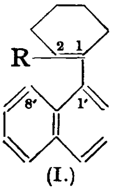
308. cyclo*Hexylnaphthalenes and Related Compounds.*

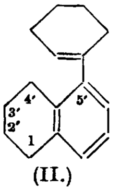
By J. W. Cook and C. A. Lawrence.

A projected synthesis of the 3 : 4-benzphenanthrene ring system from 2-(1′-naphthyl)-*cyclo*hexanol was frustrated by the fact that this carbinol could neither be converted into the bromide (Cook, Hewett, and Lawrence, this vol., p. 71) nor oxidised to the corresponding ketone. Under all the conditions used for oxidation (with chromic acid, vanadic acid, potassium permanganate, and copper oxide at 300°) the carbinol was partly or completely transformed into resinous products, and no ketonic derivative could be isolated. Evidently the ketone was more readily attacked than the carbinol. If this were due to the susceptibility to oxidation of the naphthalene nucleus, then it should have been possible to overcome the difficulty by the use of 2-(5′-*tetralyl*)cyclo*hexanol*, which was prepared from 5-tetralyl-lithium and *cyclo*hexene oxide. Although a *semicarbazone* was isolated after oxidation of this carbinol with chromic acid, the yield was so trivial that the reaction was useless for synthetic purposes. Nevertheless, a study of the properties of various hydrocarbons related to the two carbinols already mentioned has provided results of interest.

The ethylenic bond in 1-(1′-naphthyl)-Δ^1-*cyclo*hexene (I; R = H) was unexpectedly resistant to catalytic hydrogenation, the unsaturated hydrocarbon being only partly reduced to 1-cyclo*hexylnaphthalene* by shaking for 30 hours with hydrogen in the presence of Adams's platinum catalyst and acetic acid. The inertness of the double bond is most satisfactorily attributed to a mutual saturation of the free affinities of the carbon atoms 2 and 8′, which can come within atomic distances of each other without appreciable distortion of the molecule. This explanation is supported by the fact that 1-(5′-*tetralyl*)-Δ^1-cyclo*hexene* (II), in which such mutual deactivation cannot occur, behaved normally on hydrogenation, being rapidly reduced to 5-cyclo*hexyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*.



(I.)



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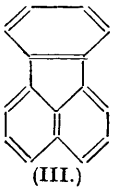

(III.)

Analogous examples of low reactivity have recently been recorded by Ingold, Parekh, and Shoppee (this vol., p. 142), who observed a mutual suppression of activity of the two double bonds in certain derivatives of $\Delta^{\alpha\epsilon}$-hexadiene, and by Fries and Bestian (*Ber.*, 1936, **69**, 718), who found that *o*-divinylbenzene, unlike styrene, has little tendency to polymerise.

Although 1-(1'-naphthyl)-Δ^1-*cyclo*hexene (I; R = H) is readily dehydrogenated by sulphur to 1-phenylnaphthalene (Weiss and Woidich, *Monatsh.*, 1925, **46**, 456; Sherwood, Short, and Stansfield, J., 1932, 1832), it underwent a dismutation to 1-phenylnaphthalene and 1-*cyclo*hexylnaphthalene when heated with selenium or platinum-black. This behaviour recalls that of oleanolic acid, which is converted into a saturated hydrocarbon by selenium at 330—350° (Ruzicka, Hösli, and Ehmann, *Helv. Chim. Acta*, 1934, **17**, 442) in spite of the fact that its double bond cannot be hydrogenated by the normal catalytic method. From previous studies of the influence of structure on dehydrogenation processes (compare Cook and Hewett, this vol., p. 62) it was anticipated that 1-*cyclo*hexylnaphthalene would be readily dehydrogenated to 1-phenylnaphthalene by platinum-black, and probably also by selenium, at 300—320°. This proved not to be the case, for the *cyclo*hexyl compound withstood the dehydrogenating action of both catalysts. It was also largely unattacked by sulphur at 220°, although in this case a little phenylnaphthalene was formed. Dehydrogenation experiments were also carried out with 2-*cyclo*hexylnaphthalene, a crystalline hydrocarbon isolated by Bodroux (*Ann. Chim.*, 1929, **11**, 511) from the products of interaction of naphthalene and *cyclo*hexene, in presence of aluminium chloride. This hydrocarbon was dehydrogenated to 2-phenylnaphthalene by selenium at 300—320° (Bodroux dehydrogenated it with sulphur), but was unaltered when heated with platinum-black at 300—320°. The unexpected resistance to dehydrogenation with platinum-black shown by the two *cyclo*hexylnaphthalenes is very remarkable, and at present no explanation is available.

