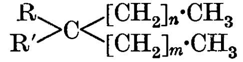
XXXVI.—cyclo*Hexane*spirocyclo*hexane.*

By WOODFORD STANLEY GOWAN PLUCKNETT NORRIS.

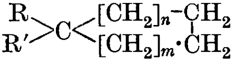
THERE is remarkable agreement between the relative ease of production of homologous alicyclic rings, the " formation numbers " calculated from the interatomic angle (115°) in saturated carbon chains (Ingold, J., 1921, **119**, 305), and the heats of ring formation (Stohmann and Kleber, *J. pr. Chem.*, 1892, **45**, 475). The effect of substitution (particularly substitution of a *gem*-grouping) on the ease of closure in any of the simple *cyclo*paraffins is very pronounced, even in comparison with the difference, in ease of ring formation, between one member of the series and the next. If, therefore, the above agreement is fundamental and not fortuitous, the introduction of a substituent should cause an alteration in the heat of formation of a *cyclo*paraffin ring comparable with the differences, in heat of formation, between successive ring homologues; indeed, the alteration should be much greater than the accuracy of any individual determination. The application of thermochemical methods to the more complex cyclic substances encountered in the study of *spiro*-compounds and of condensed alicyclic systems should therefore be capable of giving an actual quantitative measure of the influence of substituents on ease of ring formation.

It would, for example, be possible, by determining the heats of combustion of two corresponding series of hydrocarbons (A) and (B), in which R and R′ are progressively altered, to obtain a measure

(A.)



$$\begin{matrix}R\\ R'\end{matrix}{>}C{<}\begin{matrix}{[CH_2]_n}\cdot CH_3\\ {[CH_2]_m}\cdot CH_3\end{matrix}$$

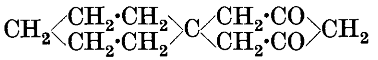


$$\begin{matrix}R\\ R'\end{matrix}{>}C{<}\begin{matrix}{[CH_2]_n}-CH_2\\ {[CH_2]_m}\cdot CH_2\end{matrix}$$

(B.)

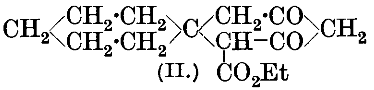
of the effect of substitution on the ease of closure of the ring present in (B). The chief interest of such a line of work would lie in the spirocyclic series. Spiran hydrocarbons have not, however, hitherto been described.* One such hydrocarbon, cyclo*hexane*-spirocyclo*hexane*, has now been prepared.

An account of the initial stages of the synthesis has already appeared (Norris and Thorpe, J., 1921, **119**, 1199). *cyclo*Hexane-*spirocyclo*hexane-3 : 5-dione (I) was obtained by hydrolysing the ester (II); the latter was prepared by the condensation of Wallach's ketone, *cyclo*hexylideneacetone, $C_5H_{10}{>}C{:}CH{\cdot}COMe$, with ethyl sodiomalonate. The reduction of the diketone (I) has now been



$$CH_2{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}C{<}\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}{>}CH_2$$

(I.)

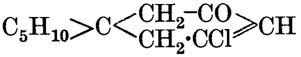


$$CH_2{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}C{<}\begin{matrix}CH_2\cdot CO\\ \underset{CO_2Et}{CH}-CO\end{matrix}{>}CH_2$$

(II.)

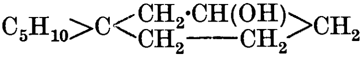
accomplished by indirect methods similar in general to those by which Crossley and Renouf (J., 1905, **87**, 1494; 1907, **91**, 63) prepared 1 : 1-dimethyl*cyclo*hexane.

Crossley and Le Sueur (J., 1903, **83**, 110) found that dimethyldihydroresorcinol was converted into 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one by means of phosphorus trichloride in chloroform



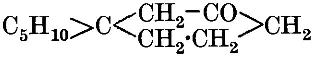
$$C_5H_{10}{>}C{<}\begin{matrix}CH_2-CO\\ CH_2\cdot CCl\end{matrix}{\gg}CH$$

(III.)



$$C_5H_{10}{>}C{<}\begin{matrix}CH_2\cdot CH(OH)\\ CH_2-\!\!-\!\!-CH_2\end{matrix}{>}CH_2$$

(IV.)



$$C_5H_{10}{>}C{<}\begin{matrix}CH_2-CO\\ CH_2\cdot CH_2\end{matrix}{>}CH_2$$

(V.)

solution. The *spiro*-diketone (I) similarly gives the unsaturated *chloro-ketone* (III). Reduction of this with sodium and moist ether

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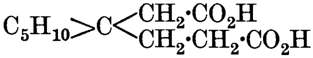
* Ingold (J., 1923, **123**, 1706) has shown conclusively that the hydrocarbon hitherto represented to be *cyclo*propane*spirocyclo*propane consists essentially of methyl*cyclo*butene, unaccompanied by any of its isomerides in the *cyclo*-propane series.

