Mode of Cyclopropane Ring Opening of 1a,2,3,7b-Tetrahydro-1-phenyl-1*H*-cyclopropa[*a*]naphthalene: a Correction

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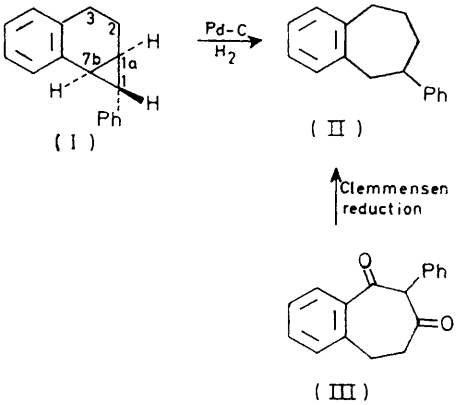
Catalytic hydrogenolysis of 1a,2,3,7b-tetrahydro-1-phenyl-1*H*-cyclopropa[*a*]naphthalene (I) and of the corresponding 1a,7b-dihydro-derivative provides 2-benzyltetralin (VI) and not 6,7,8,9-tetrahydro-6-phenyl-5*H*-benzocycloheptene (II) as previously reported.

CATALYTIC hydrogenolysis of the cyclopropanaphthalene (I) over palladium–charcoal (10%) in ethanol was reported by Heller *et al.*[1] to give the known phenylbenzocycloheptene (II),[2] m.p. 38—39°, by cleavage of the 1a,7b-bond. Similar reduction of the 1a,7b-dihydro-analogue of (I) had been reported by Nozaki and his co-workers [2] to furnish the same compound (II), identified by comparison with an authentic sample prepared [2] through Clemmensen reduction of the known 1,3-diketone (III).[3]

It has recently been demonstrated [4] that catalytic hydrogenolysis (Pd–C) of *trans*-1,2-diphenylcyclopropane cleaves the 1,2-bond exclusively; we report here that similar cleavage of the cyclopropane compounds (I) and its 1a,7b-dihydro-analogue furnishes the tetralin derivative (VI), and not the cycloheptene (II).

Hydrogenolysis of the cyclopropane derivatives (IV) catalytically or with sodium–liquid ammonia always, in our hands,[5] afforded the corresponding acid (V) (diastereoisomeric mixture), by cleavage of the 1,7b-bond. No product of 1a,7b-bond cleavage could be isolated.

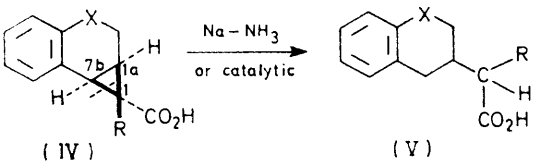


(I) (II) (III)

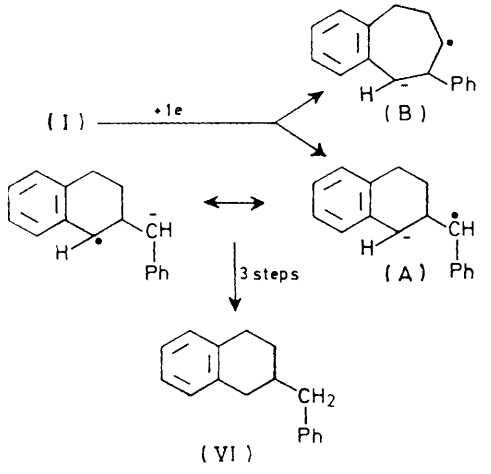
Reduction of compound (I), obtained by the reported [1] procedure, with sodium–ammonia furnished, in excellent yield a crystalline product, m.p. 37—38°, showing u.v. absorptions [$\lambda_{max.}$ 261, 265, and 273 nm (log ε 2.83, 2.88,

