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ALLENES. II. THE PREPARATION OF 1-CYCLOHEXYL-2,3-PENTADIENE

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The structure of the five-membered side-chain of pyrethrolone, the cyclopentenolone component of the pyrethrins, still remains the only feature of the molecule which has not been definitely established. Staudinger and Ruzicka[1], who first isolated and studied pyrethrolone, concluded that a side-chain containing a cumulated system of double bonds corresponded best to its chemical behavior. LaForge and Haller[2] have reported results of experiments directed to the solution of this problem, but without reaching a definite conclusion. Their experimental results, especially in regard to the behavior of pyrethrolone and its reduction product, pyrethrone, toward bromine, were difficult to explain with the assumption of the presence of the cumulated system, and they were still more contrary to the known behavior of conjugated systems.

The purpose in preparing substituted allenes was to perform on these compounds the reactions that had been applied to pyrethrolone and pyrethrone and to compare their respective behaviors.

In the first article of this series[3] the preparation of 1-phenyl-1,2-butadiene, $C_6H_5CH{=}C{=}CHCH_3$, was reported. Since this hydrocarbon contains but four members in the side-chain, its analogy with pyrethrolone was not considered sufficiently close. Moreover, it is now contemplated to extend the investigation into the field of ultraviolet absorption study, and for this purpose 1-phenyl-1,2-butadiene is unsuitable as a reference compound because of the presence of the phenyl group. A compound offering a closer analogy with pyrethrone, on the assumption that it contains the cumulated system, and at the same time one that would satisfy the requirements of ultraviolet absorption spectrum study, would be 1-cyclohexyl-2,3-pentadiene, the preparation of which is the subject of this article. It was obtained by the following series of reactions: α-chlorocrotonic aldehyde furnished 1-cyclohexyl-2-hydroxy-3-chloro-3-pentene, $C_6H_{11}CH_2CHOHCCl{=}CHCH_3$ (I), by the Grignard reaction with

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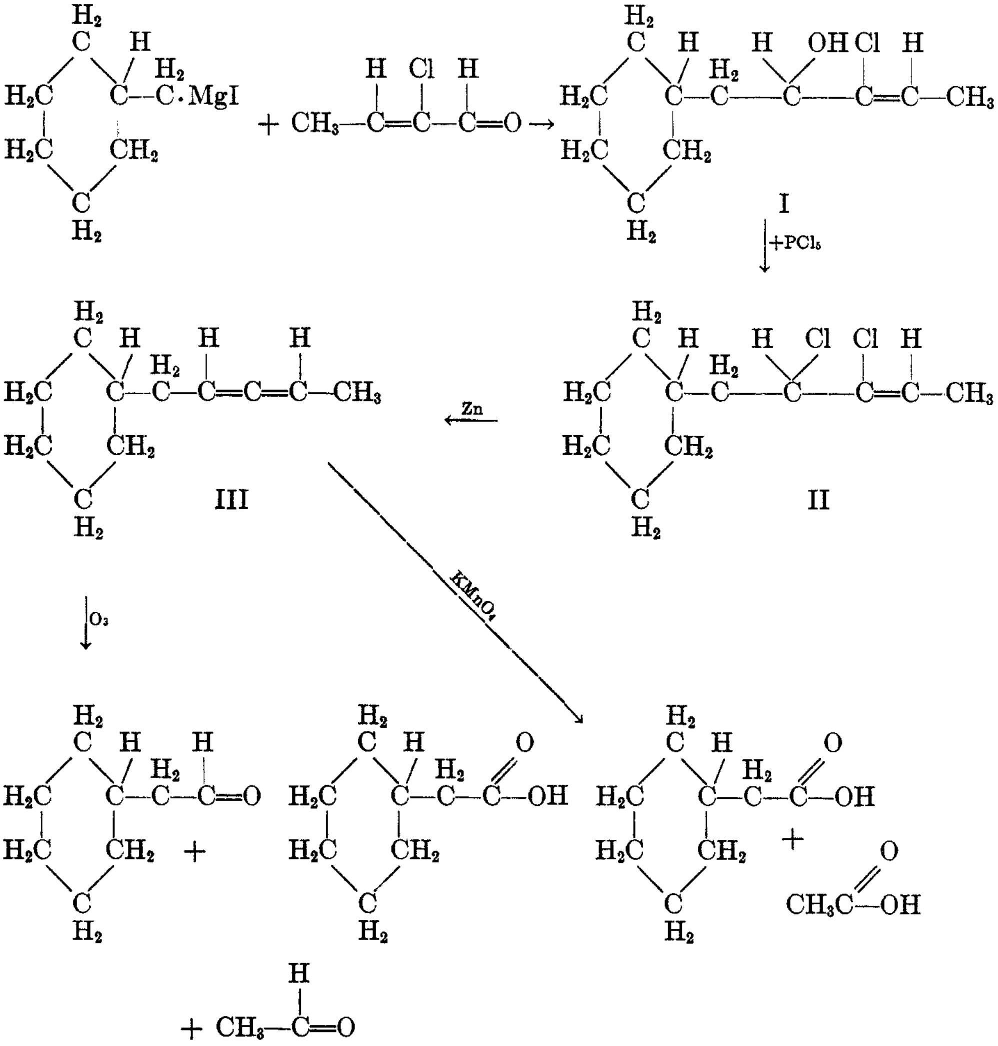
[1] STAUDINGER AND RUZICKA, *Helv. Chim. Acta*, **7**, 212 (1924).

