STEREOCHEMISTRY OF ADDITIONS TO A TRIPLE BOND

COMMUNICATION 5. STEREOCHEMISTRY OF THE ADDITION OF BROMINE TO DISUBSTITUTED ACETYLENES

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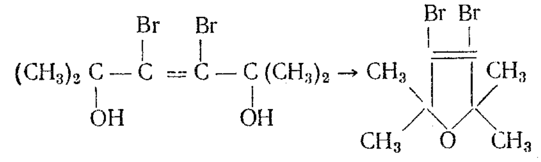
In previous investigations [1, 2] we have studied the stereochemistry of the addition of bromine to monosubstituted acetylenes RC ≡ CH under various conditions. It was shown that the steric orientation in the reaction depends on its mechanism: under conditions of ionic reaction addition is mainly trans, whereas for photochemical bromination in a nonpolar medium cis-dibromo olefins are also formed in an amount which depends on the size of the substituent R. In the present paper we describe the results of a study of the stereochemistry of the addition of bromine to disubstituted acetylenes: diphenylacetylene, 2,5-dimethyl-3-hexyne-2,5-diol, and acetylenedicarboxylic acid.

Under the conditions of photochemical bromination 2-butyne-1,4-diol and 2,5-dimethyl-3-hexyne-2,5-diol form the previously described crystalline dibromo compounds of m.p. 114° [3] and 150° [4], whose configurations have not yet been established. Study of the infrared spectra (absence of a band at 900 cm^{-1}) showed that these bromo compounds are cis isomers. Also, the cis configuration of the dibromide of 2,5-dimethyl-3-hexyne-2,5-diol, m.p. 150°, was confirmed by its dehydration to 3,4-dibromo-2,5-dihydro-2,2,5,5-tetramethylfuran:



The photochemical addition of bromine to 2,5-dimethyl-3-hexyne-2,5-diol is less stereospecific than in the case of 2-butyne-1,4,-diol, and it is accompanied by the formation of about 22% of the previously undescribed trans-dibromide, m.p. 129-130°. Still less stereospecific is the photochemical addition of bromine to diphenylacetylene. When the reaction was carried out in hexane we isolated trans-α,α'-dibromostilbene in 69% yield (m.p. 204-206°) and a little of the cis isomer (as a molecular compound with diphenylacetylene, m.p. 76-77°).

In the study of steric orientation in the ionic reaction, the addition of bromine to 2-butyne-1,4-diol and 2,5-dimethyl-3-hexyne-2,5-diol was investigated in acetic acid in the dark, i.e., under conditions which led mainly to trans-dibromides in the case of propargyl alcohols. It was found, however, that acetylenic diols do not give dibromides under these conditions, because the addition of bromine is suppressed by the participation of the anions of the solvent. Thus, on bromination in acetic acid 2-butyne-1,4-diol gives, as the main reaction

Steric Orientation in the Addition of Bromine to Disubstituted Acetylenes

Acetylenic compound	Bromination conditions	Yield of stereoisomeric dibromides(%)	
		cis	trans
2-Butyne-1,4-diol	In CCl_4 with irradiation*	84	
	In methanol in the dark	67	
	In N,N-dimethylformamide in the dark	51	
	In N,N-dimethylformamide in the dark in presence of LiBr	48	
2-Butyne-1,4-diol diacetate	In hexane with irradiation*	78	
Acetylenedicarboxylic acid	In ether with irradiation	82	
	In methanol in the dark	12	44
	In N,N-dimethylformamide in the dark		70
2,5-Dimethyl-3-hexyne-2,5-diol	In CCl_4 with irradiation*	78	16
	In N,N-dimethylformamide in the dark		78
Diphenylacetylene	In hexane with irradiation*		69
	In ether in the dark		81

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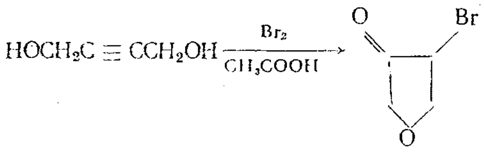
* Irradiation with a quartz mercury lamp.

product, a substance to which the structure of 4-bromodihydro-3(2H)-furanone must be attributed on the basis of chemical and spectrum data:



