169. *Alkyl–Oxygen Fission in Carboxylic Esters. Part IV.*

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Esters of optically active anisyl-1-naphthylcarbinol and anisylmethylcarbinol react, with racemisation, with carboxylic acids and with alcohols. When the hydrogen phthalates of these alcohols are hydrolysed by dilute aqueous alkali racemisation occurs, but optical purity is maintained on hydrolysis by concentrated alkali in alcoholic solution. From aqueous solutions of sodium salts of the optically active hydrogen phthalates, half-racemised neutral esters separate; in the presence of sodium *p*-toluenesulphinate, the sodium salts are converted into racemic sulphones. The hydrogen succinate of anisyl-1-naphthylcarbinol undergoes similar reactions. These reactions are similar to those described in Parts I (*J.*, 1942, 556), II (*J.*, 1942, 605), and III (previous paper).

The dependence of alkyl–oxygen fission on electron-release in the carbinol radical, stability of the anion, and ionising power of the medium is surveyed. The solubility of acid esters in dilute alkaline media is a factor which makes the occurrence of alkyl–oxygen fission, during alkaline hydrolysis, more common in acid than in neutral esters.

(+)Anisylnaphthylcarbinol is obtained *via* fractional crystallisation of the brucine salt of the *dl*-hydrogen phthalate or succinate, and (+)anisylmethylcarbinol similarly from the cinchonidine salt of the *dl*-hydrogen phthalate. The reactions of the hydrogen phthalate and succinate of these carbinols, which are exactly analogous to those of *p*-methoxybenzhydrol (Part II, *loc. cit.*) and other carbinols (Part III, *loc. cit.*), are described below, and need little further discussion. To four points, brief reference is desirable. (i) The neutral phthalate (*lævo*-anisyl-1-naphthylcarbinyl phthalate), deposited from a solution of (—)anisyl-1-naphthylcarbinyl hydrogen phthalate in one molecular proportion of aqueous sodium hydroxide, is obtained in crystalline form, as were those of *p*-methoxy-*p*′-methyl- and p-methoxy-*p*′-*iso*propyl-benzhydrols (Part III, *loc. cit.*) [the neutral phthalate originally prepared by this method {that of *p*-methoxybenzhydrol, Part II, *loc. cit.*) did not crystallise].

(ii) The *dl*-neutral phthalate is formed from the (—)hydrogen phthalate in chloroform solution, with deposition of phthalic acid. This complete racemisation is in contrast to the half-racemisation which occurs when the neutral phthalate is deposited from aqueous solution. In chloroform, the neutral ester remains dissolved, and there is a continued interchange of anisylnaphthylcarbinol kations, leading to complete racemisation; from aqueous solution it separates when only half the anisylnaphthylcarbinol groups have undergone racemisation.

(iii) A half-racemised *laevo*-neutral succinate is obtained from the (—)hydrogen succinate of anisyl-1-naphthylcarbinol, in the same way as the *laevo*-neutral phthalate.

(iv) The α-methyl group in anisylmethylcarbinol enables its kation to decompose to an olefin. *p*-Methoxystyrene is formed from the carbinol on heating (or slowly at room temperature) and also during hydrolysis of the hydrogen phthalate (by steam-distillation from alkaline solution) under conditions where alkyl–oxygen fission occurs.

1 : 1′ Di-*p*-methoxyphenyldiethyl ether is also formed under the above conditions, presumably by interaction of carbinol molecules with anisylmethylcarbinol kations. Corresponding ethers are formed on heating *p*-methoxybenzhydryl- or anisylnaphthyl-carbinol, but were not observed in the products of hydrolysis of their hydrogen phthalates, possibly because the carbinols crystallised rapidly from the warm alkaline solutions, thus avoiding the prolonged heating of steam-distillation.

It is convenient to summarise the general conclusions so far drawn in these investigations (on the particular points of the mechanisms of the neutral ester and sulphone formations, we are not yet able to add to the discussion given in Part II, *loc. cit.*).