On account of the difficulty of hydrogenation of naphthyl*cyclo*hexene (I; R = H) an alternative route to 1-*cyclo*hexylnaphthalene was sought in the interaction of α-tetralone with *cyclo*hexylmagnesium chloride. This gave, in poor yield, 1-cyclo*hexyl*-3 : 4-*dihydronaphthalene*, which was dehydrogenated to 1-*cyclo*hexylnaphthalene. A by-product of the reaction was a *ketone*, $C_{20}H_{18}O$, evidently formed by condensation between two molecules of α-tetralone.

Further evidence of the inertness of the ethylenic bond in 1-(1'-naphthyl)-Δ^1-*cyclo*hexene (I; R = H) was provided by the fact that the hydrocarbon was neither cyclised nor polymerised by aluminium chloride in cold carbon disulphide. In the hope of promoting cyclisation by the presence of a suitably disposed methyl group a similar experiment was carried out with 1-(1'-*naphthyl*)-2-*methyl*-Δ^1-cyclo*hexene* (I; R = Me). This hydrocarbon which was dehydrogenated by selenium to 1-o-*tolylnaphthalene*, was partly cyclised by aluminium chloride at 0°, for subsequent selenium dehydrogenation gave fluoranthene (III) in poor yield.

EXPERIMENTAL.

1-cyclo*Hexylnaphthalene*.—An impure specimen of this hydrocarbon was separated by Bodroux (*loc. cit.*) from the products of interaction of naphthalene and *cyclo*hexene. He described no derivatives.

(*a*) A solution of 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (α-tetralone) (36·5 g.) in anhydrous ether (100 c.c.) was added during 2 hours to a well-stirred ice-cold Grignard solution prepared from *cyclo*hexyl chloride (30 g.), magnesium turnings (6·6 g.), and anhydrous ether (140 c.c.). After being kept at 0° for ½ hour, and boiled for 1½ hours, the reaction mixture was allowed to stand overnight, and then decomposed with ammonium chloride solution. The crude product was heated with potassium hydrogen sulphate in order to ensure dehydration of the tertiary carbinol, and was then separated by distillation into 3 fractions : (i) b. p. 134—150°/12 mm. (21·5 g.), (ii) b. p. 128—132°/0·4 mm. (3·8 g.), and (iii) b. p. 216°/0·4 mm. (10·2 g.). Fraction (i) was unchanged tetralone. Fraction (ii) was 1-cyclo*hexyl*-3 : 4-*dihydronaphthalene*, which, after several distillations over sodium, had b. p. 140°/1 mm. or 172°/10 mm.; $n_D^{12\cdot2^\circ}$ 1·5762; $d_{4^\circ}^{12\cdot2^\circ}$ 1·021; whence $[R_L]_D = 68\cdot79$ (calc., 67·62) (Found: C, 90·4; H, 9·6. $C_{16}H_{20}$ requires C, 90·5; H, 9·5%). Fraction (iii) formed a viscous gum which gave a solid (3·7 g.) when triturated with light petroleum. This ketone, probably 1-*keto*-2-(1'-*tetralylidene*)-1 : 2 : 3 : 4-*tetra*-

hydronaphthalene, crystallised from alcohol in colourless microscopic needles, m. p. 130—130·5° (Found : C, 87·2; H, 6·6. $C_{20}H_{18}O$ requires C, 87·5; H, 6·6%). The 2 : 4-*dinitrophenylhydrazone* crystallised from alcohol in small orange prisms, m. p. 249—250° (decomp.) (Found : N, 12·0. $C_{26}H_{22}O_4N_4$ requires N, 12·3%).