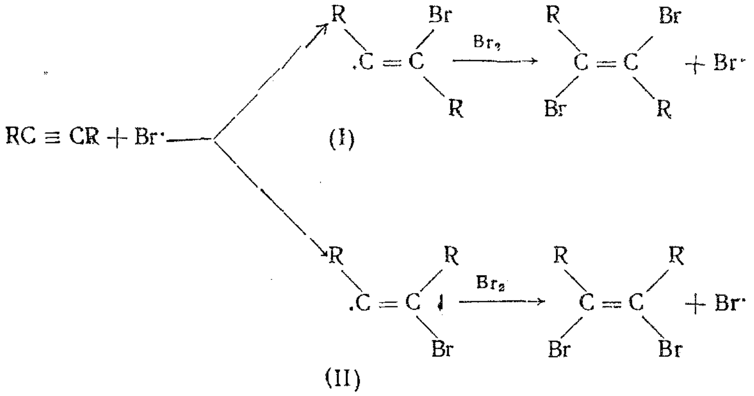
Under these conditions 2,5-dimethyl-3-hexyne-2,5-diol gives a mixture of oily products, which rapidly darken in air with elimination of hydrogen bromide.

Unlike acetylenic diols, acetylenedicarboxylic acid does not react with solvent anions when treated with bromine in an acetic acid medium, but gives a mixture of dibromofumaric and dibromomaleic acids containing not less than 75% of the trans isomer. In presence of two molecular proportions of lithium bromide the reaction becomes stereospecific and leads to pure dibromofumaric acid. We found that dibromofumaric acid and the trans-dibromide of 2,5-dimethyl-3-hexyne-2,5-diol are formed in satisfactory yields in the bromination of acetylenedicarboxylic acid and of 2,5-dimethyl-3-hexyne-2,5-diol in N,N-dimethylformamide. Though more polar than acetic acid, N,N-dimethylformamide does not give anions which interfere in the bromination reaction. In the case of 2,5-dimethyl-3-hexyne-2,5-diol and acetylenedicarboxylic acid the polarity of the solvent is sufficiently high to suppress, apparently completely, homolytic bromination. The reaction becomes stereospecific, and there is scarcely any formation of cis-dibromides.

Unlike these acetylenes, 2-butyne-1,4-diol reacts with bromine in N,N-dimethylformamide with formation of cis-dibromide together with a liquid product, which possibly contains the trans form. Addition of large amounts of lithium bromide does not change the steric orientation in the reaction, though in this case the amount of liquid product becomes greater.

On the basis of data on the isomerization of monosubstituted trans-dibromoethylenes to cis-dibromides under the conditions of photochemical reaction [1, 2] it may be assumed that in the case of disubstituted acetylenes the primary products of photochemical reaction are again trans-dibromides. However, our attempts to isomerize trans-2,5-dimethyl-3-hexyne-2,5-diol and dibromofumaric acid in a short irradiation at room temperature in presence of traces of bromine were not successful. Thus, these disubstituted trans-dibromo olefins do not pass into the cis isomers under the conditions of photochemical bromination. This confirms our previous conclusion [2] that cis-dibromides can be formed in the photochemical bromination of acetylenes as a result of "true" cis addition of bromine.

As will be seen from the table, in the disubstituted acetylenes RC ≡ CR the tendency for the formation of cis-dibromides under the conditions of photochemical reaction falls with increase in the size of the substituent R. Such an effect of the substituent on steric orientation in the photochemical reaction may be explained if we assume that this reaction has the character of a chain process:



The stereochemistry of this process is determined in the main by the thermodynamic stabilities of the radicals (I) and (II), which depend in their turn on the relative mutual repulsion of two R substituents (R↔R) on the one hand, and that of a bromine atom and an R substituent (R↔Br) on the other. When R↔Br > R↔R, the radical (II) may be found to be more stable than the radical (I), and the over-all result of the reaction will be cis addition. If, however, the mutual repulsion of two R substituents exceeds the repulsion R↔Br (e.g., when the substituent R is greater in size), trans addition will predominate. In accordance with this the substituents may be arranged in the following series, in which the tendency for the disubstituted acetylene to undergo trans addition of bromine increases

$$\mathrm{CH_2OH} < \mathrm{COOH} < \mathrm{(CH_3)_2C(OH)} < \mathrm{C_6H_5} < \mathrm{(CH_3)_3C}\,^{*}$$
$$\xrightarrow[\text{Tendency for trans addition}]{\qquad\qquad\qquad\qquad\qquad\qquad}$$

Hence, the size of a substituent has a specific effect on steric orientation in the photochemical addition of bromine to disubstituted acetylenes, and this is in the opposite direction to that observed in series of monosubstituted acetylenes [1, 2].

