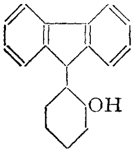
605. *Dehydration of 2-9′-Fluorenyl*cyclo*hexanol.*

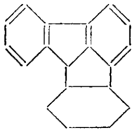
By J. W. Cook and L. Hunter.

Catalytic hydrogenation of 2-9′-fluorenyl*cyclo*hexanone gave *cis*- and *trans*-2-9′-fluorenyl*cyclo*hexanol (I), both of which were dehydrated by phosphoric acid to 9-*cyclo*hex-1′-enylfluorene (IV), the structure of which has been established. This work extends and corrects that of Hurd and Mold (*J. Org. Chem.*, 1948, **13**, 339), who regarded the dehydration product as 1 : 9-*cyclo*hexylenefluorene (II).

By dehydration of 2-fluorenyl*cyclo*hexanol * (I) with syrupy phosphoric acid at 230°, Hurd and Mold (*J. Org. Chem.*, 1948, **13**, 339) obtained a hydrocarbon which they described as 1 : 9-*cyclo*hexylenefluorene (II). They supported their claim that *cyclo*dehydration had taken place by a statement that the hydrocarbon was inert towards bromine and towards potassium permanganate, and was therefore saturated. Its dehydrogenation to 9-phenylfluorene by heating it with palladium–charcoal or with selenium was attributed by Hurd and Mold to pyrolytic fission of a carbon–carbon bond.

The structure (II) seemed to us very improbable for the hydrocarbon in question, for it contains a highly strained ring system (III). von Braun and his collaborators (*Ber.*, 1917, **50**, 56; 1928, **61**, 956) have recorded unsuccessful attempts to prepare derivatives of (III) by internal Friedel–Crafts reactions (but cf. Koelsch, *J. Amer. Chem. Soc.*, **1932**, **54**, 4746). It was suggested, therefore (Cook, *Nature*, 1949, **163**, 443), that the dehydration of 2-fluorenyl*cyclo*hexanol might be analogous to *cyclo*dehydration of 2-benzyl*cyclo*hexanol, and that the product is a derivative of the strainless 1 : 3 : 3-bi*cyclo*nonane.


(I)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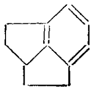
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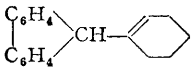
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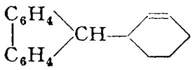
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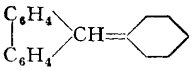
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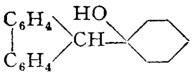

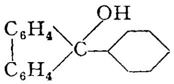
(VIII)

We have re-examined the dehydration of 2-fluorenyl*cyclo*hexanol under the conditions described by Hurd and Mold and have obtained a hydrocarbon having a m. p. (110·5—111°) in reasonable agreement with their figure (111·5—112°). This hydrocarbon was certainly not a product of *cyclo*dehydration for it was oxidised by chromic acid to fluorenone and not fluorenone-1-carboxylic acid. It was formed also by treatment of the alcohol with the milder dehydrating agent, potassium hydrogen sulphate, and was shown to be 9-*cyclo*hex-1′-enylfluorene (IV). On catalytic hydrogenation it was converted into the known 9-*cyclo*hexylfluorene. The presence of an ethylenic bond was confirmed by the formation of an epoxide with monoperphthalic acid, and of a diol with osmium tetroxide. The alternative structure of 9-*cyclo*hex-2′-enylfluorene (V) was made very improbable by the fact that the same hydrocarbon was obtained by dehydration of 1-fluorenyl*cyclo*hexanol (VII). Moreover, the possibility that double-bond migration had occurred to give *cyclo*hexylidenefluorene (VI) was excluded by the fact that the latter hydrocarbon (VI), prepared by dehydration of 9-*cyclo*hexylfluorenol (VIII), was distinct from the dehydration product of (I) and (II). The ultra-violet absorption spectra of the hydrocarbons (IV) and (VI) are in accord with the structures assigned to them. The Figure shows that 9-*cyclo*hex-1′-enylfluorene (IV) has a spectrum closely resembling that of fluorene, whereas the

