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DEPARTMENT OF CHEMISTRY
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Mixed Esters of Lactic and Fatty Acids¹

BY M. L. FEIN

Earlier papers^{2,3,4,5} described the preparation and properties of acylated derivatives of various

These esters are the pelargonates of some lactic esters and the laurates of ethyl and butyl lactyl-lactate corresponding to the general formulas $\text{CH}_3(\text{CH}_2)_7\text{COOCH}(\text{CH}_3)\text{COOR}$ and $\text{CH}_3(\text{CH}_2)_{10}\text{COOCH}(\text{CH}_3)\text{COOCH}(\text{CH}_3)\text{COOR}$. The latter may be considered as a derivative of lactyl-lactic acid.

Experimental

Materials.—2-Butoxyethyl, 2-(2-butoxyethoxy)-ethyl and 2-chloroethoxyethyl lactates were prepared as described previously.^{2,6} Ethyl lactyl-lactate was obtained by distillation of ethyl polylactate prepared by the self-alcoholysis of ethyl lactate.⁷

TABLE I

PROPERTIES OF PELARGONATES AND LAURATES OF LACTIC ESTERS

	Yield, %	B.p. °C.	Mm.	n_{20}^D	d_{20}^{20}	Viscosity at 20°C., centi- poises	Ester equivalent		Carbon, ^a %		Hydrogen, %	
							Found	Calcd.	Found	Calcd.	Found	Calcd.
2-Butoxyethyl lactate pelargonate	64	160	2.8	1.4379	0.9564	...	165.2	165.2	65.32	65.42	9.98	10.37
2-(2-Butoxyethoxy)-ethyl lactate pelargonate	79	168	1.0	1.4402	0.9740	13.74	186.4	187.2	63.86	64.17	9.89	10.23
2-Chloroethoxyethyl lactate pelargonate	85	178	3.0	1.4496	1.0530	17.98	56.23	57.05	8.39	8.68
Ethyl lactyl-lactate laurate	83	171	0.9	1.4392	0.9810	25.24	125.3	124.2	64.84	64.48	9.82	9.74
Butyl lactyl-lactate laurate	..	186-190	1.2	1.4415	0.9677	22.38	132.6	133.5	65.47	65.97	10.02	10.07

^a The author is indebted to C. L. Ogg and Mary J. Welsh for analytical data. ^b % Cl 10.62 (found); 10.53 (calcd.).

lactic esters. This paper reports several additional members of this group of mixed esters of lactic acid.

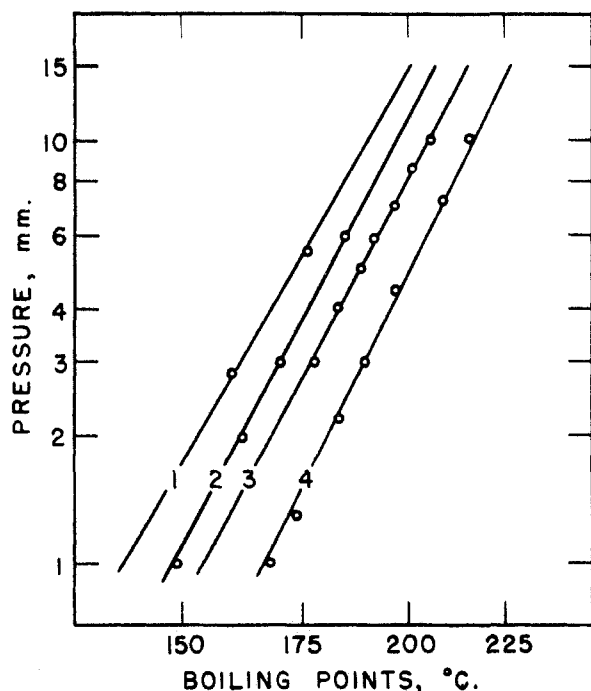


Fig. 1.—Boiling points of lactate pelargonates: 1. 2-butoxyethyl lactate pelargonate; 2. *n*-butyl phthalate; 3. 2-chloroethoxyethyl lactate pelargonate; 4. 2-(2-butoxyethoxy)-ethyl lactate pelargonate.

- (1) Not copyrighted.
- (2) M. L. Fein and C. H. Fisher, *THIS JOURNAL*, **68**, 2631 (1946).
- (3) M. L. Fein and C. H. Fisher, *ibid.*, **70**, 52 (1948).
- (4) M. L. Fein and C. H. Fisher, *J. Org. Chem.*, **15**, 530 (1950).
- (5) J. K. Weil, A. J. Stirton and A. A. Stawitzke, *J. Am. Oil Chemists Soc.*, **27**, 187 (1950).