With regard to the reactions of esters with acids or alcohols:

(i) The reactivity of the esters decreases as electron-availability at the carbinol carbon atom decreases, the order in terms of the carbinols from which the esters are derived being: (*a*) Anisyl-1-naphthylcarbinol, *p*-methoxybenzhydrol, and other *p*-alkoxyarylcarbinols, roughly in order of electron release from the substituent groups (see Parts II, III, V). (*b*) Anisyl alcohol (see Part III). (*c*) α- and γ-Substituted allyl alcohols (see Part I). (*d*) 1-Naphthylmethylcarbinol, and *o*-chloro- and *m*-methoxy-benzhydrol (see Part III). (*e*) Phenylmethylcarbinol (see Part III).

(ii) The solvent-reactants can be arranged in order of decreasing reactivity: formic acid > acetic acid > ethyl or methyl alcohol. Some esters which do not react with anhydrous solvents do so when water is added to the solution (Part III).

(iii) Increase in ease of separation of the anion favours the reaction. Thus the *p*-toluenesulphinate of phenylmethylcarbinol reacts with anhydrous acetic acid (*J.*, 1933, 173) while its hydrogen phthalate does not (compare K of toluenesulphinic acid, *ca.* 10^{-2}; first K of phthalic acid, *ca.* 10^{-3}).

(iv) The above observations agree with the suggested unimolecular mechanism (Part I), the ionisation of the ester being promoted by electron-release in the carbinol radical, by stability of the anion, and by the dissociating effect of the solvent. When these factors result in alkyl–oxygen fission, a state of equilibrium is set up, and the reaction is forced to completion in accordance with the mass-action principle; in our experiments there is usually excess of one reactant (*e.g.*, acid or alcohol), and one product (*e.g.*, phthalic acid) separates from the solution.

With regard to alkaline hydrolysis, our results are complementary, not contradictory, to previous investigations in which alkyl–oxygen fission was found not to occur. The most relevant case is that of Ingold and Ingold (*J.*, 1932, 756), who found that rearrangement did not occur in the hydrolysis of α-methylallyl acetate by 0·2N-sodium hydroxide. This ester is less likely to react by alkyl–oxygen fission than the esters of the αγ-disubstituted allyl alcohols which we described in Part I (see Balfe, Hills, Kenyon, Phillips, and Platt, *J.*, 1943, 348), and the medium used by Ingold and Ingold contained a higher concentration of hydroxyl ions than the weak alkalis found to promote alkyl–oxygen fission in esters of the substituted allyl alcohols. It is to be observed that our experiments, as yet, have been confined to the hydrolysis of acid esters, in which the main effect of weak alkalis is to bring the ester into solution in an ionising medium (water) in which the concentration of free hydroxyl ions is not high, but from which the carbonium kation can extract hydroxyl ions. Thus, as Day and Ingold (*Trans. Faraday Soc.*, 1941, **37**, 686) pointed out, the hydrolysis with " weak alkali " is in effect hydrolysis in neutral solution. Ionisation of the free carboxyl group, though necessary in the above scheme, does not in itself promote alkyl–oxygen fission, but must act against it, though, as the results show, does not prevent it. The point is discussed in more detail by Arcus and Kenyon (*J.*, 1938, 1912), though the suggestion there made, that in weakly alkaline solutions the hydrogen phthalates dissolve partly in the un-ionised form, cannot be upheld. In both strong and weak alkali (*i.e.*, at any pH value above about 7·5) the acid ester can only be present as an anion, and the different results obtained with alkaline solutions of different strengths must be ascribed to variations in their hydroxyl-ion concentrations. These variations are the controlling factor in the hydrolysis of esters in which there is a moderate tendency to alkyl–oxygen fission (*e.g.*,, substituted allyl esters), but is less important when the tendency to this mechanism is strong (*e.g.*, in *p*-alkoxybenzhydryl esters); in this case alkyl–oxygen fission occurs even when the concentration of hydroxyl ions is high, and can only be suppressed by reducing the ionising power of the solvent (*e.g.*,, replacing water by ethyl alcohol).

