284. *Syntheses of Some Asymmetric Naphthalene and Acenaphthene Hydrocarbons.*

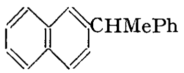
By B. R. Brown and D. Ll. Hammick.

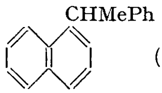
1-*Phenyl*-1-α-*naphthylethane*, 1-*phenyl*-1-β-*naphthylethane*, 2-β-naphthylbutane, 7-*methylacenaphthene*, and 7-*phenylacenaphthene* have been synthesised. The reaction between naphthalene, styrene, and concentrated sulphuric acid in carbon tetrachloride has been investigated, and the conclusions of Spilker and Schade (*Ber.*, 1932, **65**, 1686) have been corrected. A comparison of the stability of the molecular compounds of 1-phenyl-1-α-naphthylethylene, 1-phenyl-1-β-naphthylethylene, and the corresponding ethanes with picric acid and 1 : 3 : 5-trinitrobenzene is made, and it has been shown that solid compounds of racemic 7-methylacenaphthene can be obtained with racemic polynitrodiphenic esters but not with their optically active isomers.

The syntheses were carried out in order to investigate the molecular-compound formation between asymmetric aromatic hydrocarbons and racemic and optically active polynitrodiphenic acids and esters, with a view to the resolution of an asymmetric aromatic hydrocarbon. Of the hydrocarbons synthesised, only 7-*methylacenaphthene* yielded a molecular *compound* of this type (with racemic dimethyl 4 : 6 : 4′ : 6′-tetranitrodiphenate), but no solid compounds were obtained with optically active acids or esters.

In the course of the work the reaction between naphthalene, styrene, and concentrated sulphuric acid in carbon tetrachloride was investigated. Spilker and Schade (*loc. cit.*) report that this reaction yields two products, a solid of m. p. 69° (from light petroleum) and an oil of b. p. 221—224°/15 mm. Oxidation of the solid with chromic acid yielded a small amount of β-benzoylnaphthalene, and on this evidence Spilker and Schade concluded that the solid was 1-phenyl-1-β-naphthylethane (I), and that the oil was probably 1-phenyl-1-α-naphthylethane (II).

(I.)

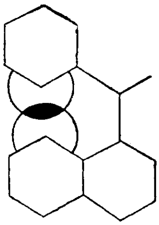




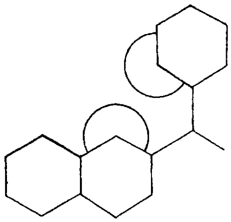
(II.)

In the present work, these hydrocarbons were prepared by unambiguous synthetical methods. 1-*Phenyl*-1-α-*naphthylethane* (II) was obtained as a solid of m. p. 65—66°, and 1-*phenyl*-1-β-*naphthylethane* (I) as a solid of m. p. 37—38°. Repetition of Spilker and Schade's work yielded an oil which corresponded in analysis and molecular weight to a mixture of these two compounds. From the oil a solid of m. p. 65—66° was isolated and proved to be identical with synthetic 1-phenyl-1-α-naphthylethane. Also, another solid of m. p. 37—38° was isolated by means of its picrate, and this proved to be 1-phenyl-1-β-naphthylethane.

A comparison of the *picrates* and *trinitrobenzene* derivatives of 1-phenyl-1-α-naphthylethylene and 1-phenyl-1-β-naphthylethylene and the corresponding ethanes indicates that (taking melting-point range and effect of solvents as criteria of stability) the molecular compounds of the β-naphthalene series are the more stable. It is suggested that this is because interference between the hydrogen atoms of the phenyl group and the hydrogen atom in the *peri*-position of the naphthalene nucleus prevents the molecules of the α-compounds from assuming a planar configuration. In the β-naphthalene derivatives a planar configuration can be assumed, and this presumably facilitates compound formation. Scale drawings using interatomic distances given by Pauling (" Nature of the Chemical Bond ", 2nd ed., 1944), shows that for a planar configuration of the molecule of the α-naphthyl compound the hydrogen atoms would overlap considerably, whereas there is ample clearance in a planar molecule of the β-naphthyl compound. This is shown roughly in the accompanying diagrams.



