633. *The Resolution and Reactions of* 1 : 2 : 3 : 4-*Tetrahydro*-1-*naphthol. A New Preparation of* 1 : 2 : 3 : 4-*Tetrahydro*-1-*naphthyl Hydroperoxide.*

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1 : 2 : 3 : 4-Tetrahydro-1-naphthol has been resolved and its optically active acetate and hydrogen phthalate described. The tendency for these compounds to react by alkyl–oxygen fission is demonstrated by (*a*) the dependence of the rotatory power of the alcohol, obtained by hydrolysis of the hydrogen phthalate, upon the nucleophilic power of the hydrolytic reagent, (*b*) the formation of a sulphone from the alcohol and the hydrogen phthalate by reaction with sodium toluene-*p*-sulphinate in formic acid solution, and (*c*) the racemisation and formation of olefin by the (+)-hydrogen phthalate in acid solution. A new reaction, proceeding by an alkyl–oxygen fission mechanism, is the preparation of 1 : 2 : 3 : 4-tetrahydro-1-naphthyl hydroperoxide by reaction of the above hydrogen phthalate with 90% hydrogen peroxide.

For an investigation of 1 : 2 : 3 : 4-tetrahydro-1-naphthyl hydroperoxide, we wished to obtain the corresponding alcohol in an optically active state and to determine the ease with which it, and its derivatives, would undergo alkyl–oxygen fission.

1 : 2 : 3 : 4-Tetrahydronaphthalene was autoxidised to the hydroperoxide, and reduction of this with sodium sulphite gave 1 : 2 : 3 : 4-tetrahydro-1-naphthol as a viscous oil which crystallised after being seeded with a specimen of the solid (+)-alcohol. The alcohol was esterified by reaction with phthalic anhydride in the presence of pyridine, and the hydrogen phthalate resolved * by crystallisation of its quinidine salt from acetone solution until the melting point and specific rotatory power of the hydrogen phthalate attained a maximum value. The maximum rotatory power of the alcohol was established by hydrolysis of this ester with sodium ethoxide in 96% ethyl alcohol; from this alcohol the hydrogen phthalate was regenerated with undiminished rotatory power, confirming that no racemisation had occurred during the hydrolysis. It may thus be assumed that hydrolysis under these conditions proceeds by an acyl–oxygen fission mechanism, and that alcohol and hydrogen phthalate of similar sign of rotation have corresponding configurations. The optically active acetate was prepared by esterification of the optically pure alcohol.

The three lines of evidence presented below suggest that 1 : 2 : 3 : 4-tetrahydro-1-naphthol and its derivatives exhibit a tendency to react by alkyl–oxygen fission. Firstly, hydrolysis of the optically pure hydrogen phthalate with aqueous sodium carbonate gave the alcohol with retained configuration but only 11% of its maximum rotatory power. This is presumably due to the incursion of a unimolecular alkyl–oxygen fission mechanism (Day and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 686), as has been established in the case of analogous arylmethanols (Kenyon *et al.*, *J.*, 1942, 556, 605; 1946, 797, 803, 807; 1951, 376, 380, 382, 385, 386). Secondly, both the alcohol and its hydrogen phthalate readily yield 1 : 2 : 3 : 4-tetrahydro-1-naphthyl *p*-tolyl sulphone by reaction with sodium toluene-*p*-sulphinate in formic acid solution. This reaction necessitates alkyl–oxygen fission in the alcohol and ester and has been used as diagnostic of a tendency to reaction by that mechanism (Kenyon *et al.*, *loc. cit.*). No formation of sulphone was observed in acetic acid solution with added sulphuric acid. Thirdly, the hydrogen phthalate undergoes slow racemisation in acetic acid solution containing a trace of sulphuric acid; after 8 hours at 60° the rotatory power of the hydrogen phthalate had fallen to 60% of the initial value. It was optically and chemically stable in acetic acid solution at 60°, but in formic acid solution, after 2 hours at 47°, 1 : 2-dihydronaphthalene was isolated.

1 : 2 : 3 : 4-Tetrahydro-1-naphthyl derivatives thus appear to undergo alkyl–oxygen fission reactions somewhat more readily than the corresponding 1-phenylethyl compounds. For example, hydrolysis of 1-phenylethyl hydrogen phthalate with aqueous sodium carbonate yields an alcohol retaining 90% of the maximum activity (Balfe, Downer, Evans, Kenyon, Poplett, Searle, and Tárnoky, *J.*, 1946, 797).

