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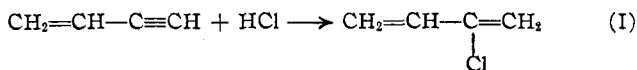
HOMOLOGS OF CHLOROPRENE AND THEIR POLYMERS (SECOND PAPER ON NEW SYNTHETIC RUBBERS)

BY WALLACE H. CAROTHERS AND DONALD D. COFFMAN

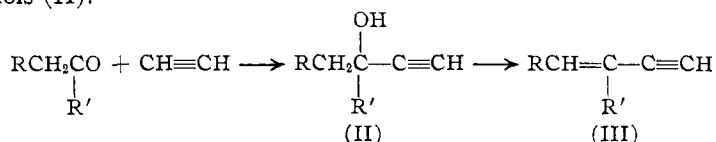
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Chloroprene (chloro-2-butadiene-1,3, I) is obtained by the addition of hydrogen chloride to vinylacetylene.¹



In the rate of its spontaneous transformation into a rubber-like polymer it greatly exceeds all previously described dienes.² The present paper is concerned with homologs of chloroprene obtained by the addition of hydrogen chloride to homologs of vinylacetylene. As Merling has shown,³ compounds (III) of the latter class can be obtained by the action of sodium acetylide on aldehydes or ketones, followed by dehydration of the resulting carbinols (II).



These reactions were in fact proposed as steps in a process for the synthesis of rubber, since in the case where $\text{R} = \text{H}$ and $\text{R}' = \text{CH}_3$, the product II can be reduced to the vinylcarbinol and then dehydrated to produce isoprene. The elegance of this method has been frequently commended, but from our own experience it appears more elegant than useful, since the yields in the first step were rather low. Nevertheless, the isolation of small amounts of the pure carbinols presents no particular difficulties, and under properly selected conditions the dehydration to the substituted vinylacetylene proceeds fairly smoothly.

In the present study the carbinols used were those represented in formulas IV-VI. These and the corresponding vinylacetylenes (VII-IX) have already been described by Merling.³ The substituted vinylacetylenes were converted into the corresponding substituted chloroprenes (X-XII) by shaking them at room temperature with concentrated hydrochloric acid containing cuprous chloride and ammonium chloride. The reactions proceeded somewhat more slowly than the formation of chloro-

¹ Carothers, Berchet and Collins, *THIS JOURNAL*, **54**, 4066 (1932).

² Carothers, Williams, Collins and Kirby, *ibid.*, **53**, 4203 (1931).

³ Merling, Friedr. Farbenfab. von Bayer & Co., German Patents 280,226, 286,920, 285,770, 288,271; Scheibler and Fischer, *Ber.*, [2] **55**, 2903 (1922); Sung Wouseng, *Ann. chim.*, [10] **1**, 343-416 (1924).

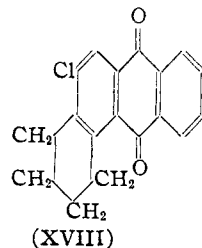
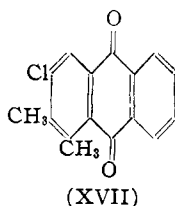
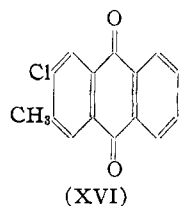
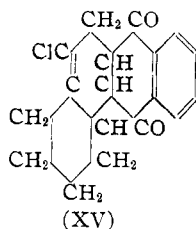
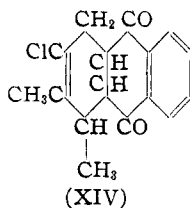
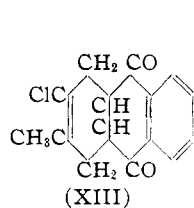
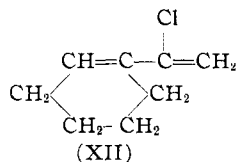
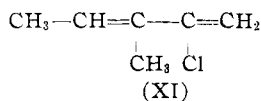
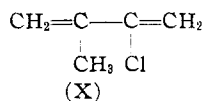
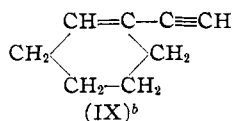
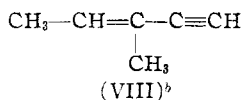
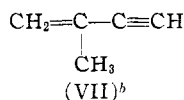
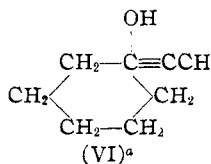
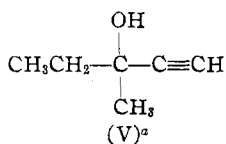
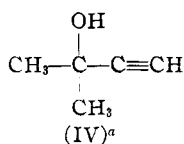
prene itself by the same process. The yields obtained were rather low but this was due chiefly to incomplete conversion. The substituted chloroprenes reacted smoothly with α -naphthoquinone to form crystalline addition products (XIII–XV), which were readily oxidized to the corresponding anthraquinones (XVI–XVIII).

