85. *Alkyl–Oxygen Fission in Carboxylic Esters. Part IX. Methyl-2-thienylcarbinol.*

By I. G. ANDERSON, M. P. BALFE, and J. KENYON.

Optically impure di(methyl-2-thienylcarbinyl) phthalate and methyl-2-thienylcarbinyl *p*-tolyl sulphone are prepared.

BY the methods described in Parts II (*J.*, 1942, 605), IV (*J.*, 1946, 803), and V (*J.*, 1946, 807), optically impure di(methyl-2-thienylcarbinyl) phthalate and methyl-2-thienylcarbinyl *p*-tolyl sulphone have been prepared from the hydrogen phthalate: the latter reaction is accompanied by racemisation. The neutral phthalate is obtained in 20%, and the sulphone in 30% yield; from substituted diphenylcarbinols (*loc. cit.*), yields of approximately 100% are obtained. Anderson, Balfe, and Kenyon (*J.*, 1950, 1866) have shown that when the hydrogen phthalate is hydrolysed in 0·4N-alcoholic alkali containing 1% of water, the resulting methyl-2-thienylcarbinol is 97% optically pure. Hydrolysis by approximately 10N-aqueous alkali gives a carbinol which is 88% optically pure. *p*-Methoxyphenyl-α-naphthylcarbinol (Part IV, *loc. cit.*) is about 50% racemised when prepared by hydrolysis of its hydrogen phthalate with 10N-aqueous alkali. It therefore appears that the tendency to alkyl–oxygen fission in the ester of methyl-2-thienylcarbinol is less than in the esters of substituted diphenylcarbinols, but greater than in the esters of substituted allyl alcohols (Part I, *J.*, 1942, 556) which yield neither the neutral ester nor the sulphone by the methods now under discussion.

EXPERIMENTAL.

The preparation of (+)- and (−)-methyl-2-thienylcarbinol is described by Anderson, Balfe, and Kenyon (*loc. cit.*).

Di(methyl-2-thienylcarbinyl) Phthalate.—The oil which separated during 12 hours from a solution of the (+)-hydrogen phthalate (5 g.) and sodium hydroxide (0·18 g.) in water (100 c.c.) was dissolved in ether, and the solution dried and concentrated. Methyl-2-thienylcarbinol (1·5 g.; b. p. 99°/18 mm.; n_D^{20} 1·5413) was distilled from the residue, leaving the crude neutral *phthalate* as a gum (0·7 g.) (Found, by hydrolysis with boiling alcoholic potassium hydroxide: equiv., 203. $C_{20}H_{18}O_4S_2$ requires equiv., 193); it could not be crystallised. The aqueous residue was acidified and filtered, evaporated to dryness, and extracted with ethyl alcohol; a combined yield of 2·6 g. of phthalic acid, m. p. 198° (decomp.), was obtained.

Methyl-2-thienylcarbinyl p-*Tolyl Sulphone.*—A filtered solution of the (−)-hydrogen phthalate (2 g.; $[\alpha]_D^{20}$ −10·0° in benzene) in 0·5N-aqueous sodium hydroxide (20 c.c.) was quickly mixed with a solution of sodium toluene-*p*-sulphinate (1·5 g.) in water (25 c.c.). After 24 hours the crystalline deposit (0·6 g.) was separated and recrystallised from ethyl alcohol, yielding the crude *sulphone*, m. p. 89—91° (Found: C, 58·4; H, 5·0; S, 22·2. $C_{13}H_{14}O_2S_2$ requires C, 58·6; H, 5·3; S, 24·2%), which was optically inactive.

Hydrolysis of (−)-Methyl-2-thienylcarbinyl Hydrogen Phthalate.—The acid ester (4·3 g.; $[\alpha]_D$ −20·5° in benzene, *i.e.*, 35% of the maximum rotatory power) was dissolved in a very concentrated solution of sodium hydroxide (1·6 g.) through which a current of steam was passed and the volume of the solution kept below about 5 c.c. The recovered alcohol (1·7 g.) had b. p. 89°/10 mm., $[\alpha]_D^{18}$ −7·6° (*l*, 2; *c*, 5·00 in benzene).

Thanks are expressed to Imperial Chemical Industries Limited for grants and to the Department of Scientific and Industrial Research for a maintenance grant (to I. G. A.).

BATTERSEA POLYTECHNIC, LONDON, S.W.11.

[*Received, October* 10*th*, 1950.]