[CONTRIBUTION NO. 120 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. XV. Halogen-4-butadienes-1,2. The Mechanism of 1,4-Addition and of α,γ-Rearrangement

BY WALLACE H. CAROTHERS AND GERARD J. BERCHET

The reactions of vinylacetylene (I) and some of its derivatives exhibit peculiar features which provide a unique opportunity for testing certain assumptions concerning the mechanism of 1,4-addition and of α,γ-rearrangement. We have already shown[1] that the primary product of adding hydrogen chloride to (I) is chloro-4-butadiene-1,2 (II) which is readily rearranged to chloroprene (III).[2]

$$\underset{\text{(I)}}{CH\equiv C-CH=CH_2} \qquad \underset{\text{(II)}}{CH_2=C=CHCH_2X} \qquad \underset{\text{(III)}}{CH_2=CX-CH=CH_2}$$

We now present further analogous facts as a basis for discussion.

The bromide II is obtained by the action of liquid hydrogen bromide on I at low temperature and by the action of sodium bromide on the chloride II at room temperature. The second method has also been applied to the preparation of the iodide II, and in both cases the product is free from the isomeric halide III.

The chloride and the bromide II react readily with hot water (preferably in the presence of sodium carbonate) and yield the corresponding carbinol, a strongly lachrymatory liquid, which can then be converted back to the chloride or the bromide II by the action of phosphorus trihalide in the presence of pyridine. The carbinol II is also converted to the chloride II by boiling dilute hydrogen chloride (18%). The action of sodium acetate on the chloride or bromide in boiling acetic acid solution yields the acetate II. The latter is also obtained from the carbinol by the action of acetic anhydride plus sulfuric acid. These reactions all proceed normally, *i. e.*, none of the isomeric compounds III has been detected in the products. In this respect they differ from those involving Grignard reagents described in the next paper.[3] Phenylmagnesium bromide acts on the chloride II yielding a mixture of phenyl-4-butadiene-1,2 (normal) and phenyl-2-butadiene-1,3 (abnormal). Methyl- and heptylmagnesium halides gave only abnormal products, while benzylmagnesium chloride gave only the normal product. The isomeric chloride III does not react with Grignard reagents.

The bromide II, like the chloride,[4] is rapidly converted to the isomeric compound III by dilute HX containing CuX. The iodide isomerizes still

---

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

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

(3) Carothers and Berchet, *ibid.*, **55**, 2813 (1933).

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

more readily: when heated alone to about 130° it suddenly evolves heat and the lower-boiling iodide III rapidly distils. It may be inferred that this transformation also occurs spontaneously at the ordinary temperature since, within one or two days, the iodide II is completely converted to a granular polymer almost certainly derived from III. Deliberate attempts to rearrange the acetate and the carbinol II have been unsuccessful.

In résumé the facts are:

Normal Metathetical Reactions of II: RCl $\longrightarrow$ RBr (I); RCl(Br) $\longrightarrow$ ROH(OAc); ROH $\longrightarrow$ RCl(Br, OAc).

Rearrangements: RCl(Br, I) II $\longrightarrow$ III.

Abnormal Reactions: RCl (II) with Grignard reagents gives both normal and abnormal products.

The halides of series III polymerize rapidly: the speeds for chloroprene and bromoprene[5] are roughly 700 and 1100 times that of isoprene, and iodoprene polymerizes so quickly as to interfere with the determination of its physical properties. None of the compounds of series II shows any tendency to polymerize spontaneously. (The apparent polymerization of the iodide II is accounted for by prior rearrangement.)

Theories[6] concerning the mechanism of 1,4-addition and of α,γ-rearrangements are too numerous to review but, with some concession for differences in terminology, the following propositions (1–4) will be recognized as pertinent to various suggestions that have from time to time been published.

1. That all apparent examples of 1,4-addition really involve (completed) 1,2-addition followed by α,γ-shift. This once attractive hypothesis appears to have been generally abandoned; the facts now show that it cannot possibly be true. The rearrangement of the halides II $\longrightarrow$ III is irreversible, hence II, the 1,4-product, must be a primary product.