The amounts of the substituted chloroprenes available did not suffice for a very detailed study of their polymerization. The results obtained, however, indicated quite definitely that, of the three dienes, only chloro-2-methyl-3-butadiene (X) is likely to deserve serious consideration as a precursor of rubber. It polymerizes at approximately the same rate as chloroprene; the polymer obtained is definitely rubber-like; a plastic form of the rubber-like product is readily isolated by distilling the unchanged diene from the viscous sirup or the soft jelly obtained by incomplete polymerization; this plastic material is vulcanized by the action of heat alone without the addition of sulfur. Samples thus obtained were strong, very tough and quite elastic, but their extensibility was rather low. The ultimate product of the spontaneous polymerization of the diene in a sealed tube containing a very little air was rather similar in its properties to the vulcanizate described above; it was a black, lustrous solid very strong and tough, but it had a low extensibility.

The dimethyl compound (XI) polymerized very much more slowly than chloroprene—apparently not much more rapidly than isoprene. The product was elastic, but soft and sticky, and attempts to vulcanize it resulted in only partial loss of the plastic properties. The vulcanizate was coherent and rather strong; its extensibility was fairly high (about 500%) but recovery from stretch was slow.

The tetramethylene compound (XII) also polymerized very slowly, and the product obtained was a very soft and plastic mass. The attempt to vulcanize it was almost entirely unsuccessful; the plastic properties were not appreciably affected, but after standing for several months the compounded sample had become quite brittle although it contained an antioxidant.

These observations together with others already available permit some conclusions concerning the effect of the position and the nature of substituting groups on the polymerization of butadiene. Since butadiene, isoprene, and β,γ -dimethylbutadiene do not very greatly differ in the rate of their spontaneous polymerization, it is evident that methyl is not an activating group. The fact that chloroprene polymerizes about seven hundred times as fast as isoprene illustrates the powerful activating effect of a chlorine atom at the β -position. The introduction of a methyl group at the other interior carbon does not greatly modify this effect, although the polymer obtained is somewhat less extensible; but the introduction of a second methyl group at one of the terminal carbons almost completely checks the activating effect of the chlorine atom.



^a See Friedr. Farbenfab. von Bayer & Co., German Patents 280,226, 284,764, 286,920, 289,800. ^b German Patent 290,558.

Experimental Part

Acetylenic Carbinols.—The general method used for the preparation of the acetylenic carbinols has already been described in the literature.⁴ The ketone (2 moles) was slowly introduced into an ethereal suspension (1 l. abs. ether) of sodamide (2 moles) at -10° with vigorous agitation. After five hours, when the evolution of ammonia had become very slow, acetylene was passed during eight hours into the reaction mixture at -10° , under 10–15 pounds pressure with constant shaking. The reaction mixture was then poured onto crushed ice, acidified with dilute sulfuric acid, subjected to ether extraction, the extract dried and distilled. The yields were: ethinyldimethylcarbinol (IV), b. p. $104-108^\circ$, 36%; ethynylmethylethylcarbinol (V), b. p. $119-123^\circ$, 33%; ethynyl-1-cyclohexanol-1 (VI), b. p. 174° at 760 mm., $53-55^\circ$ at 2 mm., 50%.

⁴ Sung Wouseng, *Ann. chim.*, [10] I, 343–416 (1924).

