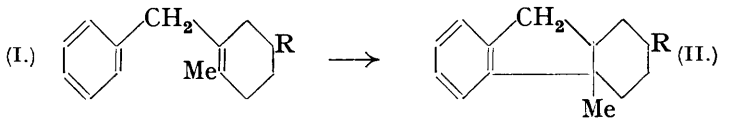
15. *The Dehydration of Benzyl*cyclo*hexanols.*

By J. W. Cook and C. L. Hewett.

In our preliminary survey of the synthesis of polycyclic hydroaromatic compounds by cyclisation of unsaturated compounds of suitable structure (J., 1933, 1098) we found that 1-benzyl*cyclo*hexanol was converted by phosphoric oxide at 160° into a saturated hydrocarbon, which we suggested was hexahydrofluorene. Further investigation was clearly desirable in view of our failure to obtain fluorene by selenium dehydrogenation of this hydrocarbon. We attributed this failure to the use of too low a temperature, consequent upon the relatively low boiling point of the hydrocarbon. If our proposed structure were correct, then similar hydrofluorene hydrocarbons (II) should be obtained more readily by cyclisation of the intermediate unsaturated hydrocarbons (I; R = H or Pr^{β}) resulting from dehydration of the *carbinols* obtained from benzylmagnesium chloride and 2-methyl*cyclo*hexanone or tetrahydrocarvone (for a discussion of the influence of a methyl group in promoting cyclisation see J., 1934, 653, 1727).



In agreement with this view, both hydrocarbons (I; R = H and Pr^{β}) were converted in good yield by aluminium chloride at 0° into saturated *isomerides*, whereas 1-benzyl-Δ^1-*cyclo*hexene is mainly polymerised. Both tricyclic hydrocarbons resisted the dehydrogenating action of selenium, and in the case of the methyl*iso*propyl compound this was certainly not due to the b. p. being too low. The methyl compound (from I; R = H) was likewise unaffected by 7 hours' treatment with palladised charcoal at 300°.

In the meantime, experiments in other directions made it difficult to assess the significance of these unsuccessful attempts to dehydrogenate the hydrocarbons in question. For instance, it was found (in collaboration with G. A. D. Haslewood and F. L. Warren) that saturated sterol derivatives (dihydrocholesterol, cholestane, and perhydrocalciferol) were not dehydrogenated by heating with selenium at 300—320° for 60 hours, and cholestane was only partly dehydrogenated at 340—350° (30 hours). Moreover, it was shown (in collaboration with A. Dansi) that 2-*benzyldecalin* was unaffected by selenium at 320—330°, although it was dehydrogenated to 2-benzylnaphthalene by platinum-black at 300°. A single double bond in the molecule destroyed this resistance to selenium dehydrogenation, for 2-*benzyloctalin*, obtained by dehydrating 2-*benzyl*-trans-2-*decalol*, gave 2-benzylnaphthalene with selenium at 300—320°. This difference in behaviour between platinum and palladium, on the one hand, and selenium and sulphur (which, unlike the noble metals, are able to bring about elimination of quaternary methyl groups), on the other hand, points to different mechanisms for the two types of dehydrogenating agents. Probably in the case of sulphur and selenium intermediate compounds are formed by combination with an unsaturated centre or an aromatic ring. If neither of these is present, dehydrogenation does not occur. An apparent exception to the generalisation that completely reduced rings are resistant to selenium dehydrogenation was recently given by Barrett, Cook, and Linstead (J., 1935, 1067), who obtained 2-methylnaphthalene from *trans*-2-methyldecalin, but these authors used a higher temperature (320—350°) than that which we normally employ (300—320°), and in any case they state that the yield was poor.

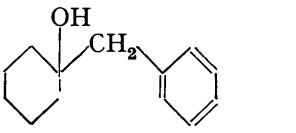
As we could not be certain that the resistance to selenium dehydrogenation shown by the tricyclic hydrocarbons from (I) was not due to the presence of the isolated *cyclo*hexane ring in (II), we decided to make a detailed study of the structure of the original tricyclic hydrocarbon from 1-benzyl*cyclo*hexanol, and also to synthesise hexahydrofluorene by an independent method. The results have shown that the dehydration product of benzyl-*cyclo*hexanol is not hexahydrofluorene, but a bridged-ring compound (VII): *hexahydro-*

fluorene, synthesised by the method described below, was smoothly dehydrogenated to fluorene by selenium at 300—320°, and was also dehydrogenated with great facility by platinum-black at 250—260°. Hence the cyclisation products of (I; R = H and Pr^{β}) cannot be hexahydrofluorene derivatives, although in the absence of further evidence we are not prepared to assert that they are homologues of (VII). It is also evident that the structure of a methyl*iso*propylhexahydrofluorene attributed by Ruzicka and Peyer (*Helv. Chim. Acta*, 1935, **18**, 678) to a hydrocarbon which they found to be unaffected by heating with selenium at 360° for 60 hours cannot be correct.

The evidence for the bridged-ring structure (VII) of the hydrocarbon from 1-benzyl-*cyclo*hexanol is as follows: (a) Oxidation with dilute nitric acid at 180° gave phthalic acid, showing that in the cyclisation the alicyclic part of the molecule becomes attached at position 2 of the aromatic ring.

(b) Oxidation with cold chromic acid in acetic acid gave, in good yield, a *ketone* which formed a characteristic well-crystallised *semicarbazone* and an *oxime*. Hence the methylene group of the original benzyl group must be preserved intact. Moreover, the same ketone was formed by oxidation of the tricyclic hydrocarbon resulting from the phosphoric oxide dehydration of 1-benzyl*cyclo*hexanol (III), 2-*benzyl*cyclo*hexanol* (IV), and phenyl-*cyclo*hexylcarbinol (V). The great stability of this ketone is incompatible with the spiran structure (VI), the only structure which could arise from all three carbinols without migration of a double bond in the hypothetical intermediate unsaturated hydrocarbon. The inevitable conclusion is that such a migration does occur during the cyclisation.

