indicate that the molecules of these two acids contain the planar cyameluric nucleus of Pauling and Sturdivant.

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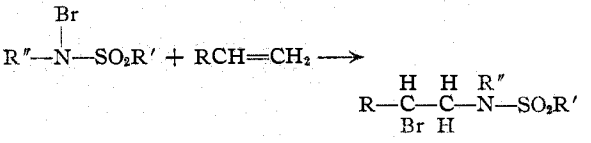
[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

The Addition of N-Haloamides to Olefins

BY M. S. KHARASCH AND HILL M. PRIESTLEY

An unsuccessful attempt to add N-haloamides to olefins is recorded by Seliwanoff.[1] Foldi,[2] however, showed that 1-phenylpropene and N-bromo-N-methylbenzenesulfonamide ($C_6H_5SO_2NBrCH_3$) react to give at least two addition isomers. The reaction was considered by Földi to be of limited applicability, since all the purely aliphatic olefins tried by him yielded the dibromo derivatives when treated with the N-bromo-N-methylbenzenesulfonamide.

We have succeeded in extending this interesting reaction to include aliphatic olefins such as propene, 2-methylpropene, and vinyl chloride, as well as styrene. We have also demonstrated that in the reaction



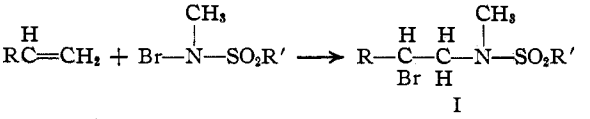
the radicals R, R′ and R″ play only a minor part, since we have employed in these reactions with equal success the phenyl-, *p*-tolyl-, and benzylsulfonyl derivatives of methylamine, benzylamine, phenethylamine, and β-bromo-α-phenylethylamine.

The addition of the bromo derivatives of the sulfonamides to olefins appears to be a unique reaction. We have been unable to obtain addition products of olefins with the following N-bromo-compounds: N-bromobenzamide, N-bromo-N-methylbenzamide, N-bromo-N-methyl-N-carbobenzoxamine, N-bromo-triphenylmethylamine, N-bromosaccharine, N-bromophthalimide, and N-bromosuccinimide.

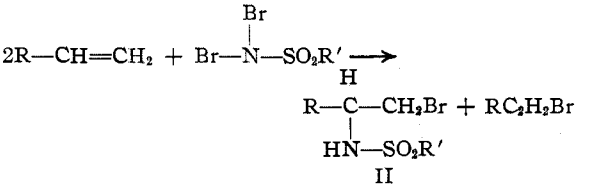
In addition to standardizing the conditions of addition of N-bromosulfonamides to olefins, we have succeeded in effecting the addition of N,N-dibromo derivatives of aromatic sulfonamides, *e. g.*, N,N-dibromo-*p*-toluenesulfonamide, to styrene, anethole, and isosafrole.

(1) Seliwanoff, *Ber.*, **26**, 426 (1893).
(2) Földi, *ibid.*, **63**, 2257 (1930).

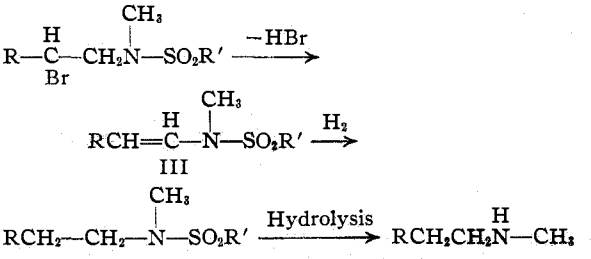
The positions taken by the nitrogen and bromine atoms of the N-bromo- and N,N-dibromosulfonamides is of considerable theoretical interest. The N-bromo-N-methyl aromatic sulfonamides add to propene, 2-methylpropene, vinyl chloride, and styrene to yield products in which the bromine atom takes the same position as the bromine atom in the "normal" addition[3] of hydrogen bromide to these olefins



The N,N-dibromosulfonamides, on the other hand, add to olefins to yield products in which the bromine takes the same position as in the "abnormal" addition of hydrogen bromide. A brominated olefin is formed at the same time.



The structure of the products of reaction I was proved by conversion into known compounds by the following series of reactions. The intermediates cited were all isolated and characterized.



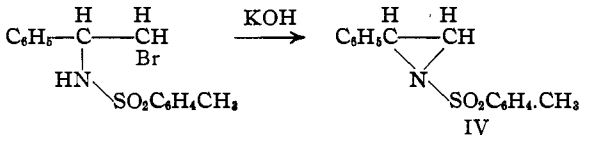
The elimination of hydrogen bromide from I usually was effected by heating the addition product with quinoline or with sodium ethoxide in al-

(3) For definition of "normal" and "abnormal" additions of hydrogen bromide consult the paper by Kharasch, Englemann, and Mayo, *J. Org. Chem.*, **2**, 288 (1937); Kharasch, Kleiger and Mayo, *ibid.*, **4**, 428 (1939).

cohol. Palladium, on barium sulfate, usually served as the catalyst in the hydrogenation reactions, and the hydrolysis was effected with the aid of hydrogen chloride at 150°. The same end-product, namely, $R-CH_2-CH_2-NH-CH_3$, also was obtained in one step if sodium was added to an amyl alcohol solution of the addition product.

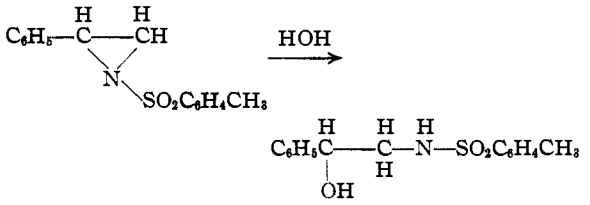
In the course of study of the structure of the products formed by the addition of aromatic N,N-dibromosulfonamides to styrene, anethole, and isosafrole, a number of extremely interesting intermediates were isolated.

Thus, when the addition product of styrene and N,N-dibromo-*p*-toluenesulfonamide was treated with aqueous or alcoholic alkali, the N-*p*-tolylsulfonyl derivative of phenylethylenimine (styrenimine) was obtained.