2. That addition at conjugated systems is a two stage process: the cation of the addendum first attacks one end of the system yielding isomeric ions (or intermediate fragments) corresponding to the two isomeric products. The ions arising from attack of (I) by hydrogen ion would be $CH_2{=}C^+{-}CH{=}CH_2$ (III) and $CH_2{=}C{=}CHCH_2^+$ (II). Thus in the addition of HX to (I), the hydrogen ion attacks the acetylenic (positive?) end of the molecule; the resulting ions are those involved in the isomerizations discussed under 4 below.

3. That the probable nature of the predominating hypothetical intermediate or of the predominating product can be inferred from conclusions based on fact or on speculation as to which is the more stable.

The facts show that this is not possible, since in the addition of hydrogen

---

[5] Carothers, Collins and Kirby, THIS JOURNAL, **55**, 789 (1933).

[6] See for example, Gillet, *Bull. soc. chim. Belg.*, **31**, 366 (1922); Prévost, *Bull. soc. chim.*, **43**, 996 (1928); Burton, *J. Chem. Soc.*, 1651 (1928); Burton and Ingold, *ibid.*, 904 (1928); Whitmore, THIS JOURNAL, **54**, 3274 (1932).

chloride or hydrogen bromide to (I) the unstable isomer (II) is a primary product, and is in all probability the only primary product.

4. (a) That in triad systems it is the ion R^+ not the molecule RX which rearranges. (b) That R^+ is a necessary intermediate in metathetical reactions of RX involving the formation of X^-. (c) That the ion R^+, whether formed directly by dissociation of RX or as an intermediate in metathetical reactions of RX, will immediately assume the forms corresponding to the equilibrium products.

The practical implication of (c) is that metathetical reactions of triad systems (involving X^-) must yield an equilibrium mixture of the isomers. This has been taken so much for granted that it forms the basis of a supposed demonstration[7] of the intimate mechanism in the hydrolysis of carboxylic esters. It is now obviously directly opposed to the facts, since a whole series of metathetical transformations in compounds of type II has been carried out without any rearrangement to the corresponding isomers III. Not only does no isomerization occur under these conditions where, according to (b), ionization must be assumed to occur, but the iodide II rearranges under conditions that appear to be especially unfavorable to ionization. This throws considerable doubt on assumption (4a).

Abnormal reactions of triad systems do, nevertheless, exist. The action of RMgX on the chloride II furnishes an unambiguous demonstration of this fact. The isomeric chloride III is (experimentally) incapable of reacting with RMgX; hence completed rearrangement cannot precede reaction. The isomeric hydrocarbons II and III cannot rearrange under the conditions used. The isomerization is therefore an integral part of the metathesis. Three explanatory assumptions appear to be possible:

(a) The abnormal reaction consists in addition of RMgX at the double bond followed by elimination of MgX_2. This has the disadvantage of being *ad hoc* since addition of RMgX at simple ethylenic linkages has never been realized.

(b) The initiating step results in the formation of a cation (or some other fragment) which adjusts itself before entrance of the anion of RMgX. This is the currently popular assumption (4a and b above). It presents this difficulty as shown in the comment under 4: the facts now require that these intermediate fragments (if they exist at all) must be capable (contrary to 4c) of resisting or escaping rearrangement under some conditions and not under others. In either case the conditions cannot be specified in advance and the assumption of intermediate ions contributes nothing to the explanation of the facts, but, at best, serves merely as a pictorial method of rationalizing the facts after they are known.

(c) The initiating step is the formation of a complex (coördination compound). This assumption also, in the present state of knowledge

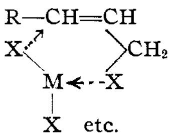
---

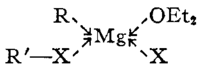
[7] Ingold and Ingold, *J. Chem. Soc.*, 756 (1932).

concerning complexes, is too vague to furnish a basis for detailed predictions. It is, however, unquestionably closer to reality than the assumption of *free* ions or radicals as intermediates. The closest approach to a simple free alkyl anion is probably found in the alkali alkyls. These materials are extraordinarily reactive; the ethyl anion, for example, is capable of reducing the sodium ion to sodium hydride at temperatures below 100°.[8] Experimentally, simple alkyl cations are completely unknown; it is reasonable to suppose that they would be still less stable than alkyl anions. Metathetical reactions of organic compounds that can be formulated as proceeding through the intervention of ions generally involve media or catalysts capable of giving rise to coördination compounds.[9]

Johnson[10] has shown that coördination and chelation are probably involved in the mechanism of many types of organic reactions including abnormal reactions and α,γ-rearrangements. Our application of his ideas to the present case is illustrated below.