(compare Crossley and Renouf, *loc. cit.*) produced much resinous matter, from which only a trace of the *spiro*-alcohol (IV) could be isolated. However, by the action of zinc dust on the chloro-ketone in boiling glacial acetic acid solution, cyclo*hexane*spirocyclo*hexan-*3-*one* (V), which is analogous to Kon's *cyclo*hexane*spirocyclo*butan-3-one (J., 1922, **121**, 515), was obtained in reasonable yield.

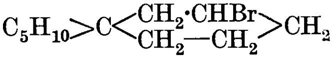
The refractive power of the ketone (V) was measured for sodium light and for the red and blue hydrogen lines, but not for the violet line on account of selective absorption. The molecular refraction shows inappreciable exaltation (0·08), in contrast with the increase (0·77) observed by Kon in the molecular refraction of his ketone; moreover, the molecular dispersion between the red and the blue shows no increase over the theoretical value. This result will not be surprising when it is remembered that *cyclo*pentanes and *cyclo*hexanes normally show scarcely any optical anomaly (compare Eisenlohr, " Spektrochemie organischer Verbindungen "), and that the figure of instability * (maximum valency curvature) for *cyclo*hexane*spirocyclo*hexane is only 0·22, as against 0·18 for 1 : 1-dimethyl*cyclo*hexane, 0·08 for *cyclo*hexane itself, and 0·13 for *cyclo*pentane.

The ketone (V) gave, on reduction with sodium and moist ether, a good yield of cyclo*hexane*spirocyclo*hexan*-3-*ol* (IV). The constitution of this alcohol was confirmed by oxidising it with nitric acid to *cyclo*hexane-1-acetic-1-propionic acid (VI).



$C_5H_{10}{>}C{<}\begin{matrix}CH_2\cdot CO_2H\\ CH_2\cdot CH_2\cdot CO_2H\end{matrix}$

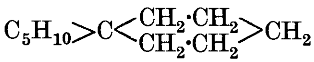
(VI.)



$C_5H_{10}{>}C{<}\begin{matrix}CH_2\cdot CHBr\\ CH_2-CH_2\end{matrix}{>}CH_2$

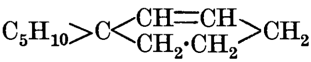
(VII.)

The conversion of the *spiro*-alcohol (IV) into the *bromo*-derivative (VII) by the action of fuming hydrobromic acid presented unexpected difficulties. Not only did the replacement of the hydroxyl group by bromine proceed with great reluctance, but the boiling points of the two compounds lie very close together, rendering even partial separation a very tedious process. The same difficulty was encountered in attempts to isolate the corresponding *chloro*-derivative.



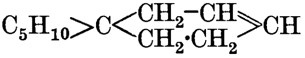
$C_5H_{10}{>}C{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}CH_2$

(VIII.)



$C_5H_{10}{>}C{<}\begin{matrix}CH{=}CH\\ CH_2\cdot CH_2\end{matrix}{>}CH_2$

(IX.)



$C_5H_{10}{>}C{<}\begin{matrix}CH_2-CH\\ CH_2\cdot CH_2\end{matrix}{>}CH$

(X.)

By reducing the impure bromo-compound (VII) in alcohol with zinc dust, *cyclo*hexane*spirocyclo*hexane (VIII) was obtained together

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* The figure of instability for a 6-carbon ring is expressed by

$$[\delta a/\delta S]_{S=0} = \sin\theta - \sqrt{3}\,.\cos\theta.$$

with an unsaturated hydrocarbon (IX or X), evidently produced by loss of hydrogen bromide; a result contrasting with the production under similar conditions of 1 : 1-dimethyl*cyclo*hexane only from 3-bromo-1 : 1-dimethyl*cyclo*hexane (Crossley and Renouf, *loc. cit.*).

The final stage in the reduction was effected by shaking the mixture of saturated and unsaturated hydrocarbons with colloidal palladium in an atmosphere of hydrogen.