These considerations need not apply to the hydrolysis of esters of monobasic acids, which is commonly brought about by strong alkali, which favours acyl–oxygen fission because of the high concentration of hydroxyl ions. It is also possible that when the ester remains as a separate phase the hydrolysis is initiated by attack of hydroxyl ions, on surface ester molecules, a bimolecular process favouring acyl–oxygen fission. When the ester is brought into solution by addition, *e.g.*, of ethyl alcohol, the alkyl–oxygen mechanism is again retarded because the ionising power of the medium is diminished.

EXPERIMENTAL.

dl-Anisyl-1-naphthylcarbinol (prepared by Grignard reaction) has m. p. 87° (Shurakowski, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1692, gives m. p. 87°). A mixture of the carbinol (26·5 g.), powdered phthalic anhydride (15 g.), benzene (30 c.c.), and pyridine (10 c.c.), brought to solution by gentle warming then left 3 days at room temperature (development of yellow colour indicates decomposition), yielded the *dl*-phthalate, which, recrystallised from benzene–light petroleum and then from benzene, was obtained in prisms, m. p. 151° (40 g.) (Found, by rapid titration with 0·1N-sodium hydroxide: *M*, 410. Calc. for $C_{26}H_{20}O_5$: *M*, 412). From acetone the phthalate separated with 1 mol. of solvent, m. p. 85° (Found: equiv., 471. Calc. for $C_{26}H_{20}O_5,C_3H_6O$: equiv., 470). A solution of these crystals in ethyl alcohol yielded the 2 : 4-dinitrophenylhydrazone of acetone, m. p. and mixed m. p. 128°. The m. p. of these crystals slowly rose and after 10 weeks was 151°. From the phthalate (104 g.) and brucine (117 g.) in a mixture of acetone (100 c.c.) and ethyl acetate (200 c.c.) after 2 days a brucine salt separated. After 4 recrystallisations from acetone–ethyl acetate, this yielded brucine (—)anisyl-1-naphthylcarbinyl phthalate (100 g., m. p. 129—130°, decomp.) from which the (—)hydrogen phthalate was obtained as crystalline powder, m. p. 62—63° (Found: *M*, 415). Rotatory powers are in Table I.

The (—)hydrogen phthalate rapidly racemised in solution; in the solid state it slowly changed to a gummy mass, with extensive racemisation, and was then largely neutral phthalate.

(—)*Anisyl-1-naphthylcarbinol.*—From the (—)phthalate (2 g., $[\alpha]_{5893}$ —58° in carbon disulphide) in ethyl alcohol

(120 c.c.) by sodium hydroxide (0·5 c.c. of 50%). M. p. 113—114°. Recrystallised from ether–light petroleum, it had m. p. 114—115° [1·1 g., bulky clusters of needles, $[\alpha]_{5893}$ −60·5° in carbon disulphide (*l*, 2; *c*, 1·5)]. Hydrolysis of the (−)phthalate with 10N-sodium hydroxide (excess) gave a *laevo*-carbinol, m. p. 80—96°, $[\alpha]_{5893}$ −29·2° (*l*, 2; *c*, 1·0 in carbon disulphide); 0·3N-sodium carbonate (excess) gave a carbinol with $[\alpha]_{5893}$ −14·4° (*l*, 2; *c*, 1·0 in carbon disulphide), m. p. 72—83°. From the mother liquors from recrystallisation of the above brucine salt, a *dextro*-carbinol was obtained, m. p. 73—76°, $[\alpha]_{5893}$ +42° in carbon disulphide. Twice recrystallised from ether–light petroleum, it had m. p. 114—115°, $[\alpha]_{5893}$ +60·2° (*l*, 2; *c*, 1·5 in carbon disulphide). The *dl*-carbinol, m. p. 87°, crystallised from the ether–light petroleum filtrate.