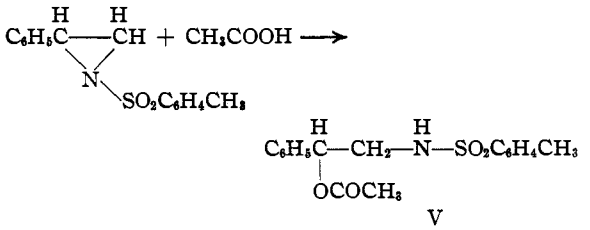


IV

The imine derivative was easily cloven by many reagents. When boiled with water it was easily transformed into the expected *p*-toluenesulfonyl derivative of 2-phenyl-2-hydroxyethylamine.

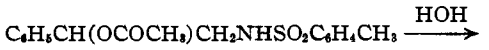


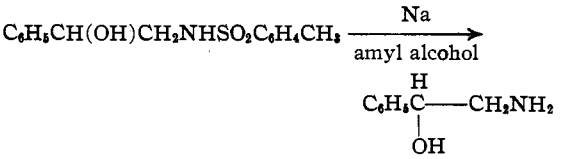
From cold glacial acetic acid the imine derivatives could be recovered unchanged, but heating the mixture for a short time caused the following reaction to take place



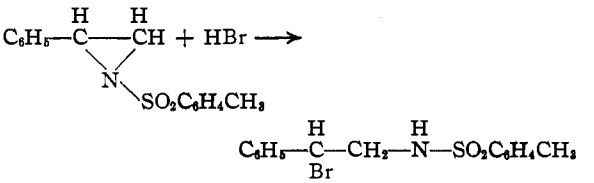
V

The structure of this compound was proved by saponification of the acetate group and treatment of the resulting compound, dissolved in boiling amyl alcohol, with sodium, to yield 2-phenyl-2-hydroxyethylamine.





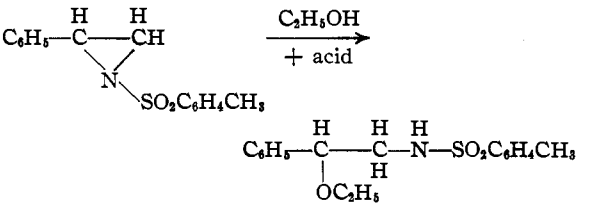
The N-substituted imines combined, at room temperatures, very readily with hydrogen chloride, hydrogen bromide, and hydrogen iodide, but with trichloroacetic and crotonic acids only upon warming. The nature of the products formed is best illustrated by a study of the addition of hydrogen bromide to the substituted imine. When the N-substituted imine, derived from styrene, is treated with hydrogen bromide at room temperatures, a compound of melting point 111° (VI) is obtained.



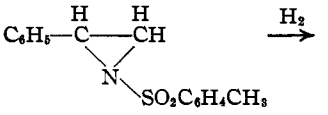
VI

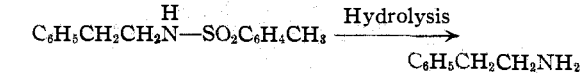
This substance is isomeric with the compound II (m. p. 167°) from which the imine is prepared. Furthermore, treatment of VI with sodium acetate yielded the same product as was obtained by direct action of acetic acid on the substituted imine IV.

Ethyl alcohol, even at the boiling point, does not cause the cleavage of the substituted imine. However, boiling an ethyl alcohol solution of it in the presence of a small amount of trichloroacetic acid, or the addition of a little cold 50% solution of sulfuric acid in alcohol to an alcoholic solution of the imine, causes the following reaction to take place



Catalytic reduction of IV, N-(*p*-toluenesulfonyl)-styreneimine gave N-phenethyl-*p*-toluenesulfonamide, which upon hydrolysis yielded phenethylamine.

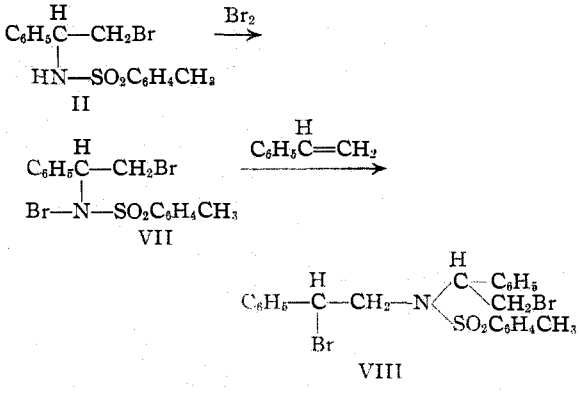




The same end-product was obtained by treating a solution of IV in amyl alcohol with sodium.

Compounds III and IV, obtained by elimination of hydrogen bromide from I and II, respectively, can be differentiated by their reactions with a neutral solution of potassium permanganate. The unsaturated compound III decolorizes the solution instantly, while the substituted imine IV is not affected by it.

It is of interest to note here that compound II, since it is a N-substituted *p*-toluenesulfonamide, reacts with bromine to give the N-bromo derivative of the substituted *p*-toluenesulfonamide VII which reacts smoothly with styrene to give an addition product VIII



Experimental

The sulfonamides and the corresponding N-bromosulfonamides were prepared by well-known methods or suitable modifications thereof.

1-Phenyl-1-bromo-2-(N-methylbenzenesulfonamido)-ethane (IX).—To 10 g. of N-bromo-N-methylbenzenesulfonamide was added 8 cc. of styrene. The mixture was warmed by the hand, until a reaction set in, after which it was cooled immediately in running water. After reaction was complete (disappearance of yellow color), the excess styrene was removed under reduced pressure. The residue was a thick sirup, which on cooling became a hard, glassy mass, but did not crystallize. For analysis, it was purified by dissolving in 25 cc. of warm absolute alcohol, and chilling the solution. A sirup separated. The alcoholic solution was decanted, and the sirup was washed with 10 cc. of cold alcohol. The substance was freed from alcohol by drying *in vacuo* for two hours at 70°, and then overnight in a vacuum desiccator over sodium hydroxide.