α-Naphthyl compound.



β-Naphthyl compound.

EXPERIMENTAL.

(Analyses are by Drs. Weiler and Strauss, Oxford. M. p.s are uncorrected.)

1-*Phenyl*-1-α-*naphthylethylene*.—This was prepared by the method of Stoermer and Simon (*Ber.*, 1904, **37**, 4167); short needles, m. p. 58—59°. A trace of the ethylene gave a deep purple colouration with concentrated sulphuric acid. No picrate was obtained. The *trinitrobenzene* derivative crystallised from alcohol as clusters of golden-yellow needles, m. p. 90—93° (Found : C, 65·5; H, 3·9; N, 9·7. $C_{24}H_{17}O_6N_3$ requires C, 65·0; H, 3·8; N, 9·5%). Recrystallisation from alcohol or chloroform caused decomposition.

1-*Phenyl*-1-α-*naphthylethane* (II).—The above ethylene (5·8 g.) was hydrogenated at room temperature and 2·5 atmospheres in the presence of alcohol (120 c.c.) and Raney nickel (1·5 g.). Reduction was complete in ½ hour. The catalyst was filtered from the solution, the alcohol distilled, and the oily residue kept overnight, during which time solidification occurred. Two recrystallisations from alcohol yielded 3·2 g. (55%) of 1-*phenyl*-1-α-*naphthylethane* in the form of flat colourless hexagons, m. p. 65—66° (Found : C, 93·1; H, 6·95. $C_{18}H_{16}$ requires C, 93·1; H, 6·9%). The *picrate* separated from alcohol as bright yellow microscopic crystals, m. p. 74—79° (Found : C, 62·6; H, 4·1. $C_{24}H_{19}O_7N_3$ requires C, 62·5; H, 4·1%). Recrystallisation caused decomposition. The *trinitrobenzene* derivative separated from alcohol as feathery yellow needles, m. p. 74—80° (Found : C, 64·8; H, 4·3. $C_{24}H_{19}O_6N_3$ requires C, 64·7; H, 4·3%). Recrystallisation caused decomposition.

1-*Phenyl*-1-β-*naphthylethylene*.—This, prepared according to Bergmann and Bondi (*Ber.*, 1933, **66**, 286), separated from alcohol in the form of colourless plates, m. p. 54—55°. The compound gave a crimson colouration with concentrated sulphuric acid. Two recrystallisations from alcohol yielded the *picrate* as orange-yellow rods, m. p. 81—82° (Found : C, 62·5 ; H, 3·8. $C_{24}H_{17}O_7N_3$ requires C, 62·8 ; H, 3·7%). The *trinitrobenzene* derivative crystallised from alcohol in the form of canary-yellow needles, m. p. 100—101° (Found : C, 64·8 ; H, 3·7 ; N, 9·9. $C_{24}H_{17}O_6N_3$ requires C, 65·0 ; H, 3·8 ; N, 9·5%).

1-*Phenyl*-1-β-*naphthylethane* (I).—This *hydrocarbon* was prepared by reduction of the β-ethylene using the conditions described for the preparation of 1-phenyl-1-α-naphthylethane. Crystallisation from methyl alcohol yielded narrow colourless hexagons, m. p. 37—38° (Found : C, 93·0 ; H, 7·1. $C_{18}H_{16}$ requires C, 93·1 ; H, 6·9%). The *picrate* crystallised from alcohol as bright yellow needles, m. p. 87—88° (Found : C, 62·1 ; H, 4·3. $C_{24}H_{19}O_7N_3$ requires C, 62·5 ; H, 4·1%). The *trinitrobenzene* derivative was obtained from alcohol as stout yellow needles, m. p. 109—110° (Found : C, 64·3 ; H, 3·8 ; N, 9·6. $C_{24}H_{19}O_6N_3$ requires C, 64·7 ; H, 4·3 ; N, 9·4%).