(c) The fact that this ketone was different from the hexahydrofluorenone synthesised from 2-phenylhexahydrobenzoic acid is fairly conclusive disproof of the hexahydrofluorene structure for the hydrocarbon from (III), (IV), and (V).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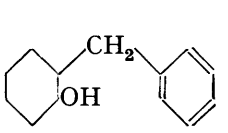
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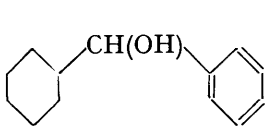
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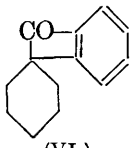
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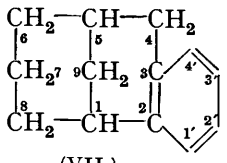
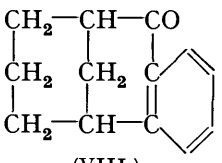
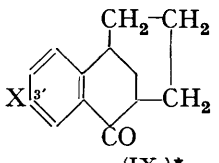

(VII.)


(VIII.)


(IX.)*

(d) The ketone (VIII) was converted by nitric acid into a crystalline *nitro*-derivative (IX; X = NO_2), in which the nitro-group evidently occupies the *m*-position with respect to the carbonyl group. This was reduced to a primary *amine* (IX; X = NH_2), which was oxidised by chromic acid to *cis*-hexahydro*iso*phthalic acid. This acid was obtained in better yield by permanganate oxidation of the *phenol* (IX; X = OH) formed by decomposition of the corresponding diazonium sulphate.

These results present some points of interest. The formation of 2 : 3-*benz*-1 : 3 : 3-bicyclo-Δ^2-*nonene* (VII) by dehydration of the carbinols (III), (IV), and (V), in preference to the alternative hexahydrofluorene, is another instance of the extreme sensitivity of the course of cyclisation processes to factors of molecular environment (compare J., 1934, 653, 1727; 1935, 667, 1635). In the present instance a determining factor is probably the complete absence of strain of the *bicyclo*nonane system present in (VII); the hexahydrofluorene structure is a strained system, although not, in the *cis*-form, extensively so. A noteworthy feature is a the facility with which the centre of unsaturation resulting from elimination of the hydroxyl group from the carbinols (III, IV, and V) moves round the *cyclo*hexane ring to the point necessary for the formation of the most favoured structure.

* This alternative representation of the benz*bicyclo*nonene system shows the relationship of these compounds to tetralin.

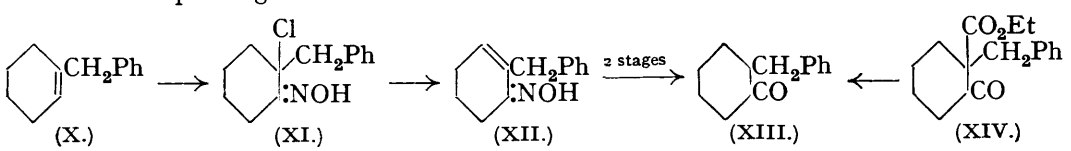
This is particularly remarkable with (V), which gave almost as good yield of (VII) as the other carbinols. The parent hydrocarbon, 1 : 3 : 3-*bicyclo*nonane, and many of its simple derivatives were prepared by Meerwein (*Annalen*, 1913, **398**, 196; *J. pr. Chem.*, 1922, **104**, 161) and their formation and properties reflect the strainless character of this system * (for a theoretical discussion of this and other strainless polycyclic systems see Mohr, *J. pr. Chem.*, 1918, **98**, 315). In our tricyclic hydrocarbon (VII) condensation with the aromatic nucleus presumably introduces a slight strain on account of the deviation from the tetrahedral angle of the valencies of carbon atoms 2 and 3, but it is apparent from a model that any strain so introduced is inappreciable.

We could obtain no evidence of dehydrogenation of benz*bicyclo*nonene (VII) either with selenium (see above), or with platinum-black at 300°, or with platinised asbestos at 340—360°, using the technique of Ehrenstein (*Arch. Pharm.*, 1931, **269**, 648). This cannot be attributed entirely to absence of strain, for Kasansky and Plate (*Ber.*, 1935, **68**, 1259) have shown that a methyl derivative of 2 : 2 : 2-*bicyclo*octane, which also is a completely strainless system (Aschan, *Acta Soc. Sci. Fennicae*, 1896, **21**, No. 5, 124; compare Mohr, *loc. cit.*), is susceptible to the action of a dehydrogenating catalyst.

The great stability of the benz*bicyclo*nonene ring system is reflected in the properties of 2 : 3-benz-1 : 3 : 3-*bicyclo*-Δ^2-nonen-4-one (VIII). This ketone was unaffected by sodium dichromate in boiling glacial acetic acid (10 hours); with potassium permanganate in pure acetone, only the solvent was oxidised; bromine in carbon disulphide had no action in 48 hours. The last is remarkable, as the ketone appears to contain an enolisable hydrogen atom. The inactivity towards bromine may be due to suppression of enolisation on account of the reluctance of the system to assume a double bond at the position 4 : 5, although, as Hückel ("Theoretische Grundlagen der organische Chemie," 1934, I, 74) has pointed out, Bredt's rule for the camphane system is not valid for more complex systems. An attempt to methylate the ketone (VIII) with sodamide and methyl iodide gave only unchanged ketone; boiling concentrated nitric acid had no oxidising action on the ketone, but merely led to the nitro-ketone (IX; X = NO_2).

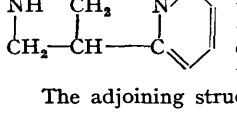
From the theoretical standpoint, the oxidation of 3'-hydroxy-2 : 3-benz-1 : 3 : 3-*bicyclo*-Δ^2-nonen-4-one to *cis*-hexahydro*iso*phthalic acid provides experimental proof of the *cis* attachment of the " bridge " carbon atom to the 1 : 5-carbon atoms of the eight-membered ring, which is in fact the only possible mode of attachment on the carbon tetrahedral theory.

At an early stage in this investigation it became necessary to review the evidence for the structure of the unsaturated hydrocarbons resulting from dehydration of the carbinols (III) and (V). Auwers and Treppmann (*Ber.*, 1915, **48**, 1207) dehydrated these carbinols with various agents. In all cases they claimed to have obtained 1-benzyl-Δ^1-*cyclo*hexene (X), which they transformed through its nitrosochloride (XI) (the same nitrosochloride was stated to be obtained from both carbinols) into an unsaturated oxime (XIII), and thence into the corresponding saturated ketone :



(X.) (XI.) (XII.) (XIII.) (XIV.)