[2] LAFORGE AND HALLER, J. ORG. CHEM., **2**, 546 (1938).

[3] ACREE AND LAFORGE, *Ibid.*, **4**, 40 (1939).

hexahydrobenzyl iodide. Substitution of chlorine for the hydroxyl group gave 1-cyclohexyl-2,3-dichloro-3-pentene, $C_6H_{11}CH_2CHClCCl{=}CHCH_3$ (II)*. Dehalogenation of the dichloro compound furnished 1-cyclohexyl-2,3-pentadiene, $C_6H_{11}CH_2CH{=}C{=}CHCH_3$ (III).



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* Regarding the possibility of the allylic rearrangement having occurred in the process of chlorination with the formation of 1-cyclohexyl-3,4-dichloro-2-pentene, see the previous article[3].

The structure of III was proved both by ozonization and by oxidation with permanganate. Acetaldehyde was isolated as its dimethone derivative from the water-soluble reaction products after decomposition of the ozonide, while from the product soluble in the organic solvent both cyclohexylacetaldehyde and cyclohexylacetic acid were isolated, the former as its semicarbazone, and the latter as its amide. Oxidation of III with permanganate furnished acetic acid, which was characterized as acetyl-*p*-toluidide, and cyclohexylacetic acid which was isolated as its amide.

An attempt to apply the general series of reactions used previously for 1-phenyl-1,2-butadiene[3] to the preparation of 1-cyclohexyl-2,3-pentadiene failed because hexahydrobenzylmagnesium iodide reduced 2,2,3-trichlorobutanal to the alcohol instead of giving the expected addition reaction.

EXPERIMENTAL

1-Cyclohexyl-2-hydroxy-3-chloro-3-pentene (*I*).—Thirty-five grams of α-chlorocrotonic aldehyde[4] dissolved in 200 cc. of dry ether was added slowly to the ice-cold Grignard reagent prepared from 84 grams of hexahydrobenzyliodide[5] and 10 grams of magnesium in 300 cc. of ether.

The reaction was allowed to continue in the cold for 16 hours. The Grignard reaction product was added slowly to a stirred solution of 25 grams of ammonium chloride in 150 cc. of water to which ice was added in quantity sufficient to maintain a temperature of 0°. Fifteen cubic centimeters of glacial acetic acid was added to break the emulsion that formed, and the reaction products were extracted with ether. The ethereal solution was washed successively with a cold saturated solution of sodium bisulfite, cold 5 per cent. sodium carbonate solution, and water, and then dried over anhydrous sodium sulfate. The solvent was removed by evaporation, and the residue was distilled, yielding 30 grams of oil boiling at 130–135°, $p = 9$ mm.; $n_D^{25} = 1.4893$. The distillate crystallized after standing several hours in the refrigerator. It was recrystallized by dissolving in 1 to 2 volumes of low-boiling petroleum ether, cooling to −18°, and filtering at the same temperature. It melted at 39–40°.

Anal. Calc'd for $C_{11}H_{19}ClO$: Cl, 17.5. Found: Cl, 17.2.

The compound did not form a crystalline phenylurethane.

Hydrogenation of 1-cyclohexyl-2-hydroxy-3-chloro-3-pentene (*I*).—One and one-half grams of the alcohol was reduced in the presence of palladium-calcium carbonate catalyst[6] in ethanolic potassium hydroxide solution, absorbing 310 cc. of hydrogen (calc'd for 2 moles, 332 cc.). The reaction product was isolated and distilled, yielding 1 gram of material boiling at 112–114°, $p = 9$ mm.; $n_D^{26} = 1.4620$. From its method of preparation this material hardly could be other than 1-cyclohexyl-2-pentanol, a compound that does not appear to be described in the literature.

Anal. Calc'd for $C_{11}H_{22}O$: C, 77.64; H, 12.94.
Found: C, 77.64; H, 12.73.

It did not form a crystalline phenylurethane.

1-Cyclohexyl-2,3-dichloro-3-pentene (*II*)*.—Six grams (10 per cent. excess) of

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[4] MOUREU, MURAT, AND TAMPIER, *Bull. soc. chim.*, [4], **29**, 32 (1921).

