Summary

Benzalquinaldine and *p*-chlorobenzalquinaldine react with phenylmagnesium bromide to give α-benzohydrylquinaldine and α-(*p*-chlorobenzohydryl)-quinaldine, respectively.

In the case of benzalquinaldine the same transformation is effected by the use of benzene in the presence of anhydrous aluminum chloride.

p-Chlorobenzalquinaldine, however, reacts with benzene in the presence of anhydrous aluminum chloride to give not the expected α-(*p*-chlorobenzohydryl)-quinaldine but the corresponding chlorine-free compound, α-benzohydrylquinaldine. This dehalogenation is being investigated.

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Acetylene Polymers and their Derivatives. XI. Dichloro-2,3-butadiene-1,3 and Trichloro-1,2,3-butadiene-1,3

BY GERARD J. BERCHET AND WALLACE H. CAROTHERS

Chloroprene (I) under ordinary conditions polymerizes to a rubber-like product about 700 times as rapidly as isoprene (or butadiene).[1] Hence in the diene polymerization a chlorine atom at the β-position has a powerful activating influence. A bromine atom in the same position has an even greater positive effect.[2] On the other hand α-chlorobutadiene polymerizes not much more rapidly than isoprene, and the product, though elastic, has very little strength.[3] The corresponding bromine compound also polymerizes spontaneously but no rubber-like properties have been ascribed to it.[4] Hence the activation produced by the halogen atom is very sensitively related to its position, and multiple substitution does not modify this conclusion, for tetrachloro-1,2,3,4-butadiene-1,3 has been described without any indication that it polymerizes at all.[5] The effect of a single β-halogen atom on diene behavior is in fact unique so far as recorded facts go. No other type of substitution has yielded a compound that greatly exceeds butadiene in the speed of its spontaneous polymerization and at the same time leads to a rubber-like product. In the methyl series isoprene polymerizes somewhat more rapidly than butadiene, and β,γ-dimethylbutadiene perhaps yet faster;[6] and the product from the latter, though somewhat inferior in snap and extensibility, is still rubber-like. On the other hand,

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(1) Carothers, Williams, Collins and Kirby, THIS JOURNAL, **53**, 4203 (1931).

(2) Carothers, Collins and Kirby, *ibid.*, **55**, 789 (1933).

(3) Unpublished results.

(4) Willstätter and Bruce, *Ber.*, **40**, 3979 (1907).

(5) Müller and Hüther, *ibid.*, **64**, 589 (1931). *Cf.* also pentachloro and hexachlorobutadiene-1,3, Beilstein, 4th ed., Vol. 1, p. 250.

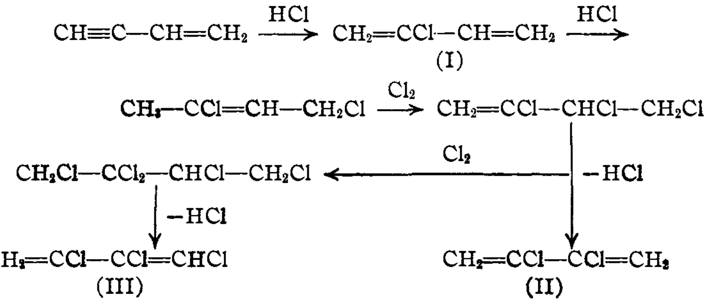
(6) Whitby and Crozier, *Canadian J. Research* **6**, 203 (1932); Whitby and Katz, *ibid.*, **6**, 398 (1932).

α-substitution by methyl reduces the tendency to polymerize and unfavorably affects the quality of the product.[7] It appears that both the terminal methylene groups of butadiene must be free: if either of them is substituted even by an activating group the speed of polymerization is diminished and/or the properties of the product are adversely affected.[8]

These conclusions stimulated interest in dichloro-2,3-butadiene-1,3 (II) which has at once the two unsubstituted terminal methylene groups and two chlorines properly located to produce a doubly activating effect. To provide further comparisons trichloro-1,2,3-butadiene-1,3 (III) was also prepared.

Dibromo-2,3-butadiene-1,3 has already been described, but not very fully: "In a sealed tube it remains limpid for several hours, then becomes turbid, and is gradually transformed into a white polymer, but the transformation is complete only at the end of several days."[9] Otherwise information concerning its behavior is lacking.