1-*cyclo*Hexyl-3 : 4-dihydronaphthalene was dehydrogenated by heating at 300—320° with platinum-black (6 hours) or selenium (15 hours) to 1-cyclo*hexylnaphthalene*, which after purification through its picrate had b. p. 118—120°/0·3 mm., and $n_D^{11°}$ 1·6000 (Found : C, 91·1; H, 8·5. $C_{16}H_{18}$ requires C, 91·35; H, 8·65%). The *picrate* formed long slender orange needles (from alcohol), m. p. 122—123·5° (Found : C, 60·3; H, 4·8. $C_{22}H_{21}O_7N_3$ requires C, 60·1; H, 4·8%); the *styphnate* formed slender yellow needles (from alcohol), m.p. 150·5—151° (Found : C, 58·5; H, 4·4. $C_{22}H_{21}O_8N_3$ requires C, 58·0; H, 4·7%); and the s.-*trinitrobenzene complex* formed slender yellow needles (from alcohol), m. p. 116·5—117·5° (Found : C, 62·4; H, 5·35. $C_{22}H_{21}O_6N_3$ requires C, 62·4; H, 5·0%). The m. p.'s of these derivatives were not depressed by admixture with the corresponding derivatives of 1-(1′-naphthyl)-Δ^1-*cyclo*hexene (I; R = H) (picrate, m. p. 124·5—125·5°; styphnate, m. p. 160·5—161·5°; *s*.-trinitrobenzene complex, m. p. 121—121·5°).

(*b*) A suspension of platinum oxide (0·25 g.) in acetic acid (25 c.c.) was reduced with hydrogen, pure recrystallised 1-(1′-naphthyl)-Δ^1-*cyclo*hexene (4·35 g.) then added, and the whole shaken with hydrogen. This experiment was carried out by each of us and repeated several times with concordant results. Absorption of hydrogen was extremely slow, and even after shaking for 30 hours the product contained appreciable amounts of unsaturated hydrocarbon (estimated at 35% by the Rosenmund and Kuhnhenn reagent). After removal of this by agitation of a *cyclo*hexane solution with sulphuric acid the product was distilled, and then gave analytical figures which showed that hydrogenation of the naphthalene nucleus had been effected to some extent under the drastic conditions employed (Found : C, 90·7; H, 9·1%). After purification through the picrate (m. p. 122—123°) this material gave 1-*cyclo*hexylnaphthalene, which had $n_D^{17·7°}$ 1·6099 and $d_{4°}^{15°}$ 1·044; whence $[R_L]_D = 69·68$ (calc., 69·93) (Found : C, 91·2; H, 8·35. Calc. for $C_{16}H_{18}$: C, 91·35; H, 8·65%).

5-cyclo*Hexyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene and its Derivatives*.—5-Bromo-1 : 2 : 3 : 4-tetrahydronaphthalene (Smith, J., 1904, **85**, 729) (10·5 g.) was slowly added to a suspension of lithium (0·75 g.; powdered under tetralin) in ether (50 c.c.). Reaction set in at once and the mixture boiled spontaneously. After the initial reaction had subsided, the whole was boiled for 3 hours and then cooled in ice during addition of *cyclo*hexene oxide (5 g.). After 15 minutes in the ice-bath the mixture was allowed to warm to room temperature, and was finally boiled for 6 hours. Ice was then added, and the carbinol isolated in the normal manner by distillation (b. p. 174—176°/1·5 mm.). This carbinol gave a 3 : 5-*dinitrobenzoate* which formed primrose-yellow microscopic plates, m. p. 163—164·5° (Found : C, 64·8; H, 5·7. $C_{23}H_{24}O_6N_2$ requires C, 65·1; H, 5·7%). Pure 2-(5′-*tetralyl*)cyclo*hexanol*, obtained by hydrolysis of this ester, was a colourless gum which did not crystallise (Found : C, 83·4; H, 9·6. $C_{16}H_{22}O$ requires C, 83·4; H, 9·65%).

