[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE STATE UNIVERSITY OF IOWA]

The Addition of Bromine to Olefinic Double Bonds. N-Bromoacetamide as a Source of Bromine.[1]

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N-Bromoacetamide has been found to react with several unsaturated compounds to form dibromides in appreciable amounts. Such formations of significant amounts of dibromides of olefins with N-bromoacetamide as the sole source of bromine have not previously been reported.[1a]

In Table I are listed the results of the reactions of various unsaturated compounds with N-bromoacetamide in chloroform. In all cases the reactions were promoted by ultraviolet light or simply by heat. Styrene reacted quite rapidly with the N-bromoacetamide. There was no appreciable bromine color in the reaction mixture. In all the other cases the reaction mixtures maintained a noticeable bromine color, and the olefin seemed to be reacting with the bromine as it formed from the decomposition of the N-bromoacetamide.[2]

TABLE I

MELTING POINTS AND YIELDS OF DIBROMIDES FROM VARIOUS SOURCES

	AcNHBr		AcNHBr + HBr (crude product)		Br_2
Olefin	Yield, %	M. p.[a]	Yield, %	M. p.[a]	M. p.[a]
Styrene	34	69–71°	93	68–70°	73–74°
	55[b]	71–72			
Ethyl cinnamate	48	74–75	99	65–71	73–74
Cinnamic acid	49	197–199	95	183–188	198–200
cis-Stilbene	18	235–237	97	85–100	110–111
trans-Stilbene	35	237–239	95	234–237	235–237
Tolan	37	210–211	98	167–199	210–211
Triphenylethylene[c]	39	112–114	99	109–112	114–115

[a] All m. p.'s corrected. [b] Dibromide isolated by distillation. [c] The product was triphenylbromoethylene.

The rapid reaction of styrene whether induced thermally or photochemically usually had an induction period. The liberation of heat which followed the induction period often caused the reaction mixture to boil violently. This behavior of styrene with N-bromoacetamide took place with chloroform, carbon tetrachloride or excess styrene as solvent. The presence of small amounts of alcohol or water in the chloroform or of *p-t*-butylcatechol in the styrene did not change the nature of the reaction. Polystyrene accompanied styrene dibromide as a product only when styrene was used as a solvent. In no case did the reaction give anywhere near a quantitative yield of the solid dibromide.

Styrene reacted with N-bromoacetamide to form dibromide at room temperature in the absence of light when the mixture merely stood overnight. When *cis*-stilbene was treated similarly there was still unchanged N-bromoacetamide after five days. A low yield of *trans*-stilbene dibromide as well as a nearly identical yield of *trans*-stilbene, itself, was obtained from the reaction mixture.

A great deal of difficulty was encountered in the isolation of reaction products which could be traced to the acetamido group of the N-bromoacetamide. It was expected at first that diacetylhydrazine would be the product, but no isolable amount of this compound was formed. The only products successfully identified were small amounts of acetamide and diacetamide hydrobromide or their hydrolysis products. These two compounds, however, have both been isolated as decomposition products of N-bromoacetamide.[2] A small amount of decomposition accompanying the olefin reaction would account for these byproducts.

In contrast to these addition reactions with N-bromoacetamide as the sole source of bromine was the formation of dibromides in a much more clean-cut fashion when the unsaturated compounds reacted with N-bromoacetamide in chloroform in presence of excess anhydrous hydrogen bromide. In every case the reaction was carried out so that there was little or no bromine color in the reaction mixture until all the olefin had reacted. In each case, also, the reaction was immediate, and heat was liberated. No external stimulus was necessary for starting the reaction. The yields of crude dibromides are listed in Table I.

Discussion

N-Bromoamides seem to be capable of supplying either bromine atoms or positive bromine[3] during a reaction. It has been reported[4] that the preferential bromination[5] of the carbon atom adjacent to the double bond is catalyzed by peroxides. Substitution reactions have also been reported for N-bromoacetamide with various olefins[6] as well as for N-bromosuccinimide at the

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[1a] Dibromides have recently been reported as the main products of the reactions of N-bromosuccinimide with certain unsaturated compounds: Buchman and Howton, THIS JOURNAL, **70**, 2517 (1948), and Southwick, private communication.

[2] (a) Edgell, Simpson and Buckles, unpublished work; (b) Hantzsch and Dollfus, *Ber.*, **35**, 249 (1902).

