STEREOCHEMISTRY OF ADDITIONS TO TRIPLE BONDS

COMMUNICATION 7. STEREOCHEMISTRY OF THE HYDROBROMINATION OF BROMOACETYLENES UNDER FREE-RADICAL CONDITIONS

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In a previous communication [1] it was shown that under the conditions of photochemical reaction bromine adds to disubstituted acetylenes in a way different from that in which it adds to their ethylene analogs: whereas the bromination of the double bond went selectively by the trans scheme, acetylenes gave considerable amounts of cis-bromination products. It was of interest to compare steric orientations in free-radical additions to acetylenes and olefins in the case of other reagents, in particular hydrogen bromide.

Several cases have been described in the literature in which the free-radical addition of hydrogen bromide to an ethylenic bond proceeds stereospecifically in accordance with the trans-addition scheme: thus, 1-methyl-, 1-chloro-, and 1-bromo-cyclohexenes react with hydrogen bromide with almost quantitative formation of the corresponding cis-1,2-substituted cyclohexanes [2, 3]. Under free-radical conditions trans-2-bromo-2-butene is converted into racemic 2,3-dibromobutane, and from cis-2-bromo-2-butene the meso-dibromide is obtained exclusively [4].

The stereochemistry of the addition of hydrogen bromide to acetylenes has not yet been studied systematically. The results obtained by Smirnov-Zamkov and Shilov [5] in a study of the hydrobromination of diethyl acetylenedicarboxylate show that under the conditions for ionic reaction (e.g., in acetic acid in presence of lithium bromide), and also in a benzene medium, mainly trans addition of the elements of hydrogen bromide occurs; in hexane a mixture of stereoisomers is formed.

In the present communication we describe the results of a study of steric orientation in the free-radical addition of hydrogen bromide to 1-bromoacetylenes:

$$RC \equiv CBr + HBr \longrightarrow RCBr = CHBr.$$

The reaction was carried out with an excess of the bromoacetylene at -70° under the radiation of a quartz mercury lamp in absence of solvent (i.e., in liquid hydrogen bromide) or in a pentane medium. The dibromides formed in the reaction were identified by comparing their constants and infrared spectra* with the constants and spectra of the corresponding substituted cis- and trans-1,2-dibromoethylenes, which have been described by us previously [6]. Our results are shown in the table.

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*Infrared spectra were determined by B. V. Lopatin.

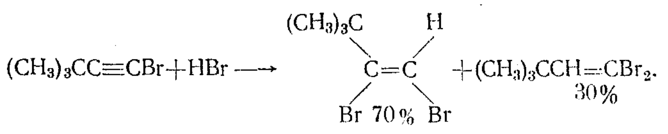
We have previously shown that trans-1,2-dibromo-3,3-dimethyl-1-butene passes almost quantitatively into its cis isomer under ultraviolet radiation at room temperature, whereas trans-1,2-dibromopropene gives a mixture of cis and trans forms in the proportions of 2 : 3 [6]. It is therefore probable that the trans-dibromoethylenes formed in the free-radical hydrobromination of bromoacetylenes at -70° arose not as a result of isomerization, but as primary products of the reaction.

A special experiment in which cis-1,2-dibromo-3,3-dimethyl-1-butene was irradiated for 20 minutes at -70° in presence of HBr did in fact show that under the conditions of hydrobromination the cis-dibromide is not isomerized. On the other hand, under the same conditions pure trans-dibromopropene was converted to the extent of about 20% into the cis isomer. It is therefore probable that the mixture of stereoisomers obtained in the hydrobromination of 1-bromopropyne is formed as a result of the isomerization of the trans-dibromopropene, which is the primary reaction product. Hence, under the conditions indicated there is selective cis addition of the elements of hydrogen bromide to the triple bond.

Original bromoacetylene	Trans-cis ratio of 1,2-dibromoethylenes in reaction product	
	in liquid HBr	in pentane
$CH_3 \equiv CBr$	85 : 15*	75 : 15*
$(CH_3)_3CC \equiv CBr$	100% trans	95 : 5

* The product contained some 1,1-dibromopropene (see Experimental).

