tity of tetraphenylethylene was obtained from 5 g. of the ethylene, 1 g. of aluminum chloride and 150 cc. of benzene which had been saturated with hydrogen chloride. The procedure was the same as that used for the conversion of triphenylethylene into *sym*-tetraphenylethane.

Dibenzyl from Tetraphenylethylene.—A solution of 7 g. of tetraphenylethylene in 150 cc. of dry benzene was saturated with dry hydrogen chloride and shaken in contact with 20 g. of aluminum chloride for three days. After decomposition and separation had been completed, the benzene was removed and the residue distilled under reduced pressure. A small amount of distillate was collected at 100–200° (8 mm.). This distillate crystallized from dilute alcohol and melted at 52–53°. It was shown by the method of mixed melting points to be dibenzyl. The residue from the distillation was unchanged tetraphenylethylene.

Summary

The production of dibenzyl by the action of benzene and aluminum chloride is a general phenomenon in the case of acetylene and ethylene derivatives in which each carbon atom bears at least one aryl group, and for similarly constituted tri- and tetraarylethanes. These transformations may be explained by assuming that hydrogen adds irreversibly to the ethylenic bond, whereas aromatic hydrocarbons add reversibly.

URBANA, ILLINOIS RECEIVED JUNE 22, 1936

[CONTRIBUTION NO. 163 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. XXVI. The Reaction of Halogen Ethers with Vinylacetylene

BY HARRY B. DYKSTRA

Isochloroprene (I) and chloroprene (II) are obtained by the addition of hydrogen chloride to

$$CH\equiv CCH=CH_2 + HCl \longrightarrow \underset{\text{(I)}}{CH_2=C=CHCH_2Cl} \longrightarrow \underset{\text{(II)}}{CH_2=CClCH=CH_2}$$

vinylacetylene.[1] The present paper is concerned with analogous compounds obtained by the addition of alpha chloroethers to vinylacetylene.

$$CH\equiv CCH=CH_2 + CH_3OCH_2Cl \longrightarrow \underset{\text{(III)}}{CH_3OCH_2CH=C=CHCH_2Cl} \longrightarrow \underset{\text{(IV)}}{CH_3OCH_2CH=CClCH=CH_2}$$

Methoxy-5-chloro-1-pentadiene-2,3 (III) and methoxy-5-chloro-3-pentadiene-1,3 (IV) are formed when vinylacetylene and chloromethyl methyl ether have reacted in ether solution containing bismuth chloride. The initial step appears to be 1,4-addition, for III is the principal product of the reaction. On treatment with hydrochloric acid and cuprous chloride, III rapidly rearranges to IV. The presence of IV in the original reaction mixture probably results from isomerization of III induced by the bismuth chloride.

The addition of alpha halogen ethers to vinylacetylene appears to be a general reaction. Compounds obtained in this manner are listed in Table I. The synthesis is a special application of the olefin–halogen ether reaction developed by Norman D. Scott.[2]

Proof of Structure of Methoxy-5-chloro-1-pentadiene-2,3 (III).—This compound is a colorless liquid having an ethereal odor. Other physical properties are recorded in Table I. Failure of III to react with alkaline mercuric iodide reagent indicates the absence of acetylenic hydrogen. It does not polymerize or react with maleic anhydride as it might be expected to do if it contained a 1,3-diene structure. Its chlorine atom is reactive, for on treatment with alcoholic silver nitrate it rapidly yields a copious precipitate of silver chloride. A substantially quantitative yield of silver chloride is obtained in twenty hours at 25°. On oxidation with potassium permanganate, III yields chloroacetic acid. These data are similar to those reported for isochloroprene[1] and indicate that III is methoxy-5-chloro-1-pentadiene-2,3.

Proof of Structure of Methoxy-5-chloro-3-pentadiene-1,3 (IV).—Physical and analytical data for this compound are given in Table I. It is a colorless liquid having weakly lachrymatory properties. It does not yield a derivative with alkaline mercuric iodide reagent, which shows that it is not a true acetylenic compound. Its chlorine atom must be attached to a carbon bearing a

---

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

(2) E. I. du Pont de Nemours & Co., U. S. Patent 2,024,749 (1935).

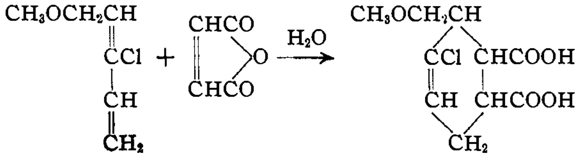
TABLE I

CHLORO ETHER–VINYLACETYLENE CONDENSATION PRODUCTS

Compound	B. p.				MR		Cl, %	
	°C.	Mm.	d^{20}_4	n^{20}_D	Calcd.	Found	Calcd.	Found
$CH_3OCH_2CH{=}CClCH{=}CH_2$	46	10	1.0351	1.4846	35.48	36.68	26.76	26.95
$CH_3OCH_2CH{=}C{=}CHCH_2Cl$	60–61	10	1.0427	1.4893	35.48	36.70	26.76	27.35
$C_2H_5OCH(CH_3)CH{=}CClCH{=}CH_2$[a]	44	4	0.9895	1.4762	44.72	45.78		
$C_2H_5OCH(CH_3)CH{=}C{=}CHCH_2Cl$[a]	56	4	.9991	1.4778	44.72	45.47		
$C_4H_9OCH(CH_3)CH{=}CClCH{=}CH_2$	67	2	.9365	1.4680	53.96	55.98	18.80	17.24
$C_4H_9OCH(CH_3)CH{=}C{=}CHCH_2Cl$	79	2	.9482	1.4705	53.96	56.84	18.80	18.71