In a triad system the usually accepted valence angles are capable of placing the unshared electrons of X fairly close to the γ-carbon atom, $R{-}\overset{\gamma}{C}H{=}\overset{\beta}{C}H{-}\overset{\alpha}{C}H_2{-}X$. Polarization at $\beta - \gamma$ favored by the proximity of these unshared electrons permits still closer approach of X toward γ and consequent loosening at α; these tendencies finally bring the two forms into equilibrium. This mechanism is in accordance with the observed order $I > Br > Cl \gg OAc$, where the effective diameters of the atoms progressively diminish and the constraints on the electrons increase, while in OAc the Ac group may besides act as a steric obstacle. This may be supposed to apply to the rearrangement of the halides II themselves at elevated temperatures. In fact, for the chloride and the bromide II rearrangement at ordinary temperature appears to require the presence of salts having great coördinating power—conditions merely favoring ionization, *e. g.*, water plus hydrogen chloride, do not suffice. On the other hand, water plus hydrogen chloride plus cuprous chloride, or dry ferric chloride alone, induces very rapid rearrangement. An easily conceivable function of the salt in this case is symbolized in the figure, where the steric factors are analogous to those involved in chelation while the metal salt acts as a carrier of the entering group. In reactions of metathesis the chloride II yields abnormal products only with RMgX. Reaction with Grignard reagents generally undoubtedly requires entrance of the reactant into the complex, $RMgX(OEt)_2$. Coupling of a halide probably involves some intermediate step such as (A). Obviously, in





A

---

(8) Carothers and Coffman, THIS JOURNAL, **51**, 588 (1929); **52**, 1254 (1930).

(9) *Cf.* Meerwein, *Ann.*, **455**, 227 (1927).

(10) Johnson, THIS JOURNAL, **55**, 3029 (1933).

view of the facts, such a purely "dative" electron shell as that which surrounds the magnesium is unusually vague and mobile. This mobility would provide the opportunity for a sufficient approach of R and R′ in forms that are essentially cation and anion without ever requiring the intermediacy of *free* alkyl ions. If R′ is a substituted allyl group the steric factors referred to above will permit the coupling to occur at the γ as well as the α carbon. Reaction of the chloride II with sodium iodide to give the corresponding iodide might appear to require intervention of the cation II indicated in 2 above, but we reject this idea also, and prefer to assume that some kind of coördination precedes reaction and that the cation is never liberated as a *free* entity. On the other hand, the coördinating power of the iodide ion is certainly relatively feeble, and there is nothing in its structure or known behavior to indicate that it could be very effective in the kind of coördination that is here suggested to account for rearrangement or abnormal reaction. The observed absence of abnormality in other reactions of compounds II can be similarly explained.

Experimental Part

Bromo-4-butadiene-1,2 (II).—Vinylacetylene (one mole) was passed into 3 moles of liquid hydrogen bromide during five to seven hours. The product, washed and distilled, gave two fractions: crude bromo-4-butadiene-1,2, 53.5% of calcd., and dibromo-2,4-butene-2[11] 36%. Careful redistillation yielded no other products. Under other conditions, bromoprene[11] was found in the reaction product. For example, liquid hydrogen bromide (2.18 moles) added to vinylacetylene (4 moles) at *ca.* −50° after three hours gave the following products: bromoprene, 10%; bromo-4-butadiene-1,2, 19%; dibromo-2,4-butene-2, 12%. The bromide II was also obtained from chloro-4-butadiene-1,2 and sodium bromide in acetone plus water. Conversion was far from complete, repeated distillation was required to obtain a pure product, and the isolated yield was poor (25%); but there was no indication of any bromoprene in the product. Better yields of the bromide II (69%) were obtained from the carbinol II plus phosphorus tribromide in the presence of a little pyridine at 10–20° (*ca.* one hour); a colorless, lachrymatory liquid; b. p. 64–66° (181 mm.), 109–111° (760 mm.); d_4^{20} 1.4255; n_D^{20} 1.5248.