[5] GUTT, *Ber.*, **40**, 2067 (1907). [Hexahydrobenzyl alcohol was prepared according to FAVORSKY AND BORGMANN, *Ber.*, **40**, 4865 (1907)].

[6] HOUBEN, "Die Methoden der organischen Chemie," 3 ed., vol. 2, p. 360.

powdered phosphorus pentachloride was slowly added to 5.2 grams of 1-cyclohexyl-2-hydroxy-3-chloro-3-pentene (I) dissolved in 25 cc. of cold petroleum ether. When the initial vigorous reaction had subsided, the mixture was boiled for a few minutes on the steam bath and then poured into water containing ice. The petroleum ether solution was separated and washed with dilute sodium bicarbonate solution and then with water. After drying over anhydrous sodium sulfate, the solvent was removed by evaporation, and the residue was distilled, yielding 4.2 grams of product which boiled at 131–133°, $p = 11$ mm.; $n_D^{26} = 1.4965$.

Anal. Calc'd for $C_{11}H_{18}Cl_2$: Cl, 32.1. Found: Cl, 31.7.

1-Cyclohexyl-2,3-pentadiene (*III*).—Ten grams of 1-cyclohexyl-2,3-dichloro-3-pentene (II) dissolved in 25 cc. of ethanol was dropped into a stirred suspension of 25 grams of zinc dust in 25 cc. of boiling ethanol. (The zinc dust had been treated previously with a large volume of very dilute hydrochloric acid to remove zinc oxide, and then washed free of acid with water and finally with ethanol.) The reaction flask was provided with a dropping funnel and a reflux condenser. The solution of the dichloride was introduced at the rate necessary to cause uniform boiling without the application of heat. Finally, the reaction solution was boiled for 15 minutes, cooled, filtered from the excess zinc, and diluted with several volumes of water. The separated oil was extracted with ether, and the solution was washed repeatedly with water and finally with dilute sodium carbonate solution, and then dried over sodium sulfate. After removal of the solvent by evaporation, the residue was distilled, yielding 4.6 grams of product boiling at 82–85°, $p = 12$ mm.; $n_D^{26} = 1.4810$.

Anal. Calc'd for $C_{11}H_{18}$: C, 88.00; H, 12.00.
Found: C, 88.50; H, 12.06.

In comparison with 1-phenyl-1,2-butadiene the compound is relatively stable. The 1-cyclohexyl-2,3-pentadiene (III) showed no evidence of reaction when treated in the usual manner with freshly prepared maleic anhydride.

Hydrogenation of 1-cyclohexyl-2,3-pentadiene (*III*).—One-half gram of III in ethanol solution, when reduced with hydrogen in the presence of platinum oxide catalyst, absorbed 165 cc. of hydrogen in a few minutes (calc'd for 2 mols, 149 cc.). The reduction product was isolated and on distillation boiled at 200–205°C., $p =$ atmos.; $n_D^{11} = 1.4474$; yield, 0.35 gram. The boiling point of *n*-amylcyclohexane is reported[7] as 198°C., $p =$ atmos.; $n_D^{11} = 1.4466$.

Ozonization of 1-cyclohexyl-2,3-pentadiene (*III*).—An excess of ozone was passed into an ice-cold solution of 1.2 grams of III dissolved in 5 cc. of carbon tetrachloride. The ozonide was decomposed by shaking with a few cubic centimeters of water containing ice and finally by warming. The aqueous solution was separated and added to a solution of 1.6 grams of dimethone dissolved in 400 cc. of water. The crystalline material that had formed by the end of 16 hours was separated and recrystallized from ethanol. It weighed 0.2 gram, melted at 138–140°, and was identified as ethylidenedimethone by the mixture melting point, 137–138°.

The carbon tetrachloride solution was extracted with 5 per cent. aqueous potassium hydroxide solution, washed with water, and dried over sodium sulfate. The solvent was removed by evaporation, and the residue was distilled, yielding 0.4 gram of product boiling at 70–120°, $p = 10$ mm. This distillate was dissolved in 2 cc. of ethanol and added to a solution of 0.4 gram of semicarbazide hydrochloride in 1 cc. of water and 1 cc. of pyridine. After standing overnight, the reaction mixture was diluted with a few cubic centimeters of water. The crystalline material that separated was removed by filtration, and recrystallized from ethanol. It weighed 0.1

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[7] STRATFORD, *Chem. Zentr.*, **1929**, **II**, 1286.

gram and melted at 157–159°. Skita[8] records the melting point of cyclohexylacetaldehyde semicarbazone as 153°.

Anal. Calc'd for $C_9H_{17}N_3O$: C, 59.02; H, 9.29.
Found: C, 58.80, 58.70; H, 9.28, 9.28.

