ALLENES. I. THE PREPARATION OF 1-PHENYL-1,2-BUTADIENE

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Pyrethrolone, the alcoholic component of the two insecticidal esters of pyrethrum flowers, pyrethrins I and II, contains an unsaturated fivemembered substituent which catalytic hydrogenation with absorption of two moles of hydrogen converts into the *n*-amyl group. According to Staudinger and Ruzicka,¹ who first investigated pyrethrolone, the compound itself has an open side-chain containing the cumulated system of double bonds. The evidence for this conclusion has always been considered inadequate, and even Ruzicka² later indicated a preference for a conjugated system.

Recently LaForge and Haller³ investigated the nature of the pyrethrolone side-chain, but were unable to reach a definite solution, although their results seemed to exclude the presence of the conjugated system. Their most striking observation had to do with the behavior of pyrethrolone (and pyrethrone, in which only the hydroxyl group of pyrethrolone had been replaced by hydrogen) toward bromine. The reaction with one mole of bromine in ethanol solution appeared to be one of substitution instead of addition, as previously supposed, and furnished a monobromo derivative with liberation of free hydrobromic acid. When the product was reduced with zinc, the original pyrethrolone (or pyrethrone) was regenerated.

Such a reaction was not in agreement with the known behavior of either the cumulated or the conjugated system. It seemed, therefore, that further investigation of the action of halogens on allenes, especially substituted methylallenes (*i.e.* 1,2-butadienes), might by analogy throw some light on the nature of the side chain of pyrethrolone. The substituted 1,2-butadienes have been considered, because evidence points to the presence of a terminal methyl group in the pyrethrolone side-chain.

This article describes the preparation of 1-phenyl-1,2-butadiene, $C_6H_5CH=C=CHCH_3$ (I), a compound not previously reported in the

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

² RUZICKA AND PFEIFFER, *ibid.*, 16, 1208 (1933).

³ LaForge and Haller, J. Org. Chem., 2, 546 (1938).

literature, by two procedures. The first procedure involves the following series of reactions: α -chlorocrotonic aldehyde furnishes 1-phenyl-1-hydroxy-2-chloro-2-butene, C₆H₅CHOHCCl=CHCH₃ (II), by the Grignard reaction with bromobenzene. Substitution of the hydroxyl group with chlorine gives 1-phenyldichlorobutene (III), in which the double bond may be in either the 1,2 position (C₆H₅CH=CClCHClCH₃) or the 2,3 position (C₆H₅CHClCCl=CHCH₃), or the product may be a mixture of the two, depending upon whether or not the allylic rearrangement has taken place. This is immaterial, however, since dehalogenation of either dichloro compound would furnish I.

The second and more convenient method of preparing the compound is by way of the following steps: 1-phenyl-2,2,3-trichloro-1-butanol, C_6H_5 -CHOHCCl₂CHClCH₃ (IV), obtained by the Grignard reaction of 2,2,3trichlorobutanal with bromobenzene, is chlorinated to furnish 1-phenyl-1,2,2,3-tetrachlorobutane, C_6H_5 CHClCCl₂CHClCH₃ (V), which on treatment in ethanol solution with zinc furnishes I.

Prepared by either method the hydrocarbon is a colorless, very mobile liquid. In contact with the air it soon turns yellow, and on longer standing it becomes a viscous mass. The changes are probably due to both oxidation and polymerization. The compound is especially sensitive to mineral acids, which cause rapid polymerization or decomposition. Because of its instability, which may be due to the presence of the styrene functional group, it should be prepared fresh before employment for reactions, and it should be distilled and kept under carbon dioxide or some other inert gas.

1-Phenyl-1,2-butadiene does not react with maleic anhydride or with α -naphthoquinone. On catalytic hydrogenation it absorbs two moles of hydrogen to form *n*-butylbenzene. It is oxidized by potassium permanganate to benzoic and acetic acids.

The behavior of 1-phenyl-1,2-butadiene and some other allenes toward halogens will be described in subsequent articles of this series.