* The same 1 : 3 : 3-*bicyclo*nonane system is apparently present in the dicyclic ketones obtained by Rabe (*Ber.*, 1903, **36**, 225; 1904, **37**, 1667, 1671) by condensing ethyl acetoacetate with cyclic ketones and by Stobbe and Rosenburg (*J. pr. Chem.*, 1912, **86**, 226) and by Georgi (*ibid.*, p. 237) by condensing cyclic ketones with $\alpha\beta$-unsaturated ketones. The latter reaction has been revived recently by Rapson and Robinson (J., 1935, 1285), and adapted for the synthesis of polycyclic ketones which probably contain condensed hydroaromatic systems. In none of the cases cited, however, has the structure of the product been proved.

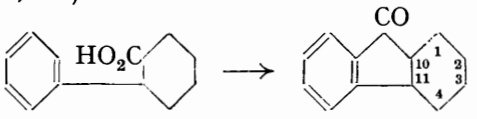


The adjoining structure proposed by Ing (J., 1932, 2778) for cytisine shows very close analogy to the structure of our benz*bicyclo*nonene. The same ring system is apparently present in anagyrine (Ing., J., 1933, 504).

This ketone was not benzoyl*cyclo*hexane and hence was assumed to be 2-benzyl*cyclo*hexanone (XIII). More recently, Prévost, Donzelot, and Balla (*Compt. rend.*, 1934, **198**, 1041) concluded from physical data that the hydrocarbon resulting from the dehydration of phenyl*cyclo*hexylcarbinol (V) with potassium hydrogen sulphate was benzylidene*cyclo*hexane. Moreover, Kurssanoff (*Ber.*, 1931, **64**, 2297) dehydrated this carbinol by pyrolysis of its methyl xanthate and oxidised the product to benzoic acid and *cyclo*hexanone. This also is compatible only with the benzylidene*cyclo*hexane structure.

In the case of the potassium hydrogen sulphate dehydration product of 1-benzyl*cyclo*hexanol we verified completely the results reported by Auwers and Treppmann. The constitution of the final saturated ketone was established by direct comparison with 2-benzyl*cyclo*hexanone prepared from *α-benzylpimelic acid*, which was obtained by hydrolysis of *ethyl* 2-*benzyl*cyclo*hexanone*-2-*carboxylate* (XIV). In the case of phenyl*cyclo*hexylcarbinol no satisfactory dehydration product was obtained by the use of potassium hydrogen sulphate, in spite of many attempts. The carbinol was largely converted into high-boiling material (possibly an ether); the small low-boiling fraction was incompletely dehydrated. Similar failure attended the use of anhydrous oxalic acid. The only other method of dehydration reported by Auwers and Treppmann for this carbinol was heating with phosphoric oxide at 160°! By the use of zinc chloride, a reagent employed for this carbinol by Sabatier and Mailhe (*Compt. rend.*, 1904, **139**, 345), we obtained a good yield of hydrocarbon, which contained only 55% of unsaturated compound. Considerable conversion into benz*bicyclo*nonene (VII) had taken place, as was shown by first destroying the unsaturated compound by oxidation with permanganate, and then oxidising the saturated residue with chromic acid, the tricyclic ketone (VIII) being identified by its semicarbazone. The original hydrocarbon mixture obtained by the zinc chloride dehydration gave in rather poor yield a nitrosochloride which was certainly not (XI). Elimination of hydrogen chloride led to a product, the indefinite m. p. of which was depressed by (XII). This definitely establishes the fact that the unsaturated hydrocarbon from phenyl*cyclo*hexylcarbinol and zinc chloride was not benzyl-Δ^1-*cyclo*hexene. It may have been largely the benzylidene*cyclo*hexane obtained by Prévost and his collaborators, and by Kurssanoff, but as we were unable to obtain a constant-melting oxime we did not pursue this question. The essential point is that, contrary to the assertion of Auwers and Treppmann, there is no evidence of the production of benzyl-Δ^1-*cyclo*hexene (X) by migration of the double bond of benzylidene*cyclo*hexane.*

The preparation of hexahydrofluorene by hydrogenation of fluoreneoneoxime with palladium oxide–palladium-black was claimed by Nakamura (*Proc. Imp. Acad. Japan*, 1929, **5**, 469), but by this method we obtained only fluorene and a base. *Hexahydrofluorenone* (XVI) was readily formed by an internal Friedel–Crafts reaction with 2-phenylhexahydrobenzoic acid (XV), an acid first described by Kipping and Perkin (J., 1890, **57**, 316). Our earlier experiments were made with a specimen of this acid obtained by hydrogenating the 2-phenyl-Δ^3-tetrahydrobenzoic acid of Lehmann and Paasche (*Ber.*, 1935, **68**, 1146), but the acid (XV) was more conveniently prepared in quantity by reduction of *o*-phenylbenzoic acid with sodium and amyl alcohol (Ranedo and León, *Anal. Fís. Quím.*, 1925, **23**, 113).

(XV.) 

(XVI.)

The isomeric hexahydro-acid obtained by catalytic hydrogenation of *o*-phenylbenzoic acid (Ranedo and León) was not affected by cold concentrated sulphuric acid, and gave no hexahydrofluorenone when its acid chloride was treated with aluminium chloride. Therefore, it was not a stereoisomeride of (XV), but *o-cyclo*hexylbenzoic acid (compare the reduction and hydrogenation of *o*-benzylbenzoic acid; Cook, Hewett, and Lawrence, this vol., p. 74). This structure was confirmed by oxidation to phthalic acid.

* Since the present paper was submitted for publication Auwers (*Ber.*, 1935, **68**, 2174) has reaffirmed his previous statement that dehydration of phenyl*cyclo*hexylcarbinol leads to benzyl-Δ^1-*cyclo*hexene.

The ketone (isolated only as the semicarbazone, m. p. 220°) obtained by Vocke (*Annalen*, 1934, **508**, 8) by pyrolysis of hexahydrodiphenic acid is presumably identical with our hexahydrofluorenone (semicarbazone, m. p. 212—213°), as, although *cis*- and *trans*-forms are theoretically possible, stereochemical considerations require an equilibrium in favour of the *cis*-form (compare hexahydro-α-hydrindone; Hückel, Sachs, Yantschulewitsch, and Nerdel, *Annalen*, 1935, **518**, 158, 169).

Hexahydrofluorenone was reduced to *hexahydrofluorene* by Clemmensen's method. The density and refractive index of this hydrocarbon were almost identical with those of the isomeric benz*bicyclo*nonene (VII).