Preparation of Dichloro-2,3-butadiene-1,3 and Trichloro-1,2,3-butadiene-1,3.—Starting materials for the preparation of the two dienes were found in the series of products obtained by chlorinating the hydrogen chloride addition products of vinylacetylene.[10] The dichlorobutadiene was obtained from trichloro-1,2,3-butene-3, and the trichlorobutadiene from pentachloro-1,2,3,3,4-butane. The reactions starting from vinylacetylene are



$$CH{\equiv}C{-}CH{=}CH_2 \xrightarrow{HCl} \underset{(I)}{CH_2{=}CCl{-}CH{=}CH_2} \xrightarrow{HCl} CH_3{-}CCl{=}CH{-}CH_2Cl \xrightarrow{Cl_2} CH_2{=}CCl{-}CHCl{-}CH_2Cl$$

$$CH_2{=}CCl{-}CHCl{-}CH_2Cl \xrightarrow{Cl_2} CH_2Cl{-}CCl_2{-}CHCl{-}CH_2Cl \xrightarrow{-HCl} \underset{(III)}{CH_2{=}CCl{-}CCl{=}CHCl}$$

$$CH_2{=}CCl{-}CHCl{-}CH_2Cl \xrightarrow{-HCl} \underset{(II)}{CH_2{=}CCl{-}CCl{=}CH_2}$$

The elimination of hydrogen chloride from the trichlorobutene proceeds very rapidly under a variety of conditions. When the trichloro compound is mixed with a slight excess of approximately 6 *N* methyl alcoholic potassium hydroxide, the theoretical amount of potassium chloride precipitates out within fifteen minutes. Dilution with water then precipitates the dichlorobutadiene as a heavy oil, which, after being stabilized with hydroquinone, is obtained in 86% yield by vacuum distillation. The losses are almost entirely due to polymerization. There is no evidence of the forma-

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[7] Macallum and Whitby, *Trans. Roy. Soc. Can.*, **22**, 39 (1928); Fisher and Chittenden, *Ind. Eng. Chem.*, **22**, 869 (1930); Whitby and Gallay, *Can. J. Res.*, **6**, 280 (1932).

[8] This statement is also supported by observations on the following compounds in which the speed of polymerization is in the indicated order: $CH_2{=}CCl{-}CH{=}CH_2$, $CH_2{=}CCl{-}CMe{=}CH_2 \gg MeCH{=}CCl{-}CH{=}CH_2$, $CH_2{=}CCl{-}CMe{=}CHMe$; Jacobson and Carothers, THIS JOURNAL, **55**, 1624 (1933); Carothers and Coffman, *ibid.*, **54**, 4071 (1932).

[9] Lespieau and Prevost, *Compt. rend.*, **180**, 675 (1925).

[10] Carothers and Berchet, THIS JOURNAL, **55**, 1628 (1933)

tion of any by-products. Dichloro-2,3-butadiene-1,3 is also obtained by the action of alcoholic potash on butadiene tetrachloride (tetrachloro-1,2,3,4-butane) but the yields are less favorable.

The dichlorobutadiene could not be induced to react with naphthoquinone or with maleic anhydride, and hence no direct and decisive proof of its structure was possible. The structure dichloro-1,3-butadiene-1,3 is not excluded by the methods of synthesis used, but this structure seems very unlikely in view of the rapidity with which the compound polymerizes.

Pentachloro-1,2,3,3,4-butane also reacts rapidly with alcoholic potash. Besides the trichlorobutadiene the product was found to contain some tetrachloro-1,2,2,3-butene-3 whose identity was established by its oxidation to α,α,β-trichloropropionic acid.[11] This compound is doubtless an intermediate in the formation of the trichlorobutadiene, and the latter should therefore have the structure (III).

Polymerization of Dichloro- and Trichlorobutadiene.—Under ordinary conditions dichlorobutadiene polymerized completely in about twenty-four hours, at 85 to 90° in about forty minutes. The corresponding times for chloroprene are about ten days, and about twelve hours (estimated). Thus the dichloro compound reacts about ten times as rapidly as chloroprene and about seven thousand times as rapidly as isoprene. The polymerization is inhibited by hydroquinone and accelerated by air or by benzoyl peroxide. The polymer is almost entirely devoid of rubber-like properties. It is a white, opaque, tough, hard mass, non-plastic and lacking in extensibility. It is somewhat (or partly) soluble in chloroform, but very slightly soluble in other common organic solvents including dichlorobutadiene, and under most conditions it separates as an opaque precipitate from the dichlorobutadiene as it is formed. At elevated temperatures (*e. g.*, 85 to 90°), however, the polymer remains dissolved until the polymerization is practically complete. The product is at first a soft, colorless, transparent, sticky, elastic mass, but it becomes opaque, hard, and tough in a very short time. The absence of rubber-like properties in the polymer is consistent with other observations on the influence of substituents: the spontaneous polymers from $CH_2{=}CCl{-}CMe{=}CH_2$[12] and from $CH_2{=}CMe{-}CMe{=}CH_2$ are both deficient in extensibility and snap as compared with those from the monosubstituted dienes $CH_2{=}CCl{-}CH{=}CH_2$ and $CH_2{=}CMe{-}CH{=}CH_2$.