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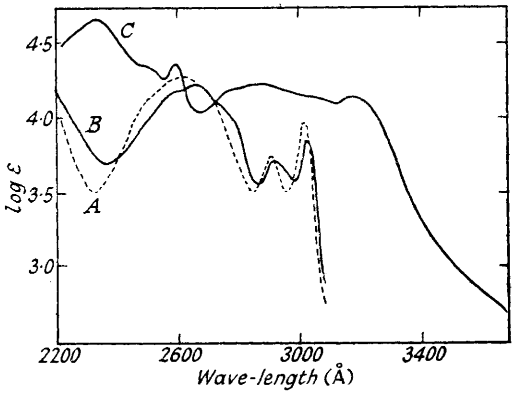
* Throughout this paper, fluorenyl refers to the 9-fluorenyl radical.

spectrum of *cyclo*hexylidenefluorene (VI), in which the double bond is conjugated with both aromatic nuclei, is widely different. The spectrum of 9-*cyclo*hexylfluorene is almost indistinguishable from that of the *cyclo*hexenyl compound (IV).

For the preparation of 2-fluorenyl*cyclo*hexanol (I) we used Hurd and Mold's method (*loc. cit.*), namely, catalytic hydrogenation of 2-fluorenyl*cyclo*hexanone over copper chromite. This gave not only the alcohol, m. p. 123° (phenylurethane, m. p. 145°), which they described, but also a stereoisomeric alcohol, m. p. 127° (phenylurethane, m. p. 172°), and a hexahydride, m. p. 177—181°, of one of these. When the hydrogenation was carried out with a very active catalyst at a much lower temperature the sole product was the alcohol, m. p. 123°, which is therefore considered to be the *cis*-isomer. Both the *cis*- and the *trans*-alcohol were dehydrated by syrupy phosphoric acid to 9-*cyclo*hex-1'-enylfluorene (IV).

A, *Fluorene* (*after Ramart-Lucas*, Bull. Soc. chim., 1935, **2**, 1377).
B, 9-cyclo*Hex-1'-enylfluorene*.
C, 9-cyclo*Hexylidenefluorene*.



EXPERIMENTAL

*Ethyl 1-Fluorenyl-2-keto*cyclo*hexane-1-carboxylate.**—Hurd and Mold (*loc. cit.*) prepared this ester in 35% yield by interaction of 9-chlorofluorene and the potassio-compound of ethyl 2-keto-*cyclo*hexanecarboxylate. We found that the yield could be increased to 75% by using 9-bromofluorene and the sodio-derivative of the keto-ester. 9-Bromofluorene was obtained in yields of 75—80% by the action of hydrobromic acid on fluorenol (Bachmann, *J. Amer. Chem. Soc.*, 1933, **55**, 2135), formed in 90% yield by hydrogenation of a solution of fluorenone in ethanol over Raney nickel. 9-Bromofluorene was obtained in 65% yield by direct bromination of fluorene with *N*-bromosuccinimide (Wittig and Felletschin, *Annalen*, 1944, **555**, 133).

Sodium (2·2 g.) was atomised in boiling purified toluene, and the toluene replaced by pure benzene (140 c.c.). Ethyl 2-keto*cyclo*hexanecarboxylate (15·9 g.) was added and the mixture kept overnight, the sodium being replaced by a voluminous precipitate of the sodio-compound. 9-Bromofluorene (23·7 g.) was then added, and the whole boiled under reflux (oil-bath) for 24 hours. The solution was slowly poured into water, and the benzene layer collected, washed, and dried (Na_2SO_4). The benzene was removed under reduced pressure and the residue was triturated with light petroleum (b. p. 60—80°). The undissolved solid was recrystallised from acetic acid and then had m. p. 133—134° (Hurd and Mold give m. p. 133—133·5°) (23·8 g.).

*2-Fluorenyl*cyclo*hexanone.*—Decarbethoxylation with aqueous-alcoholic potassium hydroxide gave yields of less than 20%. By use of barium hydroxide the yield of ketone was increased to 50%. A solution of ethyl 1-fluorenyl-2-keto*cyclo*hexane-1-carboxylate (10 g.) in 90% ethanol (100 c.c.) was heated under reflux with barium hydroxide (15·4 g.) for 22 hours. The solvent was distilled under reduced pressure and the residue treated with hydrochloric acid. The white solid so formed was replaced by a pale yellow oil after brief heating. This was extracted with ether. The ketone recovered from the washed and dried extract crystallised from ethanol in lustrous leaflets (3·91 g.), m. p. 111·5—112·5° (Hurd and Mold give 112·5—113·5°) (Found : C, 87·0; H, 6·9. Calc. for $C_{19}H_{18}O$: C, 87·0; H, 6·9%). The semicarbazone had m. p. 235—238° (decomp.) (Hurd and Mold give 220°) (Found : C, 75·4; H, 6·7; N, 13·5. Calc. for $C_{20}H_{21}ON_3$: C, 75·2; H, 6·6; N, 13·2%), and was hydrolysed by 6N-hydrochloric acid to the ketone of unchanged m. p.