dl-1-*Naphthylcarbinyl Hydrogen Succinate.*—Prepared in the same way as the phthalate, this formed clusters of prisms, m. p. 125° (Found: *M*, 362. Calc. for $C_{22}H_{20}O_5$: *M*, 364). Its brucine salt, prepared in, and thrice recrystallised from, the minimum of acetone, yielded the salt of the (+)succinate (39 g. from 36 g. of *dl*-hydrogen succinate), m. p. 122—123° (decomp.). From this salt the (+)hydrogen succinate (12 g.), m. p. 55—57°, was obtained as an oil which solidified, and was ground and dried in a vacuum. Rotatory powers are in Table II. The more soluble fraction of the brucine salt gave a *laevo*-hydrogen succinate (23 g.) the cinchonidine salt of which, thrice recrystallised from acetone, yielded the cinchonidine salt of (−)-anisyl-1-naphthylcarbinyl hydrogen succinate (30 g. irregular prisms, m. p. 160°). From this salt (−)*anisyl*-1-*naphthylcarbinyl hydrogen succinate* (15 g.) was obtained; $[\alpha]_{5893}$ −49·9° in benzene (*l*, 2; *c*, 1), m. p. 53—55° (Found: *M*, 386. $C_{22}H_{20}O_5$ requires *M*, 364).

The (+) and (−)hydrogen succinates, on hydrolysis with alcoholic sodium hydroxide (see above) yielded respectively (+) and (−)anisyl-1-naphthylcarbinols, both m. p. 114—115°. On hydrolysis with 5N-sodium hydroxide, the (+)hydrogen succinate yielded carbinol with $[\alpha]_{5893}$ +25·5° in carbon disulphide (*l*, 2; *c*, 1·0), m. p. 76—89°.

dl-*Anisyl*-1-*naphthylcarbinyl phthalate* was prepared from the acid ester in aqueous sodium hydroxide. From a solution of the *dl*-ester (10 g.) in 81 c.c. of 0·3N-sodium hydroxide, the neutral *ester* crystallised (7·8 g.; calc., 8·0 g.). It recrystallised from benzene–*cyclo*hexane in clusters of small nodules, m. p. 127—128° (decomp.) (Found: C, 79·7; H, 5·6; equiv., 326. $C_{44}H_{34}O_6$ requires C, 80·2; H, 5·2%; equiv., 329. Further recrystallisation did not give a product of better analysis). The aqueous filtrate yielded phthalic acid (1·85 g.; calc., 2·0 g.). From the (−)hydrogen phthalate (2·0 g., $[\alpha]_{5893}$ −58·0° in carbon disulphide) the *lævo*-neutral ester (1·6 g.) crystallised, $[\alpha]_{5893}$ −24·6° (in carbon disulphide). This ester (0·8 g.) on hydrolysis with 0·5 c.c. of 50% sodium hydroxide in 120 c.c. of ethyl alcohol, gave a *laevo*-carbinol, m. p. 72—76° with $[\alpha]_{5893}$ −29·2° (*l*, 2; *c*, 1·5) in carbon disulphide, *i.e.*, approximately half the rotatory power of the optically pure carbinol.

Similarly, anisyl-1-naphthylcarbinyl succinate separated from a solution of the acid ester (7·3 g., $[\alpha]_{5893}$ −50·2° in benzene) in aqueous sodium hydroxide (67 c.c.; 0·3N) (5·7 g.; calc., 6·1 g.). It crystallised with difficulty, m. p. 57—58°, $[\alpha]_{5893}$ −28·0° in benzene (*l*, 2; *c*, 1·00) (Found: equiv., 298. Calc. for $C_{40}H_{34}O_6$: equiv., 304). This neutral ester (4 g.) was warmed on the steam-bath for 3 minutes with sodium hydroxide (1 c.c. of 50%) in 200 c.c. of ethyl alcohol. On dilution with water, the carbinol (3 g.) crystallised, m. p. 70—73°, $[\alpha]_{5893}$ −28° (*l*, 2·0; *c*, 1·5) in carbon disulphide, *i.e.*, approximately half-racemised. This carbinol, by one recrystallisation from ether–light petroleum, was separated into approximately equal amounts of (−)carbinol (needles, m. p. 112—113°, $[\alpha]_{5893}$ −58° in carbon disulphide) and almost racemic carbinol (prisms, m. p. 87°).

