were employed. The spectra of the liquid ethers and phenols were determined from thin films of the pure liquids, whereas the urethans were used as mulls in perfluorokerosene.

CORVALLIS, OREGON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Unsaturated Sulfonic Acids. IV. Preparation and Properties of α-Bromoalkenesulfonyl Chlorides

BY CHRISTIAN S. RONDESTVEDT, JR.[1]

RECEIVED NOVEMBER 18, 1953

Unsaturated sulfonyl chlorides are readily prepared in good yields from β-chlorosulfonyl chlorides (from β-hydroxysulfonic acids) through the action of hindered bases at low temperatures. Unsaturated sulfonamides are available through reaction with amines, using low temperatures to suppress the competing addition to the double bond. Bromine adds to the chlorides in non-polar media to form dibromides which can be smoothly dehydrobrominated to α-bromo-α,β-unsaturated sulfonyl chlorides by hindered bases at low temperatures. α-Bromoethylenesulfonyl chloride reacts with triethylamine at −70° to form an unidentified compound, possibly acetylenesulfonyl chloride. α-Bromostyrenesulfonyl chloride reacts sluggishly with bases to eliminate (at least partially) the sulfo group; this effect is ascribed to its geometrical configuration.

Previous work with unsaturated sulfonic acids[2] indicated that its extension to acetylenic sulfonic acids would be of considerable interest. Accordingly, it was necessary to devise a synthetic procedure. There is only one report on an acetylenic sulfonic acid,[3] and the evidence for its structure is only an analysis. It seems likely that the product obtained was derived by addition to the acetylenic triple bond rather than by hydrogen substitution. Accordingly, we sought other methods of synthesis.

An attempt to sulfonate phenylacetylene with dioxane–sulfotrioxide was unsuccessful. The bulk of the sulfur trioxide was converted to forms other than sulfate, but it was not possible to isolate a pure unsaturated sodium salt. The reaction of sodium phenylacetylide with dioxide–sulfotrioxide was likewise unsuccessful. A further study of these sulfonations is being made. Metal phenylacetylides did not appear to react with sulfur dioxide under standard sulfination conditions.

It then seemed reasonable to attempt the introduction of a triple bond by the dehydrobromination of either an α,β-dibromoalkanesulfonic acid or an α- or β-bromoalkenesulfonic acid. Accordingly, attention was turned to the synthesis and reactions of these compounds. It was previously known that α,β-unsaturated sulfonic acids were brominated rapidly in aqueous solution by substitution at the position *alpha* to the sulfo group.[4,5] On the other hand, styrenesulfonyl chloride and styrenesulfonamide had been shown to brominate only slowly in carbon tetrachloride or acetic acid by (presumably) a free-radical mechanism. The products are dibromides which eliminate hydrogen bromide on treatment with base. It was known that dehydrobromination of α-bromoethylenesulfonic acid[5] or α-bromostyrenesulfonic acid[6,7] by the action of alkalies converted either compound largely into tarry materials and liberated sulfite ion. However, it seemed that dehydrobromination of a covalent derivative of the sulfonic acid might be successful.

Bromination and Dehydrobromination.—It was known that addition of bromine to styrenesulfonyl chloride in carbon tetrachloride solution is strongly light catalyzed and appears to be oxygen catalyzed.[4] In the dark, no visible reaction occurred in fifteen days, and we found that addition was not accelerated by iodine. In ordinary room fluorescent illumination, the addition of one mole of bromine to the double bond was substantially complete in four to eight hours; under direct illumination by a 50-watt bulb, only an hour was needed. Oxygen is actually an anticatalyst for the bromination in carbon tetrachloride or acetic acid solution since, when the separate solutions of styrenesulfonyl chloride and bromine in carbon tetrachloride or acetic acid were first deaerated by bubbling nitrogen through them, the addition required only ten minutes.[8] The oily dibromide could not be induced to crystallize, but it could be converted to α-bromostyrenesulfonyl chloride by 2,6-lutidine or triethylamine. The crystalline unsaturated bromosulfonyl chloride (82% yield) formed an amide identical with that prepared in low yield from sodium α-bromostyrenesulfonate by the action of phosphorus pentachloride and ammonia.[6]

