The Action of Hydrogen Bromide and Oxygen on α,α'-Dimethylstilbene and Related Compounds

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A combined action of hydrogen bromide and oxygen on ethylenic compounds induces remarkable reactions involving free radicals :[2–5] to mention a few examples which have some bearing on the subject treated in this paper, the action of hydrogen bromide on isostilbene in the presence of oxygen causes the isomerization[3,4] to stilbene, and, if a larger amount of oxygen is present, the formation of stilbene dibromide takes place[2a,4]; and the joint action of hydrogen bromide and oxygen on various ethylenic compounds causes copious liberation of bromine with those compounds which add bromine to the double bond only to a limited extent, as tetraethyl α, γ-dicarboxy-α-bromoglutaconate, and with some of those which will not do so at all, such as dimethyl dimethylfumarate.[5] These reactions are completely inhibited by a small amount of catechol. The action of hydrogen bromide and oxygen on some α, α'-disubstituted stilbene has now been investigated with special reference to the dimethyl derivative, on reactions of which some observations have been reported in a previous paper.[6]

The passage of hydrogen bromide alone (without special measures to exclude air from the apparatus) or of a mixture with oxygen through a solution of *trans*-dimethylstilbene in carbon tetrachloride in the dark at room temperature caused no reaction whatever; but, on the contrary, *cis*-dimethylstilbene, similarly treated with hydrogen bromide, isomerized partly to the trans isomer, crystals melting at 54 to 71° being recovered, and in the presence of a large amount of oxygen, it underwent a profound change giving acetophenone (9 to 20%), α-bromoacetophenone (20 to 28%) and 1,4-dibromo-2,3-diphenyl-2-butene (3 to 4%) (for a typical run see the experimental part, Expt. No. 14). These reactions were completely inhibited by catechol (37 mol.% of dimethylstilbene) added to a reaction mixture beforehand. Thus, the combined action of hydrogen bromide and oxygen caused the same type of reaction with *cis*-dimethylstilbene as observed with stilbene and other ethylenic compounds. A further point of interest is that the ethylenic bond of *cis*-dimethylstilbene was cleaved so easily

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[2] (a) Y. Urushibara and O. Simamura, This Bulletin, **14**, 323 (1939).
(b) O. Simamura, ibid., **17**, 274, 326 (1942).
(c) O. Simamura and M. Takahashi, ibid., **22**, 60 (1948).

[3] Y. Urushibara and O. Simamura, ibid., **12**, 507 (1937).

[4] Idem, ibid., **13**, 566 (1938).

[5] O. Simamura, ibid., **15**, 292 (1940).

[6] O. Simamura and H. Suzuki, ibid., **27**, 231(1954).

at room temperature to give ketones. It was temporarily considered that the remarkable difference in behavior towards hydrogen bromide and oxygen between the cis and trans isomers of dimethylstilbene might be due to some difference in the electronic state of the central double bond arising from a difference in the extent of its conjugation with the two phenyl groups which are twisted out of a coplanar configuration owing to inevitable steric requirements.[7] It soon became evident, however, that the findings had been spurious. It was found that a specimen of *cis*-dimethylstilbene purified by filtering a petroleum ether solution through a chromatographic column of alumina was no more subject to the action of hydrogen bromide and oxygen than the trans isomer. The specimen which reacted with this gas mixture showed no apparent difference from that purified by the chromatographic method, as far as the melting point and the ultraviolet absorption spectrum were concerned, but the former, on standing in a bright diffuse light of summer days, decomposed slightly and the product, when treated with ferrous ammonium sulfate and aqueous ammonium thiocyanate, developed a red color revealing the presence of a peroxidic substance. It was therefore concluded that the *cis*-dimethylstilbene had retained tenaciously, through a series of purification by repeated crystallizations, traces of peroxidic impurities or those impurities which readily yielded peroxides on autoxidation. With the trans isomer, which is less soluble and crystallizes very well, the impurities must have been easily removed by mere recrystallization. Such traces of impurities undoutedly induced the autoxidative decomposition of dimethylstilbene in air producing peroxidic molecules or very reactive intermediates of a free radical nature and thus catalyzed the reaction with hydrogen bromide and oxygen. It was indeed demonstrated by separate experiments that traces of a peroxide can in fact catalyze the combined attack by hydrogen bromide and oxygen on dimethylstilbene. Thus, in the presence of traces of bonzoyl peroxide the passage of hydrogen bromide through a solution of *trans*-dimethylstilbene in carbon tetrachloride in the dark produced a mixture of the cis and trans forms (Expt. No. 55); if oxygen was passed simultaneously, the cleavage of the double bond occurred yielding the same products (Expt. No. 27) as in the case of the impure *cis*-dimethylstilbene. Similarly, traces of the impure specimen could catalyze the reaction of *trans*-dimethylstilbene. Catechol inhibited these peroxide catalyzed reactions, a fact which is in accord with the view that reactions resulting from the action of hydrogen bromide and oxygen on the ethylenic compounds involves a radical mechanism.