Dismutation of the Hydrogen Phthalate of Anisyl-1-*naphthylcarbinol.*—From the *dl*-hydrogen phthalate (8·25 g.), heated under reflux in dry chloroform (30 c.c.) for several hours, phthalic acid (1·6 g.; calc., 1·7 g.) separated. On evaporation of the filtrate, trituration of the residue with light petroleum, and crystallisation from benzene–*cyclo*hexane, the neutral phthalate (m. p. 127—128°) was obtained (6·45 g.; calc., 6·6 g.). From a solution of the (−)hydrogen phthalate (4·2 g.) in chloroform, after 48 hours at room temperature, phthalic acid and the *dl*-neutral phthalate, m. p. 122—123° (3·1 g.; calc., 3·3 g.) were obtained in a similar way.

p-*Tolyl Anisyl*-1-*naphthylmethyl Sulphone.*—A solution of the *dl*-hydrogen phthalate (4·1 g.) in sodium hydroxide (34 c.c. of 0·3N) was filtered rapidly into a solution of sodium *p*-toluenesulphinate (2·2 g.) in water (50 c.c.). After 2 days, the crystalline mass of dl-*sulphone* was removed, washed, and dried (3·9 g.; calc., 4·0 g.). Twice recrystallised from water it was obtained in prisms, m. p. 141° (Found: S, 8·1. $C_{25}H_{22}O_3S$ requires S, 8·0%). The filtrate yielded phthalic acid (1·6 g.; calc., 1·7 g.).

From the (−)hydrogen phthalate, and the *dl*- and (+)hydrogen succinate, the *dl*-sulphone, m. p. 141°, was obtained.

Anisyl-1-*naphthylmethyl Ethyl Ether.*—The *dl*-hydrogen phthalate (4·1 g.) was heated under reflux in ethyl alcohol (200 c.c.) for 6 hours. On cooling, the ethyl ether (2·1 g.) crystallised; a further 0·75 g. (total, 2·85 g.; calc., 2·9 g.) was obtained from the filtrate together with phthalic acid (1·65 g.; calc., 1·7 g.). The dl-*ethyl ether* crystallised from ethyl alcohol in flat rhombs, m. p. 61° (Found: C, 82·4; H, 7·0. $C_{20}H_{20}O_2$ requires C, 82·2; H, 7·0%). The *dl*-ether was similarly obtained from the (−)hydrogen phthalate, the *dl*- and *laevo*-neutral phthalates, and the *dl*- and (+)-hydrogen succinates.

dl-*Anisyl*-1-*naphthylmethyl methyl ether* (rhombs, m. p. 50°) was obtained similarly from the (−)acid phthalate and succinate or *laevo*-neutral phthalate and succinate in methyl alcohol (Found: C, 81·6; H, 6·5. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%).

dl-*Dianisyl*-1-*naphthylmethyl Ether.*—The *dl*-carbinol (4 g.) was heated at 200° for 3 hours. Unchanged carbinol (2·6 g., m. p. 87°) was removed by trituration with warm ether. The residue (1·2 g., m. p. 152—154°) after three recrystallisations from benzene–ether yielded the *ether* as clusters of prisms, m. p. 160—161° (Found: C, 84·9; H, 5·8. $C_{36}H_{30}O_3$ requires C, 84·7; H, 5·9%).

dl-*Anisyl*-1-*naphthylmethyl Chloride.*—The *dl*- and the (+)-carbinol were immediately converted into the *dl*-chloride by trituration with cold concentrated hydrochloric acid. The chloride did not crystallise; it dissolved in warm light petroleum and separated on cooling as a colourless oil (Found by titration with N-sodium hydroxide: *M*, 277. Calc. for $C_{18}H_{15}OCl$: *M*, 282·5). From a solution of the chloride (2·5 g.) in ethyl alcohol (20 c.c.), on evaporation at room temperature, the *dl*-ethyl ether (2·5 g., m. p. 61°) crystallised.