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* See footnote, p. 3168.

2-*Fluorenyl*cyclo*hexanol* (I).—(*a*) A solution of 2-fluorenyl*cyclo*hexanone (2·62 g.) in purified dioxan (40 c.c.) and copper chromite catalyst (1 g.; *Org. Synth.*, Coll. Vol. II, p. 142) was placed in a stainless steel bomb which was charged with hydrogen to 90 atm. and then heated at 150° for 1¾ hours. The filtered solution, combined with two similar batches, was evaporated and the residue was dissolved in hot *cyclo*hexane. The cooled solution gave a white solid (3·3 g.), m. p. 120—123°. After 8 recrystallisations from *cyclo*hexane this gave pure (? trans-)2-*fluorenyl*-cyclo*hexanol* as a microcrystalline powder, m. p. 126·5—127·5° (0·3 g.) (Found: C, 86·4; H, 7·6. $C_{19}H_{20}O$ requires C, 86·3; H, 7·6%). The *phenylurethane* was prepared by heating a mixture of this alcohol (0·1 g.) and phenyl *iso*cyanate at 100° for 5 minutes. After several recrystallisations from light petroleum it formed silky needles, m. p. 171·5—172·5° (Found: C, 81·6; H, 6·4; N, 3·6. $C_{26}H_{25}O_2N$ requires C, 81·4; H, 6·6; N, 3·65%). Hurd and Mold (*loc. cit.*) obtained, by reduction of the ketone with sodium and moist ether, an impure product which gave a phenylurethane, m. p. 167·5—168·5°.

Evaporation of the *cyclo*hexane liquors from the first crystallisation of the alcohol gave a yellow syrup (3·9 g.) which was dissolved in hot 95% ethanol. The cooled solution slowly deposited a white solid, m. p. 146—164°, which, after crystallisation from acetone, chloroform, and then hexane, gave *hexahydro*-2-*fluorenyl*cyclo*hexanol* as fine needles, m. p. 177—181° (Found: C, 84·4; H, 10·1. $C_{19}H_{26}O$ requires C, 84·4; H, 9·7%).

Concentration of the ethanol liquors from which this last material had separated gave a yellowish syrup which slowly deposited a white solid. Six recrystallisations from ethanol gave clusters of colourless needles, m. p. 122·5—123°, consisting of (? *cis*-)2-fluorenyl*cyclo*hexanol (Found: C, 86·3; H, 7·6%). The m. p. was strongly depressed by admixture with the (?)*trans*-isomer. The phenylurethane formed silky needles (from light petroleum), m. p. 145—146°, in agreement with the figure (144·5—145·5°) given by Hurd and Mold for the phenylurethane of their alcohol, m. p. 122—122·5°.

(*b*) A much more reactive copper chromite catalyst was prepared by the procedure described by Adkins, Burgoyne, and Schneider (*J. Amer. Chem. Soc.*, 1950, **72**, 2628) for their catalyst HJS2. By its means 2-fluorenyl*cyclo*hexanone could be hydrogenated at a lower temperature, yielding a much more homogeneous product. A solution of the ketone (5·24 g.) in purified dioxan (80 c.c.) was placed in a steel bomb with 2 g. of the active catalyst and charged with hydrogen at 88 atm. Hydrogenation was effected at 80° in 2 hours. The filtered solution gave on evaporation a solid which, after two recrystallisations from ethanol, formed narrow slabs (3·5 g.), m. p. 122—123°, not depressed by the (?)*cis*-alcohol (I). When hydrogenation over this active catalyst was carried out at 150° for 1¾ hours there was formed a mixture from which the (?)*trans*-alcohol and the hexahydride, m. p. 177—181°, were both isolated.