[3] Bartlett and Tarbell, THIS JOURNAL, **58**, 466 (1936).

[4] (a) Schmid, *Helv. Chim. Acta.*, **29**, 1144 (1946); (b) Howton, THIS JOURNAL, **69**, 2060 (1947).

[5] Ziegler, Spath, Schaaf, Schumann and Winklemann, *Ann.*, **551**, 80 (1942).

[6] Wohl, *Ber.*, **52**, 51 (1919); Wohl and Jaschinowsky, *Ber.*, **54**, 476 (1921).

α-carbon atom of ketones.[7] These reactions are often promoted by ultraviolet light.[7] Reactions of this sort which exhibit catalysis by peroxides or light are generally interpreted[8] as involving bromine atoms and free radical intermediates.

On the other hand N-bromosuccinimide reacts with aromatic hydrocarbons in the presence of anhydrous aluminum chloride to give ring bromination as opposed to the side chain substitution observed with a peroxide catalyst.[4a] N-Bromoacetamide has been reported[9] to be a source of bromine for acid catalyzed olefin addition reactions of olefins in which a hydroxylic solvent is also involved; *e.g.*, water as a solvent giving rise to the bromohydrin as the predominant product. Such reactions are best interpreted[10] as ionic with the bromine behaving as if it were positive.[3]

The formation of dibromide of unsaturated molecules with N-bromoacetamide as the sole source of bromine most likely takes place through free radical intermediates. This interpretation is especially applicable in the case of styrene reacting with N-bromoacetamide because of the induction period followed by an accelerating reaction. The effect of light on the reaction also points to a free radical mechanism. The fact that *cis*-stilbene was isomerized to the *trans* isomer at room temperature in the absence of activating light shows that bromine atoms are available from N-bromoacetamide without the intermediate formation of bromine molecules. Bromine itself reacts with *cis*-stilbene at room temperature in the absence of light to give the *dl*-dibromide as the principle product.[11] On the other hand bromine atoms catalyze the *cis*-*trans* isomerization of olefins.[8] Thus, it seems reasonable to postulate that in the photochemical reaction N-bromoacetamide first forms a bromine atom (Step 1) which attacks the double bond (Step 2). The resulting radical would be capable of relatively free rotation about the bond that was originally the double bond. It would be expected to react with a N-bromoacetamide molecule to form the dibromide of most stable configuration (Step 3). At the present time it is impossible to say what might happen to the acetamidyl radical, AcNH·.

$$\mathrm{AcNHBr} + h\nu \longrightarrow \mathrm{AcNH\cdot} + \mathrm{Br\cdot} \qquad (1)$$

$$>\!\mathrm{C{=}C}\!< + \mathrm{Br\cdot} \longrightarrow\ >\!\mathrm{CBr{-}\dot{C}}\!< \qquad (2)$$

$$>\!\mathrm{CBr{-}}\underset{\cdot}{\mathrm{C}}\!< + \mathrm{AcNHBr} \longrightarrow\ >\!\mathrm{CBr{-}CBr}\!< + \mathrm{AcNH\cdot} \qquad (3)$$

$$\mathrm{Br\cdot} + \mathrm{AcNHBr} \longrightarrow \mathrm{Br_2} + \mathrm{AcNH\cdot} \qquad (4)$$

$$\mathrm{Br_2} + h\nu \longrightarrow 2\mathrm{Br\cdot} \qquad (5)$$

$$\mathrm{Br_2}\ +\ >\!\mathrm{CBr{-}}\underset{\cdot}{\mathrm{C}}\!< \longrightarrow\ >\!\mathrm{CBr{-}CBr}\!< + \mathrm{Br\cdot} \qquad (6)$$

In the cases where a definite bromine color was observed during the reaction, Steps 4, 5 and 6 must also be considered. No matter what the source of bromine atoms, however, the most stable dibromide isomer would be formed. This was found to be the case when the *meso*-dibromide was the product from either of the stilbene isomers.

