83. *Alkyl–Oxygen Fission in Carboxylic Esters. Part VII. Hydrolysis of Methyl-β-naphthylcarbinyl Hydrogen Phthalate.*

By M. P. BALFE, J. KENYON, and C. E. SEARLE.

The hydrolysis of the hydrogen phthalate in a variety of alkaline solutions confirms that the racemising mechanism (probably unimolecular) occurs in low concentrations of alkali, and at higher concentrations of alkali is suppressed by the mechanism (probably bimolecular) which results in retention of optical activity.

Ethers of methyl-β-naphthylcarbinol are described, and the *p*-tolyl sulphones of methyl-α- and -β-naphthylcarbinols. Reduction of methyl β-naphthyl ketone by zinc in alkaline solution gives the corresponding glycol, which readily undergoes the pinacone rearrangement.

IN previous communications in this series (*J.*, 1942, 556, 605; 1945, 797, 803, 807), the observations of the effect of strength of alkali on the rotatory powers of carbinols with electron-releasing substituents, obtained by hydrolysis of their hydrogen phthalates, have been confined to experiments with "strong alkali" (*e.g.*, excess of 10N-sodium hydroxide) and "weak alkali" (*e.g.*, sodium carbonate or sodium hydroxide in small excess). We have thought it of interest to examine the effect of intermediate alkalinities, and have used (+)-methyl-β-naphthylcarbinyl hydrogen phthalate as substrate. During the hydrolysis, the alkalinity of the solution necessarily decreases, and it is undesirable to counteract this by the use of buffered solutions, since the anions thus introduced might divert a part of the reaction. To keep the decrease of alkalinity as small as possible, we have used as low a concentration of hydrogen phthalate as is consistent with isolation of the liberated carbinol; the table gives the percentage of racemisation observed in carbinols formed by hydrolysis of the hydrogen phthalates in a variety of alkaline solutions, the initial and final alkalinities (hydroxyl-ion

Hydrolysis of optically active hydrogen phthalates
(at 90° unless otherwise stated).

Hydrogen phthalate. of :		Alkali.		OH′ activity.†		Racemisation, %, of liberated carbinol.
	*c.**		*c.**	Initial.	Final.	
Methyl-*β*-naphthylcarbinol	0·62	NaOH	2·50	2500 ‡	—	nil
,, ,,	0·025	,,	0·50	339	302	3
,, ,,	0·079	Na_3PO_4	0·67	76	7·9	4
,, ,,	0·031	NH_4OH §	19·6	11·2	1·3	2
,, ,,	0·021	Na_2CO_3	0·28	3·3	0·35	19
,, ,,	0·21	,,	0·09	0·66	0·12	43
,, ,,	0·083	,, ‖	0·05	0·22	0·07	48
2-Octyl alcohol	0·055	Na_3PO_4	0·73	43·7	5·5	nil
,, ,, ...	0·024	Na_2CO_3	0·28	3·2	0·4	nil

* Moles/litre. † Millimoles/litre.
‡ Calc. from *c*, an activity coefficient of 1·0 being assumed.
§ At 20°, hydrolysis not completed. ‖ At 100°.

activities) of which are recorded. The increase in racemisation, with decreasing alkalinity of solution, is clearly illustrated, and a plot of percentage racemisation against mean alkalinity gives a fairly smooth curve. On the other hand, no racemisation occurs during the hydrolysis of (+)-2-octyl hydrogen phthalate in solutions which produce nearly 50% racemisation in the hydrolysis of the methyl-β-naphthylcarbinyl ester.

Methyl and ethyl methyl-β-naphthylcarbinyl ethers are formed when the (±)-hydrogen phthalate is heated with the appropriate alcohol, and di(methyl-β-naphthylcarbinyl) ether is formed on heating the carbinol at 200°. *p*-Tolyl sulphones are formed on warming methyl-α- and -β-naphthylcarbinyl hydrogen phthalates with sodium toluene-*p*-sulphinate in formic acid.

Aluminium *iso*propoxide is the best reducing agent for preparation of methyl-β-naphthylcarbinol from the ketone. Sodium amalgam gives a higher proportion of by-products, and zinc with alcoholic sodium hydroxide gives only 1 : 2-dimethyl-1 : 2-di-β-naphthylethylene glycol, which when heated in acetic anhydride undergoes the pinacol–pinacone transformation.

EXPERIMENTAL.