[a] Impure.

double bond, for it does not react appreciably with alcoholic silver nitrate. When heated with an equivalent amount of maleic anhydride, it forms a viscous mass from which a chloro acid can be obtained by extraction with hot water. This acid melts at 163–165° and has a neutral equivalent of 123.3 as compared with a calculated value of 124.3 for $C_{10}H_{13}O_5Cl$ (V)



(V)

The reaction with maleic anhydride shows that IV is a 1,3-diene.[3] The 1,3-diene structure is further evidenced by the ease with which IV polymerizes. On oxidation with alkaline potassium permanganate, IV yields carbon dioxide, oxalic acid and methoxyacetic acid. These data indicate that IV has one of the structures

$$CH_3OCH_2CH{=}CHCCl{=}CH_2 \qquad (A)$$
$$CH_3OCH_2CH{=}CClCH{=}CH_2 \qquad (B)$$

The formation of IV from III and the close analogy which these compounds bear to chloroprene and isochloroprene, respectively, strongly favor structure B for compound IV.

Polymerization of Methoxy-5-chloro-3-pentadiene-1,3 (IV).—On standing at room temperature in the presence of air and diffused light, IV polymerizes slowly to a soft, rubber-like resin. The rate of polymerization is accelerated by light, heat and the presence of certain catalysts, *e. g.*, benzoyl peroxide and maleic anhydride. Exposure of IV to ultraviolet light from a mercury arc causes 65% to polymerize in forty-eight hours. When IV is heated in contact with air at 80°, 72% polymerizes in ten hours. In the presence of 1% benzoyl peroxide, a 95% yield of polymer is obtained in five hours at 75°. A comparison of these data with those reported for isoprene[4] and for chloroprene[5] indicates that IV polymerizes about 115 times as fast as isoprene and one-sixth as fast as chloroprene.

Polymers of IV are for the most part light colored resins which are soluble in acetone, ethyl acetate and benzene. Polymers prepared at low temperatures are somewhat rubber-like; they are elastic and resilient but lack the snap and strength of polychloroprene. Similar polymers are obtained from the analogs of IV described in Table I.

Experimental Part

Preparation of Methoxy-5-chloro-1-pentadiene-2,3 (III) and Methoxy-5-chloro-3-pentadiene-1,3 (IV).—During the course of two hours, 156 g. of vinylacetylene and 241 g. of chloromethyl methyl ether were added to a well-stirred mixture of 100 g. of ether, 1 g. of pyrogallol (antioxidant), and 3 g. of bismuth chloride maintained at 5–15°. The stirring was continued at this temperature for nine hours with periodic additions of bismuth chloride until a total of 13 g. had been added. The reaction mixture was then washed with water, dried over magnesium sulfate and distilled under reduced pressure. This yielded 60 g. of impure IV boiling at 46° (10 mm.), 138 g. of III boiling at 60–61° (10 mm.), 21 g. of liquid boiling at 78–85° (2 mm.) (probably resulting from addition of two mols of chloro ether to one of vinylacetylene), and 38 g. of non-volatile resin. Compound IV was obtained in pure form from the fraction boiling at 46° (10 mm.) by shaking with sodium methylate and redistilling. This removed an impurity containing active chlorine.

The analogs of III and IV described in Table I were prepared in a similar manner using alpha-chloroethyl ethyl ether and alpha-chloroethyl butyl ether.

Isomerization of Methoxy-5-chloro-1-pentadiene-2,3 (III).—A mixture of 200 g. of III, 50 g. of ether, 10 g. of cuprous chloride, and 50 g. of 18% hydrochloric acid was stirred at 20–40° for two hours. The ether layer was separated, dried over magnesium sulfate, and distilled. This gave 162 g. of IV boiling at 46° (10 mm.) and corresponding in properties with that separated from the reaction of chloromethyl ether with vinylacetylene.

Reaction of Methoxy-5-chloro-3-pentadiene-1,3 (IV) with Maleic Anhydride.—Twenty-seven grams of IV, 20 g. of maleic anhydride and 30 g. of acetone were heated to-

---

(3) Diels and Alder, *Ber.*, **62**, 2337 (1929).

(4) Whitby and Crozier, *Can. J. Research*, **6**, 203 (1932).

