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A Series of Mono and Diesters of Itaconic Acid: Synthesis and Structural Determination

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Summary. A series of mono and diesters of itaconic acid containing alkoxy and sulfide side chains of variable lengths has been synthesized. Their structures have been established on the basis of their spectral data.

Keywords. Diitaconic acid ester; Monoitaconic acid ester.

Eine Serie von Mono- und Diestern von Itaconsäure: Synthese und Strukturbestimmung

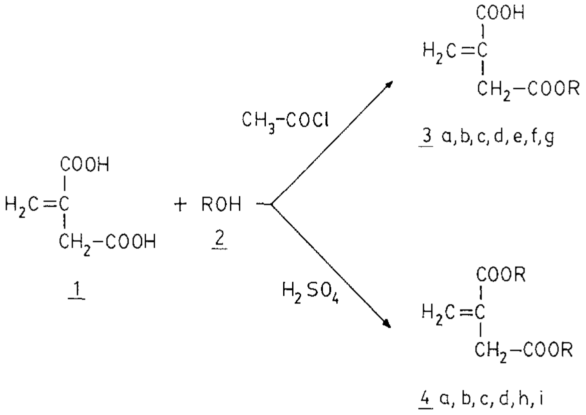
Zusammenfassung. Es wurde eine Serie von Mono- und Diestern von Itaconsäure mit Alkoxy- und Sulfidseitenketten variabler Länge synthetisiert. Die Strukturaufklärung erfolgte mittels spektroskopischer Daten.

As a part of a programme of research directed towards the study of the non-classical free-radical polymerization of itaconate esters [1], we had to deal with the preparation of a series of mono and diitaconate esters. In recent years, interest has been focused on itaconic acid **1** and its derivatives due to the fact that they are the starting point of a variety of polymers and copolymers [2]. Moreover, the diacid itself can be easily obtained from fermentation processes [3].

Most of the work reported to date has been concerned with copolymers of itaconic acid with styrene, acrylonitrile, butadiene, vynil chloride, acrylic and methacrylic esters, due to their industrial applications [4].

Work on polymerization of diester derivatives has also been reported [5]. Thus, materials with side chains lengths from methyl to hexyl [6], dibenzyl itaconates [7], diitaconate esters containing methyl-terminated poly(ethyleneoxide) side chains [8], dialkylitaconic acid esters with side chain lengths C_7 to C_{20} [9] have been described.

Less has been done with the corresponding monoester derivatives although they were found to polymerize more rapidly than the corresponding diesters [4]. On the other hand, the radical polymerization of monoitaconate esters is known to be very sensitive to steric effects due probably to the influence of the side group [1].



R: a) $-(CH_2)_2-O-(CH_2)_3-CH_3$; b) $-(CH_2)_3-O-CH_2-CH_3$;
c) $-(CH_2)_2-S-CH_2-CH_3$; d) $-(CH_2)_2-S-Ph$
e) $-(CH_2)_3-Ph$; f) $-(CH_2)_4-Ph$; g) $-(CH_2)_5-Ph$;
h) $-(CH_2)_2-O-CH_3$; i) $-(CH_2)_2-O-CH_2-CH_3$

Now we report on the preparation and spectroscopic characterization of a series of monoesters and diesters of itaconic acid which carry an oxide or sulfide function and also some containing phenyl-terminated alkyl side chains. Taking into account that the sulfur atom is larger, less electronegative and more polarizable than the oxygen atom, we considered that it could be of interest to dispose of this monomers series, in order to study comparatively the corresponding polymers as it might be expected to give rise to further interesting effects in the polymers.

Experimental

Melting points (°C) were determined with a Büchi apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer and only selected absorptions (cm^{-1}) are reported. NMR spectra were recorded at 250.13 MHz for ^1H (δ, Me_4Si, $CDCl_3$) and 62.83 MHz for ^{13}C on a Bruker WM-250, and on a Perkin-Elmer R-12B (60 MHz) spectrometers. Combustion analyses were performed with a Perkin-Elmer model 240 B apparatus and are in good agreement with the proposed structures. All reactions were monitored by thin-layer chromatography (tlc) carried out on 0.2 mm silica gel 60 GF-254 (Merck) plates using UV light as the developing agent. Flash column chromatography was conducted with silica gel 60, 0.040–0.063 nm, 230–400 mesh (Merck) [10]. Refraction indices were measured with a refractometer Warszawa P20 RL1.

