

### 615. The Resolution and Reactions of Tertiary Alcohols : 2-1'-Naphthylbutan-2-ol.

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2-1'-Naphthylbutan-2-ol is very readily resolved through the brucine salt of its hydrogen phthalate. The reactivity of this alcohol, and of 2-1'-naphthylpentan-2-ol, by unimolecular alkyl-oxygen heterolysis has been investigated.

Few optically active tertiary alcohols are available for stereochemical studies, and the resolutions which have been described are often tedious.<sup>1</sup> We have therefore investigated the resolution of 2-1'-naphthylbutan-2-ol.

This alcohol reacts with phthalic anhydride in the presence of triethylamine,<sup>1</sup> giving a crystalline hydrogen phthalate. Three recrystallisations of its brucine salt from acetone give the optically pure (−)-hydrogen phthalate,  $[\alpha]_D -52.6^\circ$  (in EtOH); the mother liquors yield the (+)-ester,  $[\alpha]_D +51.6^\circ$ .

The optically pure hydrogen phthalates yielded the (−)- and the (+)-alcohol respectively,  $[\alpha]_D \pm 7.6^\circ$  (in EtOH), m. p. 29–30°. On mixture these give the (±)-alcohol, m. p. and mixed m. p. 51–52°, and the infrared absorption spectra of the (+)-, (−)-, and (±)-alcohol were identical; resolution is therefore not accompanied by structural change.

Both the magnitude and the sign of the optical rotatory power of the alcohol and its hydrogen phthalate may vary as the solvent or the wavelength of light is changed; values are given in Tables 1 and 2.

TABLE 1. Specific rotatory power of 2-1'-naphthylbutan-2-ol (l l).

Solvent	6563 Å	5893 Å	5463 Å	4861 Å	c	Temp.
Acetone	− 8.8°	− 11.3°	− 14.4°	− 19.8°	3.62	18°
EtOH	− 5.9	− 7.6	− 9.8	− 12.6	4.6	16.5
CHCl <sub>3</sub>	− 1.6	− 2.4	− 4.4	—	2.5	19
Pyridine	0.0	0.0	—	—	1.39	18 *
CS <sub>2</sub>	+16.4	+19.8	+21.4	—	2.79	18

\* The alcohol recovered from this solution was optically pure.

TABLE 2. Specific rotatory power of 1-methyl-1-1'-naphthylpropyl hydrogen phthalate (l l).

Solvent	6563 Å	5893 Å	5463 Å	4861 Å	c	Temp.
Acetone	− 42.1°	− 52.1°	− 71.4°	− 88.4°	4.30	16.5°
EtOH	− 39.1	− 51.8	− 61.1	− 82.4	4.72	18.5
CHCl <sub>3</sub>	− 37.8	− 48.4	− 61.5	− 85.1	3.22	19
C <sub>6</sub> H <sub>6</sub>	− 14.0	− 16.4	− 19.7	− 28.1	2.13	19
Pyridine	+ 1.5	+ 0.6	− 1.9	− 5.0	4.80	19
CS <sub>2</sub>	+100	+134	+162	+222	1.82	19

This alcohol is resolved much more readily than 2-phenylbutan-2-ol<sup>2,1</sup> and 2:4-dimethylhexan-4-ol<sup>3</sup> which each need about fifteen crystallisations of the brucine salt before optical purity is attained; together with 3-methylpent-1-yn-3-ol<sup>4</sup> it affords the most readily available active tertiary alcohol of simple structure for stereochemical studies.

2-1'-Naphthylpentan-2-ol similarly gives a crystalline hydrogen phthalate, but no crystalline brucine salt could be obtained.

These two alcohols and their hydrogen phthalates undergo fairly readily the reactions which are characteristic of unimolecular alkyl-oxygen heterolysis.<sup>5</sup> The hydrogen

<sup>1</sup> References are given in the preceding paper.

<sup>2</sup> Zeiss, *J. Amer. Chem. Soc.*, 1951, **73**, 2391.