(5) Carothers, *Ind. Eng. Chem.*, **26**, 30 (1934).

gether at 50° for two hours. The acetone was then removed by distillation and the residue refluxed with water for two hours. The aqueous portion on evaporation yielded 15 g. of chloro acid. After two recrystallizations from hot water, the chloro acid melted at 163–165°. The acid had a neutral equivalent of 123.3 as compared with a calculated value of 124.3 for $C_{10}H_{13}O_5Cl$ (V).

Oxidation of Methoxy-5-chloro-3-pentadiene-1,3 (IV).—To a vigorously stirred mixture of 20 g. of IV, 80 g. of potassium carbonate and 200 g. of water, maintained at 10–25°, 165 g. of potassium permanganate was added during the course of six hours. The mixture was then decolorized with sulfur dioxide, acidified with sulfuric acid and extracted with ether. The ether extract yielded 0.8 g. of oxalic acid and 2 g. of crude methoxyacetic acid, b. p. 70–110° (25 mm.); n^{20}_D 1.4140. The oxalic acid was identified by its melting point (97–101°) and its transformation into oxal-*p*-toluidide (m. p. 266°). The methoxyacetic acid was characterized by conversion into its amide, which melted, after one crystallization from alcohol, at 92–94°, as compared with a recorded value of 92°.[6]

Oxidation of Methoxy-5-chloro-1-pentadiene-2,3 (III).—One hundred and sixty grams of potassium permanganate was added during the course of five hours to a well-stirred mixture of 20 g. of III and 200 g. of water. The mixture was then decolorized with sulfur dioxide, filtered, acidified with sulfuric acid (carbon dioxide evolved) and extracted with ether in the usual way. The ether extract yielded 0.3 g. of oxalic acid (identified by its m. p. of 99–101°, and its *p*-toluidide, m. p. 267–269°) and 6 g. of liquid boiling at 95–110° (25 mm.). On cooling, the liquid fraction deposited chloroacetic acid, m. p. 48–53°. The chloroacetic acid was further identified by conversion into its amide, which melted at 118–120° as compared with a recorded value of 119.5°.[7]

The author wishes to express his thanks to Dr. Wallace H. Carothers for his interest in this work and for his helpful suggestions.

Summary

The reaction between alpha chloro ethers and vinylacetylene is shown to be closely analogous to the addition of hydrogen chloride to vinylacetylene to form isochloroprene and chloroprene. The initial step appears to be 1,4 addition of the chloroethers $\begin{matrix}\text{R}'\\|\\\text{(ROCHCl)}\end{matrix}$ to vinylacetylene with the formation of products of the formula $\text{RO}\overset{\overset{\text{R}'}{|}}{\text{C}}\text{HCH{=}C{=}CHCH}_2\text{Cl}$. In the presence of cuprous chloride and hydrochloric acid these products readily isomerize to compounds of probable structure $\text{RO}\overset{\overset{\text{R}'}{|}}{\text{C}}\text{HCH{=}CClCH{=}CH}_2$. The latter compounds polymerize to form resins which are somewhat rubber-like.

---

[6] Gauthier, *Ann. chim. phys.*, [8] **16**, 307 (1909).

[7] Menschutkin and Jermolajew, *Z. Chem.*, [2] **7**, 5 (1871).

WILMINGTON, DEL. RECEIVED JULY 16, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS AND SCIENCES OF TEMPLE UNIVERSITY]

The Synthesis of 4-Methyl-6-oxypyrimidine-5-acetic Acid and 4-Methyluracil-5-methylamine

BY WILLIAM T. CALDWELL AND WILLIAM M. ZIEGLER

The first structure[1] for vitamin B_1 proposed by Williams contained an ethyl group in the pyrimidine nucleus. Later, Windaus, Tschesche and Grewe[2] expressed the opinion that the existence of two methyl groups rather than that of a single ethyl group in the primidine nucleus was in better harmony with their experimental results. Cleavage of the vitamin by sulfite[3] formed an amino sulfonic acid from which a corresponding hydroxy acid was obtained in which the sulfonic acid group presumably would be attached to the pyrimidine nucleus in position 5, in accord with the hypothesis of the existence of two free methyl groups in the nucleus.

A search of the literature, however, failed to disclose to us a case in which a pyrimidine with sulfonic acid group in position 5 had been isolated, and although this was no proof that a substance of the latter type was not formed by the sulfite cleavage, it nevertheless led us to consider the synthesis of compounds containing an amino methyl group in position 5.

The formula proposed by Makino and Imai[4] expresses the same conclusion as to the likelihood of an amino methyl group in this position. We set about, accordingly, to synthesize a compound of the structure

---

[1] Williams, THIS JOURNAL, **57**, 229 (1935).

[2] Windaus, Tschesche and Grewe, *Z. physiol. Chem.*, **237**, 98 (1935).

[3] Williams, Buchman and Ruehle, THIS JOURNAL, **57**, 1093 (1935).

[4] Makino and Imai, *Z. physiol. Chem.*, **239**, I, 7 (1936).