Anal. Calcd. for C_4H_5Br: C, 36.09; H, 3.76; Br, 60.15. Found: C, 36.61; H, 3.91; Br, 60.13.

Iodo-4-butadiene-1,2 (II).—Chloro-4-butadiene-1,2 with one mole of sodium iodide was allowed to stand in 80% alcohol or in acetone at room temperature for three hours. The heavy yellow oil precipitated by dilution with water was distilled; yield, 46%; b. p. 43–45° (38 mm.); estimated b. p. at 760 mm., 130°; d_4^{20} 1.7129; n_D^{20} 1.5709.

Anal. Calcd. for C_4H_5I: C, 26.66; H, 2.77; I, 70.55; mol. wt., 180. Found: C, 27.00; H, 2.97; I, 70.40; mol. wt. (in freezing benzene), 184.

It reacted instantly with aqueous silver nitrate. When it was allowed to stand at ordinary temperature solid particles began to separate within twenty-four hours; within forty to fifty hours the transformation was usually complete and the product was a granular mass of amorphous, insoluble particles similar to the granular polymers obtained from chloroprene and bromoprene.[5] The polymerization is doubtless preceded by isomerization.

---

(11) Carothers, Collins and Kirby, THIS JOURNAL, **55**, 786 (1933).

Anal. Calcd. for $(C_4H_5I)_n$: I, 70.55. Found: I, 69.49, 69.44.

Iodoprene (III).—When the iodo compound (II) was heated at 125–130° a short but lively reaction took place; the product then distilled at 111–113° (760 mm.), while a large amount of viscous residue remained in the flask. The change in physical properties indicated that the distillate was the isomeric compound, iodo-2-butadiene-1,3; n^{20}_{D} 1.561. It polymerized completely within forty-eight hours.

Hydroxy-4-butadiene-1,2 (II).—Chloro-4-butadiene-1,2 (6 moles) was stirred at 60–90° with 6 moles of sodium carbonate in 1500 cc. of water for fifteen hours. Ether extraction and distillation gave the carbinol in 50% yield (losses were due to solubility in water and formation of higher-boiling products); colorless liquid miscible with water and most organic solvents; sharp pungent odor, lachrymatory, strongly vesicant; b. p. 68–70° (53 mm.), 126–128° (756 mm.); d^{20}_{4} 0.9164; n^{20}_{D} 1.4759. The carbinol was also obtained in 50% yield by similarly hydrolyzing the bromide II.

Anal. Calcd. for C_4H_6O: C, 68.57; H, 8.57. Found: C, 68.65; H, 8.68.

Hydrogenation of the carbinol gave *n*-butyl alcohol identified through its 3-nitrophthalic ester (mixed m. p. 145°).

The carbinol was recovered unchanged after being refluxed with sodium ethylate in ethanol, 25% aqueous sulfuric acid, or 2% aqueous hydrogen chloride.

When the carbinol (0.5 mole) was refluxed with 100 cc. of 18% hydrogen chloride for one hour, a 9% yield of chloro-4-butadiene-1,2 was obtained; the rest was unchanged carbinol. By the action of phosphorus trichloride on the carbinol in the presence of a little pyridine a 62% yield of chloro-4-butadiene-1,2 was obtained. No chloroprene was found in the product.

Acetate of Hydroxy-4-butadiene-1,2.—To hydroxy-4-butadiene-1,2 with excess acetic anhydride was added a drop of sulfuric acid. The lively reaction was moderated by cooling and the mixture was finally refluxed for one-half hour. Dilution with water, extraction, and distillation gave a 75% yield of the acetate; b. p. 85–86° (125 mm.), 140–140.5° (780 mm.); d^{20}_{4} 0.9641; n^{20}_{D} 1.4504. The same compound was obtained by refluxing for seven hours one mole of chloro-4-butadiene-1,2 with 2 moles of sodium acetate dissolved in 200 cc. of glacial acetic acid; yield 59%. Similarly from bromo-4-butadiene-1,2 a 73% yield of pure acetate was obtained. There was no indication in either case of the presence of any isomeric compound.