Preparation of the Monoitaconate Esters 3. *General Procedure*

Freshly distilled acetyl chloride was added dropwise to catalyze the reaction between itaconic acid (1 mol) and the appropriate alcohol (3 mol). The reaction mixture was refluxed until complete consumption of the itaconic acid (thin-layer chromatography monitored) was achieved. After cooling dichloromethane added and the resulting solution showed the presence (t.l.c.) of three spots attributable to the expected monoester, the diitaconate and the excess of the used alcohol. Then the

Table 1. Preparation of monoitaconate esters **3**

Product no.	M.p.[a]	n_{20}	R_f[b]	Yield (%)	Reaction time
3a		1 450	0.36	60	1 h
3b		1 363	0.52	70	1 h
3c		1 492	0.43	50	1 h 30 min
3d	74–76		0.32	55	1 h
3e	35–38		0.58	63	20 min
3f		1 700	0.55	57	35 min
3g		1 496	0.28	48	1 h 40 min

[a] Crystallization from petroleum ether

[b] Eluent: dichloromethane/methanol (9.5 : 0.5)

Table 2. Preparation of diitaconate esters **4**

Product no.	n_{20}	R_f[a]	Yield (%)	Reaction time
4a	1 436	0.78	80	3 h
4b	1 366	0.74	75	3 h 30 min
4c	1 476	0.76	78	3 h
4d	1 564	0.85	83	2 h 30 min
4h	1 420	0.67	87	2 h 30 min
4i	1 442	0.71	85	3 h

[a] Eluent: dichloromethane/methanol (9.5 : 0.5)

mixture was washed with aqueous NaOH (0.5 *M*). The aqueous phase was separated, treated with HCl (0.5 *M*) and extracted with dichloromethane. Evaporation of the solvent from the combined washed and dried extracts afforded the corresponding monoitaconate which was flash column chromatographed on silica gel by eluting with dichloromethane/methanol to afford the monoester in sufficient purity for crystallization in the cases of solid derivatives. In other cases, liquid monoitaconate esters appeared as oils. Synthetical and spectral data are recorded in Tables 1 and 3.

Preparation of the Diitaconate Esters **4**. *General Procedure*

Sulphuric was added dropwise to catalyze the diesterification reaction between itaconic acid (1 mol) and the appropriate alcohol (3 mol). The reaction mixture was refluxed until complete consumption of the itaconic acid (t.l.c. monitored). After this, the reaction mixture was cooled and the crude was washed with aqueous $NaHCO_3$. The organic phase was separated, dried and flash column chromatographed by eluting with dichloromethane to afford diesters **4** as the major compounds. Synthetical and spectral data are recorded in Tables 2 and 3.

Table 3. Spectral data for the itaconate esters **3** and **4**[a]