dl-Anisylmethylcarbinol (88% yield), from methylmagnesium bromide (1 mol.) and anisaldehyde (110 g.; 0·8 mol.) at 0° (the complex being decomposed with ice and ammonium chloride), has b. p. 140—141°/17 mm., $n_{\mathrm{D}}^{24^\circ}$ 1·531. Klages (*Ber.*, 1903, **36**, 3592) gives n_{D} 1·537. The residue from distillation of the carbinol yields 1 : 1′-di-*p*-methoxyphenyldiethyl ether (3 g.), m. p. 51°.

TABLE I.

Specific Rotatory Powers of (−)*Anisyl*-1-*naphthylcarbinyl Hydrogen Phthalate in Various Solvents* (*l*, 2; *c*, 1·00).

Solvent.	*t*.	λ_{6438}.	λ_{5893}.	λ_{5780}.	λ_{5461}.	λ_{4800}.	λ_{4358}.
Carbon disulphide	17·2°	−20·4°	−58°	−66·7°	−77·1°	−120°	−131·0°
Benzene	17·2	−16·00	−32·2	−33·5	−41·1	− 58	− 65
Dioxan	17·2	− 4·3	−10·9	−12·1	−14·0	− 22	− 24·0

TABLE II.

Specific Rotatory Powers of (+)*Anisyl*-1-*naphthylcarbinyl Hydrogen Succinate in Various Solvents* (*l*, 2; *c*, 1·0).

Solvent.	*t*.	λ_{6438}.	λ_{5893}.	λ_{5780}.	λ_{5461}.	λ_{4800}.	λ_{4358}.
Benzene	20°	+39·0°	+50·1°	+53·2°	+62·4°	+87·3°	+112·1°
Chloroform	20	+29·0	+33·2	+35·5	+40·2	+50·0	+ 70·3
Ethanol	20	+26·0	+30·1	+31·5	+37·6	+48·0	+ 65·2

TABLE III.

Specific Rotatory Powers of (+)*Anisyl*-1-*naphthylcarbinol* * *in Various Solvents* (*l*, 2).

Solvent.	*c*.	*t*.	λ_{6438}.	λ_{5893}.	λ_{5780}.	λ_{5461}.	λ_{4800}.	λ_{4358}.
Carbon disulphide	1·50	18°	+48·3°	+60·9°	+64·5°	+74·8°	+ 90·8°	+149·6°
Ethanol	1·51	17·5	−24·8	−31·5	−33·1	−37·1	− 50·2	− 70·4
Ether	1·50	17·5	−49·9	−64·3	−66·6	−78·6	−113·9	−162·4

* We define as (+), the carbinol obtained from the (+)hydrogen phthalate and succinate.

Decomposition of the carbinol with formation of *p*-methoxystyrene (approx. 10%) and 1 : 1′-di-*p*-methoxyphenyldiethyl ether (approx. 20%) occurs (i) if during the Grignard reaction the temperature rises above 0°, (ii) if during isolation of the carbinol temperatures above 60° are used, (iii) on heating the pure carbinol on the steam-bath (1 hour), (iv) when the pure carbinol is kept at room temperature for 30 months.

p-Methoxystyrene has b. p. 84—87°/12 mm., $n_D^{24\cdot5^\circ}$ 1·5569. Klages (*loc. cit.*) gives n_D 1·5642. It yields 1 : 2-*dibromo*-1-p-*methoxyphenylethane* (1 : 2-dibromo-1-anisylethane), needles, m. p. 80° (decomp.) from ether–light petroleum (Found : Br, 53·8. $C_9H_{10}Br_2$ requires Br, 54·4%).