[1] H. G. Heller and R. A. N. Morris, *J. Chem. Soc.* (*C*), 1966, 1004.
[2] H. Nozaki, M. Yamabe, and R. Noyori, *Tetrahedron*, 1965, **21**, 1657.
[3] G. L. Buchanan and D. B. Jhaveri, *J. Org. Chem.*, 1961, **26**, 4295.
[4] A. L. Schultz, *J. Org. Chem.*, 1971, **36**, 383.
[5] A. Chatterjee, R. Mallik, and B. Bandyopadhyay, *Tetrahedron Letters*, 1973, 1683; and unpublished results.

and 2.86)] similar to those reported [2] for (II). On mechanistic grounds [6] (Scheme 1), cleavage of (I) should



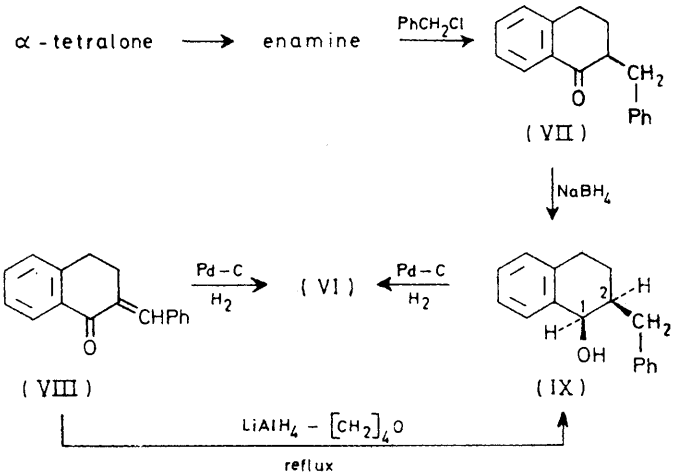
provide predominantly, if not exclusively, 2-benzyl-1,2,3,4-tetrahydronaphthalene (VI) (lit.,[7] m.p. 38—39°), since the intermediate anion radical (A) is expected to be more stable than the alternative (B).



SCHEME 1

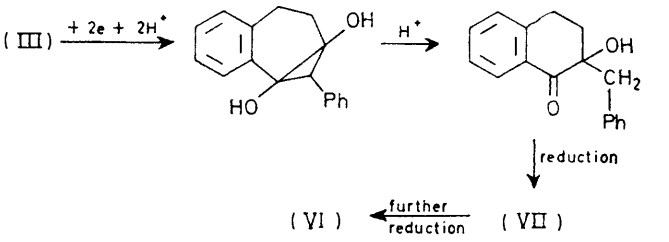
The n.m.r. spectrum of our compound [τ 7.76—8.69 (3 H, m), 7.09—7.61 (6 H, m), and 2.88—3.09 (9 H, m)] unambiguously establishes the structure (VI). In the mass spectrum an intense peak at *m/e* 131 ($M^+ - PhCH_2$) further confirms the assignment. Hydrogenolysis of (I) according to the reported procedure [1] gave the same product (VI). Authentic samples of (VI) (m.p. 38—39°), prepared by different routes (Scheme 2), were also identical (mixed m.p. and u.v. and n.m.r. spectra) with our compound. In one of the routes, 1,2-dihydro-4-pyrrolidinonaphthalene [8] was alkylated with benzyl chloride to give (VII) in very poor yield. Reduction of (VII) with sodium borohydride gave a crystalline alcohol tentatively identified as the *cis*-alcohol (IX) from the coupling constant (7.2 Hz) of the C-1 benzylic hydrogen doublet at τ 5.53. Reduction of the $\alpha\beta$-unsaturated ketone (VIII) [9] with lithium aluminium hydride gave exclusively the same *cis*-alcohol (IX). The complete stereospecificity observed in this reduction can be rationalised in terms of a cyclic metallo-organic intermediate, as observed [10] in an analogous acyclic system.

The method employed by Nozaki *et al.*[2] for the preparation of an authentic sample of (II) is ambiguous since it is well known [11] that Clemmensen reduction of 1,3-diketones proceeds mainly with rearrangement. Reduction of the 1,3-diketone (III) thus actually afforded the



SCHEME 2

rearrangement product (VI) and not the normal product (II) claimed.[2] The formation of (VI) may be rationalised by the mechanism (*cf.* refs. 11*c* and *d*) shown in Scheme 3. The drastic nature of the conditions * employed [2] for the reduction of (III) to give the hydrocarbon (VI) in only 20% yield lends additional support to the proposed mechanism.