Ethylenesulfonyl chloride added bromine more rapidly than its phenylated analog. In this case, the dibromide could be isolated by distillation (with partial dehydrobromination). The crude material was also converted directly into α-bromoethylenesulfonyl chloride, by the action of 2,6-lutidine in ether at −50°, in 68% yield based on ethylenesulfonyl chloride.

Further Dehydrobromination.—α-Bromoethylenesulfonyl chloride in absolute ether at −70° reacted vigorously with triethylamine to precipitate triethylamine hydrobromide. The filtrate upon

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[1] The author is indebted to the Horace H. Rackham School of Graduate Studies for a Summer Faculty Research Fellowship which made possible this work. Presented before the Los Angeles meeting of the American Chemical Society, March, 1953.

[2] C. S. Rondestvedt, Jr., and J. C. Wygant, THIS JOURNAL, **76**, 509 (1954), and previous papers.

[3] F. Krafft and G. Heizmann, *Ber.*, **33**, 3586 (1900). *Cf.* C. M. Suter, "Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 175.

[4] F. G. Bordwell and C. S. Rondestvedt, Jr., THIS JOURNAL, **70**, 2429 (1948).

[5] E. P. Kohler, *Am. Chem. J.*, **21**, 349 (1899).

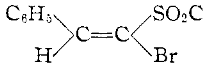
[6] W. E. Truce, Ph.D. thesis, Northwestern University, 1943.

[7] T. Y. Yu, unpublished experiments in this Laboratory.

[8] C. D. Ver Nooy and R. L. Grimsley, unpublished results in this Laboratory.

distillation yielded a violently lachrymatory liquid of approximately the same boiling point as ethylenesulfonyl chloride. The infrared spectrum showed no band in the $HC\equiv C$— region at 4.4–4.6 μ, but it was quite different from the spectra of ethylenesulfonyl chloride and α-bromoethylenesulfonyl chloride. Although satisfactory analyses could not be obtained upon this material, the boiling point indicated that it might be impure acetylenesulfonyl chloride. Attempts to prepare derivatives of this compound have, so far, been unsuccessful.

α-Bromostyrenesulfonyl chloride did not react with hindered bases at low temperature. At temperatures approximating 50°, there was a slow reaction with the liberation of sulfite, chloride and bromide ions, and a small quantity of β-bromostyrene was obtained. However, there was no evidence of phenylacetylenesulfonyl chloride. Sodium α-bromostyrenesulfonate is not readily attacked by weak bases (compare ref. 6 and 7 where alkali was used), but heating with 2,6-lutidine caused slow decomposition. These results are evidence in favor of the geometrical configuration shown in structure I, in which the hydrogen and bromine atoms are *cis* to each other. This configuration is that expected from *trans* addition of bromine to *trans*-styrenesulfonyl chloride, followed by *trans* dehydrobromination. However, the stereochemistry of addition of bromine *atoms* to double bonds has not been established. Elimination is well-known to occur much more readily from a *trans* than a *cis* configuration, and the fact that the more vigorous conditions partially eliminate the sulfonyl group is further support for this contention. It will be verified by preparation of the geometrical isomer of I from *cis*-styrene sulfonic acid.[9]