Reaction between Styrene and Naphthalene.—The directions of Spilker and Schade (*loc. cit.*) were followed. A colourless oil was obtained, b. p. 225—235°/20 mm. [Found : C, 93·2, 93·1 ; H, 7·1, 7·1 ; *M* (camphor), 228. Calc. for $C_{18}H_{16}$: C, 93·1 ; H, 6·9 ; *M*, 232].

After 6 months at room temperature, colourless crystals began to appear in the liquid, which was then kept at 0° for a week. The crystals were isolated by centrifuging and decanting as much as possible of the viscous liquid. After the adhering liquid had been removed on a porous plate, the solid was twice recrystallised from alcohol, yielding colourless plates, m. p. 65—66°, unchanged on admixture with a synthetic specimen of 1-phenyl-1-α-naphthylethane of m. p. 65—66°.

The liquid which had been decanted from the crystals was dissolved in hot alcohol and treated with an equal weight of picric acid in boiling alcohol. On cooling, a picrate separated in the form of yellow needles. These were decomposed by means of warm aqueous sodium hydroxide, and the liberated hydrocarbon isolated by means of ether. Two recrystallisations from methyl alcohol yielded colourless crystals, m. p. 37—38°, unchanged on admixture with a synthetic specimen of 1-phenyl-1-β-naphthylethane of m. p. 37—38°.

2-β-*Naphthylbut*-2-*ene* (Ruzicka and St. Kaufmann, *Helv. Chim. Acta*, 1941, **24**, 939).—An impure picrate (orange prisms, m. p. 56—58°) and an impure trinitrobenzene derivative (stout golden-yellow needles, m. p. 70—73°) were obtained from alcohol. Recrystallisation caused decomposition.

2-β-*Naphthylbutane* (Bergmann and Weizmann, *J. Org. Chem.*, 1944, **9**, 356).—The *picrate* separated from alcohol as felted yellow needles, m. p. 64—68° (Found : C, 58·6 ; H, 4·6. $C_{20}H_{19}O_7N_3$ requires C, 58·1 ; H, 4·6%). Recrystallisation caused decomposition. The *trinitrobenzene* derivative crystallised from alcohol in fine lemon-yellow needles, m. p. 80—83° (Found : N, 11·0. $C_{20}H_{19}O_6N_3$ requires N, 10·6%). Recrystallisation caused decomposition.

7-*Methylacenaphthylene.*—To the Grignard reagent prepared from magnesium (1·44 g.) and methyl iodide (8·5 g.) in ether (60 c.c.) was added an ice-cold solution of acenaphthenone (8·4 g.) in dry benzene (70 c.c.). The ether was removed and the Grignard complex decomposed by shaking with dilute hydrochloric acid. The benzene layer was separated and evaporated to 20 c.c. On addition of an alcoholic solution of picric acid (15 g.), the *picrate* of 7-methylacenaphthylene separated as a mass of brick-red needles, m. p. 174—179°. Three recrystallisations from alcohol yielded 8·8 g. (46%) of orange-red needles, m. p. 178—179° (Found : C, 57·8 ; H, 3·4. $C_{19}H_{13}O_7N_3$ requires C, 57·7 ; H, 3·3%).

Decomposition of the picrate with sodium hydroxide solution and extraction with ether yielded 7-*methylacenaphthylene* as a mobile orange oil, b. p. 130—136°/0·15 mm. (Found : C, 94·2 ; H, 6·2. $C_{13}H_{10}$ requires C, 94·0 ; H, 6·0%). The distillation was carried out rapidly, but a dark-red viscous residue of polymer remained in the distilling flask. The *trinitrobenzene* derivative crystallised from alcohol in vermillion needles, m. p. 191—193° (Found : C, 60·1 ; H, 3·5. $C_{19}H_{13}O_6N_3$ requires C, 60·2 ; H, 3·4%).

