138. *Fused Carbon Rings. Part X. Some Fundamental Properties of the* 0 : 3 : 3-bicyclo*Octane Ring.*

By J. W. Barrett and R. P. Linstead.

The experiments described in this paper bring to light a number of fundamental differences between the 0 : 3 : 3-*bicyclo*octane ring system, formed by ortho-fusion of two 5-membered rings, and the decalin system, formed similarly from two 6-membered rings. We find that (1) *trans*-0 : 3 : 3-*bicyclo*octane has a higher heat of combustion than its *cis*-isomeride, whereas in the decalin series the reverse is true. (2) Two well-known reactions of *cis*-decalin are its dehydrogenation to naphthalene and its rearrangement over aluminium chloride to the *trans*-isomeride. Neither of these reactions is paralleled in the *bicyclo*octane series.

Heats of Combustion.—In an earlier paper (J., 1935, 436) it was shown that the heat of combustion of *trans*-β-*bicyclo*octanone, measured in the liquid state at constant volume, exceeded that of the *cis*-isomeride by 6·8 kg.-cals. (If the heats of combustion are calculated for the vapour state, by the application of Trouton's rule, the corresponding difference is 6·7 kg.-cals.) This was correlated with the deviation of the carbon valencies of the *trans*-ketone from the tetrahedral arrangement. Both the *cis*- and the *trans*-ketone have now been obtained in sufficient quantity for thorough purification and reduction by both the Clemmensen and the Kishner–Wolff method. The samples of the *cis*-hydrocarbon prepared by the two methods were almost identical in density, boiling point, refractivity, and heat of combustion. The *trans*-hydrocarbon prepared by both methods melted at — 30°, and in this case, owing to the comparative scarcity of *trans*-material, only the carefully purified product of the Clemmensen reaction was used for the determination of the heat of combustion. The fact that the *trans*-ketone was comparatively difficult to reduce by the Clemmensen method suggests that the reaction proceeds through the stage of an unsaturated compound; the entry of a double bond into the strained *trans*-ring would be less easily effected than in the case of the *cis*-compound. The thermochemical measurements were carried out by Dr. G. Becker of Braunschweig, to whom our thanks are due. The experimental results are on p. 614 and the mean derived values, calculated in the usual way, are below :

Heats of Combustion of 0 : 3 : 3-bicyclo*Octanes.*

	cals./g.	Kg.-cals./mol.			
	Liquid at const. vol.	Liquid at const. vol.	Liquid at const. press.	Vapour at const. press.	B. p.
cis- (Clemmensen)	10,879 ± 2·3 *	1197·7	1199·7	1208·3	136°
cis- (Kishner–Wolff)	10,878 ± 2 *				
trans- (Clemmensen)	10,934 ± 3·2	1203·8	1205·8	1214·3	132

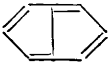
* The close agreement between these values shows that the value previously given (10,785 cals./g.; *oc. cit.*) for this hydrocarbon is erroneous, owing either to an accidental transposition of figures or to incomplete elimination of ketone during purification.

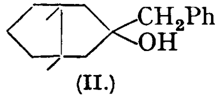
The *trans*-hydrocarbon has the higher heat of combustion by 6·0 kg.-cals. (vapour) and this confirms the result obtained with the ketones.

Hückel has calculated that the strain of the *trans*-0 : 3 : 3-*bicyclo*octane system is almost identical with that of the norcamphane (1 : 2 : 2-*bicyclo*heptane) ring. The thermochemical measurements of Becker and Roth (*Ber.*, 1934, **67**, 627) on Alder and Stein's tetrahydrodi*cyclo*-pentadienes and -hexadienes (*Annalen*, 1932, **496**, 197, 204, etc.) indicate that compounds containing the norcamphane ring have heats of combustion about 6 kg.-cals. above those calculated from the values for strain-free compounds of similar structure (cf. Pirsch, *Ber.*, 1934, **67**, 1303). This is in satisfactory agreement with the difference between the *trans*- and the *cis*-0 : 3 : 3-*bicyclo*octane system.