(−)-Methyl-*β*-naphthylcarbinyl hydrogen phthalate, prepared as described by Collyer and Kenyon (*J.*, 1940, 676), had m. p. 91—93°, $[\alpha]_D^{17}$ −49·9° in ethyl alcohol (*c*, 2·5). The (+)-2-octyl ester was prepared as described by Kenyon (*Org. Synth.*, Coll. Vol. I, 410).

Hydrolysis.—Solutions of the hydrogen phthalate (3-g. portions) in the appropriate alkali (see table) were heated, mostly at 90° (table). The carbinols separated as oils, and heating was continued for 2 hours after this separation ceased (total times ranged between 2 and 4 hours). pH values of initial and final solutions were measured with the "Alki" electrode on a Cambridge pH meter at 20°, and hydroxyl-ion activities were calculated from the appropriate value of K_w. The liberated carbinols were isolated in approximately theoretical yield by extraction of the final solution with ether; which extracts were then dried (K_2CO_3) and freed from solvent. The carbinols were converted into hydrogen phthalates by the usual method, and these esters extracted from ethereal solution with aqueous sodium carbonate, precipitated with hydrochloric acid, washed, and dried ($CaCl_2$). The % racemisation in the table is the rotatory power of the recovered phthalate as a percentage of that of the original phthalate. Recrystallisation of the recovered phthalate was not permissible since it might effect optical enrichment.

Methyl-β-naphthylcarbinyl Ethers.—The (±)-hydrogen phthalate (4 g.) was heated under reflux in 75% aqueous ethyl alcohol (60 c.c.) for 60 hours. The mixture was then diluted with water and extracted with ether. The extract was washed with sodium carbonate solution, dried (Na_2SO_4), and concentrated. Distillation of the residual oil (2·6 g.) yielded the *ethyl ether*, b. p. 145—148°/16 mm., n_D^{18} 1·5743 (Found: C, 84·1; H, 8·4. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%). The *methyl ether*, prepared similarly by use of aqueous methyl alcohol, had b. p. 148—151°/18 mm., n_D^{15} 1·5829 (Found: C, 83·7; H, 7·6. $C_{13}H_{14}O$ requires C, 83·9; H, 7·5%). *Di(methyl-β-naphthylcarbinyl) ether* was formed on heating the carbinol at 200° for 3 hours. A little carbinol was distilled from the product, and the residue, on redistillation, gave the ether, b. p. 240—245°/14 mm. (Found: C, 88·0; H, 6·7. $C_{24}H_{22}O$ requires C, 88·3; H, 6·7%).

Methyl-α- and -β-naphthylcarbinyl p-*Tolyl Sulphones.*—The hydrogen phthalate (2·0 g.) of the α-carbinol (*J.*, 1946, 797) and of the β-carbinol were separately heated at 90° with sodium toluene-*p*-sulphinate (1·3 g.) in formic acid (25 c.c.), then diluted with water, and the precipitates recrystallised from ethyl alcohol. The *sulphone* of the α-carbinol had m. p. 144·5° (Found: S, 10·5%); that of the β-carbinol had m. p. 153—154° (Found: S, 10·2. $C_{19}H_{18}O_2S$ requires S, 10·3%).

Reduction of Methyl β-Naphthyl Ketone.—*With aluminium* iso*propoxide.* See Collyer and Kenyon (*loc. cit.*).

With zinc and alcoholic alkali. The ketone (10 g.), zinc dust (10 g.), and sodium hydroxide (10 g.) were heated under reflux in ethyl alcohol (100 c.c.) for 5 hours. The mixture was filtered and diluted with water, and the precipitate recrystallised from ethyl alcohol, yielding 1 : 2-*dimethyl*-1 : 2-*di-β-naphthylethylene glycol*, m. p. 184° [Found, after heating at 110°/20 mm. over P_2O_5 for 1 hour: C, 83·9; H, 6·2%; *M* (Rast), 310. $C_{24}H_{22}O_2$ requires C, 84·2; H, 6·4%; *M*, 342]. The glycol was heated under reflux in acetic anhydride for 1½ hours, and the mixture diluted with water; the precipitate, recrystallised from aqueous ethyl alcohol, yielded a *compound*, m. p. 144—145° (Found: C, 88·5; H, 6·4. $C_{24}H_{20}O$ requires C, 88·9; H, 6·2%), probably the pinacone (or mixture of the two possible pinacones), since it gave a precipitate (difficult to purify) with 2 : 4-dinitrophenylhydrazine.

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

BATTERSEA POLYTECHNIC, LONDON, S.W.11.

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