I

Preparation of Ethylenesulfonyl Chloride and its Derivatives.—Ethylenesulfonyl chloride has been prepared previously[10] in low yields by a rather tedious procedure. We found that β-chloroethanesulfonyl chloride (prepared from commercial sodium isethionate[11] by the action of phosphorus pentachloride[12]) can be converted to ethylenesulfonyl chloride in approximately 70% yield by the action of 2,6-lutidine in dry ether at $-50°$. Lower yields were obtained with the less hindered pyridine. Sodium isethionate and its homologs are readily prepared from sodium bisulfite and alkylene oxides[13] and their conversion to chlorosulfonyl chlorides is smooth. In contrast, the previous method involving the preparation of ammonium ethylenesulfonate is quite inconvenient. An entirely similar procedure gives the homolog, propene-1-sulfonyl chloride, although in somewhat lower yields.[14]

Although styrenesulfonamides are easily prepared,[2,15] the preparation of ethylenesulfonamides is far more difficult because of the pronounced tendency for addition of ammonia or an aliphatic amine to the double bond, besides reaction with the sulfonyl chloride group.[12] We prepared N,N-diethylethylenesulfonamide from molar quantities of diethylamine and triethylamine and ethylenesulfonyl chloride at $-70°$ in 47% yield. An analogous procedure has been used for the homologous amide.[14] Ethylenesulfonanilide was prepared from β-chloroethanesulfonyl chloride and aniline in the presence of two moles of triethylamine at $-55°$. The yield was slightly better than previously reported.[12]

Ethylenesulfonate esters have been previously made by essentially this procedure at 0°,[16] although in low yields. Unfortunately, yields of the methyl and butyl esters were not significantly higher at $-50°$ than at 0°.

Experimental

Sulfination of Metal Phenylacetylides.—Lithium phenylacetylide was prepared from β-bromostyrene by the method of Curtin and Harris[17] or from phenylacetylene by the action of lithium amide in ether or dioxane solution.[18] When excess sulfur dioxide was passed into the suspension of the acetylide in ether at -20 to $-50°$ and the mixture was hydrolyzed, acidification of the aqueous layer produced no precipitate of the expected phenylacetylenesulfinic acid nor was any found by ether extraction. Most of the phenylacetylene was recovered from the original ether layer.

A suspension of sodium phenylacetylide in ether was saturated with sulfur dioxide at 0° for one hour. The ether was evaporated and alcohol extraction of the residue gave, after evaporation, a small amount of solid. The latter did not form a sulfone with *p*-nitrobromobenzene nor did it react rapidly with permanganate.[19]

Sulfonation of Phenylacetylene.—Phenylacetylene was sulfonated with a suspension of dioxane sulfotrioxide[4] at 0°. When the clear solution was worked up with barium hydroxide and the soluble barium salts were converted to sodium salts by metathesis, a small amount of material soluble in absolute alcohol was obtained. This material was water soluble and gave no precipitate with barium chloride; it contained 9.7% sodium and formed a benzylthiuronium salt, m.p. 216–218°.[20] Since the compound reduced potassium permanganate only slowly, it apparently was not an unsaturated sulfonate.

A second sulfonation was carried out in 0.5 *M* ethylene chloride *solution* at $-35°$. After hydrolysis, bromate–bromide titration of the aqueous phase indicated that 3.6% had formed water-soluble unsaturated material. There was found as barium sulfate 6.2% of the sulfur trioxide charged, and the solution decolorized permanganate. Neutralization and evaporation of the aqueous phase, followed by extraction with 95% alcohol gave a tan solid which decolorized permanganate and bromine. A sample of this solid was converted to a benzylthiuronium salt in fair yield, m.p. 125–130°. This, on recrystallization from aqueous ethanol, melted at 111–113°.

When a suspension of sodium phenylacetylide in ether was treated with 0.5 *M* dioxane sulfotrioxide in ethylene chloride at $-60°$, there was no vigorous reaction. On processing in the usual way, about 65% of the phenylacetyl-

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[9] A. P. Terent'ev, R. A. Gracheva and Z. F. Shcherbatova, *Dokl. Akad. Nauk S.S.S.R.*, **84**, 975 (1952); *C. A.*, **47**, 3262e (1953).

[10] E. F. Landau, THIS JOURNAL, **69**, 1219 (1947).