The trichlorobutadiene polymerized much more slowly than the dichloro compound. At the ordinary conditions it changed to a jelly-like mass containing about 50% of unchanged diene in ten to twelve days. After one month polymerization was apparently complete. The product was a dark colored, rather soft and friable mass.

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[11] The structure $CHCl{=}CH{-}CCl_2{-}CH_2Cl$ is not absolutely excluded but it seems very unlikely in view of the ease with which hydrogen chloride is lost from the group $CH_2Cl{-}CHCl_2{-}$.

[12] Carothers and Coffman, THIS JOURNAL, **54**, 4071 (1932).

Conclusions.—The chlorinated 1,3-butadienes now known may be arranged in the following order so far as the speed of their spontaneous transformation into high polymers is concerned

$$\beta,\ \gamma \gg \beta \gg \alpha,\ \beta,\ \gamma > \alpha \gg \alpha,\ \beta,\ \gamma,\ \delta$$

and only the second member of the series yields a polymer that is definitely rubber-like. The generalizations outlined in the introduction thus receive further confirmation.

Preparation of Dichloro-2,3-butadiene-1,3 (a) from Trichloro-1,2,3-butene-3.—253 g. (15% excess) of potassium hydroxide dissolved in 760 cc. of methanol was placed in a flask provided with a stirrer and an efficient reflux condenser, and 634 g. of trichloro-1,2,3-butene-3 was added with stirring at such a rate that the temperature of the mixture remained between 10 and 15°, the flask being cooled in a bath of ice and water. After all the trichlorobutene had been added the mixture was stirred for two hours, and the potassium chloride was filtered off; yield, 293 g. or 99.4% of the theoretical. The filtrate was poured into a large volume of water and the heavy oil was separated, dried with calcium chloride and distilled in the presence of hydroquinone. The product boiled at 39 to 41° at 80 mm.; yield, 304 g. or 86% of the theoretical. Other properties determined on a purified specimen are: b. p. 41 to 43° at 85 mm., 98° at 760 mm.; n^{20}_{D} 1.4890; d^{20}_{4} 1.1829; M_R calcd., 29.47; found, 30.21.

Anal. Calcd. for $C_4H_4Cl_2$: C, 39.02; H, 3.25; Cl, 57.72. Found: C, 38.76; H, 3.78; Cl, 57.09.

(b) From Tetrachloro-1,2,3,4-butane.—The tetrachlorobutane was prepared by chlorinating butadiene. The sample used was a mixture which contained the solid and liquid isomers in the ratio 1:1.12.[13] In a flask provided with a stirrer and a reflux condenser was placed a solution of 150 g. of potassium hydroxide in 500 cc. of methanol. To this solution 234 g. of the tetrachlorobutane mixed with 100 cc. of methanol was slowly added. The temperature of the mixture was kept between 10 and 18°. Potassium chloride separated immediately. After the addition was complete, the mixture was stirred for two hours at 25° and then filtered. The yield of potassium chloride was 156 g. (88%). The filtrate was poured into a large volume of water and the heavy oil which separated was dried and distilled over hydroquinone. The distillate segregated into two fractions (1) b. p. 39 to 45° at 80 mm., 57 g., and (2) b. p. 45 to 110° at 80 mm., 41 g. The first fraction was β,γ-dichlorobutadiene; on redistillation it boiled 39 to 40° at 80 mm. and it showed the correct refractive index and chlorine content. The second fraction on redistillation boiled chiefly at 84 to 86 at 27 mm. Its chlorine content (found, 57.67, 57.75) agreed with that required for a dichlorobutadiene, and it was perhaps an impure isomeric dichlorobutadiene: d^{20}_{4} 1.287; n^{20}_{D} 1.4999.