1 : 1′-*Di*-p-*methoxydiphenyldiethyl ether* crystallises from aqueous acetone or methyl alcohol in needles, m. p. 51°, b. p. 212°/16 mm. (Found : C, 75·5; H, 8·0. $C_{18}H_{12}O_3$ requires C, 75·5; H, 7·7%).

dl-Anisylmethylcarbinyl hydrogen phthalate (from the alcohol, b. p. 131—133°/13 mm., phthalic anhydride, and pyridine, 1 mol. of each at 50° for 30 minutes, then decomposed with hydrochloric acid) formed short needles (m. p. 86—87°), from carbon disulphide or ether–light petroleum (yield 90%) (Found, by rapid titration with NaOH : *M*, 295. Calc. for $C_{17}H_{16}O_5$: *M*, 300). Phthalic acid was deposited from solutions of the phthalate in chloroform, methyl alcohol, or ethyl alcohol. The cinchonidine salt (needles, m. p. 150—152°) from the *dl*-phthalate and cinchonidine, in acetone, separated as the salt of the *laevo*-phthalate; decomposed with hydrochloric acid it gave *laevo*-phthalate, from which the (−)phthalate, irregular prisms, m. p. 110—115° (Found : *M*, 301), was obtained after three recrystallisations from methylene chloride–light petroleum (from the mother liquors, only *dl*-phthalate was obtained). From the more soluble fraction of the cinchonidine salt, the (+)phthalate was obtained in a similar way, m. p. 110—115° (Found : *M*, 302). Rotatory powers are in Table IV. The above procedure is quicker and more efficient than resolution by fractional crystallisation of the cinchonidine or brucine salts.

From the (+)hydrogen phthalate, the (+)carbinol was obtained on hydrolysis (9 g. of phthalate, 3 g. of sodium hydroxide, 50 c.c. of ethyl alcohol, 15 c.c. of water; one hour on steam-bath, followed by dilution with water, extraction of the liberated alcohol with ether, and subsequent distillation), b. p. 140—142°/23 mm. Rotatory powers of the (+)carbinol are in Table V.

On hydrolysis of the (+)phthalate with 3N-sodium hydroxide, some racemisation occurred, the alcohol having $\alpha_{5461}^{20^\circ}$ +26·4° (*l*, 0·5); with more dilute aqueous alkali, the amount of racemisation increased, and some *p*-methoxystyrene and di-*p*-methoxyphenyldiethyl ether were formed.

TABLE IV.

Specific Rotatory Powers of Anisylmethylcarbinyl Hydrogen Phthalate in Various Solvents (20°).

Solvent.	*c*, g. per 100 c.c.	λ_{6438}.	λ_{5893}.	λ_{5780}.	λ_{5461}.	λ_{4358}.
		(−)*Phthalate.*				
Carbon disulphide	0·101	—	−50°	−74°	−79°	−198°
Pyridine	5·005	−26·5°	−30·5	−37·9	−39	− 62
Benzene	1·195	−23·0	−30·5	−37·2	−37·6	− 69
Acetic acid	5·000	—	−20·9	—	−23·7	− 40·5
Methylene chloride	5·011	−12·8	−14·6	−15·7	−16·4	− 24·3
Methyl alcohol	5·001	+11·2	+15·2	+18·2	+19·0	+ 44·8
Ethyl alcohol	5·000	+17·5	+21·5	+22·1	+26·9	+ 59·0
		(+)*Phthalate.*				
Chloroform	4·390	+10·0	+12·1	+12·4	+14·5	+ 15·4
Ethyl alcohol	5·429	−17·7	−23·0	−23·2	−29·0	− 66·8

* We define as (+), the hydrogen phthalate which yields (+)carbinol (Table V) on hydrolysis.

TABLE V.