For oxidation, a solution of this carbinol (10 g.) in glacial acetic acid (100 c.c.) was treated with a solution of chromic acid (3·2 g.) in 80% acetic acid (20 c.c.), and kept at room temperature for 24 hours. The acetic acid was removed on the water-bath under reduced pressure, the residue extracted with water and ether, and the ethereal extract washed with dilute acid and alkali and distilled. The distillate (7·1 g.) was heated with semicarbazide in aqueous-alcoholic solution for 18 hours, and gave only 0·2 g. of the *semicarbazone* of 2-(5′-tetralyl)*cyclo*hexanone, m. p. 198—200° (decomp.) (Found : N, 14·35. $C_{17}H_{23}ON_3$ requires N, 14·7%). The unreacted gum contained some of the original carbinol, of which the 3 : 5-dinitrobenzoate was isolated. The yield of ketone was not improved by modification of the conditions, or by the use of permanganate for oxidation.

1-(5′-*Tetralyl*)-Δ^1-cyclo*hexene*.—The foregoing crude carbinol (8·7 g.) was heated with zinc chloride (15 g.) at 160—180° for ¾ hour. The resulting *hydrocarbon* (II) was extracted with benzene and distilled, forming a colourless liquid, b. p. 181°/15 mm. (Found : C, 89·15; H, 9·4. $C_{16}H_{20}$ requires C, 90·5; H, 9·5%). When shaken with hydrogen and Adams's platinum catalyst in acetic acid, this hydrocarbon rapidly absorbed a molecule of hydrogen and gave a product which was almost saturated towards bromine. Purified by shaking with sulphuric acid, it formed a colourless liquid, mainly 5-cyclo*hexyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 118°/0·2 mm. (Found : C, 88·7; H, 10·3. $C_{16}H_{22}$ requires C, 89·6; H, 10·4%).

Dismutation of 1-(1′-*Naphthyl*)-Δ^1-cyclo*hexene* (I; R = H).—(*a*) The unsaturated hydrocarbon (3 g.) was heated with platinum-black (0·3 g.) at 300—320° for 4 hours, during which

60 c.c. of gas were liberated. Complete dehydrogenation to 1-phenylnaphthalene should have given 645 c.c. of hydrogen. The product, which was almost saturated, was treated with picric acid in alcoholic solution. The hydrocarbon recovered from the crystalline picrate was shaken in *cyclo*hexane solution with sulphuric acid, whereby a little unsaturated compound was removed. The unattacked hydrocarbon was then distilled over sodium and was shown to be 1-*cyclo*hexylnaphthalene (1·5 g.) (Found : C, 91·5; H, 8·2. Calc. : C, 91·35; H, 8·65%). The alcoholic liquors from which the picrate of this hydrocarbon had been separated were freed from picric acid and solvent, and the resulting hydrocarbon was nitrated with nitric acid in acetic acid, by which procedure 1-phenylnaphthalene, a liquid which forms no crystalline picrate, is converted into a nitro-compound, m. p. 132° (Weiss and Woidich, *loc. cit.*). Our material gave a crystalline derivative, m. p. 126—127°, not depressed by the compound similarly prepared from authentic 1-phenylnaphthalene.