1-Phenyl-1-bromo-2-(N-methyl-*p*-toluenesulfonamido)-ethane (X).—To 16 cc. of styrene was added, in 5 g. portions, at first with cooling, a total of 32 g. of N-bromo-N-methyl-*p*-toluenesulfonamide. After the reaction, the warm mixture was dissolved in 60 cc. of absolute alcohol and seeded with a crystal from a previous preparation. The solid mass was collected on a filter, washed with a little alcohol, and finally crystallized from 120 cc. of alcohol. The yield was 32 g.

1-Phenyl-1-acetoxy-2-(N-methyl-*p*-toluenesulfonamido)-ethane (XI).—Ten grams of (X) was refluxed with 100 cc. of glacial acetic acid and 6 g. of sodium acetate for four hours. The cooled solution was decanted from the sodium bromide, concentrated to about one-third volume, and poured into 300 cc. of ice-cold water. On standing the material crystallized. Crystallization may be hastened by rubbing a part of the semi-solid mass with a little alcohol, and introducing the crystals into the main portion. The material was recrystallized from 30 cc. of 95% alcohol, and the crystals were washed with 10 cc. of ice-cold alcohol; yield, 3.5 g. A second crop of 5 g. of less pure material was obtained by working up the mother liquor.

1-Phenyl-1-hydroxy-2-(N-methyl-*p*-toluenesulfonamido)-ethane (XII).—The 3.5 g. of (XI) was dissolved in 25 cc. of absolute alcohol, and was treated with a solution of 0.6 g. of sodium hydroxide in 3 cc. of water. The resulting solution was heated on the water-bath for half an hour under reflux. The alcohol was then removed by evaporation, and to the residue water was added. The resultant oil was dissolved in benzene, washed with a little water, and the benzene solution was concentrated under reduced pressure. A pale-yellowish, thick oil remained. It was dried in the vacuum desiccator over sulfuric acid, but did not crystallize.

Methyl-(2-phenyl-2-hydroxyethyl)-amine.—A solution of 2 g. of (XII) in 60 cc. of amyl alcohol was brought to boiling, and 3.6 g. of sodium was added in small pieces. After the sodium had all dissolved, the amyl alcohol solution was shaken with 25 cc. of water to decompose the sodium amylate. The alcohol solution was separated and extracted several times with 5% hydrochloric acid. The combined hydrochloric acid extracts were evaporated on the water-bath to a small volume, extracted twice with ether to remove amyl alcohol, and made alkaline with solid potassium hydroxide. On cooling of the solution, the base separated in crystalline form. It was extracted with ether, the ether was distilled, and the solid residue was dried *in vacuo* over sulfuric acid. The yield was 0.8 g. (80% of the calculated).

1-Phenyl-2-(N-methyl-*p*-toluenesulfonamido)-ethylene (XIII).—A solution of 2.5 g. of (X) in 2.5 cc. of anhydrous quinoline was boiled for ten seconds. To the cooled solution was added dilute hydrochloric acid, and the crystalline precipitate was thoroughly washed with water. The material was crystallized from 25 cc. of alcohol; yield, 1.4 g., m. p. 106–107°. The alcoholic filtrate was examined for any possible isomers, but was found to contain the same compound in less pure form (m. p. 105°). The same compound was also prepared by treating a solution of 2.5 g. of (X) in 10 cc. of absolute alcohol, and refluxing for ten minutes with 15 cc. of a 3% solution of sodium ethoxide. Eight ml. of water was added to the hot solution; on cooling, 1.5 g. of white plates, m. p. 107°, was obtained.

Catalytic Reduction and Subsequent Hydrolysis to Methylphenethylamine.—A solution of 2.5 g. of (XIII) in 5 cc. of methyl alcohol was hydrogenated, with the aid of 0.8 g. of a 5% palladium–barium sulfate catalyst. In 10

minutes, 98 cc. of hydrogen (1 mole) was taken up, and absorption ceased. The alcohol was allowed to evaporate spontaneously. The residue was a sirup, which could not be brought to crystallization. It was heated with 6 cc. of concentrated hydrochloric acid at 150° for two hours. The contents of the tube were diluted with a little water, 0.5 g. of charcoal was added, and the mixture was filtered. Steam was passed into the filtrate until 50 cc. of distillate (which was discarded) had collected. The solution in the distilling flask was concentrated to a small volume on the water-bath, made alkaline, and steam-distilled until no more amine passed over (litmus). The volume of the distillate was about 50 cc. It was extracted with an equal volume of ether, the ethereal solution was washed with a little water, and dried over solid sodium hydroxide for two days. On passage of dry hydrogen chloride into the clear ethereal solution, the amine hydrochloride separated in the form of white plates. The precipitate was collected by filtration, washed with ether, and dried *in vacuo* over solid sodium hydroxide. The substance melted at 162°. It was not hygroscopic. The melting point of methylphenethylamine hydrochloride is reported by Johnson and Guest[4] as 152–154°, and by Decker and Becker[4] as 156–157°. Methyl-(1-phenylethyl)-amine hydrochloride is reported[5] to melt at 173°. To remove all doubt, the mercuric chloride double salt, the oxalate, and the urea derivative were prepared, the melting points of which were, respectively, 174, 186, and 143°. The corresponding melting points recorded in the literature[6] are 173, 184, and 141°.

Reduction of 1-Phenyl-1-bromo-2-(N-methyl-*p*-toluenesulfonamido)-ethane (X) with Sodium in Amyl Alcohol Solution.—The reduction was carried out in the manner described for the preparation of methyl-2-phenyl-2-hydroxyethylamine, excepting that the acid extract was not concentrated prior to the addition of alkali. Pure methyl-1-phenylethylamine hydrochloride, m. p. 162°, was obtained.

Reduction of 1-Phenyl-1-bromo-2-(N-methylbenzenesulfonamido)-ethane (IX) with Acid and Iron Filings.—In absolute alcoholic hydrogen chloride IX was reduced to the corresponding ethane with iron filings. The gummy product was then hydrolyzed with concentrated hydrochloric acid (two hours, 150°). The resultant methylphenethylamine hydrochloride was purified by solution in alcohol and precipitation with ether; m. p. 152–154°.