Strainless isomeric dicyclic compounds should have the same heats of combustion in the vapour state whatever the carbon skeleton. In agreement with this, Pirsch's value for 2 : 2 : 2-*bicyclo*octanone, 1104·9 (*loc. cit.*), is practically identical with our value for *cis*-0 : 3 : 3-β-*bicyclo*octanone, 1105·4 (calculated from the value for the liquid given in our previous paper, and the b. p. 195°).

Dehydrogenation.—One of the most interesting substances of the *bicyclo*octane series is the bridged *cyclo*octatetraene (I) (compare Armit and Robinson, J., 1922, **121**, 827).


(I.)



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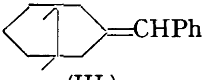
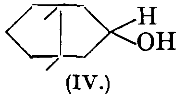


(III.)



(IV.)

It would be of considerable interest to know if this hydrocarbon exhibited any aromatic properties. It has some formal resemblance to naphthalene but cannot contain an electron sextet. In view of the ease with which derivatives of naphthalene are formed by dehydrogenation, we have examined the behaviour of suitable *bicyclo*octanes both in the vapour phase over platinum and in the liquid phase over selenium. *cis-bicyclo*Octane itself was unchanged by a platinum catalyst which dehydrogenated decalin. For work with selenium, substances of higher boiling point were necessary. *cis*-0 : 3 : 3-β-*bicyclo*Octanone was condensed with benzylmagnesium chloride to 2-*benzyl*-cis-β-0 : 3 : 3-bicyclo*octan*-2-*ol* (II). This was obtained in two stereoisomeric forms corresponding with the two possible positions of the benzyl group with respect to the remote *cyclo*pentane ring (compare the isomeric *cis*-β-hydrindanols of Hückel *et al.*, *Annalen*, 1926, **451**, 132; 1935, **518**, 155). When the 2-*benzylidene*-cis-0 : 3 : 3-bicyclo*octane* (III), obtained by their dehydration, was heated with selenium at 300—330°, it was partly unchanged and partly decomposed. In control experiments, 2-benzyl-*trans*-octalin was smoothly dehydrogenated at 300—330° to 2-benzylnaphthalene. Our experiments with the latter substances differ only in detail from those of Cook and Hewett (this vol., p. 62), an account of which appeared while this paper was being prepared. Although the unsaturated hydrocarbon of the decalin series presumably contains the double bond in the 6-membered ring by analogy with benzyl*cyclo*hexene (Cook and Hewett, *loc. cit.*), we think it more probable that the corresponding *bicyclo*octane derivative is the benzylidene compound (III) because of the comparative instability of the *cyclo*pentene ring. The benzyl*bicyclo*octene formula is not, of course, excluded. These results, although negative, provide some experimental support for the view that naphthalene is a unique dicyclic hydrocarbon and that the *bicyclo*octatetraene (I) does not possess aromatic characteristics.

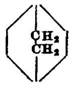
On reduction, either catalytically or by means of sodium, *cis*-β-*bicyclo*octanone yielded the corresponding *alcohol* (IV). This was obtained as a mixture of two stereoisomeric forms, corresponding to the two forms of benzyl*bicyclo*octanol. The pure isomerides were not isolated. The mixed *cis*-β-*bicyclo*octanol was mainly unchanged by selenium at 300°, yielding only a little *bicyclo*octene. *trans*-β-Decalol also appeared to be stable under these conditions.

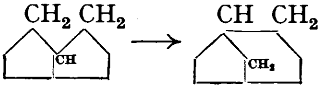
Action of Aluminium Chloride.—Zelinski and Turowa-Pollak (*Ber.*, 1932, **65**, 1299; compare *ibid.*, 1925, **58**, 1292; 1929, **62**, 1658) have shown that *cis*-decalin is converted apparently irreversibly into the *trans*-isomeride by standing at room temperature in contact with aluminium chloride. When *cis*-0 : 3 : 3-*bicyclo*octane was similarly treated, a more fundamental change occurred. The bulk of the hydrocarbon was converted into a crystalline isomeride, m. p. 132°. This was saturated and hence dicyclic. Molecular-weight determinations showed it to be monomeric, and in agreement with this it was extremely volatile. It was clear that a rearrangement of the carbon skeleton had occurred, and from the high melting point it was probable that one or more carbon atoms were present in a bridge. A strain-free stable substance which might be formed in this way was 2 : 2 : 2-*bicyclo*octane (V), but this was excluded by its m. p. (168°; Alder and Stein, *Annalen*, 1934, **514**, 13; Komppa, *Ber.*, 1935, **68**, 1267). The bold crystalline form of our material precluded its being an impure specimen of (V) and we thought it most probable that it was 1 : 2 : 3-*bicyclo*octane (VI).