<sup>3</sup> Doering and Zeiss, *ibid.*, 1948, **70**, 3966; 1950, **72**, 147.

<sup>4</sup> Hickman and Kenyon, *J.*, 1955, 2051.

<sup>5</sup> Davies and Kenyon, *Quart. Rev.*, 1955, **9**, 203.

phthalates in aqueous sodium hydroxide disproportionate to phthalic acid and the corresponding dialkyl phthalates, and the alcohols and hydrogen phthalates give sulphones with sodium toluene-*p*-sulphinic acid in formic acid solution.

#### EXPERIMENTAL

*2-1'-Naphthylbutan-2-ol.*—A solution of methyl 1-naphthyl ketone (17 g.) in dry ether was slowly added to a Grignard reagent prepared from ethyl bromide (11 g.) and magnesium (2.5 g.), and the product decomposed with ice and ammonium chloride. The resultant alcohol, b. p. 120—130°/0.2 mm., separated from ether-light petroleum in rhombs (12.8 g.), m. p. 51—52° alone or when mixed with a specimen prepared by the interaction of ethyl methyl ketone and 1-naphthylmagnesium bromide. The former method gives a better yield (Found: C, 83.4; H, 7.6. Calc. for  $C_{14}H_{16}O$ : C, 83.9; H, 8.0%). The alcohol readily forms a picrate, deep yellow prisms (from ethanol), m. p. 93—95° (Found: C, 55.7; H, 4.4; N, 9.6. Calc. for  $C_{20}H_{18}O_3N_3$ : C, 55.9; H, 4.5; N, 9.7%). Marco<sup>6</sup> reports m. p. 52.5—53.5° for the alcohol and 93.5—95° for the picrate.

The alcohol did not react with phenyl or 1-naphthyl isocyanate, but when it (2 g.) in ether (10 c.c.) containing a trace of triethylamine was mixed with benzoyl isocyanate (1.5 g.) reaction occurred at room temperature. The resulting *1-methyl-1-1'-naphthylpropyl N-benzoylcarbamate* separated from ethanol in needles (2.7 g.), m. p. 121—122° (decomp.) (Found: C, 75.7; H, 6.1; N, 4.0.  $C_{22}H_{21}O_3N$  requires C, 76.1; H, 6.1; N, 4.0%).

*(±)-1-Methyl-1-1'-naphthylpropyl Hydrogen Phthalate.*—A mixture of the (±)-alcohol (20 g.), phthalic anhydride (14.8 g.), and triethylamine (11.1 g.) was kept at 90—95° for 16 hr. The resultant viscous product was washed in ether with hydrochloric acid, and the ethereal solution, after drying and treatment with charcoal (1 g.), evaporated to dryness. The residual crystals, dissolved in warm acetone, yielded the *hydrogen phthalate* (18 g., 53%) in plates, m. p. 131° (decomp.). Varying the time of heating did not improve the yield. When the triethylamine was replaced by pyridine the yield fell to 16%. On the other hand when the potassio-derivative of the alcohol was heated at 75° for an hour with a benzene solution of phthalic anhydride the yield of ester was 60%. The ester had m. p. 130° alone or when mixed with that prepared by using triethylamine or pyridine (Found: C, 75.5; H, 5.6%; *M*, 347.  $C_{22}H_{20}O_4$  requires C, 75.9; H, 5.7%; *M*, 348).

*(-)-1-Methyl-1-1'-naphthylpropyl Hydrogen Phthalate.*—A solution of the (±)-hydrogen phthalate (50 g.) and brucine (57 g.) in hot acetone (500 c.c.), on being kept overnight, deposited the crystalline brucine salt (60 g.; crop A). This was crystallised 3 times from chloroform (120 c.c.)-acetone (90 c.c.), giving crop D (18 g.). The (-)-hydrogen phthalates liberated from each of these four crops of brucine salt had respectively  $[\alpha]_D^{16}$  -29°, -45°, -51°, and -52° (in EtOH). The last fraction separated from carbon disulphide in needles, m. p. 115° (decomp.),  $[\alpha]_D^{16}$  -52.6° (*l* 2; *c* 4.670 in EtOH) (*M*, 347).