This investigation cannot be continued for the present, but it will, it is hoped, be concluded at some future date.

EXPERIMENTAL.

cyclo*Hexane*spirocyclo*hexan*-3 : 5-*dione* (I).—The diketone of Norris and Thorpe (*loc. cit.*) has been further characterised by the formation, on hydrolytic fission, of cyclo*hexane*-1-*acetone*-1-*acetic acid*,  $C_5H_{10}{>}C{<}\genfrac{}{}{0pt}{}{CH_2{\cdot}COMe}{CH_2{\cdot}CO_2H}$. The diketone (1 g.) and 6 g. of crystalline barium hydroxide dissolved in 25 c.c. of water were heated at 200° for 24 hours. The ethereal extract of the acidified liquid left, after evaporation of the solvent, a pale yellow oil (yield practically quantitative), which set on cooling to a white solid and gave no colour with ferric chloride. The *keto-acid*, which is volatile in steam, is very soluble in ether, benzene, or alcohol, less so in water, or light petroleum (b. p. 40—60°); it separates from the latter in short, colourless needles, m. p. 67° (Found: C, 66·8; H, 8·8. $C_{11}H_{18}O_3$ requires C, 66·7; H, 9·1%). The *semicarbazone* separates from methyl alcohol in colourless plates, m. p. 183·5° (decomp.) (Found: C, 56·55; H, 8·4; N, 16·6. $C_{12}H_{21}ON_3$ requires C, 56·4; H, 8·3; N, 16·5%).

Action of Phosphorus Trichloride on the Diketone (I). cyclo*Hexane*spiro-5-*chloro*-Δ^4-cyclo*hexen*-3-*one* (III).—A mixture of 67 g. of the diketone (which must be dry and free from resinous matter and hydrochloric acid), 250 c.c. of dry chloroform, and 17·5 g. of phosphorus trichloride was heated under reflux for 3 hours, cooled, and the unchanged diketone filtered off. The residue after distillation of the chloroform was dissolved in a little ether and poured into 1300 c.c. of water, which was then extracted with ether four times. The ethereal solution, after being thoroughly washed with 10% sodium hydroxide solution (from which more of the diketone was obtained on acidification), was washed once with 25% sulphuric acid, twice with water, and dried over calcium chloride. The residue, after the ether had been removed through a column, was distilled under reduced pressure. The *chloro-ketone*, b. p. 167°/30 mm., 160°/17 mm., 157°/12 mm., solidified, on cooling, to a white, crystalline mass, which had a pungent camphor-like odour and separated from light petroleum (b. p. 60—80°) in large, colourless prisms, m. p. 47° (Found : Cl, 17·8. $C_{11}H_{15}OCl$ requires Cl, 17·8%).

The *semicarbazone* separates from methyl alcohol in glistening plates, m. p. 219° (decomp.) (Found : N, 17·0, 16·2. $C_{12}H_{18}ON_3Cl$ requires N, 16·4%).

The recovered diketone (24%) was purified with difficulty, owing to the presence of resinous phosphorus compounds, and in many cases could not be used again.

Reduction of the Chloro-ketone with Zinc Dust in Glacial Acetic Acid. cyclo*Hexane*spirocyclo*hexan*-3-*one* (V).—Zinc dust (33 g.) was added, the first portions in very small quantities because of the violence of the reaction, during 24 hours to a solution of 25 g. of the chloro-ketone in 80 c.c. of glacial acetic acid, boiling under reflux. The liquid was neutralised with caustic soda solution and steam-distilled. From the distillate, ether extracted the ketone (yield 86%).

The *semicarbazone* separated from ethyl alcohol in colourless, flattened needles, m. p. 224·5° (decomp.) (Found: N, 18·9. $C_{12}H_{21}ON_3$ requires N, 18·8%).

The *ketone*, regenerated from the semicarbazone by boiling with oxalic acid and water in a current of steam, and extracted from the distillate with ether, was a colourless, mobile liquid, b. p. 225°/772 mm. or 130°/15 mm., having a pungent odour similar to that of cedarwood oil (Found: C, 79·8; H, 10·7. $C_{11}H_{18}O$ requires C, 79·5; H, 10·9%). The freshly distilled ketone had $d^{21\cdot7^\circ}$ 0·98417, n_C 1·48432, $n_D = 1{\cdot}48685$, n_F 1·49322 (no violet light was transmitted). Hence $[R_L]_D = 48{\cdot}55$; $[R_L]_{F-C} = 0{\cdot}76$, the calculated values being 48·61 and 0·75, respectively.

