$CH—C\equiv C—R$ are described in which R is methyl, ethyl, *n*-butyl and *n*-heptyl.

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Acetylene Polymers and their Derivatives. IX. 1-Alkyl-2-chloro-1,3-butadienes and their Polymers (Fourth Paper on New Synthetic Rubbers)

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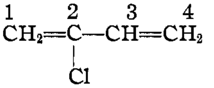
Chloroprene (I) polymerizes very rapidly to form a rubber-like product of excellent quality.[1]

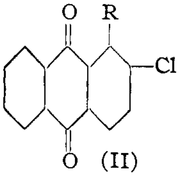

(I)

$$\overset{1}{CH_2}=\underset{\substack{|\\Cl}}{\overset{2}{C}}—\overset{3}{CH}=\overset{4}{CH_2} \quad (I)$$

Replacement of the hydrogen at the 3-position by methyl does not appreciably affect the rate of spontaneous polymerization, but the rubber-like product is somewhat deficient in extensibility.[2] On the other hand, the introduction of methyl at both the 3- and the 4-positions greatly diminishes the tendency to polymerize, and the product, although highly extensible, is lacking in resilience.[2]

The present paper is concerned with chloroprenes in which a hydrogen in the 1-position has been replaced by alkyl. These compounds are readily obtained by the action of hydrogen chloride on the corresponding α-substituted vinylacetylenes. The latter have already been described.[3] Doubtless because of their lesser solubility in water they react more slowly with aqueous hydrochloric acid than does the parent hydrocarbon, which reacts practically completely when shaken for five hours at room temperature with two moles of concentrated hydrochloric acid containing cuprous chloride.[4] Under the same conditions α-methylvinylacetylene is less than 40% utilized. Reaction of the higher homologs is still slower, so that elevated temperature was needed for the butyl compound, and the heptyl compound required the addition of alcohol to function as a solvent.

The physical properties of the new homologs of chloroprene are indicated in Table I. They are colorless liquids with characteristic odors. Like chloroprene, they react with α-naphthoquinone to form addition products, which are readily oxidized to α-alkyl-β-chloroanthraquinones (II), and their identity is established by this reaction.



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

[2] Carothers and Coffman, *ibid.*, **54**, 4071 (1932).

[3] Jacobson and Carothers, *ibid.*, **55**, 1622 (1933).

[4] Carothers, Berchet and Collins, *ibid.*, **54**, 4066 (1932).

No additions to systems of the type alkyl—$\overset{(1)}{\mathrm{C}}\equiv\overset{(2)}{\mathrm{C}}$—CH=$CH_2$ have been recorded hitherto. It is therefore of interest to observe that the result of adding hydrogen chloride under the conditions described is to place H at (1) and Cl at (2), but in view of the mechanism already established for vinylacetylene[4] it seems probable that the first product is alkyl—CH=C=CH—CH_2Cl, which then rearranges to the substituted chloroprene. In any event, current theories, either empirical or electronic, do not appear to account for this result.

TABLE I

PROPERTIES OF CH_2=CH—CCl=CH—R

Nature of R	B. p., °C.	Pressure in mm.	n^{20}_{D}	d^{20}_{4}	M_R Calcd.	M_R Found	Exaltation
H[1]	59.4	760	1.4583	0.9563	24.61	25.27	0.66
CH_3	99.5–101.5	759	1.4785	.9576	29.22	30.32	1.10
C_2H_5	68.2–69	117	1.4770	.9390	33.84	35.05	1.21
n-C_4H_9	64–65	18	1.4794	.9366	43.04	43.77	0.73
n-C_7H_{15}	74–76	1	1.4785	.9141	56.93	57.79	0.86