*(+)-1-Methyl-1-1'-naphthylpropyl Hydrogen Phthalate.*—After removal of the brucine salt, crop A, the filtrate and washings were concentrated to about 80 c.c. and set aside. A further crop of brucine salt separated. This (8 g.) was removed and the filtrate decomposed with dilute acid. The liberated acid ester (16 g.) had m. p. 113—114° (decomp.) and  $[\alpha]_D^{16}$  +48.2°, a value raised on three recrystallisations from carbon disulphide to  $[\alpha]_D^{16}$  +51.6° (*l* 2; *c* 3.97 in EtOH).

Equal weights of (+)- and (-)-hydrogen phthalate were dissolved in acetone: after evaporation the crystalline (±)-hydrogen phthalate separated (m. p. and mixed m. p. 130°).

*(-)-2-1'-Naphthylbutan-2-ol.*—(a) The (-)-hydrogen phthalate (6 g.) was added to ethanol (25 c.c.) in which sodium (1.2 g.) had been dissolved, and the mixture heated on the steam-bath for 1 hr. Dilution with water and extraction with ether yielded the (-)-alcohol, needles (see Table), m. p. 29—30° (Found: C, 84.3; H, 8.1.  $C_{14}H_{16}O$  requires C, 83.9; H, 8.0%).

(b) The (-)-hydrogen phthalate (1 g.) in dry ether (20 c.c.) was allowed to react with lithium aluminium hydride (0.34 g.); the liberated alcohol (0.4 g.) had m. p. 29—30°,  $[\alpha]_D^{16}$  -7.5°.

*(+)-2-1'-Naphthylbutan-2-ol.*—By method (a) the (+)-alcohol, m. p. 29—30°, was obtained from the (+)-hydrogen phthalate (see Table).

Equal weights of the (+)- and the (-)-alcohol regenerated the (±)-alcohol, rhombs, m. p. 51—52°.

<sup>6</sup> Marco, *Uch. Zap. Molotov. Gosudarst. Univ.*, 1939, **3**, 15; *Khim. Referat. Zhur.*, 1941, **4**, 50 (*Chem. Abs.*, 1943, **37**, 5716).

2-1'-Naphthylpentan-2-ol.—A solution of methyl *n*-propyl ketone (21.5 g.) in ether (50 c.c.) was slowly added to a cold stirred Grignard reagent prepared from 1-bromonaphthalene (52 g.) and magnesium (6.1 g.) After removal of the naphthalene in steam the main fraction (28 g.) was the required alcohol, b. p. 122—130°/0.5 mm., m. p. 63—64°, too soluble for convenient recrystallisation (Found: C, 83.7; H, 8.2. Calc. for C<sub>15</sub>H<sub>18</sub>O: C, 84.0; H, 8.4%). Its picrate separates from ethanol in yellow prisms, m. p. 146° (Found: C, 56.7; H, 4.4; N, 9.6. Calc. for C<sub>21</sub>H<sub>21</sub>O<sub>8</sub>N<sub>3</sub>: C, 56.9; H, 4.7; N, 9.5%). Marco<sup>6</sup> reports m. p. 64.5—65.5° for the alcohol and m. p. 147—149° for the picrate.

1-Methyl-1-1'-naphthylbutyl Hydrogen Phthalate.—The alcohol (10.75 g.), phthalic anhydride (7.4 g.), and triethylamine (5.5 g.) were heated on the steam-bath for 16 hr. After acidification the resultant hydrogen phthalate separated from light petroleum in plates (9.8 g.), m. p. 96° (decomp.) (Found: C, 76.2; H, 6.2%; M, 362. C<sub>23</sub>H<sub>22</sub>O<sub>4</sub> requires C, 76.1; H, 6.1%; M, 362).