Experimental.

Cyclisation of Benzyl-Δ^1*-*cyclo*hexenes by Aluminium Chloride.*—*1-Benzyl-2-methyl-*Δ^1*-*cyclo*hexene* (I; R = H). 2-Methyl*cyclo*hexanone (24·6 g.) was added to an ice-cold Grignard reagent prepared from benzyl chloride (25·2 g.), magnesium turnings (4·8 g.), and anhydrous ether (80 c.c.). After being kept at room temperature for 3 hours, the product was decomposed with ammonium chloride solution. The resulting 1-benzyl-2-methyl*cyclo*hexanol (25 g.; b. p. 115°/0·8 mm.) could not be obtained analytically pure, probably on account of the presence of dibenzyl, which was isolated when the dehydrated carbinol was oxidised with chromic acid. Dehydration by potassium hydrogen sulphate (1·5 parts) at 160—175° (1 hour) led to *1-benzyl-2-methyl-*Δ^1*-*cyclo*hexene* (95% yield), which formed a colourless liquid, b. p. 158—160°/19 mm., and had $n_D^{17\cdot8°}$ 1·5445 and $d_{4°}^{17\cdot8°}$ 0·9938 * (Found: C, 89·7; H, 9·2. $C_{14}H_{18}$ requires C, 90·3; H, 9·7%). For cyclisation, this unsaturated hydrocarbon (10 g.), dissolved in carbon disulphide (100 c.c.), was treated with anhydrous aluminium chloride (16 g.) and kept at 0° for 3 hours and then over-night at room temperature. The resulting *hydrocarbon* (7 g.) absorbed no bromine, and had b. p. 141°/18 mm., $n_D^{17\cdot8°}$ 1·5438, and $d_{4°}^{17\cdot8°}$ 0·9837 * (Found: C, 90·6; H, 9·7. $C_{14}H_{18}$ requires C, 90·3; H, 9·7%).

When this saturated hydrocarbon (4 g.) was heated with selenium (5·5 g.) at 300—320° for 100 hours, it became very dark. Distillation gave 1·5 g. of liquid, b. p. 150—160°/20 mm., which appeared to be unchanged hydrocarbon (Found: C, 90·6; H, 9·0%). Palladised charcoal at 300° (7 hours) likewise appeared to have no dehydrogenating action. That cyclisation had occurred in the *o*-position of the benzyl group was shown by oxidation of the hydrocarbon (1 g.) with nitric acid (*d* 1·42; 7 c.c.) and water (15 c.c.) at 180—185° for 5½ hours. The only oxidation product which could be isolated was phthalic acid (Found: C, 57·0; H, 3·7. Calc.: C, 57·9; H, 3·6%). The identification was completed by sublimation as phthalic anhydride (mixed m. p. with an authentic specimen).

*1-Benzyl-2-methyl-5-*iso*propyl-*Δ^1*-*cyclo*hexene* (I; R = Pr^β). Tetrahydrocarvone (for the preparation of which we are indebted to Messrs. Howards and Sons, Ltd.) (38·5 g.) was added to an ice-cold Grignard reagent from benzyl chloride (40 g.), magnesium turnings (7·5 g.), and anhydrous ether (125 c.c.). After being boiled for an hour, the whole was decomposed with ammonium chloride solution. The resulting *1-benzyl-2-methyl-5-*iso*propyl*cyclo*hexanol* (43 g.) formed a colourless viscous liquid, b. p. 140—142°/0·6 mm. (Found: C, 83·1; H, 10·6. $C_{17}H_{26}O$ requires C, 82·85; H, 10·6%). Dehydration to *1-benzyl-2-methyl-5-*iso*propyl-*Δ^1*-*cyclo*hexene* was not complete with potassium hydrogen sulphate, but was effected by heating with an equal weight of anhydrous zinc chloride at 160°. This hydrocarbon formed a colourless liquid, which absorbed the amount of bromine required for one double bond, and had b. p. 159°/12 mm., $n_D^{15\cdot8°}$ 1·5331, and $d_{4°}^{15\cdot8°}$ 0·9448; whence $[R_L]_D$ = 74·98 (calc., 74·44) (Found: C, 89·6; H, 10·6. $C_{17}H_{24}$ requires C, 89·4; H, 10·6%).

Cyclisation of this compound (I; R = Pr^β) by aluminium chloride at 0° was complete in 5 hours. The resulting saturated hydrocarbon (75% yield) was distilled over sodium and formed a colourless liquid, b. p. 160—161°/13 mm., $n_D^{15\cdot2°}$ 1·5300, and $d_{4°}^{15\cdot2°}$ 0·9607; whence $[R_L]_D$ = 73·35 (calc., 72·71) (Found: C, 89·5; H, 10·4. $C_{17}H_{24}$ requires C, 89·4; H, 10·6%).

This tricyclic hydrocarbon (3·8 g.) was heated with selenium (4 g.) at 310—320° for 40 hours. After distillation over sodium, 2·7 g. of liquid were recovered which had undergone very little dehydrogenation (Found: C, 90·1; H, 9·6%).

*Benz*bicyclo*nonene and its Derivatives.*—For the preparation of this tricyclic hydrocarbon

* No significance attaches to the values for molecular refraction on account of the presence of dibenzyl in the original hydrocarbon. These figures are recorded merely to show the inappreciable change in refractive index after cyclisation.

the standard procedure was as follows: The carbinol (III, IV, or V) was heated with 2 parts of phosphoric oxide at 150° for 20—30 minutes, after which a vacuum was applied and the hydrocarbon distilled. The distillate occasionally contained traces of unsaturated hydrocarbon, which were removed by agitation with concentrated sulphuric acid, followed by redistillation. Formation of the tricyclic hydrocarbon took place during the phosphoric oxide dehydration, and was in no way dependent upon this sulphuric acid treatment. The approximate yields were (a) from 1-benzyl*cyclo*hexanol, 50—70%; (b) from phenyl*cyclo*hexylcarbinol, 30%; from 2-benzyl*cyclo*hexanol, 55%. The last specimen had b. p. 125—126°/10 mm. and $n_D^{12\cdot8°}$ 1·5523.