9-cyclo*Hex*-1′-*enylfluorene* (IV).—(*a*) The (?)*cis*-alcohol (I) was heated with phosphoric acid at 230° for ½ hour, as described by Hurd and Mold. The resulting 9-*cyclo*hex-1′-enylfluorene, obtained in 45% yield, crystallised from methanol in colourless needles, m. p. 110·5—111° (Found: C, 92·6; H, 7·4. Calc. for $C_{19}H_{18}$: C, 92·7; H, 7·4%). Light absorption in ethanol: $\lambda_{max.}$ 2665, 2920, 3025 Å; log ε = 4·23, 3·72, 3·85. Both micro-hydrogenation with palladium black in acetic acid and titration with monoperphthalic acid gave values corresponding with one double bond. A solution of the hydrocarbon in carbon tetrachloride reacted only slowly with bromine in the same solvent, and with aqueous permanganate in acid or neutral solution. This relative inertness of the double bond is possibly to be ascribed to steric hindrance.

(*b*) The same hydrocarbon (IV) was obtained by similar treatment with phosphoric acid of the (?)*trans*-alcohol.

(*c*) Powdered (?)*cis*-2-fluorenyl*cyclo*hexanol (1 g.) was mixed with powdered anhydrous potassium hydrogen sulphate (0·1 g.) and heated gradually to 180° in an evacuated sublimation apparatus (*ca.* 15 mm.). The sublimate was twice recrystallised from methanol and then had m. p. 110—111°, alone or mixed with the hydrocarbon prepared by use of phosphoric acid.

Reactions of 9-cyclo*Hex*-1′-*enylfluorene*.—(*a*) A solution of chromium trioxide (1·5 g.) in water (1·5 c.c.) and acetic acid (1 c.c.) was added dropwise to an almost boiling solution of the unsaturated hydrocarbon (IV) (0·25 g.) in acetic acid (6·5 c.c.). The solution was boiled for 1½ hours, kept overnight, and then diluted with water and extracted with ether. The product recovered from the washed and dried ethereal extract crystallised from benzene–light petroleum as yellow needles, m. p. 80—81·5°, not depressed on admixture with authentic fluorenone. Identification was completed by preparation of the oxime, m. p. 192—193·5° (lit., 195°).

(*b*) 9-*cyclo*Hex-1′-enylfluorene (0·35 g.) was dissolved in ether (60 c.c.) containing monoperphthalic acid (*ca.* 0·6 g.) (Stahmann and Bergmann, *J. Org. Chem.*, 1946, **11**, 589), and the cold solution was kept for 2 days. It was then shaken with dilute alkali, washed with water, and dried (Na_2SO_4), and the ether removed. The residual solid (0·36 g.) had m. p. 86—89°. After several recrystallisations from light petroleum (b. p. 40—60°) 9-cyclo*hex-1′-enylfluorene epoxide* formed colourless prisms, (micro-)m. p. 89—90° (Found : C, 86·7; H, 6·9. $C_{19}H_{18}O$ requires C, 87·0; H, 6·9%).

(*c*) Osmium tetroxide (0·34 g.) was added to a solution of the unsaturated hydrocarbon (0·33 g.) in pyridine (0·21 g.) and dry benzene (3·5 c.c.). The dark brown solution soon deposited a brown osmium complex. This was collected and hydrolysed by shaking its chloroform solution with mannitol (5 g.) and potassium hydroxide (0·5 g.) in water (50 c.c.) for 2½ hours. The white solid (0·3 g.) recovered from the chloroform solution was recrystallised from methanol. 9-(1 : 2-*Dihydroxy*cyclo*hexyl)fluorene* formed small colourless crystals, m. p. 183—184° (Found : C, 81·5; H, 7·2. $C_{19}H_{20}O_2$ requires C, 81·4; H, 7·2%).