EXPERIMENTAL

Bromination was carried out under the conditions described in a previous paper [1]. In the case of 2-butyne-1,4-diol and acetylenedicarboxylic acid, whose bromides are readily soluble in water, the reaction mixture was not washed with water and thiosulfate solution, but the solvent and small excess of bromine were driven off in a vacuum at 25-30°. The spectra of 3,4-dibromo-2,5-dimethyl-3-hexene-2,5-diols were determined in chloroform, and the spectrum of 2,3-dibromo-2-butene-1,4-diol was determined in dioxane. As in the case of monosubstituted dibromoethylenes, the spectra of disubstituted trans-dibromides have intense bands at 900 cm^{-1}, which

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*Addition of bromine to di-t-butylacetylene in carbon disulfide gives only the trans-dibromide [5].

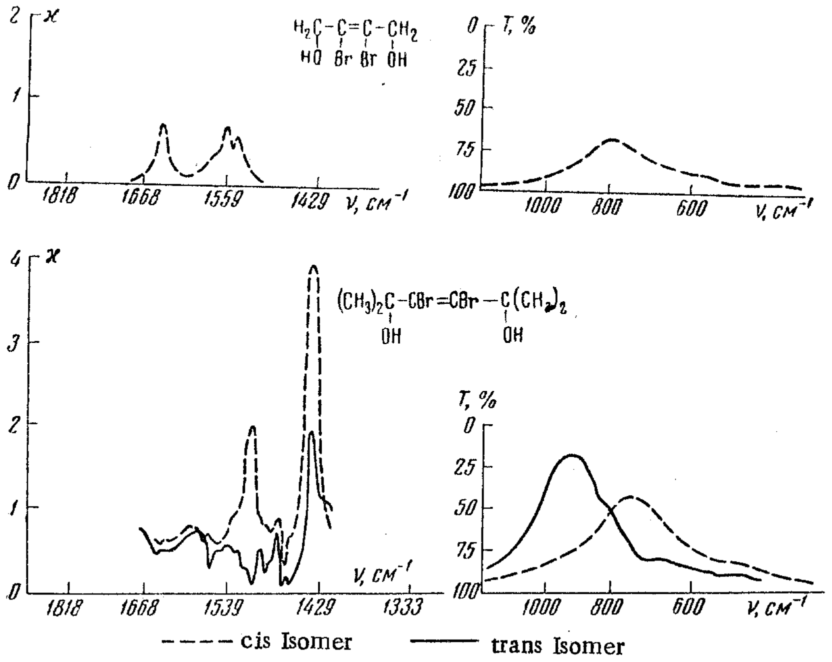

Fig. 1. Infrared spectra of cis-2,3-dibromo-2-butene-1,4-diol and of cis- and trans-3,4-dibromo-2,5-dimethyl-3-hexene-2,5-diols.

are absent in the spectra of the cis isomers. The spectra of the cis-dibromides have an intense absorption band in the region of 1600 cm^{-1} and bands of various intensities at 700 cm^{-1}, which are absent in the spectra of trans-dibromo olefins* (Fig. 1).

Bromination of 2-Butyne-1,4-diol. In carbon tetrachloride. A solution of 19.5 g of bromine in 30 ml of carbon tetrachloride was added dropwise to an irradiated stirred solution of 10 g of 2-butyne-1,4-diol (m.p. 68°) in 900 ml of dry carbon tetrachloride at 55°. When the solution was cooled, crystals were precipitated and were filtered off. Two crystallizations from a 4 : 1 mixture of benzene and alcohol gave 18.5 g of cis-2,3-dibromo-2-butene-1,4-diol, m.p. 115-117°. After distilling solvent from the mother liquor we isolated a further 6.3 g of the cis-dibromobutenediol, m.p. 114.5-116° [3]. The total yield of the cis-dibromobutenediol was 66.8%. After the evaporation of the mother liquors there remained a pale-yellow oil, n_D^{22} 1.5110, which probably consisted mainly of 3,4-dibromo-2,5-dihydrofuran. Found: Br 69.68; 69.80%. $C_4H_4OBr_2$. Calculated: Br 70.17%. When left in the air, the oil darkened in color; when vacuum-distilled, it decomposed.

In acetic acid. 2-Butyne-1,4-diol (30 g) was brominated in 95% acetic acid (two hours). Acetic acid and unchanged bromine were distilled off under the vacuum of a water pump at 30-35°. The residue consisted of crystals (58 g) and a liquid which rapidly darkened in color. After three crystallizations from a 3 : 1 mixture of alcohol and hexane we obtained 43 g (70.5%) of a substance of m.p. 59.5-61°, to which on the basis of analysis we may attribute the structure of 4-bromodihydro-3(2H)-furanone. Found: C 28.63; 28.67; H 2.92; 2.97; Br 48.70; 48.71%. $C_4H_5O_2Br$. Calculated: C 29.11; H 3.05; Br 48.44%. Mol. wt. 163 (calculated value 165).