*Oxidation of benz*bicyclo*nonene to phthalic acid.* A mixture of the hydrocarbon (1 g.), nitric acid (*d* 1·42; 7 c.c.), and water (15 c.c.) was heated at 180° for 5 hours. The tube having been opened, the solution was heated to expel nitrous gases and was then extracted once with ether. The aqueous solution was evaporated to dryness on the water-bath, and the residue recrystallised from water. The crystals (0·1 g.; m. p. 175—180°) were sublimed at 160—190°/14 mm., giving phthalic anhydride, m. p. 127—129° after crystallisation from benzene–*cyclo*hexane.

2 : 3-*Benz*-1 : 3 : 3-bicyclo-Δ^2-*nonen*-4-*one* (VIII). This could be obtained (1·65 g. of semicarbazone) when the hydrocarbon (4·8 g.) was treated with sodium dichromate (8·5 g.) in boiling acetic acid (50 c.c.) for 2½ hours, and the product fractionated. Better results were obtained by working at room temperature, the same ketone (identified by mixed m. p.'s of the semicarbazone) being formed from the saturated hydrocarbons obtained from 1- and 2-benzyl*cyclo*hexanols and from phenyl*cyclo*hexylcarbinol. The yield was about the same in all cases; on an average, 3·5 g. of semicarbazone were obtained from 10 g. of hydrocarbon. The following experiment is typical: A solution of chromic acid (65 g.) in 80% acetic acid (130 c.c.) was added during an hour to a mechanically stirred solution of benz*bicyclo*nonene (55 g.) in glacial acetic acid (550 c.c.). After being kept at room temperature for a week, the green solution was treated with *iso*propyl alcohol to reduce any excess of chromic acid. Most of the acetic acid was removed under reduced pressure, and the residue was diluted with water and extracted with ether. The extract was washed with dilute sodium carbonate solution and with water, dried, and distilled. The lower fraction, b. p. to 155°/23 mm., was discarded. The ketone fraction (b. p. 100—110°/0·1 mm.; 26·5 g.) was treated with semicarbazide in aqueous-alcoholic solution for 2 hours. The *semicarbazone* (17·7 g.) crystallised from alcohol in small colourless needles, m. p. 222—224° (Found: C, 69·3; H, 7·2; N, 17·1. $C_{14}H_{17}ON_3$ requires C, 69·1; H, 7·0; N, 17·3%). Hydrolysis of this semicarbazone (13 g.) was effected by 3 hours' boiling with a solution of crystalline oxalic acid (32·5 g.) in water (65 c.c.). After distillation in a vacuum, 2 : 3-*benz*-1 : 3 : 3-bicyclo-Δ^2-*nonen*-4-*one* (VIII) formed a colourless viscous liquid, b. p. 108—110°/0·2 mm., $n_D^{19\cdot9°}$ 1·5770, and $d_{4°}^{19\cdot5°}$ 1·1138; whence $[R_L]_D$ = 55·38 (calc., 54·24). The optical exaltation is in agreement with a structure in which the carbonyl group is directly linked to the aromatic nucleus (Found: C, 83·5; H, 7·6. $C_{13}H_{14}O$ requires C, 83·8; H, 7·6%). The *oxime*, prepared in boiling aqueous-alcoholic solution, crystallised in long colourless needles, m. p. 123—124° (Found: C, 77·8; H, 7·6. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5%).

Pure 2 : 3-*benz*-1 : 3 : 3-bicyclo-Δ^2-*nonene* (VII) was prepared by reduction of the pure ketone by Clemmensen's method (8 g. of ketone, 24 g. of amalgamated zinc, and 40 c.c. of concentrated hydrochloric acid were boiled for 6 hours). The pure hydrocarbon (3 g.) was a colourless mobile liquid, b. p. 85°/0·3 mm., 123°/15 mm., $n_D^{14°}$ 1·5580, $d_{4°}^{14°}$ 1·020; whence $[R_L]_D$ = 54·47 (calc., 54·23) (Found: C, 90·3; H, 9·5. $C_{13}H_{16}$ requires C, 90·6; H, 9·4%).

Attempted dehydrogenation of 2 : 3-*benz*-1 : 3 : 3-bicyclo-Δ^2-*nonene*. The failure to effect dehydrogenation with selenium was recorded in our earlier communication (*loc. cit.*). When the hydrocarbon (sample prepared from 2-benzyl*cyclo*hexanol; 2 g.) was heated with platinum-black (1 g.) for 10 hours in an atmosphere of carbon dioxide, 1·5 g. of hydrocarbon were recovered which seemed to be entirely unchanged. Furthermore, when this hydrocarbon was passed over platinised asbestos (Zelinsky and Borisoff, *Ber.*, 1924, **57**, 150) at 340—360° in an apparatus similar to that described by Ehrenstein (*loc. cit.*), no hydrogen was liberated and the hydrocarbon appeared to be unchanged. The activity of the catalyst was demonstrated by the fact that when decalin was afterwards used, hydrogen was freely liberated and naphthalene was formed.

3′-*Nitro*-2 : 3-*benz*-1 : 3 : 3-bicyclo-Δ^2-*nonen*-4-*one* (IX; X = NO_2). This was obtained when the ketone was boiled with concentrated nitric acid (10 parts) for 10 minutes, or by nitration with nitric acid in sulphuric acid. The best results were obtained when the ketone (10 g.)

was added dropwise to nitric acid (*d* 1·5; 100 c.c.). Heat was evolved, but no external cooling was applied. After ¾ hour the solution was heated on the water-bath for ¼ hour, and then cooled and poured into water. The *nitro*-compound crystallised from alcohol in colourless plates, m. p. 118·5—119·5° (Found: C, 67·65; H, 5·6. $C_{13}H_{13}O_3N$ requires C, 67·5; H, 5·7%).

3′-*Amino*-2 : 3-*benz*-1 : 3 : 3-bicyclo-Δ^2-*nonen*-4-*one* (IX; X = NH_2). A solution of the nitro-compound (5 g.) in alcohol (25 c.c.) was slowly added to a solution of stannous chloride (30 g.) in concentrated hydrochloric acid (25 c.c.), heated on the water-bath. Heating was continued for ¼ hour, and the solution was diluted with water, made strongly alkaline, and extracted with ether. The extract was dried (sodium sulphate), the ether removed, and the residue recrystallised from *cyclo*hexane with a little benzene. The *amine* (3·5 g.) formed lemon-yellow leaflets, m. p. 122·5—123·5°, readily soluble in cold dilute mineral acids to give colourless solutions (Found: C, 77·6; H, 7·7. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5%).