[11] I am indebted to the Wyandotte Chemical Corporation for a generous supply of sodium isethionate.

[12] A. Goldberg, *J. Chem. Soc.*, 464 (1945).

[13] *Cf.* R. T. E. Schenck and S. Kaizerman, THIS JOURNAL, **75**, 1636 (1953), for a discussion of the structures of the hydroxysulfonates.

[14] P. K. Chang and P. A. McVeigh, unpublished work in this Laboratory The structure was proved by infrared spectroscopy and by ozonolysis to acetaldehyde.

[15] F. G. Bordwell, C. M Suter, J. M. Holbert and C. S. Rondestvedt, Jr., THIS JOURNAL, **68**, 139 (1946).

[16] W. F. Whitmore and E. F. Landau, *ibid.*, **68**, 1797 (1946).

[17] D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 4519 (1951).

[18] B. B. Elsner and P. F. M. Paul, *J. Chem. Soc.*, 893 (1951). We noted that phenylacetylene does not form salts with calcium hydride or lithium hydride in boiling ether or dioxane.

[19] W. E. Truce, private communication, has had a similar experience with the sodium and halomagnesium salts of phenylacetylene.

[20] This is not the benzylthiuronium salt of benzoylmethanesulfonic acid since W. E. Truce and C. C. Alfieri, THIS JOURNAL, **72**, 2742 (1950), report the melting point as 152°.

ene was recovered from the organic layer. An aliquot of the aqueous phase contained 29% of the sulfur trioxide as sulfate ion, and bromate–bromide titration indicated that approximately 33% of the sulfur trioxide had formed unsaturated sulfonic acids (17% if acetylenic). On back titration with potassium iodide and thiosulfate, the end-point faded repeatedly, indicating that iodine ion was reacting with the brominated material; this then must have been a 1,2-dibromide.[2,4] When the neutralized aqueous solution was evaporated nearly to dryness and extracted with absolute alcohol, only a small amount of slimy solid was obtained, and it was not possible to isolate a pure material.

In another experiment, a suspension of sodium phenylacetylide in ether was treated with methyl chlorosulfonate at 0°. Extensive charring was observed and all that was isolated was a few drops of phenylacetylene.

Ethylenesulfonyl Chloride.—β-Chloroethanesulfonyl chloride was prepared essentially by the procedure of Goldberg.[12] It was found more convenient to reflux the reaction mixture with stirring, then to distil off the bulk of phosphorus oxychloride until the pot temperature reached 135°. The ensuing hydrolysis of the remaining phosphorus oxychloride then required only about $^1/_2$ hour. The yields of distilled material were as high as 84%.

A solution of 81.5 g. (0.5 mole) of β-chloroethanesulfonyl chloride in 300 ml. of absolute ether was cooled to −40°. A solution of 63.3 g. (0.59 mole) of dry (over KOH) 2,6-lutidine (Reilly) and 100 ml. of ether was added at such a rate that the temperature did not exceed −50°, in 18 minutes. The mixture was stirred for an additional 45 minutes while it warmed spontaneously to room temperature. After cooling to 0°, 200 ml. of ice-cold 1% sulfuric acid was added with stirring. The ether layer was washed again with cold acid, then with water, then with 20% sodium chloride solution. After drying with sodium sulfate and distillation, a fraction boiling at 34–36° (0.8 mm.), 45.6 g., 72.2% yield, was collected. The redistilled material boiled at 26.5–27.2° (0.2 mm.). The crude product decomposed when distilled at 14 mm. Ethylenesulfonyl chloride reacts explosively with pyridine or triethylamine at room temperature, less violently with 2,6-lutidine, to form black tar.