1-Methyl-1-1'-naphthylpropyl *p*-Tolyl Sulphone.—(a) From the alcohol. A solution of (±)-alcohol (0.93 g.) and sodium toluene-*p*-sulphinate (1 g.) in formic acid (99%; 20 c.c.), after being kept overnight, was diluted with ice-water. The precipitated sulphone separated from ethanol in needles, m. p. 131—132°. The (–)-alcohol similarly gave the (±)-sulphone, m. p. and mixed m. p. 131—132°. Yields were almost quantitative (Found: C, 74.1; H, 6.7; S, 9.5. C<sub>21</sub>H<sub>22</sub>O<sub>2</sub>S requires C, 74.5; H, 6.5; S, 9.5%).

(b) From the hydrogen phthalate. (i) A solution of the (–)-hydrogen phthalate (1 g.) and sodium toluene-*p*-sulphinate (0.64 g.) in formic acid (20 c.c.) was diluted next morning with water. The precipitated sulphone separated from ethanol in needles, m. p. 131—132° alone or when mixed with the specimen from (a); it was optically inactive. (ii) A solution of the hydrogen phthalate (0.5 g.) in 0.3*N*-sodium hydroxide (10 c.c.) was mixed with sodium toluene-*p*-sulphinate (0.32 g.), and the solution kept for a month. The precipitated sulphone (0.15 g.) separated from ethanol in needles, m. p. 131—132° alone or when mixed with a previous specimen.

Di-1-methyl-1-1'-naphthylpropyl Phthalate.—A solution of the (±)-hydrogen phthalate (1 g.) in 0.3*N*-sodium hydroxide (20 c.c.) after several hours began to deposit a semisolid precipitate. After a month the mixture was extracted with ether; dilution of the ethereal extract with light petroleum yielded a non-crystalline mass (0.2 g.) of the neutral ester. Acidification of the aqueous portion yielded phthalic acid (0.22 g.; calc., 0.25 g.).

1-Methyl-1-1'-naphthylpropyl Hydroperoxide.—(a) The (±)-alcohol (1 g.) was added to 90% hydrogen peroxide (7 c.c.) containing sulphuric acid (1 drop). The mixture was stirred for 3 hr., then diluted with water and extracted with ether, yielding the hydroperoxide as a pale yellow oil (0.84 g.).

(b) A solution of the (±)-hydrogen phthalate (1 g.) in 90% hydrogen peroxide; (15 c.c.) containing sodium hydrogen carbonate (0.6 g.), after 4 days, was diluted with water and extracted with ether. Again the hydroperoxide isolated (0.33 g.) did not solidify.

1-Methyl-1-1'-naphthylpropyl Triphenylmethyl Peroxide.—A solution of the oily hydroperoxide (0.21 g.) and triphenylmethanol (0.27 g.) in acetic acid (10 c.c.) containing sulphuric acid (1 drop) after 2 hr. was diluted with water. The precipitated peroxide separated, in almost quantitative yield, from aqueous ethanol in needles, m. p. 114° (Found: C, 86.4; H, 6.6. C<sub>33</sub>H<sub>30</sub>O<sub>2</sub> requires C, 86.3; H, 6.6%).

By similar procedures the following derivatives of (±)-2-1'-naphthylpentan-2-ol were prepared:

1-Methyl-1-1'-naphthylbutyl *p*-tolyl sulphone, prepared from both the alcohol and the hydrogen phthalate, separates from ethanol in needles, m. p. 136° (alone and mixed) (Found: C, 75.4; H, 6.3; S, 9.6. C<sub>22</sub>H<sub>24</sub>O<sub>2</sub>S requires C, 75.0; H, 6.8; S, 9.1%).

Di-1-methyl-1-1'-naphthylbutyl phthalate was deposited from a solution of the (±)-hydrogen phthalate (1 g.) in 0.3*N*-sodium hydroxide (20 c.c.) overnight; it separates from (ether in plates (0.4 g.), m. p. 68° (Found: C, 81.7; H, 6.5. C<sub>38</sub>H<sub>38</sub>O<sub>4</sub> requires C, 81.7; H, 6.8%).