View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1936. Downloaded by University of California - San Diego on 16/12/2016 20:01:29.

140. *The Resolution of α-Furylmethylcarbinol.*

By D. I. Duveen and J. Kenyon.

In the course of investigations on the relationship between chemical constitution and optical activity, numerous secondary alcohols of the general formula CHRMe·OH have been resolved into their optically active forms. In the compounds so far examined, R has been either an open-chain, saturated or unsaturated, or a homocyclic, aromatic or hydroaromatic, radical. With the object of extending the investigations to include alcohols in which the radical R is heterocyclic, *dl*-α-furylmethylcarbinol has been resolved into its *d*- and *l*-forms.

The following table shows that the optical rotatory dispersion of these alcohols is normal and of the same order of magnitude as that of the other secondary alcohols mentioned above.

R =	*n*-C_6H_{13}.	C_6H_{11}.	Ph.	CH_2Ph.	$CH_2Ph·CH_2$.	α-C_4H_4O.
$\alpha^{20°}_{4358}/\alpha^{20°}_{5461}$	1·65	1·74	1·74	1·83	1·67	1·68

dl-α-Furylmethylcarbinol (Peters and Fischer, *J. Amer. Chem. Soc.*, **1930**, **52**, 2079) is smoothly converted into its hydrogen phthalic ester, but it is interesting to note that when the hydrolysis of the (+)- or the (—)-acid esters is effected by dilute aqueous sodium hydroxide the rotatory powers of the resulting alcohols are much reduced, whilst when aqueous sodium carbonate or steam alone is employed, the alcohol obtained is optically inactive. This type of behaviour was not noticed in the hydrolysis of the hydrogen phthalic esters

View Article Online

Published on 01 January 1936. Downloaded by University of California - San Diego on 16/12/2016 20:01:29.

of the other alcohols enumerated above, but it occurred during the hydrolysis of (+)-γ-phenyl-α-methylallyl hydrogen phthalate (Kenyon, Partridge, and Phillips, this vol., p. 85).

A second interesting feature of (—)-α-furylmethylcarbinyl hydrogen phthalate is its interaction with cold acetic acid, by which it is converted into phthalic acid and *dl*-α-furylmethylcarbinyl acetate, whereas the hydrogen phthalic esters of purely aliphatic and of semi-aromatic (*e.g.*, phenyl-*n*-propylcarbinol) secondary alcohols are not affected by prolonged heating with glacial acetic acid.

Attempts to reduce α-furylmethylcarbinol to the corresponding tetrahydro-compound by the use of palladium and platinum catalysts under a pressure of 2 atm. were fruitless.

Specific Rotatory Powers of (—)-*α-Furylmethylcarbinyl Hydrogen Phthalate in Solvents* (*l*, 2).

Solvent.	*c*.	$[\alpha]_{5893}^{19°}$.	$[\alpha]_{5790}^{19°}$.	$[\alpha]_{5461}^{19°}$.	Solvent.	*c*.	$[\alpha]_{5893}^{19°}$.	$[\alpha]_{5790}^{19°}$.	$[\alpha]_{5461}^{19°}$.
EtOH	5·492	−3·6°	−3·4°	−3·1°	HOAc	5·050	26·9°	—	34·2°
Et_2O	4·733	9·5	10·4	11·7	$CHCl_3$	5·025	39·6	—	47·7
C_5H_5N	5·425	11·5	—	13·5	CS_2...........	5·122	68·5	75·3°	82·2

Specific Rotatory Powers of (—)-*α-Furylmethylcarbinol in Solvents.*

Solvent.	*c*.	$[\alpha]_{5893}$.	$[\alpha]_{5790}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
EtOH	6·025	−17·0°	−18·5°	−20·4°	−33·2°
Et_2O....................................	6·100	22·6	23·6	27·0	43·2
CS_2	5·473	23·6	24·9	27·5	48·0

EXPERIMENTAL.

dl-α-Furylmethylcarbinol, prepared in 56% yield by addition of furfuraldehyde (0·9 mol.) to methylmagnesium bromide (1 mol.), had b. p. 162—163° and 70°/15 mm., $n_D^{15°}$ 1·4827 (Peters and Fischer, *loc. cit.*, give $n_D^{25°}$ 1·4785) (Found : C, 63·5; H, 7·0. Calc. : C, 64·2; H, 7·1%). Its p-*xenylurethane* formed white needles, m. p. 114° from benzene (Found : N, 4·5. $C_{19}H_{17}O_3N$ requires N, 4·6%). Peters and Fischer (*loc. cit.*) were unable to prepare the *acetate* by Einhorn's method : we experienced no difficulty when the reaction was allowed to proceed at room temperature, and obtained a theoretical yield, b. p. 177°/760 mm., 85°/18 mm., $n_D^{15°}$ 1·4618 (Found : C, 62·7; H, 7·0. $C_8H_{10}O_3$ requires C, 62·4; H, 6·9%).

dl-α-Furylmethylcarbinyl Hydrogen Phthalate.—Phthalic anhydride (74 g.) was dissolved in hot pyridine (45 g.), and the cooled suspension mixed with the carbinol (56 g.). The mixture was then kept at room temperature with occasional shaking for 1·5 hours. The resulting viscous liquid, dissolved in acetone (1·5 vols.), was mixed with a slight excess of dilute hydrochloric acid and ice, followed by sufficient water completely to precipitate the oily *hydrogen phthalate*, which soon set to a crystalline mass (104 g.), m. p. 77—79°. This separated from ether and light petroleum in irregular rhombs, m. p. 80° (1·124 g. required 0·179 g. NaOH. Calc. : 0·173 g.).