(*b*) 1-(1′-Naphthyl)-Δ^1-*cyclo*hexene (2 g.) was heated with selenium (2 g.) at 300—320° for 24 hours. The product was worked up as described under (*a*) and gave much 1-*cyclo*hexylnaphthalene, and a smaller amount of 1-phenylnaphthalene (isolated as its nitro-derivative).

From these experiments, and those recorded above, it is clear that 1-*cyclo*hexylnaphthalene is not dehydrogenated by selenium or platinum-black at 300—320°. When 1-*cyclo*hexylnaphthalene (1 g.) was heated with sulphur (0·45 g.) at 220° for 5 hours, most of it was recovered unchanged (isolated as picrate). By working up the liquors in the manner described, a trace of the nitro-derivative of 1-phenylnaphthalene was isolated.

Dehydrogenation of 2-cyclo*Hexylnaphthalene*.—(*a*) The pure crystalline hydrocarbon, m. p. 31° (Bodroux, *loc. cit.*) (1 g.) was heated with selenium (1·2 g.) at 300—320° for 10 hours, and gave 2-phenylnaphthalene, m. p. 98·5—100°, after crystallisation from alcohol (Bodroux gives m. p. 101—102°).

(*b*) When 2-*cyclo*hexylnaphthalene (1 g.) was heated with platinum-black at 300—320° for 2 hours in an atmosphere of carbon dioxide, only 24 c.c. of gas were collected (complete dehydrogenation should have liberated 320 c.c. of hydrogen), and the unchanged material crystallised on cooling (mixed m. p.).

Synthesis of Fluoranthene.—2-Methyl*cyclo*hexanone (22·4 g.) was condensed in the usual way with 1-naphthylmagnesium bromide (from 41·4 g. of 1-bromonaphthalene, 5·3 g. of magnesium, and 200 c.c. of ether) and the crude distilled carbinol was dehydrated by 1 hour's heating at 160—170° with potassium hydrogen sulphate (30 g.). The resulting 1-(1′-*naphthyl*)-2-*methyl*-Δ^1-cyclo*hexene* (I; R = Me) (13·7 g.) was purified through its *s*.-trinitrobenzene complex, which had no sharp m. p. The hydrocarbon, regenerated by treatment with stannous chloride, formed a colourless liquid, b. p. about 125°/0·3 mm.; $n_D^{15\cdot5^\circ}$ 1·6111 and $d_{4^\circ}^{15\cdot5^\circ}$ 1·036, whence $[R_L]_D = 74\cdot44$ (calc., 73·98) (Found : C, 91·5; H, 8·3. $C_{17}H_{18}$ requires C, 91·8; H, 8·2%). The presence of one double bond was confirmed by titration with perbenzoic acid. When this hydrocarbon (0·5 g.) was heated with selenium (1 g.) at 300—320° for 10 hours and then distilled, it gave a greenish fluorescent oil which deposited crystals after 2 days. These were drained on a tile and recrystallised from aqueous alcohol, giving slender colourless needles of 1-o-*tolylnaphthalene*, m. p. 67·5—68·5° (Found : C, 93·5; H, 6·6. $C_{17}H_{14}$ requires C, 93·5; H, 6·5%).

For cyclisation, a solution of the unsaturated hydrocarbon (I; R = Me) (3·2 g.) in carbon disulphide (30 c.c.) was treated with anhydrous aluminium chloride (4 g.), and the mixture kept at 0° for 6½ hours. The solution was decanted from the sludge, shaken with ice-water, dried, and distilled. The product (2·1 g.), b. p. 122—130°/0·3 mm., gave no satisfactory crystalline derivatives, and was dehydrogenated with selenium at 310—320° (21 hours). After extraction and distillation, light petroleum was added, whereby crystals were obtained. These were drained on a porous tile and recrystallised from alcohol; they then formed pale yellow crystals, m. p. 107—107·5°, not depressed by authentic fluoranthene supplied by the Gesellschaft für Teerverwertung. The identification was completed by comparison of the picrates. The yield of fluoranthene was very small.

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