The aqueous alkaline extract from the carbon tetrachloride solution was concentrated to a small volume and acidified. The oil that separated was dissolved in petroleum ether, washed with water, and dried over sodium sulfate. The solvent was removed by evaporation, yielding 0.4 gram of residue. By treatment with thionyl chloride this acid reaction product was converted into its acid chloride. The addition of concentrated ammonium hydroxide precipitated a crystalline material, which was isolated and recrystallized from water. It melted at 169°C. Gutt[9] records the melting point of cyclohexylacetic acid amide as 171–172°C.

Anal.† Calc'd for $C_8H_{15}NO$: N, 9.93. Found: N, 10.00.

Oxidation of 1-cyclohexyl-2,3-pentadiene (*III*).—One gram of III was oxidized with 2 grams of potassium permanganate in 60 cc. of acetone previously treated with permanganate. The acetone solution, after being filtered from the manganese dioxide, yielded 0.5 gram of unchanged starting material.

The aqueous extract from the manganese dioxide was acidified and extracted with petroleum ether. The petroleum ether solution was washed with water, dried over sodium sulfate, and the solvent was removed. The residue was treated with thionyl chloride to convert the acid reaction product into the acid chloride. The addition of concentrated ammonium hydroxide precipitated a crystalline material, which was isolated and recrystallized from water. It weighed 0.1 gram and melted at 169°. It was identified as cyclohexylacetic acid amide by the mixture melting point method.

The aqueous solution that had been extracted with petroleum ether was steam distilled. The distillate was made alkaline and evaporated to dryness, yielding 0.4 gram of residue. Treatment of this residue with *p*-toluidine[10] yielded 0.15 gram of recrystallized material which melted at 148–149°. It was identified as acetyl-*p*-toluidide by the mixture melting point, 147–148°.

Reaction of 2,2,3-trichlorobutanal with hexahydrobenzylmagnesium iodide.—Sixty-five grams of 2,2,3-trichlorobutanal dissolved in 200 cc. of dry ether was added slowly to the cold Grignard reagent prepared from 12 grams of magnesium and 102 grams (20 per cent. excess) of hexahydrobenzyl iodide dissolved in 200 cc. of the same solvent. The reaction was allowed to continue for 4 hours. The reaction mixture was then added slowly to a stirred solution of 25 grams of ammonium chloride dissolved in 150 cc. of water to which sufficient ice was added to maintain the solution cold. Fifteen cubic centimeters of glacial acetic acid was added to break the emulsion, and the reaction products were extracted with ether. The ethereal solution was washed with a cold saturated solution of sodium bisulfite, cold 5 per cent. aqueous sodium carbonate, and water, and then dried over sodium sulfate. The solvent was removed by evaporation and the residue was distilled, yielding 58 grams of oil which boiled at 76–95°, $p = 1$ mm. After being kept cold for several

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[8] SKITA, *Ber.*, **48**, 1694 (1915).

[9] GUTT, *ibid.*, **40**, 2068 (1907).

† This nitrogen analysis was performed by T. H. Harris, Bureau of Agricultural Chemistry and Engineering, U. S. Department of Agriculture.

[10] MULLIKEN, "Identification of Pure Organic Compounds," 1st ed., John Wiley and Sons, Inc., New York City, **1904**, vol. 1, p. 80.

hours, the distillate crystallized. The crystalline material was separated from the non-crystalline portion by filtration at −18° and washing with cold petroleum ether. It weighed 22 grams, and melted at 53–55°. On redistillation it boiled at 97–98°, $p = 18$ mm. The material was obtained pure, melting point 58–59°, by one recrystallization from petroleum ether.

Anal. Calc'd for $C_4H_7Cl_3O$: Cl, 60.0. Found: Cl, 59.5, 60.0.

The properties of the compound agree with those reported for 2,2,3-trichloro-1-butanol prepared by Garzarolli-Thurnlackh[11] by the action of ethylzinc on 2,2,3-trichlorobutanal.

SUMMARY

The Grignard reaction of hexahydrobenzylmagnesium iodide with α-chlorocrotonic aldehyde furnished 1-cyclohexyl-2-hydroxy-3-chloro-3-pentene, which was converted into 1-cyclohexyl-2,3-dichloro-3-pentene by the action of phosphorus pentachloride. The 1-cyclohexyl-2,3-dichloro-3-pentene was dehalogenated with zinc to 1-cyclohexyl-2,3-pentadiene, the structure of which was proved by the identification of its products of ozonization and oxidation, namely, cyclohexylacetaldehyde, acetaldehyde, cyclohexylacetic acid, and acetic acid.

The Grignard reaction of hexahydrobenzyl iodide with 2,2,3-trichlorobutanal yielded the abnormal reaction product 2,2,3-trichloro-1-butanol.

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[11] GARZAROLLI-THURNLACKH, *Ann.*, **213**, 369 (1882).