Resolution of the dl-*hydrogen phthalate.* Quinidine (580 g.) dissolved readily in a warm solution of the *dl*-acid ester (420 g.) in acetone (1500 c.c.) : the resulting quinidine salt (470 g., m. p. 71°), after being thrice recrystallised from acetone (1200 c.c.), formed irregular prisms (415 g.), m. p. 82°; $[\alpha]_{5893}^{19°}$ + 76·8°, $[\alpha]_{5461}^{19°}$ + 91·9°, $[\alpha]_{4358}^{19°}$ +106·2° (*c*, 5·365; *l*, 2, in chloroform). This on decomposition with dilute hydrochloric acid gave *l*-α-furylmethylcarbinyl hydrogen phthalate, which crystallised from ether and light petroleum in rosettes of cotton-wool-like needles, m. p. 61°, $[\alpha]_{5893}^{19°}$ − 39·3°, $[\alpha]_{5461}^{19°}$ − 47·6° (*l*, 2; *c*, 4·515, in chloroform).

The more soluble fractions of the quinidine salt on decomposition with hydrochloric acid yielded the *d*- + *dl*-acid ester (170 g.), which was combined with brucine (255 g.) in dry acetone (800 c.c.). After two recrystallisations from dry acetone, the brucine salt (252 g.) was obtained as a mass of hairy needles, m. p. 81°, $[\alpha]_{5893}^{20°}$ + 13·4°, $[\alpha]_{5461}^{20°}$ + 13·9° (*c*, 5·025; *l*, 2, in chloroform). On decomposition as before, this yielded *d*-α-furylmethylcarbinyl hydrogen phthalate, which crystallised exactly like the *l*-ester, m. p. 61°, $[\alpha]_{5893}^{19°}$ + 39·6°, $[\alpha]_{5461}^{19°}$ + 47·7° (*c*, 5·240; *l*, 2, in chloroform).

l-α-Furylmethylcarbinol, obtained by saponification of its hydrogen phthalate with aqueous 10*N*-caustic soda, had b. p. 70°/15 mm., $n_D^{15°}$ 1·4828, $\alpha_{5893}^{19°}$ − 40·07°, $\alpha_{5790}^{19°}$ − 42·0°, $\alpha_{5461}^{19°}$ −47·7°, $\alpha_{4358}^{19°}$ −81·3° (*l*, 2). This alcohol was prepared in much larger amount than was its (+)-isomeride and thus was, during its removal by distillation in steam, in contact with concentrated alkali

View Article Online

Published on 01 January 1936. Downloaded by University of California - San Diego on 16/12/2016 20:01:29.

for a longer period. The close agreement in the magnitudes of the rotatory powers of the two alcohols suggests that but little racemisation has occurred.

The *d*-alcohol, similarly obtained, had b. p. 70°/15 mm., $n_D^{15°}$ 1·4827, $\alpha_{5893}^{18°}$ + 10·29°, $\alpha_{5790}^{18°}$ + 10·30°, $\alpha_{5461}^{18°}$ + 11·80°, $\alpha_{4358}^{18°}$ + 21·20° (*l*, 0·5). The rotatory powers of these alcohols are almost unaffected by small changes (*ca.* 5°) of temperature.

(—)-*α-Furylmethylcarbinyl acetate.* A mixture of the (—)-alcohol (5·6 g.), pyridine (6 g.), and acetic anhydride (6 g.) was kept at room temperature for two days and then worked up: the resulting acetate (8 c.c.) had b. p. 77°/11 mm., $n_D^{16°}$ 1·4616, $\alpha_{5893}^{16°}$ — 60·85°, $\alpha_{5790}^{16°}$ — 64·20°, $\alpha_{5461}^{16°}$ — 73·28°, $\alpha_{4358}^{16°}$ — 135° (*l*, 0·5).

Conversion of (—)-*α-Furylmethylcarbinyl Hydrogen Phthalate into the* dl-*Acetate.*—The rotatory power of the solution of (—)-α-furylmethylcarbinyl hydrogen phthalate in glacial acetic acid (see table) diminished slowly, becoming zero after 2 days; at the same time phthalic acid was deposited and the solution developed a strong odour of α-furylmethylcarbinyl acetate. In view of this result the following experiment was performed. A solution of *dl*-α-furylmethylcarbinyl hydrogen phthalate (12·5 g.) in glacial acetic acid (25 c.c.) was kept for 2 days at room temperature, then diluted with dry chloroform, and the crystals (7·3 g., m. p. 203°) removed. The filtrate yielded *dl*-α-furylmethylcarbinyl acetate (7 c.c.), b. p. 77°/11 mm., $n_D^{16°}$ 1·4617.

Thanks are due to the Government Grants Committee of the Royal Society and to Imperial Chemical Industries Ltd. for grants.

BATTERSEA POLYTECHNIC, LONDON, S.W. 11. [*Received, March 24th,* 1936.]