In the preparation of ethynyl-1-cyclohexanol-1 two by-products were isolated and identified: di-(hydroxy-1-cyclohexyl-1)-acetylene (10 g. from 2 moles of the ketone); crystals from carbon tetrachloride or benzene-petroleum ether, m. p. 106–107° (copper block). The literature records its melting point as 102°.⁵

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.65; H, 9.90. Found: C, 74.74; H, 10.41.

Cyclohexylidene-2-cyclohexanone-1 (35 g. from 4 moles of the ketone), colorless liquid (b. p. 143–145° at 16 mm.; n_D^{20} 1.5049; d_4^{20} 1.001) which readily formed an oxime, m. p. 146°.⁶

Ethynylmethylphenylcarbinol.—The condensation of acetylene with acetophenone gave in 2% yield ethynylmethylphenylcarbinol which boiled at 69° under 1 mm. The carbinol after three crystallizations from petroleum ether (b. p. 40–60°) melted at 52–53°.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.19; H, 6.85. Found: C, 81.71; H, 6.88.

Dehydration of the Acetylenic Carbinols.—The ethynylmethylcarbinol was heated at 90° (bath) in a distilling flask with an equal weight of *p*-toluenesulfonic acid for three hours. The methyl-2-butene-1-ine-3 (VII) distilled into the receiver as it was formed, b. p. 34°; yield, 53%.

The ethynylmethylethylcarbinol (60 g.) was slowly added during thirty minutes to 10 g. of *p*-toluenesulfonic acid contained in a distilling flask surrounded by a water-bath at 80°. The operation was carried out at slightly diminished pressure and the methyl-3-pentene-2-ine-4 (VIII) distilled into the receiver as it was formed, b. p. 68 to 71° at 760 mm.; yield, 25%.

Attempts to dehydrate ethynyl-1-cyclohexanol-1 by heating it with iodine, *p*-toluene-sulfonic acid, or anhydrous oxalic acid were unsuccessful, but excellent results were obtained by passing the carbinol in a stream of nitrogen over basic aluminum sulfate (from alum) at 240 to 260°. The yield of ethynyl-1-cyclohexene-1 (IX) boiling at 40 to 43° at 12 mm. was about 35% per passage and the remainder was chiefly unchanged carbinol.

Chloro-2-methyl-3-butadiene-1,3 (X).—Methyl-2-butene-1-ine-3 (40 g.) was shaken in a pressure bottle during four and a half hours at 20° with hydrochloric acid (105 cc., sp. gr. 1.19) containing cuprous chloride (15 g.) and ammonium chloride (6 g.). The reaction mixture was subjected to steam distillation, and the products were dried and distilled. The yield of the chlorobutadiene was 25 g. or 40%; b. p. 93° (760 mm.) with polymerization, 41° (113 mm.), 37° (105 mm.); n_D^{20} 1.4689, d_4^{20} 0.9593, M_R (obs.) 29.75, M_R (calcd.), 29.22.

Anal. Calcd. for C_5H_7Cl : C, 58.54; H, 6.83; Cl, 34.63; mol. wt. 103. Found: C, 58.55; H, 6.72; Cl, 34.39; mol. wt. (in freezing benzene), 126.

Chloro-2-methyl-3-tetrahydro-1,4,4a,9a-anthraquinone-9,10 (XIII).— α -Naphthoquinone (0.5 g.) was heated at 100° for half an hour with chloro-2-methyl-3-butadiene-1,3 (1 g.). The reaction mixture was cooled and the crystals were washed with absolute methanol. After crystallization from aqueous acetone, the white needles melted at 165–166° (uncorr.).

Anal. Calcd. for $C_{15}H_{13}O_2Cl$: C, 69.09; H, 4.99. Found: C, 68.72; H, 4.86.

Chloro-2-methyl-3-anthraquinone (XVI).—The tetrahydro compound (XIII) was suspended in dilute alcoholic sodium hydroxide. Air was bubbled through the blue solution until only a yellow color remained. The suspension was diluted with water, the yellow crystals were filtered and recrystallized from glacial acetic acid. The material

⁵ Iotsitch, *J. soc. phys.-chim. r.*, **38**, 656 (1906), G. Dupont, *Ann. chim.*, [8] **30**, 498 (1913).