The free-radical character of the photochemical reaction of hydrobromination is confirmed by the results obtained in the hydrobromination of 1-bromo-3,3-dimethyl-1-butyne with liquid hydrogen bromide in the dark in a nitrogen atmosphere. Under these conditions of ionic hydrobromination, the main product was found to be cis-1,2-dibromo-3,3-dimethyl-1-butene, i.e., the hydrobromination went by the trans-addition scheme. In addition to 1,2-dibromides, about 30% of 1,1-dibromo derivative was formed:

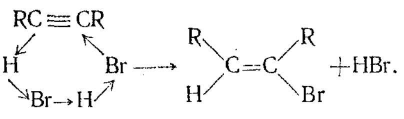


The presence of the latter was confirmed by a study of the infrared spectrum of the reaction product and the formation of 3,3-dimethylbutyric acid on treatment of the mixture of dibromides with concentrated sulfuric acid:

$$(CH_3)_3CCH{=}CBr_2 \xrightarrow{H_2SO_4} (CH_3)_3CCH_2COOH.$$

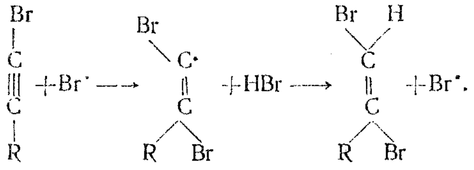
Hence, our results indicate the different steric orientation in free-radical hydrobromination in the 1-bromoethylene and the 1-bromoacetylene series. Whereas in the case of 1-bromoethylenes stereospecific trans addition of hydrogen bromide is observed [2-4], bromoacetylenes give mainly or entirely cis-addition products (trans-dibromides).

In explanation of the cis addition of hydrogen bromide to acetylenedicarboxylic ester Shilov [7] advanced the hypothesis of the formation of a trimolecular complex:

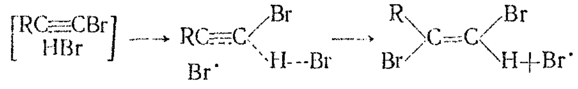


As under the conditions described in the present paper, i.e., in presence of excess of the acetylene compound, the formation of such a complex is not very probable, there remain two possibilities for the explanation of the cis addition of hydrogen bromide:

a) If the addition reaction starts with an attack on the bromine atom [8, 9], then the intermediate radical $RCBr = \dot{C}Br$ must be formed. According to Ingold and King [10], whose results indicate that the linear structure for the activated acetylene molecule is energetically unfavorable, such radicals must have an "ethylenelike" configuration. The total (steric and electrostatic) repulsion of two bromine atoms exceeds the repulsion forces between bromine and the alkyl substituent [11, 12]. Hence, the radical formed in the attack of the alkylbromoacetylene by a bromine atom must have the trans configuration. In this case reaction is completed by the cis addition of a hydrogen atom, i.e., the formation of trans-dibromoethylene:

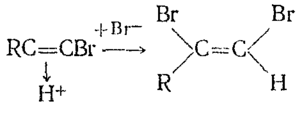


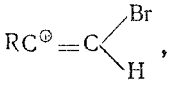
b) If, however, it is assumed that reaction starts with the formation of a complex of the acetylene compound with one molecule of hydrogen bromide, then in some moment of the reaction this complex must have a nonlinear structure:



As a result of the action of electrostatic repulsive forces, the bromine atom approaches the complex from the side opposite to that of the C − Br bond, and the trans-dibromide is formed.

The result of the ionic hydrobromination of 1-bromo-3,3-dimethyl-1-butyne was unexpected: it proceeded structurally nonselectively and differed in orientation from the hydrobromination of 1-bromo-2-alkylethylenes. The nonselectivity of the reaction appears to be the result of the competing effects of the free electron pair of the bromine and the inductive effect of the t-butyl group. It should be noted that in the case of haloacetylenes the π-electrons of the triple bond have, in general, less tendency to interact with the free electron pair of the halogen than in the case of vinyl halides; this is probably due to the lower polarizability of a triple bond, as compared with a double bond [13]. It may therefore be expected that haloacetylenes will be hydrobrominated less selectively under ionic conditions than haloethylenes. The fact that ionic hydrobromination proceeds stereospecifically by the trans-addition scheme indicates that in this case a π-complex is formed:



Actually, if the intermediate product in such a reaction was a carbanion of the type  $RC^{\ominus}{=}C\begin{smallmatrix}Br\\H\end{smallmatrix}$, it would be expected that there would be at least a partial attack by the bromide ion from the side opposite to that of the C − Br bond with formation of the trans-dibromo olefin, which is scarcely observed at all.