EXPERIMENTAL

1-Phenyl-1-hydroxy-2-chloro-2-butene (II).—The Grignard reagent was prepared from 6 grams of magnesium and 37 grams of bromobenzene in 200 cc. of dry ether. A solution of 23 grams of α -chlorocrotonic aldehyde⁴ in 200 cc. of the same solvent was slowly run into the solution of the reagent, constantly stirred, and cooled in an ice-salt mixture. After the reaction product had been kept overnight in the cold, it was decomposed by adding it, with mechanical agitation, to a solution of 25 grams of ammonium chloride in 300 cc. of water containing ice. A small quantity of acetic acid was added to clear the emulsion, and the reaction product was extracted with ether. The ethereal solution, after being washed with water and dilute sodium

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

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bicarbonate, was dried, and the solvent was removed. The product distilled at 122-124° (0.5-1.0 mm.); n_D^{20} 1.5545; n_D^{20} 1.5502. The yield was 21.8 grams. It crystallized on cooling, and was recrystallized from petroleum ether, from which it separated in long needles, m.p. 50-51°.

Anal. Calc'd for C₁₀H₁₁ClO: C, 65.75; H, 6.04.

Found: C, 65.02, 65.93; H, 6.01, 6.32.

The same compound was obtained by dehalogenation of 1-phenyl-2,2,3-trichloro-1-butanol (IV) as follows: Ten grams of IV in 25 cc. of ethanol was dropped into a stirred suspension of 10 grams of zinc dust in 25 cc. of ethanol that had been heated to the boiling point. The reaction proceeded with heat evolution sufficient to boil the solvent. After all the solution had been added, the reaction mixture was refluxed for 30 minutes, cooled, and the zinc removed by filtration. The ethanol solution was diluted with several volumes of water, and the reaction product was extracted with ether. After repeated washings with water the ethereal solution was dried, and the solvent was removed. The residue crystallized on seeding with crystals prepared by the preceding method. The yield was 7.2 grams. It was recrystallized from petroleum ether with very little loss and melted at 49° .

1-Phenyldichlorobutene (III), $C_6H_5CH=CClCHClCH_3$ or $C_6H_5CHClCCl=CHCH_3$. --Four grams of II was dissolved in 30 cc. of benzene, and 1 gram of dry hydrochloric acid (20% in excess of the theoretical equivalent) was slowly passed into the cooled solution, the amount of hydrochloric acid being determined by the gain in weight. The solution became turbid with the separation of water. The excess acid was removed by washing with water and bicarbonate solution, and the solvent was removed under reduced pressure. The residue was distilled and yielded 3.5 grams (80% of theoretical) of distillate boiling at 100° (0.7 mm.); n_p^{20} 1.5712; n_p^{20} 1.5666. In another experiment 20 grams of II yielded 19 grams of dichloro compound.

Anal. Calc'd for C₁₀H₁₀Cl₂: C, 59.70; H, 4.97; Cl, 35.28.

Found: C, 60.61, 60.93; H, 5.29, 5.28; Cl, 34.62, 34.72.

The chlorination of 1-phenyl-1-hydroxy-2-chloro-2-butene (II) was also carried out by means of thionyl chloride. In this case, as was subsequently shown, the product was essentially 1-phenyl-2,3-dichloro-1-butene. One and five-tenths grams of purified thionyl chloride was added to 2.6 grams of II. The reaction started at once with liquefaction of the mass and evolution of hydrochloric acid. After being warmed for a few minutes, the reaction mixture was poured onto cracked ice and water, and the product was extracted with ether. The ethereal solution was washed with water and sodium carbonate solution and dried. After removal of the solvent the residue was distilled and boiled at $82-87^{\circ}$ (0.5-1.0 mm.); $n_{\rm D}^{20}$ 1.5727. Anal. Calc'd for $C_{10}H_{10}Cl_2$: Cl, 35.26. Found: Cl, 35.41, 35.66.

1-Phenyl-1,2-butadiene (I) (first method).—The dehalogenation of 1-phenyldichlorobutene (III) was carried out a number of times with variations in the experimental conditions. The following procedure gave satisfactory results, but the reaction with zinc dust as applied in the dehalogenation of 1-phenyl-2,2,3-trichloro-1-butanol (IV) would have been more convenient.

A solution of 12 grams of the phenyldichlorobutene in 100 cc. of ethanol was placed in a flask provided with a condenser and equipped for mechanical stirring. The solution was warmed, and 12 grams of zinc dust was added in small portions. After the reaction had started, it proceeded with evolution of heat, sometimes making cooling necessary. Finally the reaction mixture was refluxed for several minutes. After removal of the excess zinc by filtration, part of the ethanol was removed under reduced pressure, and the solution was strongly diluted with water and extracted with ether. The ethanol was washed from the ethereal solution, which was then dried with sodium sulfate.