The methods of preparation of alkyl hydroperoxides are of two types. The first method is the autoxidation of a hydrocarbon; this has been interpreted as a free-radical reaction, and occurs most readily at the α-position to an ethylenic double bond or benzene ring (Farmer, Bloomfield, Sundralingham, and Sutton, *Trans. Faraday Soc.*, 1942, **38**, 348). 1 : 2 : 3 : 4-Tetrahydro-1-naphthyl hydroperoxide has previously been prepared only by this method (Hock and Susemihl, *Ber.*, 1933, **66**, 61; this paper). The second general method involves the use of hydrogen peroxide; all the published reactions of this type can be interpreted as involving nucleophilic attack of the $\mathrm{HO{\cdot}O^-}$ ion or $\mathrm{HO{\cdot}OH}$ molecule on a carbon atom according to the general equation :

$$\mathrm{HO{\cdot}O^- + \overset{\curvearrowleft}{R{\cdot}X} \longrightarrow HO{\cdot}OR + X^-}$$

(Davies and White, *Nature*, in the press).

It has now been established that 1 : 2 : 3 : 4-tetrahydro-1-naphthyl hydroperoxide, identical with the product obtained by autoxidation, is formed by reaction of 1 : 2 : 3 : 4-tetrahydro-1-naphthyl hydrogen phthalate with 90% hydrogen peroxide. In view of the established tendency towards alkyl–oxygen fission in the ester, and the fact that the inactive hydroperoxide is obtained from the optically active ester, it would seem that this

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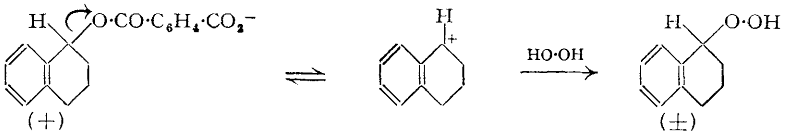
* The reference to a previous resolution of this alcohol which is given in Heilbron's " Dictionary of Organic Compounds," Vol. III, p. 698, is apparently an error and refers to the partial resolution of 1 : 2 : 3 : 4-tetrahydro-2-naphthol by Pickard and Littlebury (*J.*, 1906, **89**, 1254).

reaction may be included in the second of the above two classifications, and proceeds by a unimolecular alkyl–oxygen fission mechanism, as follows :



Experimental

1 : 2 : 3 : 4-*Tetrahydro*-1-*naphthyl Hydroperoxide*.—1 : 2 : 3 : 4-Tetrahydronaphthalene (1500 g.) was autoxidised at 75—78° for 50—60 hours (*Org. Synth.*, 1940, **20**, 94), and the product (102 g.) recovered by Robertson and Waters's method (*J.*, 1948, 1578). Recrystallisation from light petroleum gave the hydroperoxide (52 g.) as large rhombs, m. p. 55°.

1 : 2 : 3 : 4-*Tetrahydro*-1-*naphthol*.—The hydroperoxide (50 g.) was reduced by shaking it with an aqueous solution of sodium sulphite (125 g.) for 5 hours (Hock and Lang, *Ber.*, 1942, **75**, 713). 1 : 2 : 3 : 4-Tetrahydro-1-naphthol (37 g., 83%), b. p. 136°/19 mm., was obtained; this solidified to a waxy crystalline solid, m. p. 29—30°, after being seeded with a solid specimen of the (+)-alcohol (Mentzer and Billet, *Bull. Soc. chim.*, 1948, 835, record m. p. 33°). The phenylurethane had m. p. 122—123°.

1 : 2 : 3 : 4-*Tetrahydro*-1-*naphthyl Hydrogen Phthalate*.—The alcohol (30 g.) in dry benzene (15 c.c.) was added to phthalic anhydride (30 g.) in dry redistilled pyridine (24 g., 1·5 mols.); after 5 hours at 60° and 12 hours at room temperature the mixture, diluted with an equal volume of acetone, was poured on 1·5 l. of crushed ice and acidified (Congo red) with 5N-hydrochloric acid. After 2 days the 1 : 2 : 3 : 4-*tetrahydro*-1-*naphthyl hydrogen phthalate* solidified (53 g., 83%). Recrystallisation from carbon disulphide–light petroleum gave clusters of needles, m. p. 112° (Found : C, 72·7; H, 5·1%; equiv., 296. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%; equiv., 296). A similar procedure, but with the omission of benzene, gave only a 45—50% yield of a less pure product.