1-*Fluorenyl*cyclo*hexanol* (VII).—Fluorenylmagnesium bromide was prepared from fluorene (25 g.) and ethylmagnesium bromide (from 20 g. of ethyl bromide and 4·3 g. of magnesium) in xylene (Miller and Bachman, *J. Amer. Chem. Soc.*, 1935, **57**, 766). The xylene was decanted from the deposit of fluorenylmagnesium bromide, which was washed with more xylene, then covered with xylene and heated to 80°. *cyclo*Hexanone (9 g.), mixed with a little dry benzene, was added to the stirred solution. Stirring at 80° was continued for 2 hours. After being kept overnight the product was poured into cold dilute sulphuric acid. The xylene–benzene solution was worked up in the standard way, and 1-*fluorenyl*cyclo*hexanol* (6 g.) was obtained as clusters of flat colourless needles (from light petroleum, b. p. 60—80°), m. p. 130—131° (Found : C, 86·5; H, 7·7. $C_{19}H_{20}O$ requires C, 86·3; H, 7·6%). Fruitless attempts were made to prepare an acetate, a 3 : 5-dinitrobenzoate, and a phenylurethane. Dehydration with potassium hydrogen sulphate, as described for the isomer (I), gave 9-*cyclo*hex-1′-enylfluorene (IV), m. p. 110—111°, alone or mixed with a sample prepared from (I).

9-cyclo*Hexylfluorenol* (VIII).—A solution of fluorenone (2·2 g.) in dry ether was added slowly to a Grignard solution prepared from *cyclo*hexyl bromide (4·4 g.) and magnesium turnings (0·7 g.) in dry ether (50 c.c.). The solution was boiled for 3 hours and the magnesium complex then decomposed with cold ammonium chloride solution. The resulting 9-cyclo*hexylfluorenol*, isolated in the usual manner, formed colourless crystals (from aqueous methanol), m. p. 126·5—128° (Found : C, 86·5; H, 7·6. $C_{19}H_{20}O$ requires C, 86·3; H, 7·6%). The *phenylurethane* crystallised from light petroleum (b. p. 80—100°) in fine silky needles, m. p. 184—186° (decomp.) (Found : C, 81·4; H, 6·7; N, 3·8. $C_{26}H_{25}O_2N$ requires C, 81·4; H, 6·6; N, 3·7%).

9-cyclo*Hexylidenefluorene* (VI).—9-*cyclo*Hexylfluorenol (0·33 g.) was dehydrated by heating it under reduced pressure with potassium hydrogen sulphate (0·034 g.) as in the case of the isomeric alcohol (I). The resulting sublimate of 9-cyclo*hexylidenefluorene* (0·27 g.) crystallised from methanol in needles, m. p. 107—108°, depressed by admixture with the hydrocarbon formed by dehydration of 2-fluorenyl*cyclo*hexanol (Found : C, 92·6; H, 7·3. $C_{19}H_{18}$ requires C, 92·7; H, 7·3%). Light absorption in ethanol : $\lambda_{max.}$, 2330, 2500, 2595, 2870, 3185 Å; log ε = 4·67, 4·35, 4·37, 4·24, 4·14. This hydrocarbon was very unstable. The colourless crystals when kept in air slowly became yellow and finally resinous. The m. p. fell to about 90° in 24 hours.

9-cyclo*Hexylfluorene.*—(*a*) A solution of *cyclo*hexylidenefluorene (0·04 g.) in acetic acid was shaken with hydrogen and palladium black (0·05 g.). Hydrogen absorption was complete after 2 hours. The resulting 9-*cyclo*hexylfluorene had m. p. 115—115·5° (from methanol), not depressed by a specimen, m. p. 114·5—115·5°, prepared from *cyclo*hexylmagnesium bromide and 9-bromofluorene. Miller and Bachman (*loc. cit.*), who prepared 9-*cyclo*hexylfluorene by this Grignard method with 9-chlorofluorene, gave m. p. 102—103°, but this was subsequently corrected by Brown and Bluestein (*J. Amer. Chem. Soc.*, 1943, **65**, 1083) to 115—116°. Light absorption in ethanol : $\lambda_{max.}$, 2270, 2665, 2918, 3028 Å; log ε = 3·79, 4·24, 3·74, 3·88.

(*b*) 9-*cyclo*Hex-1′-enylfluorene (0·5 g.), prepared by dehydration of 2-fluorenyl*cyclo*hexanol with phosphoric acid, was likewise hydrogenated in acetic acid solution over palladium black (0·25 g.). Absorption of hydrogen was slow, and was complete only after 12 hours. The resulting 9-*cyclo*hexylfluorene had m. p. 115—115·5° (from methanol), depressed by admixture with the initial hydrocarbon, but not by admixture with authentic 9-*cyclo*hexylfluorene.

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