The residue obtained on removal of the solvent was distilled from a flask provided with a 15-cm. reflux column, and yielded 4.5 grams of colorless distillate which boiled at 44-47°, (0.5-1.0 mm.); n_D^{∞} 1.5754, $n_D^{\infty}-n_C^{\infty}$ 0.025; n_D^{∞} 1.5698; $d_4^{\pm .5}$ 0.9240 M.R. calc'd for C₁₀H₁₀: 43.84; found: 46.33. (The refractive index for 1-phenyl 1,3-butadiene is reported as n_D^{16} 1.6140).

Anal. Calc'd for C10H10: C, 92.31; H, 7.69.

Found: C, 92.65, 91.87, 91.30: H, 8.11, 7.87, 7.90.

The compound turns yellow in a short time in contact with the air, and slowly changes to a thick liquid; it is therefore necessary to keep it under some inert gas and to prepare it fresh for subsequent reactions. Owing to its tendency to oxidize and polymerize, and also because of its volatility, it is difficult to obtain sharp analytical results.

Hydrogenation of 1-phenyl-1,2-butadiene to n-butylbenzene.—One gram of I was hydrogenated with platinum oxide catalyst in ethanol solution. In 10 minutes 375 cc. of hydrogen was absorbed, and in the next 10 minutes 25 cc. The theoretical quantity of hydrogen for 2 moles is 343 cc. The hydrogenated product was isolated by dilution of the filtered solution with water and extraction with ether. The residue on distillation yielded 0.6 gram of product boiling at 183° (760 mm.); n_{12}^{12} 1.4907. $[n_{12}^{12} 1.4940$ is reported for *n*-butylbenzene, which boils at 179° (760 mm.).]

Behavior of 1-phenyl-1, 2-butadiene toward maleic anhydride and α -naphthoquinone. —The Diels-Alder reaction was attempted in order to show that the hydrocarbon prepared as above described was not 1-phenyl-1, 3-butadiene or a mixture containing this. Four-tenths of a gram of I was warmed for 30 minutes on the steam bath with 0.15 gram of pure maleic anhydride. The anhydride quickly dissolved, but no crystallization occurred. The reaction product became viscous and gummy due to polymerization, and nothing crystalline could be isolated. The result of the reaction in no way resembled that observed when 1-phenyl-1,3-butadiene was subjected to the same treatment.

Five-tenths of a gram of 1-phenyl-1,2-butadiene and the same quantity of α -naphthoquinone when heated together changed to a reddish-brown mass of gummy consistency. It was dissolved in a little methanol and seeded with 1-phenylanthraquinone, but no crystallization could be induced. Again it did not show the characteristic behavior of 1-phenyl-1,3-butadiene.

1-Phenyl-3, 2, 3-trichloro-1-butanol (IV).—Since butyl chloral hydrate is available commercially and is easily dehydrated to 2, 2, 3-trichlorobutanal, 1-phenyl-1, 2-butadiene was prepared by the following procedure:

The preparation of the carbinol from 2,2,3-trichlorobutanal and bromobenzene by the Grignard reaction has been described by Helferich and Besler⁵. Following essentially the recorded procedure, 85 grams of product was obtained from 82 grams of aldehyde, 118 grams of bromobenzene, and 18 grams of magnesium. It boiled at 140-145° (0.5 mm.); $n_{\rm D}^{25.7}$ 1.5627. The compound, which solidified on cooling, was melted and dissolved in warm petroleum ether, from which nearly all of it crystallized. The crystalline product melted at 53°. Helferich and Besler record that the compound distils at 172-173° (13 mm.), and that it melts at 53°.

1-Phenyl-1, 2, 3, 3-tetrachlorobutane (V).—By treatment with phosphorus pentachloride, 1-phenyl-2, 2, 3-trichloro-1-butanol (IV) is quantitatively converted into

⁵ HELFERICH AND BESLER, Ber., 57, 1276 (1924).

1-phenyl-1,2,2,3-tetrachlorobutane. The proportions employed in a typical experiment were 20 grams of the carbinol and the same quantity of powdered phosphorus pentachloride. When the two components were mixed, the reaction set in at once with evolution of hydrochloric acid and liquefaction of the mass. The cooled reaction mixture was warmed a few minutes, ice was added, and the product was extracted with ether. After being washed with water, and finally with bicarbonate solution, the ethereal solution was dried, and the solvent was removed. The product distilled at 110-125° (0.5-1.0 mm.); n_{D}^{20} 1.5618. The yield was 18 grams. It solidified on standing and melted at 54-55° when recrystallized from ethanol. In another experiment 50 grams of IV yielded 48 grams of V boiling at 122-125° (0.5-1.0 mm.); n_{D}^{20} 1.5625. It will be noted that the refractive index is almost the same as that of 1-phenyl-2,2,3-trichloro-1-butanol (IV).