(+)-1 : 2 : 3 : 4-*Tetrahydro*-1-*naphthyl Hydrogen Phthalate*.—The (±)-hydrogen phthalate (50 g.) in acetone (50 c.c.) was added to a hot solution of anhydrous quinidine (55 g.) in acetone (600 c.c.). On cooling, large crystals of the solvated quinidine salt separated (87 g.); seven recrystallisations from acetone gave the optically pure salt, $[\alpha]^{20}_{D}$ +63·2° (*l*, 2; *c*, 2·1 in chloroform). This (+)-quinidine salt (31 g.), as a slurry in acetone (150 c.c.), was rendered homogeneous by the addition of 5N-hydrochloric acid, which solution was filtered on to crushed ice (750 c.c.) and confirmed to be acid (Congo-red). After 4 days the precipitated (+)-hydrogen phthalate solidified; it was purified by dissolution in ether and 3 extractions with 3N-hydrochloric acid. Recrystallisation of the crude material (12 g., 81%) from carbon disulphide gave short rods, m. p. 122°, $[\alpha]^{18}_{D}$ +11·1° (*l*, 2; *c*, 4·1 in chloroform). Decomposition of the quinidine salt from the mother liquors gave, after 3 recrystallisations from carbon disulphide, the (−)-hydrogen phthalate, m. p. 122°, $[\alpha]^{15}_{D}$ −10·5° (*l*, 2; *c*, 6·8 in chloroform).

Hydrolysis of (+)-1 : 2 : 3 : 4-*Tetrahydro*-1-*naphthyl Hydrogen Phthalate*.—(a) *With sodium ethoxide in ethyl alcohol.* A mixture of the (+)-hydrogen phthalate (3 g.), $[\alpha]^{18}_{D}$ +11·1° (*l*, 2; *c*, 4·1 in chloroform), in 96% ethyl alcohol (40 c.c.), and sodium (0·5 g., 2·5 mols.) in the same solvent (10 c.c.) was heated under reflux for 1 hour, the mixture poured into water, and the resulting alcohol recovered by extraction with ether. After distillation the (+)-1 : 2 : 3 : 4-tetrahydro-1-naphthol (1·0 g., 67%) solidified to a white micro-crystalline solid, b. p. 92°/1·8 mm., m. p. 39—40°, $[\alpha]^{17}_{D}$ +32·65° (*l*, 2; *c*, 2·5 in chloroform), $[\alpha]^{17}_{D}$ +8·54° (*l*, 2; *c*, 2·0 in carbon disulphide). This alcohol was converted back into the (+)-hydrogen phthalate with undiminished rotation.

(b) *With aqueous sodium carbonate.* A solution of the (+)-hydrogen phthalate (2 g.), $[\alpha]^{18}_{D}$ +11·1° (*l*, 2; *c*, 4·1 in chloroform) in aqueous sodium carbonate (0·9 g., 2·5 mols. ; in 25 c.c. of water) was heated on the steam-bath for 15 minutes and the mixture then distilled in a current of steam. After extraction with ether, the distillate yielded the (+)-alcohol (0·7 g., 70%), b.p. 92°/2 mm., m. p. 29° $[\alpha]^{19}_{D}$ + 3·6° (*l*, 2; *c*, 3·7 in chloroform). This alcohol was converted into the hydrogen phthalate which then had no detectable activity (*l*, 2; *c*, 4·4 in chloroform).

(−)-1 : 2 : 3 : 4-*Tetrahydro*-1-*naphthyl Acetate*.—A mixture of the (+)-alcohol (0·5 g.), $[\alpha]^{17}_{D}$ +32·65° (*l*, 2; *c*, 2·5 in chloroform), acetic anhydride (0·38 g.), and pyridine (0·3 g.), after 6 hours at 60°, was poured into water (100 c.c.) containing hydrochloric acid (10 c.c.; 3N-solution). The washed and dried ethereal extract yielded (−)-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthyl acetate* (0·5 g., 78%), b. p. 112—113°/2·5 mm., n_D^{20} 1·5292, d_4^{25} 1·0816; α_D^{21} −58·1° (homogeneous; *l*, 0·5); $[\alpha]_D^{21}$ −107·4° (homogeneous; *l*, 0·5) (Found: C, 76·0; H, 7·0. $C_{12}H_{14}O_2$ requires C, 75·8; H, 6·8%). The (±)-acetate obtained by the same method from the (±)-alcohol had n_D^{20} 1·5307. Criegee (*Annalen*, 1930, **481**, 263) reported b. p. 105—110°/2 mm.