The ketone is stable towards neutral permanganate, and slowly attacked by the alkaline reagent in the cold.

The *oxime*, prepared by boiling the ketone for 1 hour with hydroxylamine hydrate (1·5 mols.) in aqueous-alcoholic solution, separated from light petroleum (b. p. 40—80°) in large, colourless prisms, m. p. 128° (Found: C, 73·1; H, 10·6. $C_{11}H_{19}ON$ requires C, 72·9; H, 10·6%).

Reduction of the spiro*Ketone with Sodium in Moist Ether.* cyclo*Hexane*spirocyclo*hexan*-3-*ol* (IV).—A solution of 18 g. of the crude ketone (from the reduction of 25 g. of chloro-ketone) in 100 c.c. of ether and 10 c.c. of alcohol was poured on to 200 c.c. of water in a separating funnel, to which was attached a reflux condenser. Sodium (19 g., in thin slices) was gradually added, the water being changed after addition of the first 10 g.; this water was extracted with a little ether, which was then transferred to the funnel. When all the sodium had been added, the ethereal solution was washed twice with water, the ether removed through a column, and the residue distilled in steam. The ethereal extract of the distillate was washed twice with a saturated solution of sodium bisulphite, and the ether distilled through a column; the residue solidified on cooling in a vacuum (yield 50% of the theoretical, calculated on the chloro-ketone used).

cyclo*Hexane*spirocyclo*hexan*-3-*ol* boils at 127—128°/15 mm. and sets to a felted mass of needles, which are too soluble in the ordinary solvents to be recrystallised, but melt quite sharply at 58° after draining well on porous porcelain (Found: C, 78·5; H, 11·75. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%). The alcohol has a pleasant camphoraceous odour.

The p-*nitrobenzoate* is produced when the hydroxy-compound and *p*-nitrobenzoyl chloride are boiled with pyridine in ethereal solution. It separates from alcohol in pearly-white plates, m. p. 102° (Found: C, 68·3; H, 7·25. $C_{18}H_{23}O_4N$ requires C, 68·1; H, 7·3%).

Oxidation of the spiro*Alcohol.* cyclo*Hexane*-1-*acetic*-1-*propionic Acid* (VI).—The hydroxy-compound (19 g.) was gradually added to 45 c.c. of boiling, concentrated nitric acid, and the liquid was then diluted with water and evaporated. This process was repeated until no more nitric acid remained. A gummy acid (19·5 g.) was thus obtained (compare Crossley and Renouf, *loc. cit.*) which did not solidify. This was kept for 36 hours with 60 c.c. of absolute alcohol and 20 c.c. of concentrated sulphuric acid. The fraction, b. p. 179—183°/14 mm., of the neutral ester thus produced (Found: C, 66·4; H, 9·5. $C_{15}H_{26}O_4$ requires C, 66·6; H, 9·7%) was hydrolysed with boiling alcoholic caustic potash, and the acid extracted from the acidified solution with ether. The residue left after evaporation of the ether gradually solidified when kept in a vacuum, and, after remaining for 3 days in contact with porous porcelain, was recrystallised from a mixture of chloroform and light petroleum (b. p. 40—60°), from which it separated in rosettes of colourless needles, m. p. 142·5° (Found: C, 61·45; H, 8·4. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·4%).

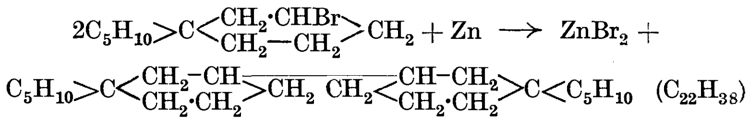
The acid may also be purified through the characteristic *calcium* salt, the solubility of which in water apparently increases with increasing temperature almost to the boiling point, and then suddenly decreases.

