer from 2a and 1,4-butanedithiol**: IR (neat) 2940, 1380, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.59–3.97 (m, 4H), 3.97–3.53 (m, 6H), 2.98–2.36 (m, 8H), 1.91–1.45 (m, 10H). **Polymer from 2b and ethanedithiol**: IR (neat) 2940, 1380, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.60–3.97 (m, 4H), 3.97–3.40 (m, 6H), 3.17–2.51 (m, 8H), 2.00–1.46 (m, 8H). **Polymer from 2b and 1,3-propanedithiol**: IR (neat) 2940, 1380, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.57–4.00 (m, 4H), 4.00–3.42 (m, 6H), 3.07–2.51 (m, 8H), 2.08–1.58 (m, 10H). **Polymer from 2b and 1,4-butanedithiol**: IR (neat) 2940, 1380, 1050 cm^1; ^{1}H NMR ($CDCl_3$) δ 4.60–4.00 (m, 4H), 4.00–3.42 (m, 6H), 3.00–2.38 (m, 8H), 2.07–1.33 (m, 12H).

Hydrolysis of Polymer. A solution of the polymer (0.164 g) obtained from **2a** and ethanedithiol in THF (4 mL)–water (1 mL) was refluxed for 4 h. After evaporation of THF in vacuo, the residue was extracted with chloroform and the organic layer was washed with brine and then dried over magnesium sulfate. Removal of chloroform under reduced pressure gave viscous liquid (0.152 g): IR (neat) 3440, 1735, 1430, 1370, 1240 cm^{-1}; ^{1}H NMR δ 5.23–4.78 (m), 4.30–3.70 (m), 3.24 (br), 2.96–2.63 (m), 2.10 (s).

Hydrolysis of 4 as a Model Reaction for the Hydrolysis of Polymer. A solution of ortho ester **4** (0.603 g, 2.9 mmol) in THF (12.6 mL)–water (3.1 mL) was refluxed for 4 h. After evaporation of THF in vacuo, the residue was extracted with dichloromethane and the organic layer was washed with brine and then dried over magnesium sulfate. After removal of the solvent, the residue was purified by column chromatography on silica gel (Wakogel C-200, eluent:hexane:ethyl acetate = 3:2) to afford **5** (0.300 g, 58% yield) and **6** (0.150 g, 29% yield): **5** R_f = 0.34 (hexane:ethyl acetate = 3:2); IR (neat) 3450, 1740, 1380, 1240, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.25–3.60 (m, 3H), 3.22–2.90 (br, 1H), 2.57 (d, J = 4.0 Hz, 2H), 2.55 (q, J = 8.0 Hz, 2H), 2.05 (s, 3H), 1.28 (t, J = 8.0 Hz, 3H). **6**: R_f = 0.30 (hexane:ethyl acetate = 3:2); IR (neat) 3450, 1740, 1380, 1240, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.12–4.63 (m, 1H), 3.68 (d, J = 6.0 Hz, 2H), 2.83 (br, 1H), 2.58 (d, J = 6.0 Hz, 2H), 2.53 (q, J = 7.0 Hz, 2H), 2.07 (s, 3H), 1.28 (t, J = 7.0 Hz, 3H).

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