7-*Methylacenaphthene.*—Reduction of 7-methylacenaphthylene in ethyl alcohol in the presence of Raney nickel was complete in 15 minutes at room temperature and 2 atmospheres. Treatment of the colourless alcoholic solution with picric acid yielded the *picrate* of 7-methylacenaphthene. Recrystallisation from alcohol yielded orange-red felted needles, m. p. 121—122° (Found : C, 57·5 ; H, 3·8. $C_{19}H_{15}O_7N_3$ requires C, 57·5 ; H, 3·8%).

Decomposition of the picrate gave the *hydrocarbon* as a colourless oil, b. p. 145—155°/28 mm. (Found : C, 92·5 ; H, 7·2. $C_{13}H_{12}$ requires C, 92·9 ; H, 7·1%). The *trinitrobenzene* derivative crystallised from alcohol as woolly yellow needles, m. p. 134—135° (Found : C, 59·5 ; H, 3·95 ; N, 10·7. $C_{19}H_{15}O_6N_3$ requires C, 59·9 ; H, 3·9 ; N, 11·0%).

The hydrocarbon in alcohol gave a molecular *compound* with racemic dimethyl-4 : 6 : 4′ : 6′-tetranitrodiphenate, as sparkling yellow plates, m. p. 136—137° (Found : C, 50·9 ; H, 3·1 ; N, 10·2. $C_{13}H_{12},2C_{16}H_{10}O_{12}N_4$ requires C 50·6 ; H 3·0 ; N 10·5%). The compound was decomposed by contact with methyl and ethyl alcohols, light petroleum, or carbon tetrachloride in the absence of excess of hydrocarbon.

7-*Phenylacenaphthylene* (cf. Ghigi, *Ber.*, 1940, **73**, 677).—This was prepared from acenaphthenone (16·8 g.) and the Grignard reagent from bromobenzene (18·8 g.). The hydrocarbon was isolated as the *picrate* (20 g., 44%), which separated from alcohol as orange-red microscopic crystals, m. p. 123° (Found : N, 9·2. $C_{24}H_{15}O_7N_3$ requires N, 9·2%).

Decomposition of the picrate yielded 7-phenylacenaphthylene, which crystallised from alcohol as sparkling yellow plates, m. p. 57—58° (Found : C, 94·3 ; H, 5·5. Calc. for $C_{18}H_{12}$: C, 94·7 ; H, 5·3%). The *trinitrobenzene* derivative separated from alcohol in the form of felted orange needles, m. p. 133—134° (Found : C, 65·4 ; H, 3·9 ; N, 9·35. $C_{24}H_{15}O_6N_3$ requires C, 65·3 ; H, 3·4 ; N, 9·5%).

7-*Phenylacenaphthene.*—7-Phenylacenaphthylene (2·3 g.) was hydrogenated under the conditions described for 7-methylacenaphthene. The resulting colourless alcoholic solution was concentrated to crystallisation ; 7-*phenylacenaphthene* (1·7 g., 74%) then separated as colourless needles, m. p. 104—105°. On recrystallisation from methyl alcohol, the m. p. was 105—106° (Found : C, 93·6 ; H, 6·2. $C_{18}H_{14}$ requires C, 93·9 ; H, 6·1%). The hydrocarbon yielded no picrate. The *trinitrobenzene* derivative separated from alcohol in the form of small yellow needles, m. p. 116—117°, unchanged by further recrystallisation (Found : C, 65·0; H, 4·3; N, 9·0. $C_{24}H_{17}O_6N_3$ requires C, 65·0; H, 3·8; N, 9·5%).

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