⁶ Wallach, *Ber.*, **29**, 2965 (1896); Mannich, *ibid.*, **40**, 157 (1907).

melted at 214–215° (uncorr.). The melting point of chloro-2-methyl-3-anthraquinone is recorded in the literature as 215° and 219° corrected.⁷

Chloro-2-dimethyl-3,4-butadiene-1,3 (XI).—Methyl-3-pentene-2-ine-4 (25 g.) was shaken in a pressure bottle during five and a half hours at 20° with hydrochloric acid (58 cc., sp. gr. 1.19), containing cuprous chloride (8.5 g.) and ammonium chloride (3.5 g.). The reaction mixture was subjected to steam distillation and the product dried and distilled. The yield of the chlorobutadiene was 9 g. or 22%. A considerable proportion of unreacted hydrocarbon was recovered; b. p. 57–60° (96 mm.), n_D^{20} 1.4671; d_4^{20} 0.9437, M_R (obs.) 34.26, M_R (calcd.) 33.84.

Anal. Calcd. for C_8H_9Cl : C, 61.80; H, 7.72; Cl, 30.44; mol. wt., 116.5. Found: C, 61.40; H, 7.55; Cl, 29.24; mol. wt., 116.

Chloro-2-dimethyl-3,4-tetrahydro-1,4,4a,9a-anthraquinone-9,10 (XIV).— α -Naphthoquinone (0.5 g.) was heated at 100° during one hour with chloro-2-dimethyl-3,4-butadiene-1,3 (1 g.). The reaction mixture was cooled, and the crystals were washed with absolute methanol. After crystallization from aqueous acetone, the white needles melted at 107° (copper block).

Anal. Calcd. for $C_{16}H_{16}O_2Cl$: C, 69.95; H, 5.47. Found: C, 69.41; H, 5.53.

Chloro-2-dimethyl-3,4-anthraquinone (XVII).—The tetrahydro compound (XIV) was suspended in dilute alcoholic sodium hydroxide. Air was bubbled through the purple solution until only a pale yellow color remained. The ethanol was diluted with water, the yellow crystals filtered and recrystallized from glacial acetic acid. The anthraquinone melted at 171.5° (copper block).

Anal. Calcd. for $C_{16}H_{14}O_2Cl$: C, 70.98; H, 4.07. Found: C, 70.22; H, 4.14.

Chloro-2-tetramethylene-3,4-butadiene-1,3 (XII).—Ethynyl-1-cyclohexene-1 (33 g.) was shaken in a pressure bottle during four and a half hours at 20° with hydrochloric acid (70 cc., sp. gr., 1.19) containing cuprous chloride (10 g.) and ammonium chloride (4 g.). The reaction mixture was subjected to vacuum steam distillation, and the product dried and fractionated. The yield of the chlorobutadiene was 14 g. or 32% of the theoretical, and a considerable amount of unreacted hydrocarbon was recovered; b. p. 55–57° (1 mm.); n_D^{20} 1.5240; d_4^{20} 1.0422; M_R (obs.), 41.84; M_R (calcd.), 40.88.

Anal. Calcd. for $C_8H_{11}Cl$: C, 67.37; H, 7.72; mol. wt., 142.5. Found: C, 67.50; H, 7.90; mol. wt. (in freezing benzene), 143.

Chloro-2-tetramethylene-3,4-tetrahydro-1,4,4a,9a-anthraquinone-9,10 (XV).— α -Naphthoquinone (2 g.) was heated at 100° during twenty minutes with chloro-2-tetramethylene-3,4-butadiene-1,3 (4 g.). On cooling crystals formed which were washed with absolute methanol. After recrystallization from absolute ethanol, the white needles melted at 191–192° (copper block).

Anal. Calcd. for $C_{18}H_{17}ClO_2$: C, 71.88; H, 5.66. Found: C, 71.42; H, 5.86.