A boiling solution of this amine (0·5 g.) in glacial acetic acid (5 c.c.) was oxidised by dropwise addition of a solution of chromic acid (3 g.) in 80% acetic acid (6 c.c.). The whole was boiled for 1¼ hours, the acetic acid removed under reduced pressure, the residue dissolved in water, the solution filtered, and the filtrate extracted four times with ether. After removal of the ether, the residue was heated at 100° under reduced pressure to remove the last traces of acetic acid. The non-volatile residue was dissolved in water, boiled with charcoal, and the filtered solution was evaporated to dryness. The resulting *cis*-hexahydro*iso*phthalic acid crystallised from water in small colourless leaflets, m. p. 160—162°, not depressed by the acid obtained from the hydroxy-ketone (below).

3′-*Hydroxy*-2 : 3-*benz*-1 : 3 : 3-bicyclo-Δ^2-*nonen*-4-*one* (IX; X = OH). An ice-cold solution of the amino-ketone (2 g.) in *N*-sulphuric acid (25 c.c.) was diazotised with aqueous sodium nitrite (0·7 g. in 3 c.c.). The diazonium sulphate separated partly as an orange crystalline precipitate, a solution of which gave a dark red precipitate with alkaline β-naphthol. After ½ hour, urea (0·1 g.) was added, and the suspension was slowly added to boiling *N*-sulphuric acid (400 c.c.). After boiling for a few minutes, the whole was cooled and extracted with ether. The phenol was removed from the ethereal extract by shaking with dilute sodium hydroxide solution, and the alkaline solution was boiled with charcoal, filtered, and acidified. After cooling, the crystalline *hydroxy-ketone* (1·45 g.) was collected, washed, and recrystallised from aqueous alcohol. For analysis, a little of the resulting leaflets was recrystallised from benzene–*cyclo*hexane, forming a colourless crystalline powder, m. p. 160·5—161·5° (Found: C, 77·4; H, 6·9. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%).

For oxidation, a solution of this phenol (IX; X = OH) (0·82 g.) in water (25 c.c.), containing potassium hydroxide (0·4 g.), was stirred mechanically during addition of an aqueous solution of potassium permanganate (5·55 g. in 110 c.c.). The oxidation was completed by heating on the water-bath for 20 minutes. The filtered solution was acidified with hydrochloric acid and evaporated to dryness on the water-bath. The residue was extracted with water, filtered from a trace of resinous matter, and extracted five times with ether. The extract was dried (sodium sulphate), the ether removed, and the residue recrystallised from a little water, with charcoal. The resulting *cis*-hexahydro*iso*phthalic acid (0·25 g.) was recrystallised from benzene, forming a colourless powder, m. p. 161·5—162·5°, not depressed by an authentic sample (Found: C, 56·5; H, 7·0. Calc.: C, 55·8; H, 7·0%). The identification was completed by conversion into the anhydride, m. p. 185—186° (Perkin, J., 1891, **59**, 813, gives 187—189°), which by brief warming with aniline gave the anilic acid, m. p. 210—211°, described by Komppa (*Ann. Acad. Sci. Fennicae*, 1933, **37**, *A*, No. 6, 1).

The authentic specimen of *cis*-hexahydro*iso*phthalic acid was prepared by hydrogenation of *iso*phthalic acid (5 g.) in alcoholic solution (250 c.c.) with a platinum oxide catalyst (1 g.) at 4 atmospheres' pressure. Hydrogenation was complete in 2 hours, and the *cis*-hexahydro-acid was purified through its sparingly soluble calcium salt (Perkin, *loc. cit.*).

Unsaturated Hydrocarbons from 1-*Benzylcyclohexanol and Phenylcyclohexylcarbinol.*—2-*Benzylcyclohexanone from* 1-*benzyl*-Δ^1-*cyclohexene*. The nitrosochloride of benzyl*cyclo*hexene (obtained from 1-benzyl*cyclo*hexanol by dehydration with potassium hydrogen sulphate) was prepared by addition during 1 hour of a mixture of acetic acid (35 c.c.) and fuming hydrochloric acid (35 c.c.) to a mixture of hydrocarbon (30 g.), glacial acetic acid (30 c.c.), and amyl nitrite (24 c.c.), cooled in ice and salt. After an hour a little methyl alcohol was added and the nitrosochloride (12·5 g.) was collected and drained on porous porcelain; it then had m. p. 97—102°. This nitrosochloride (XI) was sufficiently stable to be recrystallised in small amounts from benzene, from which it separated in snow-white needles, m. p. 116—117° (Auwers and

Treppmann, *loc. cit.*, give 110°) (Found: C, 64·85; H, 6·5. Calc. for $C_{13}H_{16}ONCl$: C, 65·7; H, 6·8%). For elimination of hydrogen chloride, a solution of the nitrosochloride (12 g.) in pyridine (60 c.c.) was boiled for 3 hours. After cooling, and dilution with water, the oxime (XII) crystallised (4·6 g.); recrystallised from methyl alcohol, it formed stout colourless needles, m. p. 138·5—139·5°. This was clearly the oxime obtained by Auwers and Treppmann, who give m. p. 136—138°. Hydrolysis to the unsaturated ketone was effected by boiling 6*N*-sulphuric acid in 1½ hours, and the distilled ketone (bath at 180°; 0·4 mm.) was hydrogenated in ethereal solution with a palladium-black catalyst. The resulting saturated ketone (XIII) gave, in good yield, a semicarbazone, m. p. 165—166°, not depressed by the semicarbazone of 2-benzyl*cyclo*hexanone prepared as described below.

*Dehydration of phenyl*cyclo*hexylcarbinol with zinc chloride.* A mixture of the carbinol (20 g.) and powdered anhydrous zinc chloride (40 g.) was heated for an hour at 170—180°. While still warm, the liquid was poured off and distilled in a vacuum, and then redistilled over sodium (Found: C, 90·3; H, 9·3. Calc. for $C_{13}H_{16}$: C, 90·6; H, 9·4%). The hydrocarbon mixture (15 g.) had b. p. 90—91°/5 mm., $n_D^{12\cdot8°}$ 1·5460, and $d_{4°}^{12\cdot8°}$ 0·9656. These values are in good agreement with those given by Auwers and Treppmann, but this is of no significance, as the product was not homogeneous.