1-Phenyl-1-bromo-2-(N-benzylbenzenesulfonamido)-ethane (XIV).—To a solution of 5.0 g. of N-benzylbenzenesulfonamide dissolved in 25 cc. of chloroform, was added 3.4 g. of bromine. Immediately thereafter there was added a solution of 1.2 g. of sodium hydroxide in 15 cc. of water. After decolorization, the chloroform layer was separated and, without drying, was treated with 4 cc. of styrene. The solution was warmed a little on the water-bath, and the chloroform was removed in a stream of air. The residue was dissolved in 15 cc. of hot absolute alcohol. On cooling, an oil separated. The supernatant solution was decanted, the sirup was washed by decantation with a little alcohol, and was dried in the vacuum desiccator over sulfuric acid. Like the corresponding phenylsulfonylmethylamido compound, this substance did not crystallize, even on standing for several months in the ice-chest.

1-Phenyl-1-bromo-2-(N-benzyl-*p*-toluenesulfonamido)-ethane (XV).—This substance was prepared in exactly the same manner as XIV. A sirup was obtained, which, on standing for two days, crystallized; recrystallization from alcohol.

1-Phenyl-2-(N-benzyl-*p*-toluenesulfonamido)-ethylene (XVI).—A solution of 2.5 g. of (XV) in 25 cc. of 2% sodium ethoxide solution was boiled for one hour. Ten milliliters of hot water was added to the hot solution to redissolve the sodium bromide. The crystalline product that separated on cooling was crystallized from alcohol.

1-Phenyl-2-(N-benzyl-*p*-toluenesulfonamido)-ethane (XVII).—A suspension of 1.4 g. of (XVI) was hydrogenated with 1.5 g. of a 5% palladium–barium sulfate catalyst. In twenty minutes, the required 90 cc. of hydrogen was absorbed. Forty milliliters of benzene was added, the solution filtered from the catalyst, evaporated to dryness, and the residue recrystallized from alcohol.

Benzylphenethylamine.—A solution of 1.8 g. of (XVII) in 60 cc. of amyl alcohol was treated with 3 g. of metallic sodium, as described for the preparation of methyl-2-phenyl-2-hydroxyethylamine, with the exception that 10% sulfuric acid was used to extract the amine from the amyl alcohol solution, and the acid solution was made alkaline without preliminary concentration. The crude benzylphenethylamine hydrochloride isolated was purified by dissolving it in a little water and adding concentrated hydrochloric acid. Pure benzylphenethylamine hydrochloride separated.

1,1-Dimethyl-1-bromo-2-(N-methylbenzenesulfonamido)-ethane (XVIII).—A fairly rapid stream of isobutylene (generated from 5 g. of *t*-butyl alcohol and 5 g. of oxalic acid) was passed through a suspension of 5 g. of N-bromo-N-methylbenzenesulfonamide in 10 cc. of chloroform, at 40°, until a colorless solution resulted. This required about fifteen minutes. A special delivery tube with a large surface exposure was used. The chloroform was allowed to evaporate spontaneously, and the solid residue was recrystallized from 15 cc. of absolute alcohol; yield 4.8 g. This substance may also be prepared by treating liquefied isobutylene in a sealed tube, as described for (XIX).

1,1-Dimethyl-1-bromo-2-(N-methyl-*p*-toluenesulfonamido)-ethane (XIX).—Eight grams of liquefied isobutylene was sealed with 10 g. of N-bromo-N-methyl-*p*-toluenesulfonamide, and the contents were allowed to reach room temperature. After all the bromo compound had dissolved, and the solution was colorless, the tube was cooled in a dry ice–acetone mixture and opened. The excess isobutylene was allowed to escape and the solid residue was recrystallized from 30 cc. of absolute alcohol; yield 9.7 g.

1,1-Dimethyl-2-(N-methylbenzenesulfonamido)-ethylene or 1-Methyl-1-methylene-2-(N-methylbenzenesulfonamido)-ethane (XX).—A solution of 8.4 g. of XVIII in 16 cc. of dry quinoline was boiled for one minute. The solution was then cooled, and acidified with dilute hydrochloric acid, and the oil was extracted with ether. The

(4) Johnson and Guest, *Am. Chem. J.*, **42**, 350 (1909); Becker and Decker, *Ann.*, **395**, 368 (1913).

(5) "Beilstein," 4th ed., Vol. XII, p. 1094.

(6) Johnson and Guest, *Am. Chem. J.*, **42**, 350 (1909).

ethereal solution was dried with calcium chloride and the ether removed by distillation. The residue was distilled *in vacuo*, and practically all of it passed over at 203° at 21 mm. The yield was 3.8 g. of a colorless, viscous oil. The substance reduced permanganate, absorbed bromine, and showed all the reactions of a double bond, including hydrogenation, described below.

Catalytic Reduction of XX, and Hydrolysis to Methylisobutylamine.—A solution of 0.87 g. of (XX) in 6 cc. of alcohol was reduced, with the aid of 0.046 g. of platinum oxide catalyst (Adams). In five minutes, 85 cc., or the theoretical molecular equivalent of hydrogen was absorbed, and further shaking produced no more absorption. The solution was filtered from the catalyst, and the alcohol was distilled. The residue from 2.0 g. of reduced substance was heated with 10 cc. of concentrated hydrochloric acid for two hours at 150°. The amine hydrochloride was isolated as described in the case of the styrene addition product (XI). The substance melted at 178°, which is the melting point recorded in the literature for methylisobutylamine hydrochloride; the melting point of the prepared chloroplatinate (192°) is also in agreement with that recorded. The substance was extremely hygroscopic.

1,1 - Dimethyl - 1 - bromo - 2 - (N-methylbenzylsulfonamido)-ethane (XXI).—Two grams of N-bromo-N-methylbenzylsulfonamide, 6 cc. of chloroform, and 2 cc. of liquid isobutylene were sealed in a Pyrex tube, and the mixture brought to 40°. When the solution had become colorless, the tube was opened, and excess isobutylene allowed to escape. The chloroform was allowed to evaporate spontaneously, and the residue was recrystallized from 40 cc. of absolute alcohol; yield 1.5 g.