The clean-cut reaction of the olefins with N-bromoacetamide in the presence of hydrogen bromide, on the other hand, most likely involves ionic intermediates (ion pairs or triplets in non-polar solvents). Such addition reactions are best interpreted as involving ionic intermediates, *e.g.*, the bromonium ion,[12] which maintain their steric identity. Only with such an interpretation can the formation of *dl*-dibromide from *cis*-stilbene be explained. Either the conjugate acid of N-bromoacetamide or molecular bromine could act as a source of positive bromine[3] for the usual ionic mechanism of bromine addition.[10]

$$\mathrm{AcNHBr} + \mathrm{HBr} \rightleftharpoons \mathrm{AcNH_2Br^+} + \mathrm{Br^-}$$

$$\mathrm{AcNH_2Br^+} + \mathrm{Br^-} \longrightarrow \mathrm{AcNH_2} + \mathrm{Br_2}$$

Experimental

N-Bromoacetamide.—This material was prepared by the reaction of equimolar amounts of acetamide, bromine and potassium hydroxide in a minimum amount of water at 0–5°.[13] The reaction product was dissolved in chloroform and the solution distilled until there was no more water in the distillate. Cooling crystallized the product. The m. p. fell somewhere between 95 and 105° with a range of several degrees. The pure anhydrous N-bromoacetamide has m. p. 108°.[2a] The yields of product were generally around 45%.

Unsaturated Compounds.—The styrene (stabilized with *p*-*t*-butylcatechol) was supplied by Eastman Kodak Co. Thanks are due Mr. Norris G. Wheeler of this Laboratory who prepared the *cis*-stilbene by the decarboxylation of α-phenylcinnamic acid.[14]

Authentic Samples of Dibromides.—These were all prepared by the action of bromine in either chloroform or carbon tetrachloride on the respective olefins. In the case of triphenylethylene the resulting dibromide lost hydrogen bromide so that triphenylbromoethylene was the product. In all cases except *cis*-stilbene the yields exceeded 80%. The *cis*-stilbene dibromide was generally obtained in about 70% yields with a small amount of *trans*-dibromide.

The m. p.'s of the dibromides check favorably with the accepted values in the chemical literature; they are tabulated in Table I. The capillary m. p. of *meso*-stilbene dibromide from the addition of bromine to *trans*-stilbene, depended on the length of time necessary to heat the sample to the m. p. Only when the sample was placed in the bath preheated to about 210° was decomposition minimized enough for the recorded m. p. of 237° to be observed. Otherwise the m. p. was much lower. On the Maquenne block the m. p. was 254–255° (dec.).

Reactions of the Unsaturated Compounds with N-Bromoacetamide.—In most of the experiments 0.005 to 0.02 mole of the unsaturated compound in 15–25 ml. of unpurified commercial chloroform containing 0.75% alcohol was treated with twice as many moles of N-bromoacetamide. In the case of triphenylethylene an equimolar amount was used. The reaction mixture was usually heated gently and illuminated with ultraviolet light. Either sunlight or a Hanovia quartz mercury arc was used as a source of illumination. Usually the solution became

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[7] Djerassi and Scholz, *Experientia*, **3**, 107 (1947).

[8] Price, "Mechanisms of Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, New York, N. Y., chap. 3, 1946.

[9] Winstein and Lucas, THIS JOURNAL, **61**, 1576 (1939); Likhosherstov and Alekseev, *J. Gen. Chem.* (*U. S. S. R.*), **3**, 927 (1933); Schmidt, Knilling and Ascherl, *Ber.*, **59**, 1280 (1926).

[10] Footnote 8, chap. 2.

[11] Wislicenus, *Chem. Zentr.*, **72**, I, 464 (1901).

[12] Roberts and Kimball, THIS JOURNAL, **59**, 947 (1937).

[13] Winstein and Henderson, *ibid.*, **65**, 2196 (1943).

[14] Taylor and Crawford, *J. Chem. Soc.*. 1130 (1934).

light brown in color and remained so for several hours. If an excess of N-bromoacetamide was used the end of the reaction was characterized by a distinct darkening of the bromine color. When no olefin was present the brown color deepened much faster. After several hours of illumination the reaction mixture was filtered and washed with warm water and chloroform. A crystalline product remained if the dibromide was an insoluble one.

The two phase filtrate was shaken, and the water layer was removed. In all cases the aqueous layer contained acetamide and bromide ion, and if it was evaporated to dryness by standing for some time the residue contained ammonium ion and acetic acid as well. In some of the experiments a small amount of a water soluble crystalline product was filtered from the chloroform solution before water was added. This compound proved to be diacetamide hydrobromide[2] of m. p. somewhere in the range 130–139°.