This hydrocarbon mixture (11 g.) was treated with amyl nitrite and hydrochloric acid as described for benzyl-Δ^1-*cyclo*hexene. The resulting nitrosochloride (1 g.) separated slowly from its solution in benzene as a white powder, m. p. 115—117° (decomp.); the mixed m. p. with the nitrosochloride of benzyl*cyclo*hexene was 106—108° (decomp.). Elimination of hydrogen chloride with boiling pyridine led to a product which crystallised in colourless needles, m. p. 128—132° after sintering; the mixed m. p. with benzyl*cyclo*hexenoneoxime (XII) was 110—115°. This experiment was repeated several times, with consistent results. The oxime mixture could be partly separated into higher-melting fractions. For example, by extraction with boiling *cyclo*hexane an insoluble residue, m. p. 155—160°, was obtained, and the filtrate deposited colourless needles, m. p. 147—155°. No homogeneous sharp-melting substance could be isolated from the small amount of material available.

The presence of benz*bicyclo*nonene (VII) in the hydrocarbon mixture (iodine value, 79. Calc. for one double bond, 148) obtained by dehydrating phenyl*cyclo*hexylcarbinol was shown as follows: The hydrocarbon mixture (8 g.) was heated on the water-bath with 5% aqueous potassium permanganate, more being added as long as it was decolorised rapidly. The manganese dioxide was reduced by sulphur dioxide, and the oil was extracted with ether, the extract dried, and the ether removed. The resulting liquid (3·5 g.) was almost completely saturated, and after oxidation with cold chromic acid in the usual way it gave 0·75 g. of the semicarbazone of benz*bicyclo*nononenone (VIII).

2-*Benzyl*cyclo*hexanone and* 2-*Benzyl*cyclo*hexanol.—Ethyl* 2-*benzyl*cyclo*hexanone*-2-*carboxylate.* The sodio-compound prepared from ethyl *cyclo*hexanone-2-carboxylate (34 g.) and powdered sodium (4·6 g.) in benzene (100 c.c.) was boiled for 5 hours with benzyl chloride (25·2 g.). After decomposition with water, the washed benzene solution was dried and distilled. *Ethyl* 2-*benzyl*cyclo*hexanone*-2-*carboxylate* (XIV), obtained in 80% yield, formed a colourless liquid, b. p. 144—145°/0·4 mm., which slowly crystallised. After recrystallisation from light petroleum and then from methyl alcohol it had m. p. 34·5—35° (Found: C, 73·8; H, 7·5. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·75%). The *semicarbazone* had m. p. 182—183° (Found: C, 64·3; H, 8·35. $C_{17}H_{23}O_3N_3$ requires C, 64·3; H, 7·3%). *α-Benzylpimelic acid*, obtained by hydrolysis of the keto-ester with alcoholic potash, separated from water in small colourless crystals, m. p. 81—82° (Found: C, 66·8; H, 7·2. $C_{14}H_{18}O_4$ requires C, 67·0; H, 7·25%).

2-Benzyl*cyclo*hexanone (XIII) was formed when α-benzylpimelic acid (75 g.) was distilled from a metal-bath at 360—380°. The ketone was purified through its sodium bisulphite compound, and was then distilled, yielding 26 g. of a colourless liquid, b. p. 155°/10 mm. (Found: C, 82·7; H, 8·7. Calc.: C, 82·9; H, 8·6%). The semicarbazone had m. p. 167—168°, in agreement with other workers who prepared this ketone by other methods (Tiffeneau and Porcher, *Bull. Soc. chim.*, 1922, **31**, 330; Cornubert and Maurel, *ibid.*, 1931, **49**, 1512, give 170—171°; Poggi and Saltini, *Gazzetta*, 1932, **62**, 684).

2-*Benzyl*cyclo*hexanol.* Water was added during 4 hours to a mechanically stirred mixture of 2-benzyl*cyclo*hexanone (26 g.), pure ether (100 c.c.), and thin slices of sodium (26 g.). The ethereal solution was washed, dried, and distilled. 2-*Benzyl*cyclo*hexanol* (IV), b. p. 154°/11 mm., crystallised from light petroleum in long colourless needles (20 g.), m. p. 75·5—76° (Found: C, 81·9; H, 9·5. $C_{13}H_{18}O$ requires C, 82·1; H, 9·8%). A more convenient route to this carbinol was subsequently found (Cook, Hewett, and Lawrence, this vol., p. 75).

Dehydrogenation of 2-Benzyloctalin and 2-Benzyldecalin.*—trans-2-*Benzyl*-2-*decalol. trans*-β-Decalone (15 g.) was added to an ice-cold Grignard solution prepared from benzyl chloride (12·5 g.), magnesium turnings (2·5 g.) and anhydrous ether (65 c.c.). The product was boiled for 2 hours, and decomposed with ammonium chloride solution. The dried ethereal solution was distilled, the carbinol fraction (16 g.) having b. p. 171°/6 mm. For characterisation, the 3 : 5-*dinitrobenzoate* was prepared by brief heating at 100° with 3 : 5-dinitrobenzoyl chloride in pyridine. It crystallised from alcohol in colourless needles, m. p. 162·5—164° (Found : C, 66·1; H, 6·0. $C_{24}H_{26}O_6N_2$ requires C, 65·7; H, 6·0%).

2-*Benzyloctalin* was obtained by dehydration of the aforesaid carbinol with potassium hydrogen sulphate at 160—170° (2 hours). It was distilled over zinc chloride and then over sodium, forming a colourless liquid, b. p. 151°/6 mm., $n_D^{12\cdot8°}$ 1·5520 (Found : C, 90·0; H, 9·8. $C_{17}H_{22}$ requires C, 90·2; H, 9·8%). For dehydrogenation, the hydrocarbon (2·2 g.) was heated with selenium (5·7 g.) at 310—320° for 48 hours. The product was distilled over sodium in a vacuum, and the distillate treated with alcoholic picric acid. The picrate of 2-benzylnaphthalene had m. p. 93°, in agreement with Roux (*Ann. Chim.*, 1887, **12**, 331), and the regenerated hydrocarbon, after crystallisation from alcohol, had m. p. 55·5°, in agreement with Vincent and Roux (*Bull. Soc. chim.*, 1883, **40**, 165) and with Dziewoński and Wodelski (*Rocz. Chem.*, 1932, **12**, 369).