An agent which initiates these reactions is obviously a bromine atom produced from benzoyl peroxide and hydrogen bromide. It adds to one carbon atom of the central double bond of dimethylstilbene forming a radical intermediate which contains a single bond between the α, α' carbon atoms. The radical can then react in the following ways. The first is the cis-trans isomerization by rotation of the groups round the single bond between the α, α' carbons followed by expulsion of the bromine atom to regenerate a double bond between the α,α' carbons. The second is a reaction with oxygen to give an oxygenated radical, which, immediately or after the formation of a hydroperoxide by abstracting a hydrogen atom from hydrogen bromide and leaving a bromine atom, decomposes in a manner generally postulated for peroxides[8] to give eventually acetophenone and fragments of radical nature. The latter are assumed to react with hydrogen bromide producing bromine atoms. Bromine atoms produced in the several ways just mentioned can again attack the double bond of dimethylstilbene continuing the chain process or combine with one another to give bromine molecules. Thus, the formation of brominated compounds such as 1, 4-dibromo-2, 3-diphenyl-2-butene and bromoacetophenone is readily understood as discussed in the previous report. The inhibitive action of catechol consists in the annihilation of chain carrying bromine atoms.

Ordinary ethylenic compounds are liable to the combined action of hydrogen bromide and oxygen leading to a complicated reaction, because in their presence bromine atoms can be formed from hydrogen bromide and oxygen, thus initiating chains carried by bromine atoms. Both *cis*- and *trans*-dimethylstilbenes undergo no such reaction in the absence of a catalyst, because they are unable by themselves to produce bromine atoms from hydrogen bromide and oxygen. This is probably attributable to the steric effect of the two phenyl and the two methyl groups, which hinder the approach of hydrogen bromide and oxygen to the double bond. On the other hand, once bromine atoms have been produced from hydrogen bromide and a peroxidic initiator, they are active enough, in spite of the steric repulsion, to attack the double bond of

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[7] H. Suzuki, This Bulletin, **25**, 145 (1952).

[8] For a leading reference see J. E. Leffler, *Chem. Rev.*, **45**, 385 (1949) and C. E. Frank, ibid., **46**, 155 (1950).

dimethylstilbene, as has previously been demonstrated,6) producing radicals which then give the isomerized product or further react with oxygen and hydrogen bromide resulting in the oxidative cleavage of the double bond.