Preparation of Esters.—The lactate pelargonates were prepared by acylating the appropriate lactate with redistilled pelargonyl chloride; ethyl lactyl-lactate laurate by acylation of ethyl lactyl-lactate with redistilled lauroyl chloride. The conventional acid chloride acylation method was employed.^{3,4} Butyl lactyl-lactate laurate was obtained as a by-product in the esterification of butyl lactate with lauric acid in a modification of the method described in an earlier paper.⁸

The esters prepared and their properties are listed in Table I. These esters exhibited slight solubility (less than 0.03 g. per liter) in water at room temperature, and were found to be compatible with ethyl cellulose though incompatible with cellulose acetate.

Vapor pressures of the lactate pelargonates were determined by distillation in a tensimeter still.⁹ The boiling points in the range of 1 to 10 mm. are shown in Fig. 1. The line for *n*-butyl phthalate is included for purposes of comparison.

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(6) M. L. Fein, W. P. Ratchford and C. H. Fisher, *THIS JOURNAL*, **66**, 1201 (1944).

(7) E. M. Filachione, E. J. Costello, T. J. Dietz and C. H. Fisher, "Lactic Acid Derivatives as Plasticizers. Esters of Polymeric Lactic Acid," U. S. Dept. Agr., Bur. Agr. and Ind. Chem., AIC-295 (ERRL) February, 1951.

(8) M. L. Fein and C. H. Fisher, *Ind. Eng. Chem.*, **40**, 584 (1948).

(9) W. P. Ratchford and C. E. Rehberg, *Anal. Chem.*, **21**, 1417 (1949).

(10) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

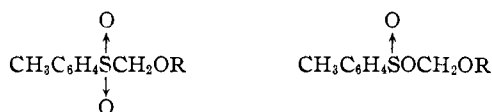
Structure of the Addition Product of *p*-Toluenesulfonic Acid and Formaldehyde

BY LAMAR FIELD AND PAUL H. SETTLAGE

The formation of an addition product from *p*-toluenesulfonic acid and formaldehyde has been reported by von Meyer,¹ who regarded it as having

(1) E. von Meyer, *J. prakt. Chem.*, [2] **63**, 167 (1901).

the structure of *p*-tolylsulfonylcarbinol (I). Other sulfinic acid-aldehyde addition products were



I, R = H
 IIIA, IIIB, R = C₆H₅CO

II, R = H
 IV, R = C₆H₅CO

subsequently investigated by Kohler and Reimer² and by Bazlen.³ These adducts were also presumed to be α -hydroxysulfones, but unlike most sulfones were unstable and easily subject to cleavage. In view of the interest attached to α -hydroxysulfones as a general class of sulfone derivatives it seemed worthwhile to determine definitely whether the sulfinic acid-aldehyde adducts are indeed the α -hydroxysulfones, such as I, that they have been presumed to be, or are actually α -hydroxymethyl sulfinates, such as II. A very similar structural question has existed in connection with the addition products of aldehydes with sodium bisulfite, and it is only in recent years that it has been established⁴ that these adducts are α -hydroxysulfonates and not sulfites.

In order to establish the structure of the *p*-toluenesulfinic acid-formaldehyde adduct, it was converted to the corresponding benzoate (IIIA) by a common acylation procedure in which rearrangement is highly improbable. Authentic *p*-tolylsulfonylcarbinyl benzoate (IIIB) was prepared for comparison with IIIA by the reaction of chloromethyl benzoate and sodium *p*-toluenesulfinate. Since it is well known that the reaction of alkyl halides with sodium arylsulfonates provides



a general and apparently unequivocal synthesis of sulfones,⁵ there can be little doubt that the reaction product of chloromethyl benzoate and sodium *p*-toluenesulfinate is the sulfone IIIB rather than the sulfinate IV.

The identity of IIIA and IIIB was established by m.p. and mixture m.p. and by identical infrared spectra, hence the original adduct is proved beyond reasonable doubt to have the sulfone structure, I. The presence of prominent bands in the spectra of IIIA and IIIB within the regions reported to be characteristic of sulfones serves to substantiate the sulfone structure, but is not in itself rigorous evidence for it because the absorption characteristics of sulfinate esters have apparently not yet been evaluated.

We are indebted to the Research Corporation for a Frederick Gardner Cottrell Grant which greatly facilitated this work. We also wish to

(2) E. P. Kohler and M. Reimer, *Am. Chem. J.*, **31**, 163 (1904).

(3) M. Bazlen, *Ber.*, **60**, 1470 (1927).