SCHEME 3

EXPERIMENTAL

U.v. spectra were measured for solutions in ethanol with a Unicam SP 500 spectrophotometer, i.r. spectra for solutions in chloroform with a Perkin-Elmer 337 instrument, and n.m.r. spectra for solutions in carbon tetrachloride with a Varian T-60 spectrometer (tetramethylsilane as internal standard).

1a,2,3,7b-Tetrahydro-1-phenyl-1*H*-cyclopropa[*a*]naphthalene (I) was prepared by the reported [1] procedure.

Reduction of the Cyclopropa-compound (I).—(a) *With sodium–liquid ammonia.* Sodium (220 mg) was cut into

* Refluxing a solution of (III) in toluene with zinc amalgam, concentrated hydrochloric acid, and water for 25 h.

[6] *Cf.* H. M. Walborsky and J. B. Pierce, *J. Org. Chem.*, 1968, **33**, 4102.

[7] R. G. Melton, E. J. Eisenbraun, P. W. K. Flanagan, and M. C. Hamming, *Org. Prep. Proced.*, 1970, **2**(1), 37 (*Chem. Abs.*, 1970, **73**, 3682s).

[8] L. A. Paquette and M. Rosen, *J. Org. Chem.*, 1968, **33**, 2130.

[9] W. S. Rapson and R. G. Shuttleworth, *J. Chem. Soc.*, 1940, 636.

[10] F. A. Hochstein and W. G. Brown, *J. Amer. Chem. Soc.*, 1948, **70**, 3484.

[11] (*a*) D. Staschewski, *Angew. Chem.*, 1959, **71**, 726; (*b*) N. J. Cusack and B. R. Davis, *J. Org. Chem.*, 1965, **30**, 2062; (*c*) E. Wenkert and E. Kariv, *Chem. Comm.*, 1965, 570; (*d*) K. M. Baker and B. R. Davis, *Chem. and Ind.*, 1966, 768.

three pieces. One piece was added to stirred liquid ammonia, followed slowly by a solution of compound (I) (500 mg) in dry ether (30 ml). The rest of the sodium was then added and the mixture was stirred for 20 min. Solid ammonium chloride was then added in small portions to discharge the blue colour, and the ammonia was allowed to evaporate at room temperature. The residue was diluted with water and the product was extracted with ether (3 × 75 ml). The extract was washed with water, dried (Na_2SO_4), and evaporated to give 2-benzyl-1,2,3,4-tetrahydronaphthalene [7] (VI) (478 mg, 95%), m.p. 38—39° [from light petroleum (b.p. 40—60°)] (lit.,[7] 38—39°) (Found: C, 91.65; H, 8.55. Calc. for $C_{17}H_{18}$: C, 91.85; H, 8.15%); $\lambda_{max.}$ 261, 265, and 273 nm (ε 676.1, 758.6, and 724.4); τ 7.76—8.69 (3 H, m), 7.09—7.61 (6 H, m), and 2.88—3.09 (9 H, m); *m/e* 222 (M^+), 131 ($M^+ - 91$), 92, and 91.

(b) *By catalytic hydrogenolysis.* Compound (I) [1] (400 mg) in ethanol (30 ml) was hydrogenated over palladium–charcoal (10%; 100 mg) at 23 °C and 1 atm (uptake 43 ml in 24 min). Filtration, evaporation, and distillation of the residue at 140—145 °C (bath) and 0.3 mmHg gave 2-benzyl-1,2,3,4-tetrahydronaphthalene [7] (VI) (400 mg, 97%), m.p. and mixed m.p. 38—39°.