Experiments on the preparation of this hydrocarbon were undertaken, but while they were still in progress Komppa, Hirn, Rohrmann, and Beckmann (*Annalen*, 1936, **521**, 242) reported a rational synthesis of 1 : 2 : 3-*bicyclo*octane, m. p. 134°, by the method which we had contemplated and which provides a proof of the structure. Through the kindness of Professor Komppa we have examined a sample of his synthetic hydrocarbon. It is identical in all respects with our material and does not depress its melting point.*

The rearrangement of 0 : 3 : 3- into 1 : 2 : 3-*bicyclo*octane is easily visualised and involves the migration of only one hydrogen atom and one carbon-to-carbon bond.

(V.)





(VI.)

Nevertheless the change is remarkable in that it involves the formation of a strained from a strain-free system. It is therefore analogous with the rearrangement of *cis*- into *trans*-

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* Professor Komppa has independently confirmed this.

hydrindane by aluminium bromide (Zelinski and Turowa-Pollak, *Ber.*, 1929, **62**, 1658) and it appears that in the presence of an aluminium halide the direction of isomeric change is not determined predominantly by questions of strain. There is, at present, no evidence that these changes are reversible and the persistence of the less stable modifications is thus easily understood.

Hydrogenation.—Willstätter and Kametaka (*Ber.*, 1908, **41**, 1480) obtained a liquid *bicyclo*octane from α-*cyclo*octadiene which resembled the 0 : 3 : 3-*bicyclo*octanes fairly closely in physical properties. This substance was formulated as a 0 : 1 : 5-, 0 : 2 : 4-, or 0 : 3 : 3-*bicyclo*octane. The bridge was reduced by hydrogen over nickel at 200° to give a mixture of hydrocarbons derived from *cyclo*octane. In view of this, the 0 : 1 : 5-structure was considered most probable.

We find that *trans*-0 : 3 : 3-*bicyclo*octane is unchanged by passage in hydrogen over platinised asbestos at 200°. There is no rearrangement to the more stable *cis*-form nor reduction of the bridge. The activity of the catalyst was checked both before and after the experiment by the conversion of benzene into *cyclo*hexane. In our experience this catalyst is more active than nickel and as it failed to reduce the *less* stable form of 0 : 3 : 3-*bicyclo*octane, it is reasonably certain that Willstätter's hydrocarbon did not contain this arrangement.

EXPERIMENTAL.

bicyclo*Octanes.*—15 G. of pure regenerated *cis*-β-0 : 3 : 3-*bicyclo*octanone, 200 g. of amalgamated zinc, 150 c.c. of glacial acetic acid, and 75 c.c. of hydrochloric acid were refluxed for 7 hours in an all-glass apparatus, a current of hydrogen chloride being passed through the mixture. The hydrocarbon formed was distilled in steam and extracted from the distillate with a little ether. The extract was washed with solutions of sodium bicarbonate and bisulphite (thrice), with concentrated sulphuric acid (twice), and with water. It was dried with calcium chloride, and the solvent removed under a column. The hydrocarbon was refluxed for 2 hours over sodium and distilled from fresh sodium. Yield, 10 g. (75%), b. p. 137°/765 mm. It was then redistilled and two fractions were collected arbitrarily; these had precisely the same physical properties: $d_{4°}^{18°}$ 0·8716; $n_{\mathrm{D}}^{18°}$ 1·4624; $[R_L]_{\mathrm{D}}$ 34·72 (calc., 34·75); b. p. 137°/765 mm., liquid at − 80°. These figures are almost identical with those reported in Part IV. The preparation of *cis*-*bicyclo*octane from *cis*-β-*bicyclo*octanone semicarbazone was carried out as described in our previous paper except that the hydrocarbon was also washed with concentrated sulphuric acid. The b. p., density and refractivity were identical with those previously found (*loc. cit.*).