(4) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 126 ff.

(5) R. Connor in H. Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 874, 916. Ref. 4, p. 667. Sulfinate salts have been reported to react with ethyl chloroformate, however, to form a sulfinate rather than a sulfone.⁶ This reaction may involve formation of the sulfinyl chloride and its reaction with alcohol; in any event, it is not surprising that ethyl chloroformate should not react in the manner characteristic of alkyl halides.

(6) R. Otto and A. Rössing, *J. prakt. Chem.*, [2] **47**, 152 (1893); *Ber.*, **18**, 2493 (1885).

thank N. Fuson, M. L. Josien and R. L. Powell of Fisk University for the infrared data.

Experimental⁷

Preparation of *p*-Tolylsulfonylcarbinyl Benzoate (IIIA) from the Carbinol I.—I was prepared, using the procedure of von Meyer¹; yield 92%; m.p. 94–95° (m.p. reported,¹ 90°). Small amounts of water lower the m.p. several degrees.

IIIA was prepared by slowly pouring 55 g. of benzoyl chloride into an ice-cold solution of 65.0 g. of I in 300 g. of pyridine. After four days the mixture was poured into 1 liter of iced 3 *N* hydrochloric acid and the resulting solid was taken up in benzene. Customary washing (dilute acid, bicarbonate and water), drying over anhydrous sodium sulfate, and removal of solvent under reduced pressure gave a tan residue which after two recrystallizations from petroleum ether-benzene (3:1) gave 51.1 g. (50%) of IIIA, m.p. 101.5–102°. Further recrystallization gave material having a constant m.p. of 102–102.5°.

Anal. Calcd. for C₁₅H₁₄O₄S: C, 62.05; H, 4.86. Found: C, 62.02; H, 4.81.

The use of aqueous sodium hydroxide instead of pyridine resulted in the formation of benzoic acid (96%). An attempt to prepare the benzoate of the acetaldehyde-*p*-toluenesulfinic acid adduct² (53%, m.p. 71–72°) by the method used for IIIA gave *p*-tolyl *p*-toluenethiolsulfonate and benzoic acid as the only pure products.

***p*-Tolylsulfonylcarbinyl Benzoate (IIIB) from Chloromethyl Benzoate and Sodium *p*-Toluenesulfinate.**—Chloromethyl benzoate was prepared⁸ from 140 g. of benzoyl chloride, 30 g. of paraformaldehyde (dried over phosphorus pentoxide) and 4 g. of freshly fused zinc chloride. The mixture was heated for 4.5 hours, after which distillation gave 85.4 g. of material, b.p. 100–105° (13 mm.). Three further distillations using a 20-cm. Vigreux column gave 32.1 g. (19%) of material having constant b.p. and *n*_D²⁰; b.p. 98–99° (6 mm.); *n*_D²⁰, 1.5328; *d*₄²⁰, 1.2329, 1.2334; *M*_D calcd. 42.06; found, 42.91, 42.93 (exaltation, 0.86).

Anal. Calcd. for C₈H₇O₂Cl: C, 56.31; H, 4.14. Found: C, 56.22; H, 3.82.

A solution of 3.00 g. of chloromethyl benzoate in 6 ml. of acetone was added during two hours to 7.30 g. of sodium *p*-toluenesulfinate (dihydrate) in 30 ml. of acetone with stirring at the reflux temperature, and the mixture was then held at this temperature for 17 hours more. The cooled mixture was poured onto ice, and an ether extract washed with 10% aqueous sodium bicarbonate and water; acidification of the bicarbonate solution gave 1.16 g. (54%) of benzoic acid, m.p. and mixture m.p. 120–120.5°. The ether solution was dried over anhydrous sodium sulfate after which concentration resulted in 1.78 g. (35%) of IIIB, m.p. 55–80°. One recrystallization gave 0.91 g. (18%) of IIIB, m.p. 93–98°, which upon further recrystallization had a constant m.p. of 102–102.5°, undepressed by IIIA (mixture m.p. 102–102.5°).

Anal. Calcd. for C₁₅H₁₄O₄S: C, 62.05; H, 4.86. Found: C, 62.05; H, 4.75.

Attempts to reduce the amount of benzoic acid formed by using anhydrous sodium *p*-toluenesulfinate in anhydrous

INFRARED ABSORPTION SPECTRA OF IIIA AND IIIB

The spectra were determined in nujol mulls; absorption positions are given in μ . Abbreviations: S, strong; M, medium; w, weak. K. C. Schreiber has reported characteristic strong bands for sulfones at 7.41–7.70 μ and 8.62–8.93 μ [*Anal. Chem.*, **21**, 1168 (1949)].