Anal. Calc'd for C10H10Cl4: Cl, 52.20. Found: Cl, 51.67, 52.68, 52.38.

1-Phenyl-1, 2-butadiene (I) (second method).—The reaction of 1-phenyl-1, 2, 2, 3-tetrachlorobutane with zinc dust proceeds with unusual, even explosive, violence when the reactants are heated in ethanol. The reaction takes place moderately, however, under the following conditions.

Ten grams of V was dissolved in 25 cc. of warm ethanol, and the solution dropped into a stirred suspension of 20 grams of zinc dust in 25 cc. of boiling ethanol. (The zinc dust had been treated with a large volume of very dilute aqueous 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 reflux condenser and a dropping funnel. After the zinc-dust suspension had been heated to the boiling point of the solvent, the solution of V was introduced at a rate necessary to cause uniform ebullition without additional application of heat. The reaction was completed by boiling for about 15 minutes; the solution was then cooled and filtered from the excess zinc. Several volumes of water were added to the filtrate, which was then extracted with ether. A white precipitate, which probably consisted of zinc compounds, appeared in the aqueous solution, but vanished upon extraction with ether. The ethereal solution was repeatedly washed with water, and finally with sodium carbonate solution, dried with sodium sulfate, and the ether was removed by evaporation on the steam bath. The residue was distilled in an atmosphere of carbon dioxide, from a flask with a 15-cm. reflux column. The yield was 3.7 grams, boiling at 76-77°, (10 mm.); n_D²⁴ 1.5716.

Anal. Cale'd for C10H10: C, 92.31; H, 7.69.

Found: C, 91.14; H, 7.88.

Oxidation of 1-phenyl-1,2-butadiene (I).—One and six-tenths grams of I was suspended in 150 cc. of water and oxidized by the gradual addition of powdered potassium permanganate while the suspension was agitated mechanically and cooled with an ice bath. The process required about 24 hours, and 7.6 grams of permanganate was added, leaving an excess in solution.

The manganese dioxide was removed by filtration, and the excess permanganate was removed by addition of a little oxalic acid to the boiling solution. After filtration the solution was neutralized and concentrated to about 10 cc. On acidification with dilute sulfuric acid the voluminous precipitate was removed by filtration and washed with water. The yield was 1 gram. It was melted at 121-122° and was identified as benzoic acid by the mixture melting point. The filtrate was distilled with steam. The distillate was neutralized with sodium hydroxide, and after complete evaporation and dehydration there remained a residue weighing 0.7 gram. It was essentially sodium acetate, for when 0.4 gram was treated with *p*-toluidine and concentrated hydrochloric acid according to Mulliken's method⁶ it yielded 0.2 gram of *N*-acetyl-*p*-toluidine, which after recrystallization from benzene melted at 146–147° and was identified as such by the mixture melting point with authentic material.

One and three-tenths grams of I was oxidized with 6.3 grams of potassium permanganate in 130 cc. of acetone previously treated with permanganate. The acetone solution combined with the aqueous extract of the manganese dioxide was evaporated and the residue dissolved in a few cubic centimeters of water and acidified. The benzoic acid was removed by filtration and identified by its melting point. The filtrate was steam-distilled, and the distillate was neutralized with potassium hydroxide, concentrated to a small volume, and treated with silver nitrate solution. The silver salt was recrystallized with some loss from water and was still not pure.

Anal. Calc'd for C₂H₃O₂Ag: Ag, 64.6.

Found: Ag, 60.0.

The silver salt was treated with hydrochloric acid, the silver chloride removed by filtration, and the filtrate neutralized and concentrated to dryness. The residue on treatment with *p*-toluidine yielded the acetyl derivative, which after recrystallization melted at 146-147° and was identified by the mixture point, 146-147°, with acetyl-*p*-toluidide. When mixed with propionyl-*p*-toluidide, the melting point was 115-118°.

SUMMARY

The preparation of 1-phenyl-1,2-butadiene by two procedures is described. This hydrocarbon is only moderately stable in contact with the air, and it is easily polymerized by acids. It does not react with maleic anhydride or with α -naphthoquinone. Its structure is proved by its oxidation to benzoic and acetic acids and by its reduction to *n*-butylbenzene.

⁶ MULLIKEN, "Identification of Pure Organic Compounds," 1st ed., John Wiley and Sons, Inc., New York City, **1904**, Vol. 1, p. 80.