Product no.	^{1}H-NMR ($CDCl_3$/*TMS*)[b] δ (ppm), *J* (Hz)	^{13}C-NMR ($CDCl_3$/*TMS*) δ (ppm)
3a	8.24 (s, 1 H, OH)[c], 6.39 (s, 1 H, $CH_2{=}C$)[d], 5.76 (s, 1 H, $CH_2{=}C$)[d], 4.16 (t, 2 H, $J = 4.6$, COO—CH_2), 3.54 (t, 2 H, $J = 4.6$, CH_2—O), 3.38 (t, 2 H, $J = 6.6$, O—CH_2), 3.28 (s, 2 H, CH_2—COO), 1.47 (m, 2 H, CH_2-*Et*), 1.27 (m, 2 H, CH_2—CH_3), 0.82 (t, 3 H, CH_3)	170.6 (COOH), 170.5 (COOR), 133.2 ($CH_2{=}C$), 130.3 ($CH_2{=}C$), 71.1 (COO—CH_2), 64.1 (CH_2—O), 61.5 (O—CH_2), 37.1 (CH_2—COO), 31.5 (OCH_2—CH_2), 19.1 (CH_2—CH_3), 13.7 (CH_3)
3b	9.90 (s, 1 H, OH)[c], 6.29 (s, 1 H, $CH_2{=}C$)[d], 5.67 (s, 1 H, $CH_2{=}C$)[d], 4.02 (t, 2 H, COO—CH_2), 3.41 (m, 4 H, CH_2—O), 3.20 (s, 2 H, CH_2—COO), 1.01 (m, 3 H, CH_3)	
3c	6.09 (s, 1 H, OH)[c], 6.38 (s, 1 H, $CH_2{=}C$)[d], 5.77 (s, 1 H, $CH_2{=}C$)[d], 4.26 (t, 2 H, $J = 7.2$, COO—CH_2), 3.32 (s, 2 H, CH_2—COO), 2.73 (t, 2 H, $J = 7.2$, CH_2—S), 2.51 (q, 2 H, $J = 7.5$, S—CH_2), 1.20 (t, 3 H, $J = 7.5$, CH_3)	173.4 (COOH), 168.3 (COOR), 131.8 ($CH_2{=}C$), 127.4 ($CH_2{=}C$), 62.6 (COO—CH_2), 35.8 (CH_2—COO), 32.8 (CH_2—S), 28.1 (S—CH_2), 13.2 (CH_3)
3d	11.60 (s, 1 H, OH)[c], 7.45 (m, 5 H, *Ar*-H), 6.72 (s, 1 H, $CH_2{=}C$)[d], 6.09 (s, 1 H, $CH_2{=}C$)[d], 4.40 (t, 2 H, $J = 7$, COO—CH_2), 3.61 (s, 2 H, CH_2—COO), 3.25 (t, 2 H, $J = 7$, CH_2—S)	
3e	10.65 (s, 1 H, OH)[c], 7.20 (s, 5 H, *Ar*-H), 6.25 (s, 1 H, $CH_2{=}C$)[d], 5.30 (s, 1 H, $CH_2{=}C$)[d], 3.05 (m, 2 H, COO—CH_2), 2.40 (s, 2 H, CH_2—COO)	
3f	9.50 (s, 1 H, OH)[c], 7.20 (s, 5 H, *Ar*-H), 6.30 (s, 1 H, $CH_2{=}C$)[d], 5.65 (s, 1 H, $CH_2{=}C$)[d], 3.8 (m, 2 H, COO—CH_2), 2.55 (s, 2 H, CH_2—COO)	
3g	8.20 (s, 1 H, OH)[c], 7.25 (s, 5 H, *Ar*-H), 6.30 (s, 1 H, $CH_2{=}C$)[d], 5.75 (s, 1 H, $CH_2{=}C$)[d], 3.65 (m, 2 H, COO—CH_2), 2.70 (s, 2 H, CH_2—COO)	

Table 3 (continued)