IIIA			IIIB		
5.74S	8.52w	12.19Mw	5.72M	8.50w	12.18Mw
6.27M	8.69S	12.38M	6.26Mw	8.71MS	12.38Mw
7.08w	9.05MS	12.51M	7.08w	9.03M	12.51M
7.50S	9.26MS	13.09M	7.48S	9.26M	13.07M
7.65	9.35MS	14.05MS	7.64	9.37M	14.03MS
7.70	9.70M		7.71	9.71Mw	
8.03S	10.42M		8.02MS	10.42Mw	

(7) Melting points are corrected and boiling points are uncorrected. Analyses are by the Clark Microanalytical Laboratory, Urbana, Ill.

(8) L. H. Ulich and R. Adams, *This Journal*, **43**, 662 (1921). See also W. R. Kirner, *ibid.*, **48**, 2750 (1926).

acetone or alcohol resulted in recovery of 80–90% of the chloromethyl benzoate.

***p*-Tolylsulfonylcarbinyl *p*-Toluenesulfonate.**—A solution of 19.7 g. of the carbinol I in 35 ml. of dry dioxane was slowly poured with cooling into 30 ml. of dioxane containing 9.5 g. of pyridine and 22.8 g. of *p*-toluenesulfonyl chloride. The mixture, after standing for ten days, was poured into water and an ether extract washed with aqueous sodium bicarbonate and water. The ether contained 17.24 g. (48%) of solid, m.p. 45–58°, which upon recrystallization from petroleum ether–benzene gave 1.01 g. (3%) of the presumed tosylate, m.p. 84–86°. Further recrystallization gave an unstable crystalline solid with a constant m.p. of 86–88°.

Anal. Calcd. for $C_{16}H_{16}O_3S_2$: S, 18.84. Found: S, 18.79.

The mother liquor yielded 11.9 g. (33%) of material which seemed to be the crude tosylate, m.p. 43–51°, undepressed by the analytically pure sample. Reduction with lithium aluminum hydride gave di-*p*-tolyl disulfide and *p*-thiocresol rather than methyl *p*-tolyl sulfone which reported reductions of tosylates to hydrocarbons⁹ might lead one to expect.

(9) J. Strating and H. J. Backer, *Rec. trav. chim.*, **69**, 638 (1950); H. Schmid and P. Karrer, *Helv. Chim. Acta*, **32**, 1371 (1949).

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Tetramethylthiophene and Tetramethylfuran

BY RUSSELL GAERTNER AND RICHARD G. TONKYN

In connection with an unsuccessful attempt to use a simple thiophene¹ as a diene in the Diels–Alder reaction,² useful syntheses for tetramethylthiophene (I) and tetramethylfuran (II) were developed.

2,5-Dimethylthiophene was chloromethylated to give 3,4-bis-(chloromethyl)-2,5-dimethylthiophene, which was reduced to I by lithium aluminum hydride. Maleic anhydride did not react with I, even in boiling nitrobenzene, but added to II at room temperature. The furan (II) was obtained by dehydration of 3,4-dimethyl-2,5-hexanedione with acetic anhydride and zinc chloride. Acetonylacetone was also converted to 2,5-dimethylfuran by these reagents³ (71% yield).

Experimental⁴

3,4-Bis-(chloromethyl)-2,5-dimethylthiophene.—To a solution of 72.4 g. of *s*-trioxane in 75 ml. of concd. hydrochloric acid which had been saturated below 50° with hydrogen chloride was added dropwise and with stirring 30 g. of 2,5-dimethylthiophene. The blue mixture was stirred for two hours, diluted with three volumes of water, and extracted with ether and petroleum ether. The extracts were washed successively with dilute hydrochloric acid, water, 5% sodium bisulfite, water, and dilute sodium hydroxide. The solid obtained by evaporation of the solvents was recrystallized from hexane by cooling the solution in the refrigerator. Colorless needles (28 g., 50% yield) were obtained; m.p. 73°.

(1) Only highly arylated, fused thiophenes have been found to add maleic anhydride as do dienes; for a summary, see Kloetzel in Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 36–37.

(2) Alkylated naphthalenes were reported by Kloetzel, *et al.*, *This Journal*, **72**, 273, 1991 (1950), to add maleic anhydride across the 1- and 4-positions in the substituted ring; it seemed likely that a similar effect might operate in the thiophene series.

(3) The use of acetic anhydride in this dehydration is apparently novel and was suggested by the observation of Hurd, Roach and Edwards, *ibid.*, **66**, 2013 (1944), that ketene effects this conversion.