What is of interest in connection with these observations is that, when traces of bromine was added to a solution of *trans*-dimethylstilbene through which hydrogen bromide was being passed, the cis-trans isomerization occurred, and similarly, when a mixture of hydrogen bromide and oxygen was passed in the presence of bromine, the cleavage of the double bond took place (Expt. No. 33). The action of bromine on dimethylstilbene gives 1, 4-dibromo-2, 3-diphenyl-2-butene.5) When oxygen was passed through a reaction mixture while bromine was being added, the yield of the dibromo-compound decreased and the formation of ketones resulting from the oxidative cleavage of the double bond was observed (Expt. No. 20). That these ketones were not formed from the 1, 4-dibromo-2, 3-diphenyl-2-butene by the action of oxygen and the hydrogen bromide primarily produced from bromine and dimethylstilbene was demonstrated by a separate experiment, in which the dibromo-compound was recovered unchanged when subjected to the action of oxygen and hydrogen bromide, even in the presence of benzoyl peroxide or of bromine. These observations are readily explained on the basis of the radical nature of the action of bromine on dimethylstilbene as has been pointed out in the previous report.5) Thus, some radicals formed in the course of the reaction between bromine and dimethylstilbene release the combined attack by hydrogen bromide and oxygen.

The action of hydrogen bromide and oxygen on some other α,α'-disubstituted stilbenes was also examined. *trans*-Diethylstilbene reacted with a mixture of hydrogen bromide and oxygen only in the presence of bromine or of benzoyl peroxide, producing the same type of cleavage of the central double bond as in the case of the dimethyl analogue (Expt. No. 97). The cis isomer was cleaved without added catalyst; the material used boiled at 177–8° at 22 mm. Hg, and probably contained some peroxidic impurities as no special measures of purification had been taken in the preparation. 1, 1, 2-Triphenylpropene did not react with hydrogen bromide and oxygen even in the presence of bromine or of benzoyl peroxide. The action of hydrogen bromide and oxygen on *trans*-α-methylstilbene gave 1, 2-dibromo-1, 2-diphenylpropane, corresponding to stilbene dibromide from stilbene, along with benzoic acid and α-bromoacetophenone (Expt. No. 69). The results of these experiments substantiate the view put forth above, that some molecule with a double bond sterically hindered to such an extent that it can not by itself initiate the chains involving bromine atoms is able to react with bromine atoms and propagate the chains. Further, the absence of reaction with 1, 4-dibromo-2, 3-diphenyl-2-butene and 1, 1, 2-triphenylpropene demonstrates that the steric hindrance is so great in these molecules that they are not only incapable of such initiation, but unsusceptible even to the action of bromine atoms or, if a bromine atom adds to the double bond, unable to propagate the chains efficiently.

Experimental

The stilbenes used in this study were prepared as reported previously.6) Hydrogen bromide was generated by dropping dried bromine on hot tetralin, passed through a bottle of cooled tetralin and a tube filled with glass wool and anthracene and then dried by passage over phosphorus pentoxide.

Typical experiments which have been referred to in the discussion are described in the following. All reactions were carried out in the dark below room temperature (0 to 10°).

Expt. No. 14 *cis*-Dimethylstilbene (0. 140 g.) was dissolved in 10 cc. of carbon tetrachloride and hydrogen bromide was passed for 45 minutes into the solution. The solvent was removed under diminished pressure, the oily residue containing a small amount of crystals was treated with alcohol to dissolve the oil; the crystals were collected on a filter and identified with 1,4-dibromo-2,3-diphenyl-2-butene, m. p. 147-152° (yield 10 mg.), which was not depressed on admixture with the specimen prepared from bromine and dimethylstilbene. The alcoholic extract, on treatment with 2, 4-dinitrophenylhydrazine deposited 0. 18 g. of yellowish brown precipitate (Found: Br, 16. 25. Calcd. for $C_{14}H_{11}BrN_4O_4$: Br, 21. 11%). This was separated into two components, 2, 4-dinitrophenylhydrazones of acetephenone and α-bromoacetophenone, m. p. 250° and 220°, respectively, by fractional crystallization from alcohol. On the basis of the bromine content of the original mixture, the amounts of the ketones produced were estimated at 0. 0735 g. of bromoacetophenone and 0. 016 g. of acetophenone.