2-Benzyl-1,2,3,4-tetrahydronaphthalene (VI).—(a) *By catalytic hydrogenation of 2-benzylidene-1-tetralone* (VIII). A solution of compound (VIII) [9] (1 g) in ethanol (70 ml) was hydrogenated over palladium–charcoal (10%; 200 mg) at 23 °C and 1 atm (uptake 310 ml in 14 h). The product was distilled at 140—145 °C (bath) and 0.3 mmHg to furnish compound (VI) (800 mg, 84%), m.p. 38—39° [from light petroleum (b.p. 40—60°)] (Found: C, 91.7; H, 8.25%).

(b) *By catalytic hydrogenolysis of* cis-*2-benzyl-1,2,3,4-tetrahydronaphthalen-1-ol* (IX). A solution of benzyl chloride (4 ml) and 1,2-dihydro-4-pyrrolidinonaphthalene [8] (5.25 g) in anhydrous dioxan (25 ml) was refluxed under nitrogen for 20 h. Acetic acid (1 ml), sodium acetate (1 g), and water (30 ml) were then added and the mixture was further refluxed for 1 h. Dioxan was removed under reduced pressure, the residue was diluted with water, and the product was extracted with ether (3 × 75 ml). The extract was successively washed with 5% hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and water, dried, and evaporated. The residue was distilled to give 2-benzyl-1-tetralone (VII) (630 mg), b.p. 150—160° (bath) at 0.2 mmHg; $\nu_{max.}$ 1 677 cm^{-1}.

To an ice-cold stirred solution of the ketone (VII) (630 mg) in a mixture of acetone-free methanol (15 ml) and water (0.7 ml) was added sodium borohydride (350 mg). The mixture was stirred at the same temperature for 4 h, then left at room temperature for 16 h. The cooled mixture was then decomposed with dilute acetic acid, and the product was extracted with ether (3 × 50 ml). The extract was washed with water, saturated sodium hydrogen carbonate solution, and water again, dried, and evaporated. Treatment of the semisolid product (630 mg) with ether–light petroleum caused partial solidification to provide *cis*-2-benzyl-1,2,3,4-tetrahydronaphthalen-1-ol (IX) (200 mg), m.p. 117—119° (from ether–light petroleum) (Found: C, 85.55; H, 7.5. $C_{17}H_{18}O$ requires C, 85.65; H, 7.6%); $\nu_{max.}$ 3 587 cm^{-1}; τ 6.78—8.87 (8 H, m), 5.53 (1 H, d, *J* 7.2 Hz), and 2.47—3.00 (9 H, m).

A solution of the alcohol (IX) (140 mg) in ethanol (20 ml) was hydrogenated over palladium–charcoal (10%; 80 mg) in the presence of concentrated hydrochloric acid (one drop). The mixture was worked up as before to give 2-benzyl-1,2,3,4-tetrahydronaphthalene (VI) [7] (120 mg, 92%), m.p. 38—39°.

The noncrystalline material (280 mg) obtained by reduction of (VII) was probably a mixture of diastereoisomers of the desired alcohol. Catalytic reduction of the mixture as above also provided (VI) (240 mg), m.p. 38—39° [total yield 69% based on ketone (VII) utilised].

This authentic sample of (VI) was identical (mixed m.p. and u.v. and n.m.r. spectra) with the product obtained by reduction of (I) with sodium–liquid ammonia.

Reduction of the Tetralone (VIII) *with Lithium Aluminium Hydride.*—To an ice-cold stirred suspension of the hydride (950 mg) in dry tetrahydrofuran (20 ml) was added dropwise a solution of 2-benzylidene-1-tetralone [9] (VIII) (2.34 g) in tetrahydrofuran (25 ml) during 30 min. The mixture was then refluxed for 3 h, left at room temperature for 20 h, cooled, and decomposed with cold water. Dilute sulphuric acid (10%; 30 ml) was then added and the product was extracted with ether (3 × 75 ml). The extract was washed with water, dried (Na_2SO_4), and evaporated to furnish *cis*-2-benzyl-1,2,3,4-tetrahydronaphthalen-1-ol (IX) (2 g, 84%), m.p. and mixed m.p. 117—119° (Found: C, 85.5; H, 7.55%).

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