(4) Melting points are corrected; boiling points are not. Microanalyses were by Micro-Tech Laboratories, Skokie, Illinois. Properties of known compounds agreed satisfactorily with those in the listed references.

The twice recrystallized material was sublimed *in vacuo* before analysis; m.p. 73.0–73.4°.

Anal. Calcd. for $C_8H_{10}Cl_2S$: C, 45.94; H, 4.82. Found: C, 46.04; H, 4.86.

The product reacted immediately with alcoholic silver nitrate. It did not form a Grignard reagent in the "cyclic reactor"⁵ as evidenced by the negative Gilman color test.⁶

Tetramethylthiophene (I).—Reduction⁷ of 13 g. of the chloromethyl compound with 6.3 g. of lithium aluminum hydride yielded 5.8 g. (67%) of colorless I⁸; b.p. 74–79° (15 mm.); n_D^{20} 1.5199. An attempted low-pressure hydrogenation of the halide over platinum oxide and then 10% palladium-on-charcoal was unsuccessful; the recovered material in dioxane was reduced with stannous chloride⁹ to give I in 54% yield. The action of phosphorus pentasulfide on 3,4-dimethyl-2,5-hexanedione¹⁰ gave I in only 8% yield in a single small run. No product could be detected in mixtures of I with a tenfold excess of maleic anhydride in boiling benzene after four days or in boiling nitrobenzene after four hours.

Tetramethylfuran (II).—A mixture of 15 g. of 3,4-dimethyl-2,5-hexanedione,¹⁰ 12 g. of acetic anhydride and 0.5 g. of anhydrous zinc chloride was heated under reflux for three hours after the initial exothermic reaction subsided. The mixture was made alkaline with 6 *N* sodium hydroxide and distilled with steam. The II¹¹ weighed 6.5 g. (49%); b.p. 145–148° (748 mm.); n_D^{20} 1.4550.

By a similar procedure, 114 g. of acetonylacetone, 112 g. of the anhydride and 1 g. of zinc chloride gave 69 g. (71%) of 2,5-dimethylfuran¹²; b.p. 92.5–94°; n_D^{20} 1.4470.

A yellow solution of 3 g. of I and 3.2 g. of maleic anhydride in 30 ml. of absolute ether was allowed to stand at room temperature overnight and then cooled at –15° for 24 hours. After being recrystallized from petroleum ether–ether, the yellow crystals gave white needles (3.2 g., 64%); m.p. 95–96°. They sublimed readily at 2 mm.; m.p. 95.8–96.6°.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 64.85; H, 6.35. Found: C, 65.00; H, 6.52.

The adduct, presumably tetramethyl-3,6-endoxotetrahydrophthalic anhydride, absorbed about a mole of hydrogen over platinum oxide.

(5) Under similar conditions 2-thenyl chloride forms high yields of Grignard reagent; *cf.* Gaertner, *This Journal*, **73**, 3934 (1951).

(6) Gilman and Schulze, *ibid.*, **47**, 2002 (1925); Gilman and Heck, *ibid.*, **52**, 4949 (1930).

(7) Johnson, Blizzard and Carhart, *ibid.*, **70**, 3664 (1948).

(8) Zelinsky, *Ber.*, **21**, 1835 (1888).

(9) Wood and Fieser, *This Journal*, **62**, 2674 (1940).

(10) Moore, *J. Chem. Soc.*, 236 (1951).

(11) Willstätter and Clarke, *Ber.*, **47**, 308 (1914).

(12) v. Auwers, *Ann.*, **408**, 271 (1915).

DEPARTMENT OF CHEMISTRY
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Streaming Birefringence in Aqueous Solutions of Poly-4-vinyl-*n*-butylpyridinium Bromide

BY RAYMOND M. FUOSS WITH RUDOLF SIGNER

Previous work¹ on polyelectrolytes suggests that the configuration of charged macromolecules is a function of the concentration: at moderate concentration, many counter ions are held in the vicinity of the polyion by electrostatic attraction, with the result that the net charge per macroion is small, and the latter can assume approximately the statistical coil configuration of a neutral polymer. On dilution, counter ions escape into the bulk of the solvent between polyions, thereby increasing the net charge, with the result that intramolecular repulsion causes the coil to expand, and in the limit of infinite dilution, to assume a rod-like configuration. Measurement of streaming bire-

(1) R. M. Fuoss and G. I. Cathers, *J. Polymer Sci.*, **2**, 12 (1947); R. M. Fuoss and W. N. Maclay, *ibid.*, **6**, 305 (1951).