5·5 G. of pure regenerated *trans*-β-0 : 3 : 3-*bicyclo*octanone were reduced similarly but for 12 hours and with one-third the quantities of reagents mentioned above. The purification was the same, except that the hydrocarbon extract was washed with sodium carbonate solution, concentrated sulphuric acid (twice), semicarbazide hydrochloride solution, and water. The yield of hydrocarbon was 2·16 g. (44%); 3 g. (54%) of *trans*-ketone were recovered by dilution of the sulphuric acid and extraction with ether; and 0·3 g. of *trans*-semicarbazone from the semicarbazide washing. The recovery of material was thus practically quantitative. The *trans*-hydrocarbon had $d_{4°}^{16°}$ 0·8648, $n_{\mathrm{D}}^{16°}$ 1·4638, $[R_L]_{\mathrm{D}}$ 35·12 (exaltation, 0·37), b. p. 134°/760 mm., m. p. (corr.) − 30°. The *trans*-hydrocarbon prepared by Kishner–Wolff reduction melts at − 29° (corr.) and not at − 36° as reported in Part IV. 3 G. of *trans*-hydrocarbon from two Clemmensen reductions were redistilled in an all-glass apparatus for the determination of the heat of combustion.

The values determined (const. vol. at *ca.* 20°) by Dr. Becker are:

cis-0 : 3 : 3-*bicyclo*Octane (Clemmensen) 10880, 10885, 10876, 10875; mean, 10879 ± 2·3 cals./g.

cis-0 : 3 : 3-*bicyclo*Octane (Kishner–Wolff) 10881, 10875, 10877; mean, 10878 ± 2 cals./g.

trans-0 : 3 : 3-*bicyclo*Octane (Clemmensen) 10941, 10927, 10936, 10930; mean, 10934 ± 3·2 cals./g.

Dehydrogenations.—A column of platinised asbestos (Zelinski and Borisoff, *Ber.*, 1924, **57**, 150) was contained in a hard-glass tube about a metre long. Dehydrogenations were carried out at 300—320° in an atmosphere of hydrogen, purified by means of acid and alkaline permanganate, silver sulphate, and potash. The substance was allowed to flow through a fine capillary into the tube and a slight suction was maintained by a siphon. The liquid products were condensed and the gas evolved was measured in a graduated reservoir. After each experiment the tube was thoroughly swept out with a current of purified hydrogen. In this apparatus decalin (3 c.c. during 2 hours) evolved hydrogen corresponding to 75% dehydrogenation and the product (2·4 g.) yielded 2·1 g. of naphthalene. *cis*-0 : 3 : 3-*bicyclo*Octane (2 c.c.) over the same catalyst yielded no hydrogen and the recovered hydrocarbon (1·8 c.c.) was analytically pure after two distillations from sodium (Found : C, 87·1; H, 12·7. Calc. for C_8H_{14} : C, 87·2; H, 12·8%). The physical properties were almost unchanged. The catalyst was still active towards decalin after this experiment.

Selenium dehydrogenation of benzylated compounds. Experiments with derivatives of 2-benzyldecalin are described only in so far as they supplement those of Cook and Hewett (*loc. cit.*). trans-2-*Benzyl*-2-*decalol* was a viscous liquid, b. p. 170°/3 mm. (Found : C, 83·8; H, 10·1. $C_{17}H_{24}O$ requires C, 83·5; H, 9·9%). Potassium hydrogen sulphate, used by Cook and Hewett, gave incomplete dehydration of this alcohol; oxalic acid was preferable. 6 G. of the alcohol were heated with 20 g. of crystalline oxalic acid for 6 hours at 120°. The product was poured into water, and the hydrocarbon isolated by means of ether. Yield, 4·5 g., b. p. 140—145°/3 mm. 24 G. of the alcohol and 40 g. of anhydrous oxalic acid, treated similarly for 5 hours, yielded 19 g. of hydrocarbon, b. p. 144—146°/3 mm. Redistillation from sodium yielded *trans*-2-benzyloctalin, b. p. 145°/3 mm., which rapidly reduced permanganate and decolorised bromine in chloroform (Found : C, 89·9; H, 9·8. Calc. for $C_{17}H_{22}$: C, 90·2; H, 9·8%). 5 G. of the hydrocarbon were heated with 10 g. of selenium for 36 hours at about 320°. The residue was extracted with ether, and the extract refluxed for several hours with sodium. After removal of solvent the residue yielded 3·5 g. of 2-benzylnaphthalene, b. p. 156—166°/3—4 mm., which soon solidified. It formed prismatic needles from alcohol, m. p. 55—56° (Found : C, 93·5; H, 6·4. Calc. for $C_{17}H_{14}$: C, 93·5; H, 6·5%). The m. p. was not depressed by authentic 2-benzylnaphthalene (m. p. 56°), but was depressed to *ca.* 40° by 1-benzylnaphthalene (m. p. 59°). The picrate melted at 93—94° alone, 93° admixed with 2-benzylnaphthalene picrate, and 81° admixed with 1-benzylnaphthalene picrate (m. p. 102°). Pure 2-benzylnaphthalene, regenerated from the picrate, melted at 57°. We are indebted to Mr. K. D. Errington for the preparation of the reference samples.

