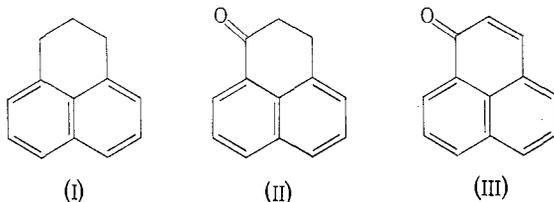


THE PREPARATION AND STABILITY OF PERINAPHTHANE*

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Possibly because of difficulties in its synthesis, perinaphthene (I; 2,3-dihydrophenalene) has been less studied than its homolog acenaphthene. The only satisfactory methods of preparation reported are the reduction of perinaphthanone (II)^{1,2} and the hydrogenation of perinaphthenone (III),³ both of which we have investigated. Other methods, such as the selenium dehydrogenation of perinaphthenone,⁴



the hydrogenation of perinaphthene,⁵ preparation from a degradation product of pyrene,⁶ the reduction of perinaphthanedione,⁷ and the hydrogenation of 6-bromoperinaphthan-1-ol,⁸ are unsuitable for the preparation of useful quantities. Perinaphthanone is prepared¹ by the cyclization of 3-(1-naphthyl)propionic acid, itself obtained in two steps from a 1-halomethylnaphthalene. Seeking an alternative synthesis we attempted ring expansion of acenaphthenone with diazomethane, avoiding strongly alkaline conditions under which biacenone is produced,⁹ by (a) passing an ethereal solution of diazomethane into a solution of acenaphthenone and (b) generating the diazomethane in the acenaphthenone solution from methylnitrosourea and sodium carbonate. Both reactions gave only a trace of ring-expanded products (gas chromatography). The related ring expansion of acenaphthenequinone is reported¹⁰ as being successful, although the yield of purified product is not quoted.

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⁵ Boekelheide, V., and Larrabee, C. E., *J. Amer. Chem. Soc.*, 1950, **72**, 1245.

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⁸ Boekelheide, V., and Goldman, M., *J. Amer. Chem. Soc.*, 1954, **76**, 604.

⁹ "Elsevier's Encyclopaedia of Organic Chemistry." Vol. 13, p. 188. (Elsevier: Amsterdam 1946.)

¹⁰ Eistert, B., and Selzer, H., *Chem. Ber.*, 1963, **96**, 314.

The Clemmensen reduction of perinaphthanone has been reported⁵ but the perinaphthane obtained was difficult to purify and no yield was given. We have checked this result and the yield is indeed low (12%).

Perinaphthenone has usually been prepared by the condensation of β -naphthol with glycerol.^{3,11} This reaction is exothermic, difficult to control, gives low and variable yields, and the product must be isolated from a viscous tar. We have employed an alternative method¹² involving the cyclization of the sodium salt produced on the condensation of the commercially available methyl 1-naphthyl ketone with ethyl formate in the presence of sodium. Yields of 80% were obtained, based on the amount of 1-isomer present in the commercial sample, and the method is suitable for the preparation of large quantities. The hydrogenation of perinaphthenone in dioxan at 250° in the presence of copper chromite has been reported³ to give perinaphthane together with some perinaphthan-1-ol. In seeking the optimum reaction conditions we varied the pressure, temperature, amount of solvent and of catalyst, and tried perinaphthenone samples of various purities. From the product mixtures we have isolated, or detected the presence of, perinaphthenone, perinaphthanone, perinaphthanol, perinaphthane, and tetrahydroperinaphthane. High yields of perinaphthane can be obtained but the amount of catalyst is critical and the perinaphthenone must be distilled prior to use.

Earlier workers reported^{6,7} that perinaphthane was unstable towards air and should be kept under carbon dioxide. Fieser and Hershberg³ agreed that it darkened on exposure to air. Similar observations have been made with 4,7-dimethylperinaphthane.¹³ There seems to be no reason for such instability and indeed we find that the compound is quite stable over long periods in a nitrogen atmosphere or in air in the absence of light. Some surface darkening occurred on leaving a sample exposed to air and light but examination (m.p., gas chromatography, i.r.) of a surface sample showed no significant amount of impurity.

Experimental

Perinaphthenone

A solution of methyl 1-naphthyl ketone (1 mole) and ethyl formate (2 moles, purified by shaking with sodium carbonate and collecting the sample b.p. 53–53.5° on fractionation) in dry ether (250 ml) was added slowly, with shaking, to sodium wire (1 mole) in dry ether (1 l.). The mixture was refluxed (4 hr) and the deposited sodium salt was then collected and washed with dry ether. The yield was almost quantitative. The salt (half quantity) was violently stirred in carbon tetrachloride (3 l.) while sulphuric acid (82%, 800 ml) was added. After stirring for a further 30 min, the mixture was poured into water (12 l.). The organic layer was washed with aqueous sodium hydroxide (2%) and with water and dried (MgSO₄). After removal of the solvent, distillation of the combined products, b.p. 180–185°/0.5 mm, gave perinaphthenone (115.4 g, 64%), m.p. 155–156° (from cyclohexane), (lit.³ m.p. 156–156.5°). (The methyl naphthyl ketone used contained 80% of the 1-isomer.)

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Perinaphthane

Perinaphthenone (10 g) in purified dioxan (30 ml) was hydrogenated in a glass vessel contained in a shaking autoclave (1 l. volume) in the presence of copper chromite¹⁴ (0.15 g). The initial pressure of hydrogen was 120 atm (room temperature) and the reaction was conducted at 260° for 8 hr. Pentane (50 ml) and water (50 ml) were then added and the organic layer was washed with water, dried (MgSO₄), and the pentane evaporated. Distillation, b.p. 120°/0.5 mm, gave perinaphthane (7.5 g, 80%), m.p. 56° (yields varied from 6.5 to 8.5 g). Fractionation through an 18-in. spinning band column followed by recrystallization from methanol gave material of m.p. 65° (lit.³ 65.4°).

Using the quantities of Fieser and Hershberg,³ namely perinaphthenone (20 g), catalyst (50 mg), and dioxan (25 ml), we obtained carbonaceous material from which small amounts of perinaphthane (picrate m.p. 149°, lit.³ 150–151°), perinaphthanone (m.p. 81–81.5°, oxime m.p. 123–126°, lit.¹ 82.6–83.2° and 127–128° respectively) and perinaphthenone (i.r. spectrum identical to authentic sample) were isolated. When the catalyst/ketone ratio was increased (200 mg catalyst per 10 g of ketone), mainly tetrahydroperinaphthane was produced (Found: C, 91.1; H, 9.0. Calc. for C₁₃H₁₆: C, 90.7; H, 9.3%). When using the given optimum conditions for the production of perinaphthane but reducing the time from 8 to 7 hr, distillation of the perinaphthane left a residue which gave an i.r. spectrum containing a very strong -OH peak, the only evidence which we discovered for perinaphthanol as an intermediate in the hydrogenation. The use of perinaphthenone purified solely by recrystallization led to lower yields of perinaphthane, and considerable quantities of carbonaceous material were obtained.

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¹⁴ Lazier, W. A., and Arnold, H. R., *Org. Synth.*, 1943, Coll. Vol. II, 142.