Action of Hydrobromic Acid on the Hydroxy-compound.—The *spiro*-alcohol (20 g.) was heated for 1·5 hours in a sealed soda-water bottle with 110 c.c. of fuming hydrobromic acid, saturated at 0°. The cooled liquid was resaturated with hydrogen bromide, and the heating repeated. The product was poured into 1500 c.c. of water, and the heavy oil extracted with ether. The ethereal solution was washed well with a solution of sodium carbonate and then with water, and dried over calcium chloride. The residue, after the ether had been removed through a column, was distilled under reduced pressure. The greater portion boiled between 133° and 136°/12 mm., but the liquid could not be separated into definite fractions, even by repeated distillation. A portion taken at 133° gave the following figures on analysis : C, 61·2 ; H, 8·7 ; Br, 29·2. $C_{11}H_{19}Br$ requires C, 57·1 ; H, 8·3 ; Br, 34·6%. These correspond to 84% of the bromo-derivative, if only bromo-compound and hydroxy-compound were present. A purer sample was not obtained.

Action of Hydrochloric Acid on the Hydroxy-compound.—The reaction was conducted as in the preceding case. The fraction of the product most rich in chlorine boiled at 142—148°/33 mm. and contained 13·7% of chlorine, corresponding with the presence of 72% of $C_{11}H_{19}Cl$ in the mixture. No fraction containing more than this amount of chlorine could be isolated.

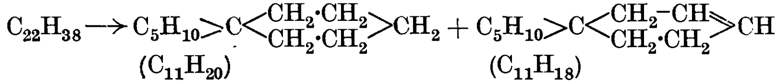
Reduction of the Bromo-derivative (VII) *with Zinc Dust and Alcohol.*—The crude bromo-compound (26·5 g.), containing 84% of the pure material, was dissolved in 90 c.c. of 90% alcohol and mixed with 46 g. of zinc dust and an equal bulk of sand. Enough absolute alcohol (*ca.* 10 c.c.) was added to form a clear solution, and the whole heated under reflux on the water-bath for 20 hours. The liquid was filtered into 1200 c.c. of water, and the aqueous liquid extracted twice with ether. The ethereal solution was washed with water, and dried over potassium carbonate, the ether removed, and the residue heated for 2 hours over metallic sodium and then distilled. After two further distillations over sodium (the third time the metal remained unattacked), a bright, colourless liquid, b. p. 204—208°/762 mm., was obtained having a penetrating odour of geranium (Found in a fraction, b. p. 204—206° : C, 87·4 ; H, 13·0. Found in a fraction, b. p. 206—208° : C, 87·35 ; H, 12·9. $C_{11}H_{20}$ requires C, 86·8 ; H, 13·2%. $C_{11}H_{18}$ requires C, 88·0 ; H, 12·0%. A 50% mixture of $C_{11}H_{20}$ and $C_{11}H_{18}$ requires C, 87·4 ; H, 12·6%).

These figures indicate that the hydrocarbon contained some unsaturated material, a conclusion which was confirmed by the ready absorption of bromine in chloroform solution and by the reduction of permanganate in acetone solution. The analytical figures are so close to those given above for a 50% mixture that at first it was thought that a reaction in the following sense must have occurred :



$$2C_5H_{10}{>}C{<}\begin{matrix}CH_2\cdot CHBr\\CH_2-CH_2\end{matrix}{>}CH_2 + Zn \longrightarrow ZnBr_2 +$$
$$C_5H_{10}{>}C{<}\begin{matrix}CH_2-CH\\CH_2\cdot CH_2\end{matrix}{>}CH_2\ CH_2{<}\begin{matrix}CH-CH_2\\CH_2\cdot CH_2\end{matrix}{>}C{<}C_5H_{10}\quad (C_{22}H_{38})$$

followed by isomeric change on distillation :



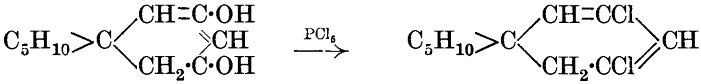
$$C_{22}H_{38}\longrightarrow \underset{(C_{11}H_{20})}{C_5H_{10}{>}C{<}\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}{>}CH_2} + \underset{(C_{11}H_{18})}{C_5H_{10}{>}C{<}\begin{matrix}CH_2-CH\\CH_2\cdot CH_2\end{matrix}{>}CH}$$

These figures have, however, never been repeated; moreover, 3 g. of the hydrocarbon mixture absorbed, in chloroform solution, 0·345 g. of bromine only, whereas for a 50% mixture 0·530 g. should have been taken up. It is concluded, therefore, that the remarkable agreement of the analytical results with the numbers required for the composition "$C_{22}H_{38}$" is accidental, and that reduction and elimination of hydrogen bromide must have occurred simultaneously.