15 G. of *cis*-0 : 3 : 3-β-*bicyclo*octanone were added slowly at room temperature to the Grignard reagent prepared from 15·5 g. of benzyl chloride and 2·9 g. of magnesium in 200 c.c. of dry ether. The mixture was refluxed for 8 hours and worked up in the usual way. The colourless viscous product (18·5 g.) quickly deposited a hard crystalline mass (12·4 g., m. p. 65°), which was separated from residual liquid by suction. Crystallisation from purified light petroleum (b. p. 40—50°) gave massive transparent prisms of the solid form of 2-*benzyl*-cis-0 : 3 : 3-bicyclo-*octan*-2-*ol* (II), m. p. 66—67° (Found : C, 83·1; H, 9·2. $C_{15}H_{20}O$ requires C, 83·1; H, 9·3%). The liquid *isomeride* deposited practically no more solid on standing (Found : C, 83·3; H, 9·4%). Both alcohols were dehydrated with crystalline oxalic acid as described above to 2-*benzylidene*-cis-0 : 3 : 3-bicyclo*octane* (III), an unpleasant-smelling liquid, unsaturated to permanganate and to bromine, b. p. 126—127°/3 mm. (Found : C, 91·2; H, 9·2. $C_{15}H_{18}$ requires C, 90·9; H, 9·1%). Yield, 3 g. from 5 g. of solid; 2·5 g. from 4 g. of liquid alcohol.

5 G. of the hydrocarbon and 9 g. of selenium powder were heated for 2 hours at 300° and 48 hours at 310—330°. Very little hydrogen selenide was evolved; the liquid residue, isolated by means of ether, boiled between 80°/768 mm. and 138°/10 mm. (2 g.). The most definite fraction (0·6 g., b. p. 137°/10 mm.) corresponded to unchanged hydrocarbon. All the fractions reduced permanganate and none yielded a picrate.

cis-0 : 3 : 3-bicyclo*Octan*-2-*ol*.—A solution of 10 g. of *cis*-β-0 : 3 : 3-*bicyclo*octanone in 200 c.c. of moist ether was reduced during 6 hours by the addition of 20 g. of sodium. The main fraction of the product boiled at 104—108°/20 mm. (3·4 g.) and a considerable amount of bimolecular material was formed. A similar reduction in the presence of an excess of acetic acid gave 6 g., b. p. 103—105°/20 mm., 92—95°/15 mm. 4·6 G. of the ketone in 50 c.c. of alcohol were hydrogenated over Adams's catalyst. 1 Mol. of hydrogen was absorbed in 12 hours, after which distillation yielded 4 g. of *bicyclo*octanol, b. p. 85—86°/10 mm. No hydrocarbon was formed. The same mixture of stereoisomeric alcohols appeared to be formed by all three methods. It had a characteristic smell and failed to crystallise even at low temperatures [Found : (method 1) C, 76·2; H, 11·0; (method 2) C, 76·0; H, 10·9; (method 3) C, 76·0; H, 11·0. Calc. for $C_8H_{14}O$: C, 76·2; H, 11·1%]. In the course of attempts to separate pure stereoisomeric forms we isolated a hydrogen phthalate, m. p. 72°, crystallising in large transparent perfect rhombs, and an apparently homogeneous phenylurethane, m. p. 116°. No solid *bicyclo*octanol could be obtained by the hydrolysis of these derivatives.