Polymerization of the Substituted Chloroprenes.—Chloroprene polymerizes practically completely to an elastic, rubber-like mass in forty-eight to eighty hours when directly illuminated by a 150-watt Mazda lamp at 30 to 35°. The substituted chloroprenes listed in Table I all polymerize much more slowly. The methyl compound requires about six or seven weeks, and the higher members of the series require still longer times. The products, with the possible exception of that derived from the heptyl compound, are definitely rubber-like but much inferior in quality to polychloroprene. The product from the methyl compound is the best. Polymerization under direct light from a 150-watt Mazda lamp during one month at the ordinary temperature gave a soft mass containing a considerable proportion of unchanged monomer. The polymer precipitated by the addition of alcohol was a soft, plastic mass resembling milled smoked sheets. It was compounded with 10% of its weight of zinc oxide and then heated at 120° for twenty minutes. The plastic properties were quite largely suppressed by this treatment, but the product appeared to be incompletely vulcanized. It was strong and tough and had a high extensibility, but it recovered from stretch rather slowly, and was deficient in resilience. Vulcanizates obtained from higher members of the series were still softer and more deficient in resilience.

Preparation of 1-Alkyl-2-chloro-1,3-butadienes.—The general procedure was similar to that already described for chloroprene.[4] One mole of the hydrocarbon was shaken with approximately 2.2 moles of concentrated aqueous hydrochloric acid containing about 0.25 mole of cuprous chloride and 0.2 mole of ammonium chloride. The nonaqueous layer was separated, stabilized with hydroquinone and distilled; or, in some cases, the reaction mixture was distilled with steam after the addition of hydroquinone. The reaction time varied from five to sixteen hours and the temperature from 23 to

ANALYTICAL DATA FOR THE 1-ALKYL-2-CHLORO-1,3-BUTADIENES

Nature of alkyl	Calculated				Found			Mol. wt. (cryoscopic in benzene)
	C	H	Cl	Mol. wt.	C	H	Cl	
CH_3	58.56	6.83	34.61	102.5	58.49	6.92	34.63	102 103
C_2H_5	61.82	7.73	30.45	116.5	61.64	7.97	30.28	116 119
n-C_4H_9	66.45	8.99	24.56	144.5	65.73	8.76	24.57	152 154
n-C_7H_{15}	70.79	10.19	19.02	186.5	70.39	10.04	19.26	189 193

45°. The product in each case appeared to consist entirely of the substituted chloroprene and the unchanged hydrocarbon. Yields were good, but conversions were not complete. No appreciable addition could be obtained with the heptyl compound in aqueous solution, but a fair conversion was obtained when the hydrocarbon was shaken with 3.4 moles of hydrochloric acid in ethyl alcohol with 0.35 mole of cuprous chloride and 0.44 mole of ammonium chloride for five hours at 70 to 80°.

Condensation of Naphthoquinone with the 1-Alkyl-2-chloro-1,3-butadienes.—The substituted chloroprenes were each heated with α-naphthoquinone in the ratio of about 1 g. to 0.5 g. at 100° for about two hours. Alcohol containing sodium hydroxide was added, and air was bubbled through the resulting suspension. The solids were crystallized as indicated below and were thus obtained in the form of yellow crystals (generally needles).

SUBSTITUTED ANTHRAQUINONES OF FORMULA II

R =	Cryst. from	M. p., °C.	Calcd. C	Calcd. H	Found C	Found H
CH_3	Acetic acid	181	70.19	3.51	70.16	3.50
C_2H_5	Alcohol	151–152	70.99	4.06	70.93	4.18
n-C_4H_9	Methanol	129–130	72.37	5.03	71.83	5.16
n-C_7H_{15}[a]	Alcohol	112.5–113.5	74.02	6.17	74.12	6.40

[a] In this case the intermediate tetrahydro compound was isolated, probably 1-heptyl-2-chloro-4,4a,9,9a-tetrahydro-9,10-anthraquinone; white crystals from methanol, m. p. 96–98°.

Anal. Calcd. for $C_{21}H_{25}O_2Cl$: C, 73.16; H, 7.26. Found: C, 72.48; H, 7.44.