Observed Rotatory Powers of (+)*Anisylmethylcarbinol at Different Temperatures* (*l*, 0·5).

t.	15·0°.	28·25°.	32·25°.	45·0°.	60·5°.
λ 5780	+29·26°	+28·25°	+27·76°	+27·09°	+25·78°
λ 5461	33·54	32·36	31·71	30·88	29·47
λ 4358	60·40	58·00	56·90	55·55	52·55

$d_{4^\circ}^{19\cdot5^\circ}$ 1·079, $d_{4^\circ}^{34\cdot5^\circ}$ 1·065, $d_{4^\circ}^{45\cdot5^\circ}$ 1·051, $d_{4^\circ}^{60^\circ}$ 1·044

Using a different specimen of the (+)alcohol, the following values were obtained (*l*, 0·5; *t*, 20·0°) :

λ	6438	5893	5780	5461	5086	4800	4358
α	+22·05°	+27·18°	+28·48°	+33·31°	+38·85°	+44·53°	+58·80°

dextro-1-*Anisylethyl Methyl Ether.*—A solution of (+)anisylmethylcarbinyl hydrogen phthalate (5 g. with $[\alpha]_{5461}$ $-21\cdot8°$ in ethyl alcoholic solution) in anhydrous methyl alcohol (30 c.c.) was kept overnight and then slowly evaporated on the steam-bath. The partly crystalline residue was separated by extraction with chloroform into phthalic acid (2·4 g.) and dextro-1-*anisylethyl methyl ether* (2 g.), b. p. 116—117°/23 mm., $n_D^{24°}$ 1·505; $\alpha_{5893}^{20°}$ $+0\cdot14°$; $\alpha_{5461}^{20°}$ $+0\cdot13$; $\alpha_{4358}^{20°}$ $+0\cdot33$ (*l*, 0·25) (Found : C, 72·3; H, 8·6. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·5%).

Action of Glacial Acetic Acid on (−)*Anisylmethylcarbinyl Hydrogen Phthalate.*—The rotatory power of a 5% solution of the (−)phthalate in glacial acetic acid (Table I) fell to half its value after 10 hours at room temperature and had become zero after 10 days. From the solution (which originally contained 5 g. of phthalate) there were obtained phthalic acid (2·4 g.) and *dl*-anisylmethylcarbinyl acetate (2 c.c.), b. p. 137°/15 mm., $n_D^{17°}$ 1·519 (Found : *M*, 192. Calc. for $C_{11}H_{14}O_3$: *M*, 194).

Action of Dilute Aqueous Sodium Hydroxide on (−)*Anisylmethylcarbinyl Hydrogen Phthalate.*—A filtered solution of the (−)acid ester (12 g., $[\alpha]_{5893}$ $-20\cdot2°$ in ethyl alcohol) in sodium hydroxide (140 c.c. of 0·3N) after being kept overnight had deposited a viscous oil. This was triturated with ethyl alcohol in order to remove traces of anisylmethylcarbinol, and dried (3·1 g.); it had $\alpha_{5893}^{17°}$ $-4\cdot3°$ (*l*, 0·5) (Found : *M*, 412. Calc. for $C_{26}H_{26}O_6$: *M*, 434).

On hydrolysis with 2·5 mols. of 5N-sodium hydroxide, this neutral ester yielded the alcohol (2·2 g.), b. p. 125—126°/10 mm., $n_D^{17.5°}$ 1·534, $\alpha_{5893}^{17.5°}$ $-8\cdot4°$ (*l*, 0·5).

dl-p-*Tolyl* 1-*Anisylethyl Sulphone.*—A solution of the hydrogen phthalic ester (3·0 g., $[\alpha]_{5893}^{20°}$ $-18°$ in ethyl alcohol) in sodium hydroxide (35 c.c. of 0·3N) was filtered into a solution of sodium *p*-toluenesulphinate (2·15 g.) in water (25 c.c.). The solution rapidly turned cloudy and crystalline dl-p-*tolyl* 1-*anisylethyl sulphone* began to separate. After several days this (1·6 g.) was removed by filtration; it was optically inactive in chloroform solution and separated from ethyl alcohol as a micro-crystalline powder, m. p. 119—120° (Found : S, 11·0. $C_{16}H_{18}O_3S$ requires S, 11·0%).

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