The mixed alcohols (5 g.), refluxed for 2 days with selenium at 300—310°, yielded much hydrogen selenide, 2 g. of unchanged alcohol, 0·5 g. of a hydrocarbon, b. p. 136—140°/760 mm., probably *bicyclo*octane, and a viscous residue which failed to give a picrate. *trans*-β-Decalol, m. p. 75°, gave no naphthalene or naphthol under the same conditions, nearly all being recovered unchanged.

Reaction with Aluminium Chloride.—2 G. of aluminium chloride were sublimed into a flask and covered with 5 g. of *cis*-0 : 3 : 3-*bicyclo*octane. The mixture, protected from moisture, was kept at room temperature for 48 hours. [Later experiments showed that the formation of the solid was almost complete after 2 hours' standing.] The hydrocarbon was then removed by means of a high vacuum into a tube cooled to − 70°. It solidified and remained mainly solid at room temperature. The liquid was removed by means of a "filter-stick" and distilled (mainly at 135—136°/758 mm.). The distillate partly solidified and was separated as before. After several repetitions of this process a "permanent" liquid, b. p. 135°, m. p. − 30° to − 15°, was isolated, but, owing to the small amount, we were unable to determine whether this was crude *trans*-0 : 3 : 3-*bicyclo*octane (m. p. − 29°) or unchanged *cis*-0 : 3 : 3-*bicyclo*octane contaminated with the solid hydrocarbon. The ratio of solid to liquid was about 6 : 1. The combined solid was purified by three vacuum sublimations at room temperature, which produced bold but irregular transparent crystals, m. p. 128°. This material was dissolved in alcohol, precipitated by the addition of water, collected rapidly, and immediately transferred to an all-glass apparatus consisting of four elongated bulbs, one containing phosphoric oxide, attached to a common tube. The substance was placed in the end bulb, the pressure reduced to 1 mm., and the apparatus sealed. After 24 hours' drying, the hydrocarbon was transferred to the third bulb by cooling this to − 75°, and was finally resublimed into the fourth bulb in the same way. The product was then practically pure 1 : 2 : 3-*bicyclo*octane, m. p. 131·5—132·5°. It had a peculiar odour, was very soluble in organic solvents and extremely volatile. It sublimed readily at room temperature and pressure and was best kept in a sealed tube. It was stable to bromine and permanganate, contained no chlorine, and left no ash on sudden ignition (Found: C, 86·6; H, 12·7; *M*, cryoscopic in benzene, 104, 108. Calc. for C_8H_{14}: C, 87·2; H, 12·8%; *M*, 110). Professor G. Komppa kindly sent us a generous sample of his synthetic 1 : 2 : 3-*bicyclo*octane. This was not quite pure, m. p. 126°. As it seemed probable that the impurity was the corresponding unsaturated hydrocarbon or ketone, the material was treated with dilute potassium permanganate solution (20% of that required for complete oxidation) and distilled in steam. The solid hydrocarbon was then purified by the method described above, and finally melted at 132°, unchanged by resublimation. A mixture of the two samples of 1 : 2 : 3-*bicyclo*octane melted at 132°.

Hydrogenations.—These were carried out with the same apparatus and catalyst as for the dehydrogenations over platinum. 3 C.c. of thiophen-free benzene were passed in a free stream of hydrogen during 2 hours, the catalyst being maintained at 190—210°. The product had $n_D^{23°}$ 1·447, $d_{4°}^{23°}$ 0·796, corresponding to about 75% hydrogenation. 2 G. of *trans-bicyclo*octane were similarly treated during 2 hours, and the product passed over the catalyst a second time. The final product (1·5 g.) was distilled from sodium and finally alone. Before treatment the hydrocarbon had $n_D^{23°}$ 1·4604, $d_{4°}^{23°}$ 0·8580; and after treatment $n_D^{22°}$ 1·4608, $d_{4°}^{22°}$ 0·8590. The catalyst was still active towards benzene after this experiment.

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