In a similar experiment with β-chloropropanesulfonyl chloride, there was no evidence of reaction with 2,6-lutidine until the temperature rose to −25°. The yield was 40%, but this could be improved to approximately 75% by substitution of triethylamine for lutidine.[14]

N,N-Diethylethylenesulfonamide.—A solution of 6.3 g. (0.05 mole) of ethylenesulfonyl chloride in 40 ml. of absolute ether was cooled to −70°. A mixture of 3.7 g. (0.05 mole) of diethylamine and 5.1 g. (0.5 mole) of triethylamine in 25 ml. of dry ether was added in one-half hour below −50°. After warming to room temperature with stirring, the mixture was poured into ice-water; the organic layer was extracted thoroughly with dilute ice-cold hydrochloric acid, and the acid extracts were extracted once with chloroform. The combined organic layers were washed with water and dried with sodium sulfate. The brown oil remaining after evaporation of the solvents was distilled; 3.8 g. (47% yield) of colorless oil was obtained, b.p. 80–82° (1 mm.). The analytical sample boiled at 86.5–88.0° (1.4 mm.); $n^{24.3}$D 1.4602; m.p. −1.3 to −0.4°.

Anal. Calcd. for $C_6H_{13}NO_2S$: C, 44.15; H, 8.02. Found: C, 43.75; H, 7.79.

1-Bromoethene-1-sulfonyl Chloride.—This compound has been previously prepared in low yield by the action of phosphorus pentachloride on sodium 1-bromoethene-1-sulfonate.[5]

Ethylenesulfonyl chloride, 25.3 g. (0.20 mole), was placed in a 300-ml. three-necked flask. To the tared flask was added 32.5 g. (0.20 mole) of bromine in two portions at 15-minute intervals. When the flask was swirled, the temperature rose rapidly to about 45°, possibly as a result of oxygen catalysis of the bromination. The flask was cooled at tinervals in a pan of cold water to maintain the temperature near 25°. After standing for 12 hours at room temperature in a pan of water, the liquid was golden yellow. There was no detectable loss in weight, although fumes (of hydrogen bromide?) were visible when the mixture became warm. After heating for ten minutes on the steam-bath, 150 ml. of dry ether was added, and the mixture was cooled to −50°. A solution of 21.4 g. (0.20 mole) of 2,6-lutidine in 40 ml. of ether was added in 20 minutes below −40°. After warming slowly to 0° with stirring, cold dilute sulfuric acid was added, and the layers were separated. The ether layer was washed with cold acid, water and saturated sodium chloride solution, dried with calcium chloride, and distilled. The product weighed 28.1 g., 68.1%, b.p. 27–38° (0.3 mm.). On standing for three weeks in daylight at room temperature in a stoppered flask, it had turned brownish-yellow, and a brown solid separated. The filtered liquid was redistilled for analysis; 24.3 g., b.p. 31–33° (0.1 mm.).

Anal. Calcd. for $C_2H_2O_2ClBrS$: C, 11.67; H, 0.98. Found: C, 12.48; H, 0.68.

The analysis indicates the presence of a small amount of ethynesulfonyl chloride, with a higher carbon content (19.25%).

In a similar run, the crude dibromide was distilled. The yield of crude product, b.p. 99–103° (3 mm.), was 49.2 g., 84%. A portion was redistilled for analysis; b.p. 76–77° (2.8 mm.).

Anal. Calcd. for $C_2H_3O_2ClBr_2S$: C, 8.39; H, 1.06. Found: C, 8.74; H, 1.13.

2-Phenyl-1-bromoethene-1-sulfonyl Chloride.—A solution of 10.1 g. (0.05 mole) of 2-phenylethene-1-sulfonyl chloride and 8.0 g. (0.05 mole) of bromine in 50 ml. of carbon tetrachloride and a few crystals of iodine was stored at room temperature in the dark. There was no visible decolorization in three days. When placed in the light, decolorization was nearly complete in 8 hours. (In other similar experiments without iodine, the bromine color disappeared in 1–12 hours, depending on the light intensity.)