EXPERIMENTAL

Preparation of 1-Bromopropyne. A solution of potassium hypobromite prepared from 45 g of potassium hydroxide and 16 g of bromine in 300 ml of water at 0° was saturated with propyne while being cooled with ice water. The course of the reaction was followed by iodometric titration of test samples taken from the reaction mixture. After five hours, after the whole of the hypobromite had reacted, the mixture was extracted with ether, and the ether extract was dried with magnesium sulfate and distilled in a nitrogen atmosphere. By fractionation through a column we isolated 14.5 g (61% on the bromine) of 1-bromopropyne; b.p. 64-65° (758 mm); d_4^{25} 1.5230 (determined in a nitrogen atmosphere). We did not succeed in measuring its refractive index because 1-bromopropyne ignites spontaneously in air. In ethereal solution 1-bromopropyne remains unchanged when kept in a refrigerator for one month. According to the literature 1-bromopropyne has b.p. 65°; n_D^{25} 1.4448; d_4^{19} 1.35015 [14] or b.p. 64-65°; d_4^{25} 1.5222 [15]. In the first case [14] the preparation was probably impure.

Preparation of 1-Bromo-3,3-dimethyl-1-butyne. To 300 ml of a 1.2 N solution of potassium hypobromite (prepared from 25 g of bromine, 180 g of potassium hydroxide, 800 ml of water, and 1 g of potassium stearate) containing a few drops of ethanol we added 25 g of 3,3-dimethyl-1-butyne with stirring and cooling with ice water and at such a rate that the temperature of the reaction mixture did not exceed 5°. The mixture was left overnight and stirred further for one hour at 20°, after which the concentration of hypobromite had fallen to 0.15 N. The mixture was extracted with hexane, the extract was dried with magnesium sulfate, and solvent was distilled off at atmospheric pressure with passage of nitrogen. Fractionation gave 34.5 g (69% on the 3,3-dimethyl-1-butyne) of 1-bromo-3,3-dimethyl-1-butyne; b.p. 113° (756 mm); n_D^{20} 1.4515; d_4^{20} 1.216; Found MR 35.69; Calculated MR 35.60. Found: C 45.56; 44.63; H 5.66; 5.95; Br 49.75; 49.87%. C_6H_9Br. Calculated: C 44.74; H 5.63; Br 49.61%.

Free-Radical Hydrobromination of 1-Bromopropyne. a) In pentane. The reaction was carried out with irradiation by means of an immersed PRK-4 quartz mercury lamp (nominal power 200 w) provided with a quartz cooling jacket. Heptane cooled to -180° was pumped through the jacket. The jacketed lamp was lowered straight into the reaction vessel, which was cooled externally with solid carbon dioxide and acetone. A solution of 12 g of 1-bromopropyne (0.1 mole) in 50 ml of pentane was introduced into the reaction vessel, which was fitted with a dropping funnel and a thermometer for the measurement of low temperatures. When the temperature of the solution had fallen to -78°, a solution of dry hydrogen bromide (0.05 mole) in 25 ml of pentane (also cooled to -78°) was added under the radiation of the ultraviolet lamp at such a rate that the temperature of the reaction mixture did not exceed -60°. The mixture was irradiated for 20 minutes at -70°, the radiation was switched off, and the temperature was raised in the dark to 0°. The solution was washed with water and with aqueous sodium bicarbonate solution, and it was dried with magnesium sulfate. Ether and unchanged 1-bromopropyne were distilled off in a stream of nitrogen, and the residue was vacuum-distilled through a column (length 30 cm). We obtained a single fraction of the dibromide (9.2 g; yield 92% on the hydrogen bromide); b.p. 63-65° (61 mm); n_D^{20} 1.5302. Judging from the infrared spectrum (κ_{980} 4.40), the preparation contained 75 ± 7.5% of trans-1,2-dibromopropene, about 15 ± 2% of the cis isomer, and a little 1,1-dibromopropene. Pure trans-1,2-dibromopropene has: b.p. 46-47° (40 mm); n_D^{20} 1.5336; κ_{980} 5.83 [6].

b) Without solvent. A mixture of 12 g of 1-bromopropyne and 4 g of liquid anhydrous hydrogen bromide was irradiated, as indicated above, for 20 minutes at -75°. The temperature was raised in the dark to 0°, when a little unchanged hydrogen bromide was liberated. Fractionation through a column gave 8.3 g of a mixture of dibromopropenes; b.p. 40-44° (30 mm); n_D^{20} 1.5266; judging from the infrared spectrum it contained 45 ± 5% of trans-1,2-dibromopropene. On standing in air the preparation yellowed with the separation of hydrogen bromide, which indicates the presence of 1,1-dibromopropene [16]. For the removal of the latter the mixture of dibromides obtained was stirred for three hours at room temperature with 30 ml of concentrated sulfuric acid, 10 g of ice was added, and the upper layer was separated, washed with water, and dried with calcium chloride. Fractionation gave a single fraction (6.5 g); b.p. 42-43° (30 mm) and n_D^{20} 1.5321; judging from its infrared spectrum it contained 85 ± 10% of trans-1,2-dibromopropene.