1 : 2 : 3 : 4-*Tetrahydro*-1-*naphthyl* p-*Tolyl Sulphone*.—(a) *From the alcohol.* A mixture of the (±)-alcohol (0·50 g.) and sodium toluene-*p*-sulphinate (0·80 g.) in 98% formic acid (20 c.c.) was kept overnight at room temperature, and was then poured on crushed ice (100 c.c.); the precipitated *sulphone* (0·62 g., 62%) was recrystallised from methyl alcohol forming well-formed rhombs, m. p. 131° (Found: S, 11·3. $C_{17}H_{18}O_2S$ requires S, 11·2%). The use of glacial acetic acid (20 c.c.) and concentrated sulphuric acid (2 drops) as solvent instead of formic acid, after 8 hours at 60°, led to the recovery of the unchanged alcohol (96%). At 100° a similar reaction mixture gave a brown non-distillable material which was not further investigated.

(b) *From the hydrogen phthalate.* The hydrogen phthalate (0·50 g.), dissolved in a little acetone, was added to a solution of sodium toluene-*p*-sulphinate (0·50 g.) in 98% formic acid (15 c.c.). After 15 minutes at 100° and 48 hours at 20° characteristic crystals of the sulphone were precipitated. More was obtained (total, 0·36 g., 75%) by pouring the reaction mixture on crushed ice. Recrystallisation from methyl alcohol gave the sulphone, m. p. 131°.

Racemisation of the (−)-*Hydrogen Phthalate in Acid Solution*.—From a similar reaction mixture in glacial acetic acid in the presence of sulphuric acid, no sulphone was isolated, but the (−)-hydrogen phthalate was recovered partially racemised: the (−)-hydrogen phthalate (1·0 g.), m. p. 119°, $[\alpha]_D^{21}$ −8·5° (*l*, 2; *c*, 8·3 in chloroform) and sodium toluene-*p*-sulphinate (1·0 g.) were dissolved in glacial acetic acid (20 c.c.) containing 2 drops of concentrated sulphuric acid. After 8 hours at 60°, the hydrogen phthalate (0·76 g.) was recovered; it had m. p. 115—117°, $[\alpha]_D^{20}$ −5·2° (*l*, 2; *c*, 6·3 in chloroform). At 100° a brown non-distillable material was again obtained.

Reaction Between (−)-*Hydrogen Phthalate and* 98% *Formic Acid*.—A solution of the (−)-hydrogen phthalate (2·5 g.), $[\alpha]_D^{20}$ −4·8° (*l*, 2; *c*, 2·8 in chloroform), in 98% formic acid (20 c.c.), after 2 hours at 47°, was poured into water (50 c.c.) and extracted with ether. From the dried ethereal extract, 1 : 2-dihydronaphthalene was obtained (0·30 g.), b. p. 56—58°/0·9 mm.; n_D^{20} 1·5820 (Found: C, 92·1; H, 7·8. Calc. for $C_{10}H_{10}$: C, 92·3; H, 7·7%). A non-distillable residue (0·46 g.) was obtained, which could not be solidified. The involatile residues, obtained in this and the preceding two experiments, may be polymerised dihydronaphthalenene.

From a similar reaction in glacial acetic acid solution, after 8 hours at 60°, the unchanged (−)-hydrogen phthalate was recovered with undiminished rotation.

Reaction of (+)-1 : 2 : 3 : 4-*Tetrahydro*-1-*naphthyl Hydrogen Phthalate with Hydrogen Peroxide*.—The (+)-hydrogen phthalate (1·1 g.), $[\alpha]_D^{19}$ +11·1° (*l*, 2; *c*, 4·1 in chloroform), was added to 90% hydrogen peroxide (10 c.c.) containing sodium hydrogen carbonate (1·4 g.) at 0°. An oil soon separated on the surface of the initially homogeneous solution. After 2 days at 0°, water was added (30 c.c.); the ethereal extract yielded, after recrystallisation from light petroleum, 1 : 2 : 3 : 4-tetrahydro-1-naphthyl hydroperoxide (0·35 g.), m. p. 54—56° undepressed by mixture with the hydroperoxide obtained by autoxidation of tetralin. No optical activity could be detected in the product (*l*, 0·5; *c*, 18·6 in chloroform).

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