Product no.	^{1}H-NMR ($CDCl_3$/*TMS*)[b] δ (ppm), *J* (Hz)	^{13}C-NMR ($CDCl_3$/*TMS*) δ (ppm)
4a	6.31 (s, 1 H, $CH_2{=}C$)[d], 5.70 (s, 1 H, $CH_2{=}C$)[d], 4.20 and 4.15 (2 t, 4 H, *J* = 4.6, 2 × COO—CH_2), 3.63 and 3.54 (2 t, 4 H, *J* = 4.6, 2 × CH_2—O), 3.44 and 3.38 (2 t, 4 H, *J* = 6.6, 2 × O—CH_2), 3.30 (s, 2 H, CH_2—COO), 1.51–1.42 (m, 4 H, 2 × CH_2-*Et*), 1.32–1.23 (m, 4 H, 2 × CH_2—CH_3), 0.82 (2 t, 6 H, 2 × CH_3)	170.6 and 166.0 (2 × COOR), 133.6 ($CH_2{=}C$), 128.6 ($CH_2{=}C$), 71.7 and 71.0 (2 × COO—CH_2), 68.4 and 68.3 (2 × CH_2—O), 37.4 (CH_2—COO), 64.0 and 61.7 (2 × O—CH_2), 31.6 (2 × OCH_2—CH_2), 19.1 (2 × OCH_2—CH_3), 13.8 (2 × CH_3)
4b	6.20 (s, 1 H, $CH_2{=}C$)[d], 5.60 (s, 1 H, $CH_2{=}C$)[d], 4.25–3.92 (m, 4 H, 2 × COO—CH_2), 3.40–3.30 (m, 8 H, 4 × CH_2—O), 3.20 (s, 2 H, CH_2—COO), 1.00 (2 t, 6 H, 2 × CH_3)	
4c	6.28 (s, 1 H, $CH_2{=}C$)[d], 5.69 (s, 1 H, $CH_2{=}C$[d], 4.24 and 4.18 (2 t, 4 H, *J* = 7.2, 2 × COO—CH_2), 2.72 and 2.65 (2 t, 4 H, *J* = 7.2, 2 × CH_2—S), 2.50 and 2.48 (2 t, 4 H, *J* = 7.5, S—CH_2), 3.29 (s, 2 H, CH_2—COO), 1.22 and 1.20 (2 t, 6 H, 2 × CH_2)	170.1 and 165.5 (2 × COOR), 133.2 ($CH_2{=}C$), 128.6 ($CH_2{=}C$), 70.5 and 70.4 (2 × COO—CH_2), 37.3 (CH_2—COO), 34.3 and 29.7 (2 × CH_2—S), 25.9 and 25.3 (2 × S—CH_2), 14.6 and 14.5 (2 × CH_3)
4d	7.38 (m, 10 H, *Ar*-H), 6.21 (s, 1 H, $CH_2{=}C$)[d], 5.63 (s, 1 H, $CH_2{=}C$)[d], 4.32 (m, 4 H, 2 × COO—CH_2), 2.82 and 2.73 (2 t, 4 H, 2 × CH_2—S), 3.15 (s, 2 H, CH_2—COO)	
4h	6.27 (s, 1 H, $CH_2{=}C$)[d], 5.64 (s, 1 H, $CH_2{=}C$)[d], 4.25 and 4.18 (2 t, 4 H, *J* = 4.5, 2 × COO—CH_2), 3.57 and 3.54 (2 t, 4 H, *J* = 4.5, 2 × CH_2—O), 3.34 and 3.33 (2 s, 6 H, 2 × OCH_3), 3.32 (s, 2 H, CH_2—COO)	170.0 and 164.2 (2 × COOR), 132.8 ($CH_2{=}C$), 127.1 ($CH_2{=}C$), 70.3 and 70.2 (2 × COO—CH_2), 63.8 (2 × CH_2O), 58.8 (2 × OCH_3), 37.7 (CH_2—COO)
4i	6.31 (s, 1 H, $CH_2{=}C$)[d], 5.69 (s, 1 H, $CH_2{=}C$)[d], 4.24 and 4.20 (2 t, 4 H, *J* = 4.8, 2 × COO—CH_2), 3.60 and 3.57 (2 t, 4 H, *J* = 4.8, 2 × CH_2—O), 3.56 and 3.46 (2 m, 4 H, OCH_2—CH_3), 3.33 (s, 2 H, CH_2—COO), 1.72 and 1.38 (2 t, 6 H, 2 × CH_3)	170.4 and 165.8 (2 × COOR), 133.4 ($CH_2{=}C$), 128.4 ($CH_2{=}C$), 67.9 and 66.3 (2 × COO—CH_2), 64.0 (2 × CH_2O), 63.8 (2 × OCH_2), 37.3 (CH_2—COO), 14.8 (2 × CH_3)

[a] The IR ($CHCl_3$) spectra of the monoitaconate esters **3** showed bands at: 3 300 (OH), 1 740 (C=O, ester), 1 720 (C=O, acid). For the diitaconate esters: 1 745 (C=O, ester)

[b] s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet

[c] Exchangeable with D_2O

[d] Indistinguishable

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