1,1-Dimethyl-2-(N-methylbenzylsulfonamido)-ethylene or 1 - Methyl - 1-methylene - 2 - (N - methylbenzylsulfonamido)-ethane (XXII).—On treatment of (XXI) with quinoline, in the usual manner, hydrogen bromide was eliminated, and the unsaturated compound was formed. The substance (XXII) was hydrogenated with platinum oxide (Adams) in alcohol solution, in the usual manner. The resultant N-methyl-N-isobutylbenzylsulfonamide melted at 83°.

1-Bromo-1-chloro-2-(N-methylbenzenesulfonamido)-ethane (XXIII).—Vinyl chloride (15 g.) and 26 g. of N-bromo-N-methylbenzylsulfonamide were sealed up and kept at room temperature until the next day. A colorless solution resulted. Excess vinyl chloride was allowed to escape, and the residue was crystallized from 125 cc. of 95% alcohol; yield 26 g.

1-Bromo-1-chloro-2-(N-methyl-*p*-toluenesulfonamido)-ethane (XXIV).—This substance was prepared in the manner described above.

1 - Chloro - 2 - (N - methyl - *p* - toluenesulfonamido)-ethylene (XXV).—A solution of 1 g. of XXIV in 5 cc. of absolute alcohol was refluxed for fifty minutes with 5 cc. of an alcoholic solution containing 2% of sodium ethoxide. Excess alcohol was removed on the water-bath. To the residue was added water and ether; the ethereal solution was separated and dried with sodium sulfate. The ether was distilled, and the oil was transferred to a desiccator. Several days later it solidified. The material, recrystallized from alcohol, melted at 91°. With the crystalline material at hand, the substance was readily prepared by heating XXIV with sodium ethoxide solution, as described above. After the refluxing was over, water was added to the warm solution to redissolve the inorganic salts, and a crystal was dropped in. On cooling, the substance of m. p. 91° separated.

1 - (N - Methyl - *p* - toluenesulfonamido) - 2 - bromopropane (XXVI).—Ten grams of N-bromo-N-methyl-*p*-toluenesulfonamide was sealed with 10 cc. of liquid propylene and 30 cc. of chloroform. After it had reached room temperature, the bomb tube was heated in a water-bath at 70–80° until the contents became colorless, which required about thirty to forty minutes. Excess propylene was allowed to escape, the chloroform was removed by distillation on the water-bath, and the residue was recrystallized from 40 cc. of absolute alcohol; yield 8.5 g.

Removal of Hydrogen Bromide from XXVI, Catalytic Hydrogenation and Subsequent Hydrolysis to Methylpropylamine.—Eight grams of the addition product XXVI was heated on the water-bath under reflux for two hours with 60 cc. of a 2% sodium ethylate solution in alcohol. The product was then worked up as described in the case of XXV. Evaporation of the ether left a semi-solid mass. The solid could be separated from the oily portion with filter paper. It melted at 54–56.

The oily portion contained 6.12% nitrogen. At 20 mm. the mixture distilled within the range 195–205°. Apparently, we are dealing here with two isomers of the formula $C_{11}H_{15}O_2NS$; $CH_2{=}CHCH_2NCH_3SO_2C_6H_4CH_3$(B) and $CH_3CH{=}CHNCH_3SO_2C_6H_4CH_3$(A). A solution of 1.37 g. of the semi-solid in 8 cc. of methyl alcohol was hydrogenated, with the aid 1.3 g. of 5% palladium–barium sulfate catalyst. After two and one-half hours, 123 cc. of nitrogen was absorbed, or about 90% of the theoretical quantity, for one double bond. After evaporation of the alcohol, the N-methyl-N-*n*-propyl-*p*-toluenesulfonamide was obtained in crystalline form.

One gram of the substance was hydrolyzed, as described previously in the case of the styrene product. The hydrochloride melted at 150°, which is in agreement with the melting point recorded in the literature[7] for methyl-*n*-propylamine hydrochloride. The hydrochloride of methylisopropylamine melts at 77°.

1 - Phenyl - 1 - *p* - toluenesulfonamido - 2 - bromoethane (II).—In an attempted preparation of N-bromo-N-acetyl-*p*-toluenesulfonamide, from N-acetyl-*p*-toluenesulfonamide and sodium hypobromite, N,N-dibromo-*p*-toluenesulfonamide, previously prepared by Chattaway, was obtained. This on interaction with styrene produced simultaneous bromination and addition. The brominated styrene remained in the chloroform solution, and the difficultly soluble addition product separated.

The addition product was conveniently prepared as follows: to 11.5 g. of *p*-toluenesulfonamide was added 6.9 cc. of bromine, the two components being intimately mixed, and then, with cooling and stirring, 27 cc. of 20% sodium hydroxide was added gradually from a separatory funnel. The lower layer containing the reaction product was dissolved in 60 cc. of lukewarm chloroform, and the chloroform layer was separated from the alkaline solution. To the chloroform solution, which was not dried, there was added drop by drop from a buret, at first with cooling and

(7) Chattaway, *J. Chem. Soc.*, **87**, 164 (1905).

stirring, 15 cc. of styrene. Toward the end of the addition, the solution was allowed to warm up, so as to complete the reaction. Usually, a small amount of a yellow substance precipitated from the hot solution toward the end of the styrene addition. This is the sodium salt of the monobromosulfonamide, which is later removed from the addition product by washing with alcohol. On cooling of the chloroform solution with ice water, the addition product separated. It was collected on a filter, washed with 20 cc. of ice-cold chloroform, and then with 30 cc. of cold absolute alcohol, and air-dried. The yield was 14.0 g. of substance, m. p. 163°, which, for the conversion into the imine, is sufficiently pure. Another 4 g. of addition product was obtained by evaporation of the filtrate to dryness, washing of the semi-solid residue with ice-cold alcohol, and recrystallization from alcohol. The bromine in the addition product is held rather firmly; none of it is precipitated by alcoholic silver nitrate solution in the course of twenty-four hours. In the corresponding methylamido addition product (X), the bromine, being attached to a carbon atom holding a phenyl group, is precipitated practically quantitatively during the first five minutes by alcoholic silver nitrate solution. Again, whereas the methylamido compound readily yielded an acetate on heating with sodium acetate and glacial acetic acid for four hours, the amido compound (II), is recovered practically unchanged under the same conditions.