Expt. No. 20 A solution of bromine in carbon tetrachloride (1 : 20) was added gradually to 0. 199 g. of *trans*-dimethylstilbene in 10 cc. of carbon tetrachloride simultaneously with the introduction of oxygen. The reaction mixture, worked up as Expt. No. 14, gave 97 mg. of 1, 4-dibromo-2, 4-diphenyl-2-butene and 0. 22 g. of 2, 4-dinitrophenylhydrazone of ketones.

Expt. No. 27 The action of hydrogen bromide and oxygen on 0. 226 g. of *trans*-dimethylstilbene and 11 mg. of benzoyl peroxide in 10 cc. of carbon tetrachloride for one hour, worked up as above, yielded 12 mg. of 1, 4-dibromo-2, 3-diphenyl-2-butene and ketones (0. 282 g. of 2, 4-dinitrophenylhydrazones).

Expt. No. 33 A mixture of hydrogen bromide and oxygen was passed into 0. 13 g. *trans*-dimethylstilbene in 10 cc. of carbon tetrachloride and a few drops of carbon tetrachloride solution of bromine (1 : 20) was added through a fine capillary tube; the passage of the gas mixture was continued for a further forty-five minutes and the solution was worked up as above to give 5 mg. of 1, 4-dibromo-2, 3-diphenyl-2-butene and ketones (0. 202 g, of 2, 4-dinitrophenylhydrazone).

Expt. No. 55 Hydrogen bromide was passed through a solution of 0. 102 g. of *trans*-dimethylstilbene, m. p. 107°, and 4 mg. of benzoyl peroxide in 10 cc. of carbon tetrachloride for one hour; the removal of the solvent gave a mixture of the cis and trans isomers melting over a range of 72° to 102°.

Expt. No. 69 A mixture of hydrogen bromide and oxygen was passed for one hour into a solution of 0. 267 g. of α-methylstilbene, m. p. 83-83. 5°, in 10 cc. of carbon tetrachloride. The mixture was shaken with dilute aqueous sodium carbonate and the aqueons layer deposited benzoic acid on acidification with sulfuric acid (the total yield of the benzoic acid, 18 mg.). The dried carbon tetrachloride solution, concentrated under diminished pressure, gave 0. 134 g. of α-methylstilbene dibromide, m. p. 127°, and an oily matter which gave 0. 132 g. of 2, 4-dinitrophenylhydrazone, m. p. 205-216°, probably of impure α-bromoacetophenone.

Expt. No. 97 A mixture of hydrogen bromide and oxygen was passed into a solution of 0. 107 g. of *trans*-α, α′-diethylstilbene, m. p. 77-8°, and 4 mg. of benzoyl peroxide in 10 cc. of carbon tetrachloride for one hour; the mixture was worked up as above to give 0. 012 g. of 2, 5-dibromo-3. 4-diphenyl-3-hexene, m. p. 155-7°, and ketones (0. 046 g. of 2, 4-dinitrophenylhydrazone). A catalytic action of bromine was demonstrated by an experiment similar to Expt. No. 33.

Summary

The action of hydrogen bromide on *cis*- or *trans*-α, α′-dimethylstilbene in the presence of a peroxidic substance or of bromine in carbon tetrachloride in the dark below room temperature caused a partial isomerization to the respective geometrical isomers. The reaction was inhibited by catechol. When oxygen was allowed to react simultaneously under otherwise the same experimental conditions, the cleavage of the central double bond took place yielding acetophenone and α-bromoacetophenone along with 1, 4-dibromo-2, 3-diphenyl-2-butene. Similar experiments with α-methylstilbene and α, α′-diethylstilbene were conducted. The action of oxygen and bromine on α, α′-dimethylstilbene caused the same oxidative cleavage of the double bond as with hydrogen bromide and oxygen. It was pointed out that an ethylenic compound which is sterically hindered to such an extent that it is unreactive towards molecular reagents can be reactive enough towards radical reagents.

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