The carbon tetrachloride was pumped off at room temperature, and the residue was dissolved in 20 ml. of benzene which was then pumped off. The oil did not solidify at −10°. It was dissolved in 50 ml. of dry ether and a solution of 5.0 g. (0.05 mole) of triethylamine (distilled from KOH) in 20 ml. of dry ether was added in 30 minutes while the internal temperature was maintained below 0°. After an additional 30 minutes of stirring below 0°, the mixture was washed with cold 1% sulfuric acid, then water, then dried and evaporated. The residue was crystallized from petroleum ether (30–40°) containing a few per cent. of ether or chloroform. The first crop weighed 9.3 g., m.p. 48.0–49.5°; the second crop 2.2 g., m.p. 46–48°, total yield 82%.

The analytical sample, recrystallized from petroleum ether–chloroform, melted at 50.5–51.1°.

Anal. Calcd. for $C_8H_6O_2ClBrS$: C, 34.12; H, 2.15. Found: C, 34.30; H, 2.25.

In another experiment in which the temperature was not carefully controlled during addition of triethylamine and the mixture was allowed to stand 48 hours before washing, the yield was only 55% and the purification was more difficult.

The sulfonamide was prepared from the chloride in absolute ether by the action of liquid ammonia. After crystallization from dilute ethanol, it melted at 132–133°, and it did not depress the melting point of a sample prepared from sodium 2-phenyl-1-bromoethene-1-sulfonate *via* the chloride.[6]

Dehydrobromination of 2-Phenyl-1-bromoethene-1-sulfonyl Chloride and its Sodium Salt.—When sodium 2-phenyl-1-bromoethene-1-sulfonate was refluxed for 12 hours with alcoholic alkali, a tar precipitated. The filtrate contained sulfite ion. When a sample was heated in aqueous alcohol with excess 2,6-lutidine for 12 hours, a test portion gave no precipitate with silver nitrate solution after acidification, though tar formation was evident.

When 2.8 g. of bromochloride was allowed to stand in dilute benzene solution at 30° for a day in the presence of a molar amount of 2,6-lutidine, some tarry material precipitated. The filtrate was washed with acid and water, then distilled. There was collected 2.0 g. of material, b.p. 144–147° (1.4 mm.), which solidified. It did not depress the melting point of the starting material.

When 6.1 g. (0.0216 mole) of bromochloride in 20 ml. of dry benzene was treated with 2.2 g. of triethylamine, the solution warmed up to 45°. After 30 minutes, it was heated to 55° for ten minutes. After storing for 28 hours at 5°, the precipitated salts were collected and washed with dry benzene; the white solid weighed 1.5 g., and its aqueous solution gave tests for bromide and sulfite ions. The benzene solution was distilled. There was collected 1.1 g. of yellow liquid, b.p. 40–110° (0.5 mm.), but the pot residue, black and tarry, could not be further distilled. Addition of bromine to the distillate permitted isolation of a small quantity of 1,1,2-tribromo-2-phenylethane, m.p. 37–38°.[21]

Ethynesulfonyl Chloride.—A solution of 6.5 g. (0.0316 mole) of 1-bromoethene-1-sulfonyl chloride in 40 ml. of dry ether was cooled to −70°. A solution of 3.3 g. (0.0326 mole) of triethylamine in 25 ml. of ether was added below −60° in one-half hour. After an additional half-hour, the precipitated hydrobromide was filtered and washed with dry ether. After evaporation of the ether, the brown oil was distilled, giving 1.8 g., 46% yield of a yellow oil, b.p. 33–43° (0.5 mm.). The compound was a vicious lachrymator. Satisfactory analytical data have not yet been obtained; this product is doubtless contaminated with starting material. Its infrared spectrum was taken without solvent or in carbon disulfide or carbon tetrachloride on a Baird instrument in a cell 0.1 mm. thick.