The chloroform solution was distilled at reduced pressure and the dibromide residue was recrystallized from alcohol or alcohol–water. The results of these experiments are given in Table I.

The Reaction of Styrene with N-Bromoacetamide.—Several experiments with 0.1 and 0.2 mole of styrene with equivalent amounts of N-bromoacetamide were carried out. In 50 to 100 ml. of unpurified chloroform containing 0.75% ethyl alcohol the reaction was quite violent as soon as it started unless the N-bromoacetamide or the styrene was added portionwise. It was possible to start this violent reaction either by the application of heat to or illumination of the reaction mixture. It made no difference whether the N-bromoacetamide was hydrated or anhydrous. In fact the addition of a mole of water per mole of styrene had no effect on the reaction. In most of these cases the dibromide crystallized from an alcohol solution following the removal of the chloroform. In one case the dibromide was distilled from the residue, b. p. 108–110° (3–4 mm.) (see Table I).

In one experiment 15 ml. of chloroform washed with concentrated sulfuric acid and dried over anhydrous potassium carbonate was distilled into a cooled flask containing 1.4 g. (0.010 mole) of N-bromoacetamide. Two ml. of styrene was then distilled at reduced pressure into the same flask. The reaction exhibited an induction period as before, but the reaction mixture heated up noticeably once it started. A control experiment using unpurified chloroform and styrene stabilized with *p-t*-butylcatechol behaved the same way. Both reactions yielded styrene dibromide.

Similarly 0.01 mole of N-bromoacetamide reacted with styrene alone and with styrene in carbon tetrachloride to give the dibromide.

At room temperature in the absence of light, a successful reaction of 0.01 mole of N-bromoacetamide with a slight excess of styrene in chloroform was observed only if the reaction mixture stood overnight or longer.

The Reaction of *cis*-Stilbene with N-Bromoacetamide in the Absence of Light.—A solution of 1.38 g. (0.010 mole) of N-bromoacetamide in 50 ml. of chloroform was prepared in a Pyrex Lifetime Red Low Actinic glass flask. The solution was cooled, and 0.90 g. (0.005 mole) of *cis*-stilbene was added. The flask was stoppered and the solution was allowed to stand five days at room temperature. The solution was extracted with water. The aqueous phase gave an iodine color when potassium iodide was added. Chloroform was distilled from the organic layer and alcohol was added. Cooling yielded 0.13 g. (8%) of *trans*-stilbene dibromide. The solution was concentrated and cooled and 0.07 g. (8%) of *trans*-stilbene of m. p. 118–120° was isolated. Recrystallization of the *trans*-stilbene from aqueous alcohol yielded crystals of m. p. 122.5–123.5°; no depression when mixed with an authentic sample. Evaporation of the mother liquor gave a little oily residue containing no crystals.

Reactions of the Unsaturated Compounds with N-Bromoacetamide and Anhydrous Hydrogen Bromide.—A slight excess of anydrous N-bromoacetamide was added portionwise to a solution of 0.005 mole of the unsaturated compound in 15 ml. of unpurified commercial chloroform which was kept saturated with anhydrous hydrogen bromide. There was an immediate evolution of heat. The N-bromoacetamide was added at a rate such that only local concentrations of bromine were observed by color. At the end of the reaction the bromine color became pronounced and a white precipitate of diacetamide hydrobromide was observed.[2a] The reaction mixture was shaken with water, and the chloroform layer was evaporated on a tared watch glass. The solid residue was weighed and the melting point taken. These data are in Table I. The crude products were recrystallized when necessary and identified by mixed m. p. with authentic samples. When this method of isolation was attempted with the reactions of the olefins with N-bromoacetamide alone, only sticky, viscous liquids were obtained as residues.

Summary

1. N-Bromoacetamide has been shown to act as the sole source of bromine for addition to the double or triple bonds of certain unsaturated compounds.

2. The reactions of the unsaturated compounds with N-bromoacetamide have been interpreted as involving free radical intermediates.

3. N-Bromoacetamide has been shown to be a source of bromine atoms capable of isomerizing *cis*-stilbene to the *trans* isomer.

4. The reactions of unsaturated compounds with N-bromoacetamide in the presence of anhydrous hydrogen bromide have been interpreted as following the usual polar mechanism of *trans* addition.

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