Anal. Calcd. for $C_6H_8O_2$: C, 64.28; H, 7.14. Found: C, 64.30; H, 7.16.

Hydrogenation of the acetate gave pure *n*-butyl acetate. Saponification gave pure hydroxy-4-butadiene-1,2.

Rearrangement of Chloro-4-butadiene-1,2 (II).—To the observations recorded previously[1] the following may be added. The chloride II (30 g.) with 50 cc. of 18% hydrogen chloride after two hours at 70–80° gave 2 g. of *crude* III. The rest was unchanged II. The chloride II (50 g.) with 150 cc. of 18% hydrogen chloride and 10 g. of cuprous chloride shaken at 20° for sixteen hours gave a 70% yield of III. The rest was polymer; no II was recovered. When 3% of dry ferric chloride was added to the chloride II heat was evolved and distillation set in at once. The distillate was a mixture of II and III. We are indebted to Dr. D. D. Coffman for the last two of these experiments.

Summary

Compounds of the formula $CH_2{=}C{=}CHCH_2X$ in which X is Cl, Br, I, OH and OAc undergo a series of metathetical reactions without yielding abnormal (rearranged) products. The chloride and the bromide are formed by the 1,4-addition of HX to vinylacetylene. They are easily and

irreversibly rearranged to $CH_2{=}CX{-}CH{=}CH_2$. The iodide rearranges spontaneously. The direct bearing of these facts on theories concerning the mechanism of 1,4-addition and of α,γ-rearrangement is discussed.

WILMINGTON, DELAWARE
RECEIVED DECEMBER 20, 1932
PUBLISHED JULY 6, 1933

[CONTRIBUTION NO. 121 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. XVI. The Preparation of Orthoprenes by the Action of Grignard Reagents on Chloro-4-butadiene-1,2

BY WALLACE H. CAROTHERS AND GERARD J. BERCHET

The term orthoprene is here presented as a designation for derivatives of butadiene-1,3 having a single substituent and that in the 2-position (III). Isoprene is the historically important member of this class and (except for a single reference[1] to ethylbutadiene) it was the only one known until the discovery of chloroprene[2] and bromoprene.[3] The extraordinarily superior properties of these compounds from the standpoint of rubber synthesis prompted the preparation and examination of other dienes.[4] The results[5] suggested that similarly desirable properties are not likely to be found among any other types of dienes than the orthoprenes as such, and it became important to obtain further members of this class. The lack of any satisfactory general method for this purpose led to the development of the method described here, which is based on the observation that chloro-4-butadiene-1,2 (I) like other substituted allyl halides[6] reacts with Grignard reagents to produce abnormal (III) as well as normal (II) products. The theoretical implications of this fact have been discussed in the preceding paper.[7]

$CH_2{=}C{=}CHCH_2Cl$ (I) $CH_2{=}C{=}CHCH_2R$ (II) $CH_2{=}CR{-}CH{=}CH_2$ (III)

For the purpose in view the new method leaves much to be desired. Yields are rather low, and separation of the desired product from by-products is rather laborious. No doubt further study would lead to considerable improvement. In its present state, however, the method has sufficed for the isolation of two orthoprenes especially wanted: *n*-heptoprene and phenoprene. As precursors of rubber neither of these compounds approaches chloroprene; they are in fact probably inferior to isoprene. Heptoprene polymerizes rather more rapidly than isoprene but the

---

(1) Ipatiew, *J. prakt. Chem.*, [2] **59**, 534 (1899).
(2) Carothers, Williams, Collins and Kirby, THIS JOURNAL, **53**, 4203 (1931).
(3) Carothers, Collins and Kirby, *ibid.*, **55**, 786 (1933).
(4) Carothers and Coffman, *ibid.*, **54**, 4071 (1932); Jacobson and Carothers, *ibid.*, **55**, 1624 (1933).
(5) See also Whitby and Gallay, *Can. J. Research*, **6**, 280 (1932).
(6) Prévost and Daujat, *Bull. soc. chim.*, [4] **47**, 588 (1930).
(7) Carothers and Berchet, THIS JOURNAL, **55**, 2807 (1933).