1 - *p* - Anisyl - 1 - *p* - toluenesulfonamido - 2 - bromopropane (XXVII).—To a chloroform solution of the dibromoamide, prepared exactly as described above, was added, with cooling and stirring, 12 cc. of anethole. After the reaction was complete, the solution was cooled in ice water, and the product worked up as in the case of the styrene product.

1 - (3,4 - Methylenedioxyphenyl) - 1 - *p* - toluenesulfonamido - 2 - bromopropane (XXVIII).—The addition product was prepared as described above, from 12 cc. of isosafrole, and the dibromoamide was prepared from 11.5 g. of *p*-toluenesulfonamide. The chloroform solution was set aside in the ice chest for twenty-four hours, since crystallization proceeded very slowly.

1 - Phenyl - 1 - bromo - 2 - [N - (1 - phenyl - 2 - bromoethyl) - *p* - toluenesulfonamido]- ethane (VIII). (Interaction of the Bromo Derivative of 1-Phenyl-1-*p*-toluenesulfonamido-2-bromoethane with Styrene.)—To a solution of 3.5 g. of VI was added 2.5 g. of bromine and then 20% sodium hydroxide solution, drop by drop until almost all the free bromine had disappeared. A trace of free bromine was allowed to remain. At this point, 1.0 g. of unchanged starting material, m. p. 167°, precipitated. It was removed by filtration, and to the chloroform filtrate 1 cc. of styrene was added. The solution was warmed slightly on the water-bath, and the chloroform was removed by a stream of air. The residue still contained "positive" bromine (potassium iodide test). One milliliter of styrene was added, and the mixture was warmed on the water-bath until a test with potassium iodide showed the absence of "positive" halogen. The residue was dissolved in a little chloroform and ligroin was added. The precipitate was recrystallized several times from alcohol.

N-(*p*-Tolylsulfonyl)-styreneimine (IV).—A suspension of 11.5 g. of the styrene addition product (II), m. p. 167°, in 40 cc. of alcohol was brought to boiling on the water-bath. There was then rapidly added, from a pipet, 8 cc. of 20% aqueous sodium hydroxide solution. The addition product dissolved completely. To the hot solution, 8 cc. of warm water was added. On cooling the solution, styreneimine crystallized in glistening plates; yield 8.6 g. An acetone solution of the substance did not decolorize a solution of permanganate in acetone.

1 - Phenyl - 1 - halo - 2 - *p* - toluenesulfonamidoethanes (XXIX-XXXI).—A solution of 1 g. IV in 35 cc. of ether was shaken with 15 cc. of an aqueous hydrobromic acid solution. The ether was allowed to evaporate spontaneously, and the residue was washed with ice-cold alcohol. The addition product (XXIX) crystallized in needles. The corresponding chloro (XXX) and iodo (XXXI) ethanes were also prepared.

Catalytic Hydrogenation of N-(*p*-Tolylsulfonyl)-styreneimine (IV).—A suspension of 2.0 g. of the imine in 6 cc. of methyl alcohol was subjected to hydrogenation, with the aid of 0.5 g. of a 5% palladium–barium sulfate catalyst. In forty-five minutes, the calculated amount of hydrogen (172 cc.) was absorbed, and further treatment caused no more hydrogen to be taken up. The solution was filtered and washed with methyl alcohol, and the filtrate was evaporated to dryness. The N-phenethyl-*p*-toluenesulfonamide (XXXII) was left behind in the form of needles, m. p. 67°. The melting point recorded in the literature is 65–66°.

Hydrolysis of N - Phenethyl - *p* - toluenesulfonamide (XXXII).—On heating 0.7 g. of (XXXII) with 6 cc. of concentrated hydrochloric acid at 150° for two hours, the substance was recovered unchanged. The heating was then repeated for another two hours at 170°, and the hydrochloride of phenethylamine, m. p. 217°, was recovered.

Phenethylamine was obtained in one step by treating IV with an excess of sodium in boiling amyl alcohol solution, in the manner previously described. The same result was obtained by subjecting the styrene addition product (II) to the action of sodium and boiling amyl alcohol.

Treatment of the isosafrole addition product (XXVII), with sodium and amyl alcohol, gave aminoisosafrole; m. p. of hydrochloride 183°.

1-Phenyl-1-bromo-2-(N-phenethyl-*p*-toluenesulfonamido)-ethane (XXXIII).—One gram of XXXII, obtained from the catalytic reduction of IV, was dissolved in 10 cc. of chloroform, and treated successively with 1.2 g. of bromine and 0.6 g. of sodium hydroxide in 10 cc. of water. The chloroform solution was separated and treated with 0.5 cc. of styrene. The chloroform was removed in a stream of air, to the residue was added 0.2 cc. more of styrene, and the mixture was warmed for two to three minutes. It was then dissolved in 4 cc. of absolute alcohol. On cooling, a gum separated. After standing for several days in the ice chest, it solidified. The material was recrystallized several times from alcohol.

N - (2 - Phenyl - 2 - hydroxyethyl) - *p* - toluenesulfonamide (XXXIV).—A suspension of 0.2 g. of IV in 150 cc. of water was boiled under reflux for two hours. On cooling, white needles crystallized.

1 - Phenyl - 1 - trichloroacetoxy - 2 - *p* - toluenesulfonamidoethane (XXXV).—A mixture of 10 g. of IV and 10 g. of trichloroacetic acid was warmed on the water-bath until a homogeneous solution resulted. The gum was poured

in a thin stream into 100 cc. of water contained in a large mortar. The gum was rubbed with a pestle, the supernatant liquor being replaced with fresh water, until crystallization took place. The material, after several recrystallizations from alcohol, melted at 125°. The compound was stable toward boiling water or alcohol but hydrolyzed by alkali to XXXIV.