Free-Radical Hydrobromination of 1-Bromo-3,3-dimethyl-1-butyne. a) In pentane. The reaction was carried out under the conditions described for 1-bromopropyne. From 16 g of 1-bromo-3,3-dimethyl-1-butyne (0.1 mole) and 4 g of hydrogen bromide (0.05 mole) in 50 ml of pentane, after removal of solvent and unchanged 1-bromo-3,3-dimethyl-1-butyne, we obtained 10.7 g (89% on the hydrogen bromide) of 1,2-dibromo-3,3-dimethyl-1-butene; b.p. 68-70° (16 mm); n_D^{20} 1.5171; judging from the infrared spectrum it contained 95 ± 5% of trans isomer (κ_{980} 0.56) [6].

b) Without solvent. Under the conditions of the free-radical hydrobromination of 1-bromopropyne, from 16 g of 1-bromo-3,3-dimethyl-1-butyne and 4 g of liquid anhydrous hydrogen bromide we obtained 9.1 g (75% on the hydrogen bromide) of 1,2-dibromo-3,3-dimethyl-1-butene; b.p. 68° (16 mm); n_D^{20} 1.5178; the infrared spectrum of this coincided completely with the infrared spectrum of the trans-dibromide described previously [6].

Ionic Hydrobromination of 1-Bromo-3,3-dimethyl-1-butyne. Liquid anhydrous hydrogen bromide (4 g) was added to 1-bromo-3,3-dimethyl-1-butyne containing 0.3 g of diphenylamine in the dark at -70° in a nitrogen atmosphere. The mixture was kept for four hours at -78° and then treated as indicated above. Fractionation through a column gave 10.8 g of a mixture of dibromides of b.p. 51-64° (14 mm) and n_D^{20} 1.5100-1.5160 [the bulk (8.6 g) had n_D^{20} 1.5142]. The infrared spectrum of this product contained the following bands in the 700-2000 cm^{-1} region (intensities are given on a three-grade scale): 1616 (weak), 1580 (strong), 1464 (strong), 1394 (medium), 1370 (strong), 1305 (weak), 1239 (strong), 1196 (strong), 1028 (medium), 980 (very weak), 951 (weak), 943 (strong), 916 (medium), 826 (weak), 805 (strong), 775 (strong), 732 (strong) cm^{-1}. According to these data the substance was a mixture of cis-1,2-dibromo-3,3-dimethyl-1-butene (intense bands at 1580 and 732 cm^{-1} [6]) and the isomeric 1,1-dibromide (absorption bands at 1464, 1370, 1028, and 805 cm^{-1} [17]). Comparison of the intensities of the absorption bands in the region of 1580 cm^{-1} for the mixture of dibromides obtained (κ 0.45) and for the pure cis-dibromide (κ 0.64) [6] shows that the hydrobromination product contained 70 ± 7% of the cis isomer. To separate the isomeric bromides the mixture obtained (10 g) was stirred for three hours at room temperature with 30 ml of concentrated sulfuric acid; the mixture was cautiously diluted with ice and cold water and was extracted with ether. The ether extract was washed with sodium bicarbonate solution until neutral and was dried with calcium chloride. After removal of ether we obtained a single fraction (6.6 g) of b.p. 72-73.5° (16 mm) and n_D^{20} 1.5129; its infrared spectrum was identical with that of pure cis-1,2-dibromo-3,3-dimethyl-1-butene [6]. The alkaline extract was acidified with dilute hydrochloric acid and extracted with ether. After evaporation of the ether extract there remained an oil, which distilled over at 185-190° (temperature of bath) and did not freeze when cooled to -10° (3,3-dimethylbutyric acid melts at 6°). The product (0.6 g) was neutralized to phenolphthalein with 1% NaOH solution and then acidified with two drops of 1% hydrochloric acid; a suspension of 1.4 g of 2-bromo-4'-phenylacetophenone [18] in 30 ml of alcohol was added, and the mixture was boiled for two hours. On standing in a refrigerator there was a precipitate of the p-phenylphenacyl ester of 3,3-dimethylbutyric acid, which melted at 90.0-90.5° after recrystallization from 60% alcohol. The literature [19] gives m.p. 92°. Found: C 77.33; 77.47; H 7.01; 7.08%. $C_{20}H_{22}O_3$. Calculated: C 77.39; H 7.13%.

SUMMARY

The reaction of 1-bromoacetylenes with hydrogen bromide under free-radical conditions occurs mainly according to the cis-addition scheme with formation of substituted trans-dibromoethylenes.

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