The substance did not give a crystalline 2,4-dinitrophenylhydrazone. Its infrared spectrum contained a characteristic carbonyl absorption band in the region of 1700 cm^{-1}, a very intense band at 1500 cm^{-1}, and an absorption band at 600 cm^{-1}, characteristic for the C–O–C grouping (Fig. 2).

In N,N-dimethylformamide. A solution of 19.5 g of bromine in 30 ml of N,N-dimethylformamide was added dropwise in the dark to a solution of 10 g of 2-butyne-1,4-diol in 30 ml of N,Ndimethylformamide. After two hours, when the solution had almost become decolorized, solvent was distilled off at 1 mm. Water was added, and the precipitated crystals (m.p. 96-98°) were recrystallized from ether. We obtained 15.3 g (51%)

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*The spectra were determined and interpreted by B. V. Lopatin.

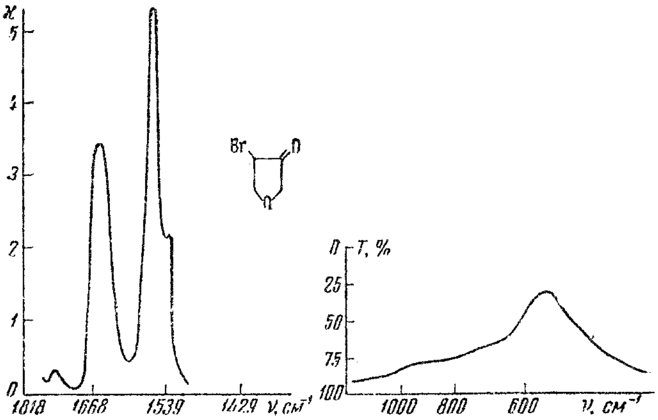

Fig. 2. Infrared spectrum of 4-bromodihydro-3(2H)-furanone.

of cis-2,3-dibromo-2-butene-1,4-diol, m.p. 114-116°. On evaporation of the aqueous mother liquor under reduced pressure there remained a sirupy substance which decomposed when distilled. When 10 g of the butynediol was brominated under the same conditions, but in presence of two moles of lithium bromide, 12.9 g of the cis-dibromobutenediol was obtained.

Bromination of 2-Butyne-1,4-diol Diacetate. 2-Butyne-1,4-diol diacetate (17 g, 0.1 mole) was brominated under standard conditions [1] with irradiation in 700 ml of hexane. The pale-yellow liquid reaction product (29.2 g) obtained after distilling off the hexane under reduced pressure crystallized on standing. Recrystallization from a 3 : 1 mixture of benzene and hexane gave 26.1 g (78%) of cis-2,3-dibromo-2-butene-1,4-diol diacetate, m.p. 62-63°. Found: C 29.02; 29.18; H 2.93; 2.90; Br 48.36; 48.28%. $C_8H_{10}O_4Br_2$. Calculated: C 29.12; H 3.05; Br 48.44%.

Acetylation of cis-2,3-dibromo-2-butene-1,3-diol. Acetic anhydride (24 g) containing p-toluenesulfonic acid (0.1 g) was added in portions to 11 g of cis-2,3-dibromo-2-butene-1,4-diol. The mixture was heated for one hour at 50° and left overnight at room temperature; 75 ml of water was then added, the mixture was heated for 90 minutes in a water bath, the oil layer was separated, and the aqueous layer was extracted with ether. The combined ether solution was washed with sodium carbonate solution and with water, and was then dried with magnesium sulfate. Ether was distilled off, and crystallization of the residue from a 1 : 3 mixture of benzene and hexane gave 12.2 g of the diacetate, m.p. 62°. A mixture with the diacetate obtained by the bromination of 2-butyne-1,4-diol diacetate melted without depression.

Bromination of 2,5-Dimethyl-3-hexyne-2,5-diol. In carbon tetrachloride. The dimethylhexynediol (15.7 g) was brominated with irradiation in carbon tetrachloride (600 ml). When the solution was left in a refrigerator, 5.8 g (19%) of crystals of the trans-dibromide were precipitated; after recrystallization from ether they melted at 120-130° (see below). After the usual treatment and evaporation of the filtrate under reduced pressure to 100 ml, 22.6 g (78%) of crystals of cis-3,4-dibromo-2,5-dimethyl-3-hexene-2,5-diol was precipitated; m.p. 149-150° (from benzene). Found: C 32.11; 32.01; H 4.65; 4.56; Br 53.08; 52.81%. $C_8H_{14}O_2Br_2$. Calculated: C 31.81; H 4.64; Br 52.93%. The mother liquor was evaporated by distillation of the residue under reduced pressure, and a substance of b.p. 84.0-86.6° (10 mm) was obtained; on standing in a refrigerator this yielded crystals. Three crystallizations from alcohol gave 4.8 g of 3,4-dibromo-2,5-dihydro-2,2,5,5-tetramethylfuran, m.p. 49.3-49.5° [4].