1 - Phenyl - 1 - ethoxy - 2 - *p* - toluenesulfonamidoethane (XXXVI).—One gram of IV was added to 7 cc. of absolute alcohol which contained 12 drops of concentrated sulfuric acid. The substance immediately dissolved with the evolution of heat. On cooling and scratching of the walls of the container with a glass rod, a precipitate separated. It was collected by filtration and washed with 5 cc. of ice-cold alcohol.

1 - Phenyl - 1 - crotonoxy - 2 - *p* - toluenesulfonamidoethane (XXXVII).—A mixture of 1 g. of IV with 2 g. of crotonic acid was heated at 160° for five minutes. A test

TABLE I

ADDITION COMPOUNDS, [a] THEIR DERIVATIVES, AND [b] CLEAVAGE PRODUCTS

Substance	M. p., °C.	Analyses, % Nitrogen Calcd.	Nitrogen Found	Halogen Calcd.	Halogen Found
1-Phenyl-1-bromo-2-(N-methylbenzenesulfonamido)-ethane (IX)	Sirup	3.95	4.03	22.6	22.6
1-Phenyl-1-bromo-2-(N-methyl-*p*-toluenesulfonamido)-ethane (X)	67	3.80	3.98	21.74	22.60
1-Phenyl-1-acetoxy-2-(N-methyl-*p*-toluenesulfonamido)-ethane (XI)[a]	94	4.03	3.81	...	...
1-Phenyl-1-hydroxy-2-(N-methyl-*p*-toluenesulfonamido)-ethane (XII)[a]	Oil	...	...	...	...
Methyl-(2-phenyl-2-hydroxyethyl)-amine[b]	78	9.27	9.33	...	...
1-Phenyl-2-(N-methyl-*p*-toluenesulfonamido)-ethylene (XIII)[a]	106–7	4.88	4.97	...	...
Methylphenethylamine hydrochloride[b]	162	8.17	8.23	...	...
1-Phenyl-1-bromo-2-(N-benzylbenzenesulfonamido)-ethane (XIV)	Sirup	3.27	3.51	...	...
1-Phenyl-1-bromo-2-(N-benzyl-*p*-toluenesulfonamido)-ethane (XV)	99	3.15	2.92	...	...
1-Phenyl-2-(N-benzyl-*p*-toluenesulfonamido)-ethylene (XVI)[a]	122	3.85	3.94	...	...
1-Phenyl-2-(N-benzyl-*p*-toluenesulfonamido)-ethane (XVII)[a]	105	3.85	4.00	...	...
Benzylphenethylamine hydrochloride[b]	265	...	...	...	...
1,1-Dimethyl-1-bromo-2-(N-methylbenzenesulfonamido)-ethane (XVIII)	95	4.57	4.64	26.1	25.4
1,1-Dimethyl-1-bromo-2-(N-methyl-*p*-toluenesulfonamido)-ethane (XIX)	93	4.37	4.49	25.8	25.2
1,1-Dimethyl-2-(N-methylbenzenesulfonamido)-ethylene (XX)[a] or 1-methyl-1-methylene-2-(N-methylbenzenesulfonamido)-ethane	Oil	6.27	6.44	...	...
Methylisobutylamine hydrochloride[b]	178	11.33	11.34	...	...
1,1-Dimethyl-1-bromo-2-(N-methylbenzylsulfonamido)-ethane (XXI)	123	4.37	4.29	...	...
1,1-Dimethyl-2-(N-methylbenzylsulfonamido)-ethylene (XXII)[a] or 1-methyl-1-methylene-2-(N-methylbenzylsulfonamido)-ethane	60	5.85	5.81	...	...
N-Methyl-N-isobutylbenzylsulfonylamide[a]	83	5.81	5.77	...	...
1-Bromo-1-chloro-2-(N-methylbenzenesulfonamido)-ethane (XXIII)	90	4.48	4.55	...	...
1-Bromo-1-chloro-2-(N-methyl-*p*-toluenesulfonamido)-ethane (XXIV)	90	4.28	4.41	35.33	34.49
1-Chloro-2-(N-methyl-*p*-toluenesulfonamido)-ethylene (XXV)[a]	91	5.70	5.78	14.44	14.05
1-(N-Methyl-*p*-toluenesulfonamido)-2-bromopropane (XXVI)	92	4.58	4.56	...	...
1-(N-Methyl-*p*-toluenesulfonamido)-propylene[a] (A)	54–56	6.22	6.16	...	...
and 3-(N-methyl-*p*-toluenesulfonamido)-propylene (B)	Oil	6.22	6.12	...	...
N-Methyl-N-*n*-propyl-*p*-toluenesulfonamide[a]	40	6.16	6.17	...	...
Methyl-*n*-propylamine hydrochloride[b]	150	12.78	12.60	...	...
1-Phenyl-1-*p*-toluenesulfonamido-2-bromoethane (II)	167	3.95	3.97	...	...
N-(*p*-Tolylsulfonyl)-styreneimine (IV)[a]	95	5.13	5.22	...	...
N-(2-Phenyl-2-hydroxyethyl)-*p*-toluenesulfonamide (XXXIV)[a]	113	4.91	4.89	...	...
2-Phenyl-2-hydroxyethylamine picrate[b]	158	15.30	15.56	...	...
1-Phenyl-1-trichloroacetoxy-2-*p*-toluenesulfonamidoethane (XXXV)[a]	125	3.20	3.47	24.4	23.5
1-Phenyl-1-ethoxy-2-*p*-toluenesulfonamidoethane (XXXVI)[a]	106	4.07	4.30	...	...
1-Phenyl-1-crotonoxy-2-*p*-toluenesulfonamidoethane (XXXVII)[a]	85	3.92	3.93	...	...
1-Phenyl-1-acetoxy-2-*p*-toluenesulfonamidoethane (XXXVIII)[a]	105	...	...	...	...
1-Phenyl-1-bromo-2-*p*-toluenesulfonamidoethane (XXIX)[a]	111	3.95	4.22	...	...
1-Phenyl-1-chloro-2-*p*-toluenesulfonamidoethane (XXX)[a]	95	4.52	4.77	...	...
1-Phenyl-1-iodo-2-*p*-toluenesulfonamidoethane (XXXI)[a]	137	3.49	3.66	...	...
N-Phenethyl-*p*-toluenesulfonamide (XXXII)[a]	67	...	...	...	...
Phenethylamine hydrochloride[b]	217	8.88	8.94	...	...
1-*p*-Anisyl-1-*p*-toluenesulfonamido-2-bromopropane (XXVII)	167	3.95	3.97	...	...
1-(3,4-Methylenedioxyphenyl)-1-*p*-toluenesulfonamido-2-bromopropane (XXVIII)	153	3.40	3.51	...	...
1-Phenyl-1-bromo-2-[N-(1-phenyl-2-bromoethyl)-*p*-toluenesulfonamido]-ethane (VIII)	158	2.60	2.69	...	...
1-Phenyl-1-bromo-2-(N-phenethyl-*p*-toluenesulfonamido)-ethane (XXXIII)	97	3.05	3.09	...	...