Preparation of Trichloro-1,2,3-butadiene-1,3 and Tetrachloro-1,2,2,3-butene-3.—One-half mole (115 g.) of pentachloro-1,2,3,3,4-butane was slowly added with stirring to a solution of one mole of potassium hydroxide in 270 cc. of methanol. The mixture was stirred at room temperature for about two hours. The precipitated potassium chloride was filtered off; yield, 61 g. or 82%. The filtrate was poured into a large volume of water, and the precipitated oil was dried and separated by distillation into two fractions (a) crude trichlorobutadiene boiling at 56 to 65° at 26 mm., 44 g.; and (b) crude tetrachlorobutene boiling at 66 to 75° at 26 mm., 24.5 g. They were further purified by distillation.

Trichloro-1,2,3-butadiene-1,3.—B. p., 33 to 34° at 7 mm.; n^{20}_{D} 1.5262; d^{20}_{4} 1.4060; M_R calcd., 34.34; M_R found, 34.39.

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(13) *Cf.* Muskat and Northrup, THIS JOURNAL, **52**, 4054 (1930).

Anal. Calcd. for $C_4H_3Cl_3$: C, 30.47; H, 1.90; Cl, 67.61. Found: C, 29.50, 29.43; H, 2.33, 2.19; Cl, 68.42, 68.50.

Tetrachloro-1,2,2,3-butene-3.—B. p. 41 to 42° at 7 mm.; n_D^{20} 1.5133; d_4^{20} 1.4602; M_R calcd. 39.67; M_R found, 39.91.

Anal. Calcd. for $C_4H_4Cl_4$: C, 24.74; H, 2.06; Cl, 73.19. Found: C, 25.49, 25.16; H, 2.23, 2.24; Cl, 72.66, 72.16.

Oxidation.—A sample (23 g.) of the tetrachlorobutene was oxidized with excess aqueous potassium permanganate. After filtration and treatment with sulfur dioxide the solution was extracted continuously with ether. Evaporation of the ether gave a liquid residue which distilled at 120 to 125° at 22 mm. It crystallized on cooling and after being washed with petroleum ether melted at 48 to 50°. Neutral equivalent found, 176.4; calcd. for trichloropropionic acid, 177.5.

Summary

Dichloro-2,3-butadiene-1,3 and trichloro-1,2,3-butadiene-1,3 have been prepared and their properties are described. The dichloro compound polymerizes more rapidly than chloroprene, the trichloro compound more slowly than chloroprene. The polymers are not rubber-like in either case. The chlorobutadienes now known may be arranged in the following order so far as their speed of spontaneous polymerization is concerned: $\beta,\gamma \gg \beta \gg \alpha,\beta,\gamma > \alpha \gg \alpha,\beta,\gamma,\delta$; and only the second member of the series (chloroprene) yields a definitely rubber-like polymer.

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Acetylene Polymers and their Derivatives. XII. The Addition of Thio-*p*-cresol to Divinylacetylene

BY WALLACE H. CAROTHERS

The reaction of acetylene with itself to form an open-chain trimer was described in the first paper of this series.[1] This compound, which has the molecular formula C_6H_6, contains no true acetylenic hydrogen; on hydrogenation it yields *n*-hexane; and it differs from the already known dimethyldiacetylene (I). It was therefore assigned the structure divinylacetylene (V).[2] The formulas II, III and IV, which are equally con-

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(1) Nieuwland, Calcott, Downing and Carter, THIS JOURNAL, **53**, 4197 (1931).

(2) This compound has perhaps been obtained in small amounts, though not completely characterized, by Farmer, Laroia, Switz and Thorpe, *J. Chem. Soc.*, 2948 (1927). See also Mignonac and de Saint-Aunay, *Compt. rend.*, **188**, 959 (1929).

Lespieau and Guillemonat in a recent publication [*Compt. rend.*, **195**, 245 (1932)] have described divinylacetylene under the title "A New Isomer of Benzene." Apparently they have entirely overlooked the paper of Nieuwland, Calcott, Downing and Carter referred to above. They also state that they have obtained about 12 cc. of (impure) vinylacetylene, of which hitherto only 1.4 g. has been prepared (referring to Willstätter and Wirth). It may, therefore, be of interest to state that in the laboratories and works of the du Pont Company many hundreds of kilograms of vinylacetylene and divinylacetylene have been prepared by the process of Nieuwland, Calcott, Downing and Carter.