Chloro-2-tetramethylene-3,4-anthraquinone (XVIII).—The tetrahydro compound (XV) was suspended in dilute alcoholic sodium hydroxide. Air was bubbled through the purple solution until only a yellow color remained. The ethanol was diluted with water, the crystals filtered and recrystallized from glacial acetic acid. The yellow needles melted at 155–156° (copper block).

Anal. Calcd. for $C_{18}H_{15}ClO_2$: C, 72.85; H, 4.38. Found: C, 72.59; H, 4.53.

Polymerization of Chloro-2-methyl-3-butadiene-1,3 (X).—When a sample of the diene was allowed to stand at the laboratory conditions in a sealed tube containing a trace of air it set up to a stiff jelly in about five days. Later the specimen became dark in color and ten months later when the tube was opened the product was a black, lustrous solid, very strong and tough but having only a slight extensibility. A sample of

⁷ Keimatsu and Hirans, *J. Pharm. Soc. Japan*, 49, 140–147 (1929).

the diene exposed to the light of a Cooper-Hewitt lamp (mercury arc in glass) at ordinary temperature contained 30% of polymer after sixty-five hours. (Under the same conditions chloroprene polymerizes at a greater rate than this—about 30% in forty hours.) The sample was then a soft jelly. The polymer was precipitated, washed with alcohol, and compounded with 1% of phenyl- β -naphthylamine, 5% of zinc oxide, 2% of stearic acid, and heated in a mold at 140 to 145° for fifteen minutes. The resulting sheet was coherent, strong, tough, and rather elastic, but it was deficient in resiliency and extensibility. It appears that the polymer from chloro-2-methyl-3-butadiene-1,3 more closely resembles the products from dimethylbutadiene (methyl rubber) than those obtained either from isoprene or from chloroprene.

Polymerization of Chloro-2-dimethyl-3,4-butadiene-1,3 (XI).—A specimen placed in a sealed glass tube under air and exposed to the light of a 100-watt Mazda lamp for two months at the ordinary temperature was converted to a very soft, sticky, elastic mass which still contained a considerable proportion of volatile material—apparently unchanged monomer. After standing for eight months more in the absence of direct light its properties had not undergone any further change.

A sample of the diene was submitted to a pressure of 8000 atmospheres for 106 hours at 40°. The product was a soft, plastic, elastic mass containing about 70% of polymer. It was compounded with 1% of phenyl- β -naphthylamine, 10% of zinc oxide, 2% of stearic acid, 1% of benzidine and 1% of tetramethylthiuramdisulfide and was then heated in a mold at 120 to 125° for seventy minutes. The product obtained in this way was rather soft and lacking in resiliency and nerve. The extensibility was fairly high (400 to 500%).

Polymerization of Chloro-2-tetramethylene-3,4-butadiene-1,3 (XII).—A specimen in a glass tube under air was exposed to the light of a 100-watt Mazda light for forty-eight days. The product was a thick, dark mass. Removal of the unchanged monomer by washing with alcohol yielded about 70% of polymer. This was very soft, plastic and sticky. It was compounded in the same manner as the polymer described in the preceding paragraph, but after being heated it still remained soft and plastic. After standing for ten months it had become brittle. A specimen of the diene was submitted to a pressure of 6000 atmospheres at 38° during ninety-six hours. The product was quite soft and plastic and when compounded as in the preceding example and heated for seventy minutes at 120° it showed no appreciable signs of vulcanization.

We are indebted to Dr. H. W. Starkweather for the experiments at high pressures.

Summary

Three substituted vinylacetylenes were treated with hydrogen chloride and thus converted to the corresponding chlorobutadienes. Chloro-2-methyl-3-butadiene-1,3 polymerized very rapidly and yielded a rubber-like polymer, which after vulcanization was less extensible than the corresponding product obtained from chloroprene (chloro-2-butadiene-1,3). Chloro-2-dimethyl-3,4-butadiene-1,3 polymerized very slowly and the product, even after vulcanization, was soft and lacking in nerve. Chloro-2-tetramethylene-3,4-butadiene-1,3 also polymerized very slowly and the product was very soft, plastic and sticky.

The structures of the three new chlorobutadienes were established through their reaction with α -naphthoquinone to form crystalline addition products, which were oxidized to the corresponding anthraquinones.