with the cooled material showed it to be completely soluble in alkali. The reaction product was treated with sodium carbonate solution, to remove unchanged crotonic acid, the residue was washed with water, and recrystallized from alcohol. When the crotonate was heated on the water-bath for fifteen minutes with 10% sodium hydroxide, and the solution acidified, XXXIV (m. p. 113°) separated.

1 - Phenyl - 1 - acetoxy - 2 - *p* - toluenesulfonamidoethane (XXXVIII).—A solution of 55 g. of IV in 100 cc. of glacial acetic acid was warmed on the water-bath until a test portion showed it to be completely soluble in alkali. This required thirty minutes. Too much heating renders the isolation of a crystalline acetate a difficult matter. The solution was poured in a fine stream into a liter of ice water. After standing for thirty minutes, the crystals were collected by filtration and air-dried. The yield was 65 g. (97% of the theoretical); m. p. 105°. The same acetate was obtained by refluxing for six hours 1 g. of XXIX (m. p. 111°) with 0.4 g. of anhydrous sodium acetate in 10 cc. of glacial acetic acid.

2-Phenyl-2-hydroxyethylamine.—A solution of 10 g. of XXXIV in 250 cc. of amyl alcohol was brought to boiling, and 18 g. of metallic sodium gradually added. The solution was then worked up in the usual manner. The amine was recovered in the form of a semi-solid mass, which when exposed to carbon dioxide yielded the known carbonate, m. p. 115°. The picrate melted at 158°.

Summary

1. Halosulfonamides of the type $R'SO_2NBrR$ react with a large number of olefins to yield products in which the bromine atom takes the same position as the bromine atom in the "normal" addition of hydrogen bromide to these substances.

2. The N,N-dibromosulfonamides, on the other hand, add to olefins to give products in which the bromine atom takes the same position as the bromine atom in the "abnormal" addition of hydrogen bromide to these compounds.

3. The preparation of N-(*p*-tolylsulfonyl)-styreneimine and its reactions with various reagents are reported.

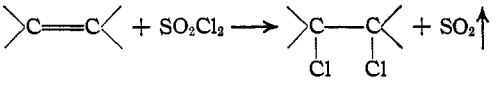
CHICAGO, ILLINOIS RECEIVED AUGUST 31, 1939

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Chlorinations with Sulfuryl Chloride. II. The Peroxide-Catalyzed Reaction of Sulfuryl Chloride with Ethylenic Compounds

BY M. S. KHARASCH AND HERBERT C. BROWN[1]

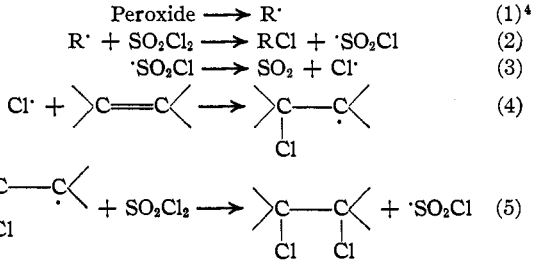
Sulfuryl chloride reacts readily with most ethylenic compounds to yield the saturated dichloro derivatives and sulfur dioxide.



Although this reaction has been used for synthetic purposes,[2] no thorough study has been made of the factors which control these additions.

We have previously shown that the presence of small quantities of organic peroxides brings about a reaction between sulfuryl chloride and saturated aliphatic hydrocarbons.[3] The characteristics of the reaction of sulfuryl chloride with olefins led us to suspect that this reaction is also peroxide-catalyzed. Investigation has confirmed this belief, and the evidence we have obtained indicates that the mechanism of this reaction is similar to that involved in the peroxide-catalyzed reaction of sulfuryl chloride with aliphatic hydrocarbons, a chain reaction involving chlorine atoms.

The following mechanism is in full agreement with the experimental facts and is advanced as representing the most probable course of the reaction in the light of our present-day information.



That the reaction is peroxide-catalyzed is indicated by a number of observations. Thus, an old sample of cyclohexene (which gave a strong test for peroxides) reacted with sulfuryl chloride with explosive violence when the two substances were mixed at room temperature. When the

(1) Eli Lilly Fellow, 1938–1939.

(2) A search of the literature reveals the use of sulfuryl chloride for the chlorination of unsaturated substances in the following instances: (a) chlorination of tetraphenylethylene and its derivatives, Norris, Thomas and Brown, *Ber.*, **43**, 2949 (1910); (b) chlorination of cinnamic acid and cinnamyl aldehyde, Durrans, *J. Chem. Soc.*, **123**, 1424 (1923); (c) chlorination of cyclohexene, Frieze and Djiang, *Ber.*, **71**, 667 (1938); and (d) chlorination of 3-hexene, Spiegler and Tinker, THIS JOURNAL, **61**, 940 (1939).

(3) Kharasch and Brown, *ibid.*, **61**, 2142 (1939).

(4) The dot denotes an unshared electron. The evidence for the assumption that the catalytic effect of peroxides in these chlorinations is due to their decomposition into organic free radicals, is discussed in the first paper of this series: *ibid.*, **61**, 2149 (1939).