In N,N-dimethylformamide. A solution of 8 g of bromine in N,N-dimethylformamide was added to a solution of 7 g of the dimethylhexynediol in 30 ml of N,N-dimethylformamide at 50°. The mixture was kept for 20 hours at 50°, and then diluted with water and extracted with four 100-ml portions of ether. After the usual treatment and drying with magnesium sulfate, the extract was vacuum-evaporated to 150 ml. This led to the precipitation of 11.7 g (78%) of trans-3,4-dibromo-2,5-dimethyl-3-hexene-2,5-diol, which melted at 129-130° after two crystallizations from ether. Found: C 32.11; 32.01; H 4.65; 4.56; Br 53.08; 52.81%. $C_8H_{14}O_2Br_2$. Calculated: C 31.81; H, 4.64; Br 52.93%. At room temperature the reaction mixture was not completely decolorized in the course of five days.

Bromination of Acetylenedicarboxylic Acid. In methanol. A solution of 8 g of bromine in 40 ml of methanol was added to a stirred solution of 2.8 g of acetylenedicarboxylic acid in 65 ml of methanol. The bromine was added over a period of one hour, during which the temperature of the mixture was kept at 0-5°. The mixture was left for 12 hours at room temperature, and methanol and unchanged bromine were then distilled off at 80 mm. Five crystallizations of the residue from a 5:1 mixture of benzene and ether gave 4.8 g (44%) of dibromofumaric acid, m.p. 231-232° (decomp.). The mother liquors were evaporated, and the liquid residue was distilled at 0.9 mm (bath temperature 130-135°). The liquid distillate (5.95 g) yielded crystals, which were filtered off and recrystallized from a 1:2 mixture of hexane and benzene. Four crystallizations gave 1.2 g of dibromomaleic acid, m.p. 139-140° (in sealed capillary). The liquid part of the distillate (3.75 g) did not crystallize when left for two months.

In ether. A solution of 2.8 g of acetylenedicarboxylic acid and 8 g of bromine in ether was kept in the light for 12 hours at room temperature. The mixture was shaken with dry thiosulfate, ether was distilled off, and the residue was fractionated by crystallization from a 1:2 mixture of hexane and benzene. We obtained 8.9 g (82%) of dibromomaleic acid, m.p. 133-139°, and 0.9 g of dibromofumaric acid, m.p. 228-234°.

Bromination of Diphenylacetylene. In hexane with irradiation. The dibromide obtained after the usual treatment [1] from 9 g of diphenylacetylene was extracted with hot alcohol, in which the trans isomer is poorly soluble [6]. The residue was crystallized from propyl alcohol. We obtained 9.1 g of trans-α,α'-dibromostilbene, m.p. 204-205° [5]. When the alcoholic extract was cooled, a further 1.7 g of the trans isomer was precipitated (total yield 69%). The filtrate was evaporated, and crystallization of the residue from methanol gave 2.7 g of the molecular compound of diphenylacetylene with cis-α,α'-dibromostilbene, m.p. 77° [6].

In ether in the dark. From 9 g of diphenylacetylene we obtained 9.8 g of trans-α,α'-dibromostilbene.

Attempts to Isomerize trans-Dibromides. The experiments were carried out in a quartz vessel. A solution of 1 g of trans-3,4-dibromo-2,5-dimethyl-3-hexene-2,5-diol, m.p. 129-130°, in 100 ml of carbon tetrachloride containing one drop of bromine was irradiated for 30 minutes at 20° with a PRK-4 quartz mercury lamp. The mixture, which had darkened appreciably, was vacuum-evaporated. We recovered 0.82 g of the original trans-dibromide, m.p. 128-129.5°.

A solution of 1 g of dibromofumaric acid in 50 ml of ether was irradiated with a quartz mercury lamp for one hour at 20°. After the solvent was distilled off the original dibromofumaric acid was recovered in almost quantitative yield.

SUMMARY

In the photochemical addition of bromine in nonpolar solvents, 2-butyne-1,4-diol, its diacetate, and 2,5-dimethyl-3-hexyne-2,5-diol form mainly cis-dibromides, whereas diphenylacetylene gives mainly the trans-addition product. Under these conditions the tendency for disubstituted acetylenes to undergo cis addition of bromine falls with increase in the size of the substituent.

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