Polymerization of the 1-Alkyl-2-chloro-1,3-butadienes

1-Methyl-2-chloro-1,3-butadiene.—A sample of 1-methyl-2-chloro-1,3-butadiene was exposed at room temperature to an ordinary incandescent light (150-watt Mazda) for one month. During this period the liquid increased in viscosity—slowly at first, but more rapidly later—until a soft, transparent, elastic, rubber-like solid was obtained. The rubber-like solid was macerated with alcohol to remove monomer and polymers of low molecular weight. The residual polymer was a tough, rubbery, plastic material. Ten per cent. by weight of zinc oxide was incorporated by means of steel rolls and the plastic mass then heated at 120° for twenty minutes. The product was strong, tough and elastic, but recovery from stretch was rather slow.

A sample of 1-methyl-2-chloro-1,3-butadiene was exposed to a 150-watt Mazda light at 30–35° for six and one-half weeks. The liquid progressively increased in viscosity until finally a pale yellow rubbery solid was obtained. This product was more completely polymerized than the product of the preceding experiment. The polymer was highly elastic and resembled cured natural rubber.

1-Ethyl-2-chloro-1,3-butadiene.—A sample of 1-ethyl-2-chloro-1,3-butadiene was exposed to the light of a 150-watt Mazda lamp at 30 to 35° for about four weeks. The product was a pale yellow, transparent, viscous sirup. This was macerated with a large volume of alcohol to remove unchanged monomer. The soft, sticky, coherent mass that remained undissolved by the alcohol was mixed with 10% of zinc oxide and heated in a mold for twenty minutes at 120°. The product was a tough, elastic material resembling the vulcanized product obtained from 1-methyl-2-chloro-1,3-butadiene, but it was softer and less resilient.

1-Butyl-2-chloro-1,3-butadiene.—A sample of 1-butyl-2-chloro-1,3-butadiene, when allowed to stand at the ordinary conditions in a stoppered bottle, after nine and one-half months had changed to a thick, sticky, brown sirup. Precipitation with alcohol then gave a 60% yield of rather soft, rubber-like material. The reaction was accelerated by light. A sample directly exposed to a 150-watt Mazda lamp at 30 to 35° for six weeks had changed to a yellow, viscous, sirup. After five weeks more it was considerably thicker. It was washed with alcohol and the residual sticky solid was mixed with zinc oxide. It vulcanized very incompletely on being heated.

A sample of 1-butyl-2-chloro-1,3-butadiene was subjected to a pressure of 6000 atmospheres at 38°. At the end of ninety-six hours it had polymerized to a transparent, soft, sticky solid; 90% of this solid was now insoluble in alcohol. The portion insoluble in alcohol was mixed with 10% of its weight of zinc oxide, 2% of stearic acid, and 1% of benzidine and then heated at 120°. The physical properties of the product indicated that it was very incompletely vulcanized. It was elastic but rather weak and somewhat sticky.

1-Heptyl-2-chloro-1,3-butadiene.—A sample of this diene showed no apparent change in color or viscosity when allowed to stand at the ordinary conditions for nine months. Polymerization occurred slowly when a sample was exposed to light from a Mazda lamp at 30 to 35°. After three and one-half weeks the sample had changed to a colorless, transparent sirup. After six more weeks it had become thick and very viscous. It was finally washed with alcohol and attempts were made to vulcanize the insoluble polymer in the presence of zinc oxide. The product was soft and sticky.

A sample of 1-heptyl-2-chloro-1,3-butadiene was subjected to a pressure of 6000 atmospheres at 38°. At the end of ninety-six hours it had polymerized to a transparent, sticky, elastic mass. Only 4% of the material was soluble in alcohol. The alcohol-insoluble polymer was mixed with 10% of zinc oxide, 2% of stearic acid, and 1% of benzidine and heated at 120°. The product was a sticky solid possessing very slight elasticity.

Acknowledgment.—We are indebted to Dr. H. W. Starkweather for the experiments at high pressure.

Summary

Substituted chloroprenes of the formula $CH_2{=}CH{-}CCl{=}CH{-}R$ in which R is methyl, ethyl, *n*-butyl and *n*-heptyl are described. These compounds all polymerize much more slowly than chloroprene and the polymers, though rubber-like, are inferior in quality to polychloroprene. The methyl compound polymerizes most rapidly and yields the best polymer, but compared with polychloroprene the polymer is lacking in resilience.

Substituted anthraquinones derived from the substituted chloroprenes are described.

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