Reduction of the Hydrocarbon Mixture with Hydrogen and Colloidal Palladium. cyclo*Hexane*spirocyclo*hexane* (VIII).—The mixed hydrocarbons (6 g.) were shaken in an atmosphere of hydrogen for 8 hours with 2·5 c.c. of a 10% solution of palladium chloride, 2·5 c.c. of a 10% solution of gum arabic in water, 5 c.c. of water, and enough alcohol to give a clear solution. The initial pressure of gas was 1070 mm.; this fell gradually to 815 mm. The product was isolated by distillation in steam and extraction of the distillate with ether.

cyclo*Hexane*spirocyclo*hexane*, b. p. 208°/777 mm., is a clear, colourless, mobile liquid having a faint odour of geranium (Found : C, 86·7; H, 13·35. $C_{11}H_{20}$ requires C, 86·6; H, 13·3%). It is quite stable to permanganate and is only slowly dissolved by boiling, fuming nitric acid; bromine, in chloroform solution, is quite without action. The freshly distilled hydrocarbon has $d^{20\cdot6^\circ}$ 0·87833, n_C 1·47048, n_D 1·47313, n_F 1·47902, n_G 1·48398. Hence $[R_L]_D = 48\cdot61$, $[R_L]_{F-C} = 0\cdot75$, $[R_L]_{G-C} = 1\cdot19$. The theoretical figures are 48·60, 0·74, 1·19, respectively. These values show no optical exaltation such as might be expected were the *cyclo*hexane rings in the *spiro*-hydrocarbon under a strain comparable with that in derivatives of *cyclo*butane, *cyclo*propane or *cyclo*heptane. Crossley and Renouf (*loc. cit.*) quote the following results, determined for 1 : 1-dimethyl*cyclo*hexane by W. H. Perkin, sen. :—$d^{15\cdot5^\circ}$ 0·78543, n_C 1·42958, n_D 1·43728, n_G 1·44203. Hence $[R_L]_C = 36\cdot85$, $[R_L]_G = 37\cdot78$, $[R_L]_{G-C} = 0\cdot93$. The calculated figures are 36·78, 37·68, 0·90, respectively. The increase shown by the experimental figures over the theoretical is inappreciable.

Action of Phosphorus Pentachloride on the spiro-*Diketone* (I). cyclo*Hexane*spiro-3 : 5-*dichloro*-$\Delta^{2:4}$-cyclo*hexadiene*.—After it had been found that the conversion of the *spiro*-alcohol into the corresponding halogen derivatives could not be carried out quantitatively, it was hoped that an increased yield of the final product might be obtained by eliminating both oxygen atoms from the molecule at an early stage of the reduction. Accordingly the action of phosphorus pentachloride on the diketone was investigated, in the hope that the latter might react in the dienol form (XI) to give the dichloro-unsaturated hydrocarbon (XII); an expectation which has been realised.



$$C_5H_{10}{>}C\begin{array}{l}\diagup CH{=}C{\cdot}OH \\ \qquad\qquad\quad {>}CH \\ \diagdown CH_2{\cdot}C{\cdot}OH\end{array} \xrightarrow{PCl_5} C_5H_{10}{>}C\begin{array}{l}\diagup CH{=}CCl\diagdown \\ \qquad\qquad\qquad\quad {>}CH \\ \diagdown CH_2{\cdot}CCl\diagup\end{array}$$

(XI.) (XII.)

The diketone (50 g.) was suspended in 130 c.c. of dry chloroform in a flask attached to a reflux apparatus; 125 g. of phosphorus pentachloride were gradually added in small quantities; after each addition the liquid boiled vigorously. The whole was heated for 3 hours on the water-bath, the cooled liquid filtered, and the chloroform distilled off. The residue was shaken well with ice-cold water, and the organic material taken up in ether. The ethereal solution, after being well washed with a dilute solution of caustic soda and then with water, was dried over calcium chloride. The residue after removal of the ether was distilled under reduced pressure. Only a very little impure diketone was recovered from the alkaline washings. cyclo*Hexane*spiro-3 : 5-*dichloro*-$\Delta^{2\cdot4}$-cyclo*hexadiene* was thus obtained (yield 65%) as a pale yellow oil, b. p. 152°/21 mm. (Found : Cl, 32·5. $C_{11}H_{14}Cl_2$ requires Cl, 32·7%).

Unfortunately it has not yet been possible, by the use either of acid or of alkaline reducing agents, to prepare from this material a pure compound free from halogen.

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