2-*Benzyldecalin.* A solution of 2-benzyloctalin (11 g.) in glacial acetic acid (50 c.c.) was shaken with hydrogen and palladium-black (from 1 g. of palladous chloride) for 6 hours. The product was freed from solvent, and its benzene solution was washed with 80% sulphuric acid until no further colour was developed by fresh portions of acid. After distillation over sodium, 2-*benzyldecalin* formed a colourless liquid, b. p. 173—175°/10 mm. (Found : C, 89·6; H, 10·35. $C_{17}H_{24}$ requires C, 89·4; H, 10·6%). This hydrocarbon was unchanged by heating with an equal weight of selenium at 320—330° for 20 hours (Found : C, 89·2; H, 10·0%), but was dehydrogenated to 2-benzylnaphthalene (identified by m. p. of hydrocarbon and picrate) by heating at 300—305° for 6 hours with one-third of its weight of platinum-black.

Synthesis of Hexahydrofluorene.—2-*Phenylhexahydrobenzoic acid from α-phenylbutadiene.* 2-Phenyl-Δ^3-tetrahydrobenzaldehyde was prepared from α-phenylbutadiene and acraldehyde (Lehmann and Paasche, *Ber.*, 1935, **68**, 1146) and was oxidised in the cold by chromic acid in acetic acid (not by warming on the water-bath as specified by Lehmann and Paasche). The acidic product was distilled. Fractional crystallisation of the distillate furnished a small amount of an acid, m. p. 119·5—120·5°. This was probably the acid (m. p. 122°) obtained by Lehmann and Paasche from phenylbutadiene and acrylic acid. They stated that this acid was 3-phenyl-Δ^4-tetrahydrobenzoic acid, as it was different from the 2-phenyl-Δ^3-tetrahydrobenzoic acid formed by oxidation of the aldehyde, but it seems equally probable that the two acids are stereoisomeric.

Hydrogenation of the crude distilled acids from the above oxidation, by palladium-black in acetic acid, gave 2-phenylhexahydrobenzoic acid, m. p. 105—107° (from light petroleum). This acid did not depress the m. p. of the acid obtained by reduction of *o*-phenylbenzoic acid with sodium and amyl alcohol (Ranedo and León, *loc. cit.*) and the latter route proved to be more convenient for preparative purposes. As it seemed possible that the acid, m. p. 102—103°, obtained by Ranedo and León by catalytic hydrogenation of *o*-phenylbenzoic acid was stereoisomeric with the above hexahydro-acid, their experiment was repeated. The new hexahydro-acid was purified by dissolution in concentrated sulphuric acid, which sulphonated or dehydrated impurities but did not affect the acid in question. The acid so purified had m. p. 104°, and its structure as *o-cyclo*hexylbenzoic acid was established by the fact that it was slowly oxidised to phthalic acid (isolated as the anhydride) by boiling 5% alkaline potassium permanganate solution.

Hexahydrofluorenone (XVI). The conversion of 2-phenylhexahydrobenzoic acid into this ketone (identified by mixed m. p. of the semicarbazone) was carried out with specimens of the acid prepared from phenylbutadiene, and also from *o*-phenylbenzoic acid. The acid (XV) (20 g.) was converted into its chloride by 1 hour's boiling with thionyl chloride (100 c.c.), excess of thionyl chloride being then removed on the water-bath under reduced pressure. An ice-cold carbon disulphide solution (100 c.c.) of the crystalline chloride was treated with anhydrous aluminium chloride (13·5 g.), kept at 0° for 3 hours, and then decomposed with ice and hydrochloric acid. After being washed (sodium carbonate solution removed a little unchanged acid) and dried, the carbon disulphide was removed, and the residue distilled. The distillate,

* The preparation and dehydrogenation of 2-benzyloctalin were carried out by Dr. A. Dansi.

b. p. 130—132°/1 mm. (14 g.), crystallised. 1 : 2 : 3 : 4 : 10 : 11-*Hexahydrofluorenone* (XVI) crystallised from light petroleum in long colourless needles, m. p. 41·5—42° (Found : C, 83·4; H, 7·6. $C_{13}H_{14}O$ requires C, 83·8; H, 7·6%). The *semicarbazone* formed a yellowish crystalline powder (from alcohol), m. p. 212—213° (Found : C, 69·5; H, 7·1; N, 18·0. $C_{14}H_{17}ON_3$ requires C, 69·1; H, 7·0; N, 17·3%). An *oxime* prepared from the crude distilled ketone formed colourless needles (from *cyclo*hexane), m. p. 183—185° (Found : C, 78·0; H, 7·3. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5%). Subsequent attempts to prepare this oxime from the pure recrystallised ketone gave products of indefinite m. p., *ca.* 130—135°.

1 : 2 : 3 : 4 : 10 : 11-*Hexahydrofluorene.* The foregoing ketone (10 g.) was reduced by boiling for 5 hours with concentrated hydrochloric acid (20 c.c.), water (40 c.c.), and amalgamated zinc (30 g.), concentrated hydrochloric acid (5 c.c.) being added after each hour. The hydrocarbon was distilled in steam, separated from the distillate with ether, dried, and distilled. *Hexahydrofluorene* (8·2 g.) formed a colourless mobile liquid, b. p. 127°/15 mm., $n_D^{10\cdot9°}$ 1·5572, $d_4^{10\cdot9°}$ 1·019; whence $[R_L]_D$ = 54·37 (calc., 54·23) (Found : C, 90·2; H, 9·2. $C_{13}H_{16}$ requires C, 90·6; H, 9·4%).

Dehydrogenation of hexahydrofluorene. (a) A mixture of hexahydrofluorene (0·7 g.) and Adams's platinum oxide (0·1 g.), reduced with hydrogen, was heated at 250—260° for 1½ hours. Evolution of hydrogen was very brisk at this temperature. Even at 160° some gas was liberated. After recrystallisation from alcohol, the product had m. p. 113·5—114·5°, alone or mixed with an authentic specimen of fluorene, and gave a picrate, m. p. 80—81° (*lit.*, 80—82°).

(b) Dehydrogenation of hexahydrofluorene with an equal weight of selenium at 300—320° for 15 hours gave fluorene in good yield.

Oxidation of hexahydrofluorene with chromic acid in acetic acid under the conditions used for benz*bicyclo*nonene led to high-boiling resinous products which could not be distilled without decomposition. No hexahydrofluorenone could be isolated.

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[*Received, November 30th*, 1935.]