ANN ARBOR, MICHIGAN

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[21] R. Fittig and F. Binder, *Ann.*, **195**, 142 (1879).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

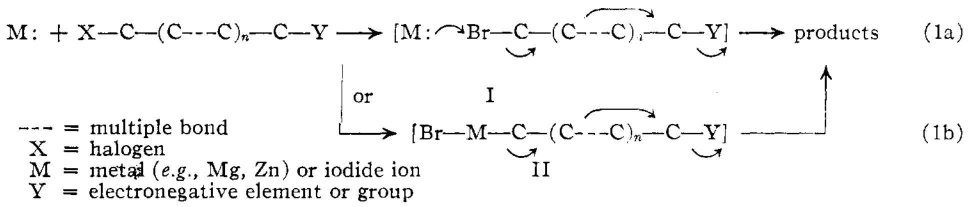
The Action of Metals on Unsaturated 1,4-Dihalides and Derivatives. I. Synthesis and Some Properties of Butatriene[1]

BY W. M. SCHUBERT, THOMAS H. LIDDICOET AND WAYNE A. LANKA

RECEIVED OCTOBER 19, 1953

As part of a study of the elimination reactions of "vinylogous" 1,2-dihalides and derivatives, butatriene has been synthesized by the action of zinc on 1,4-dibromo-2-butyne or 1-bromo-4-phenoxy-2-butyne. Butatriene, a readily polymerizable volatile substance, has been thoroughly characterized and some of its chemical properties explored. On hydration in 78% sulfuric acid it yielded methyl vinyl ketone. When added in excess and in high dilution to bromine, butatriene gave mainly 1,2,3,4-tetrabromo-2-butene. A small amount of 1,4-dibromo-2-butyne and a very easily polymerized isomeric dibromo compound were also formed. Attempted nascent hydrogen reduction, reaction with phenyl azide, diazoacetic ester, maleic anhydride or cyclopentadiene yielded only polymeric materials.

A study is being made to determine the general nature of reactions of type 1 in which *n* is greater than zero.[2] The general reaction 1 in which *n* = 0 is, of course, well-known. However, just a few isolated examples of the reaction 1 in which *n* > 0 are reported. For example, in 1899, Thiele found that 1,4-dibromo-2-butene and zinc in ethanol yielded 1,3-butadiene.[3] Later, 1,3-butadiene was obtained from 1,4-dibromo-2-butene and magnesium in ether[4,5] and from γ-phenoxycrotyl bromide and magnesium under the same conditions.[4] No Grignard reagent or coupling product was detected. Reid and Yost obtained cyclopentadiene in the reaction of magnesium and *cis*-3,5-dibromocyclopentene with magnesium in ether, whereas ethylmethylfulvenol is a reported product when the reaction was run in the presence of excess butanone.[6] The presence of reaction 1 probably also explains the failure to obtain a condensation product by treatment of the reaction mixture of magnesium and γ-methoxycrotyl bromide with the sodium salt of hydroxymethylene-β-ionone.[7] An example of the reaction 1 in which *n* = 2 is the formation of 1,3,5-hexatriene as an unstable liquid from the action of zinc on 1,6-dibromo-2,4-hexadiene.[8] Examples of reactions at least similar to 1 may exist in the tetraarylcumulene synthesis of Kuhn in which the α,ω-diols are treated with P_2I_4.[9]



--- = multiple bond
X = halogen
M = metal (*e.g.*, Mg, Zn) or iodide ion
Y = electronegative element or group

Preparation and Characterization of Butatriene.—To determine whether the multiple bond of reaction 1 can be a triple bond a study of the action of metals and iodide ion on 1,4-dibromo-2-butyne was undertaken. The first experiments, with zinc in ethanol or water, produced a volatile gas which was largely 1,3-butadiene, as evidenced by infrared, ultraviolet and mass spectra. The spectra showed the presence of another substance, shown later to be butatriene, to the extent of 10–15% of the total product.[10] Chemical tests confirmed the absence of acetylenic hydrogen. There was evidence of polymer formation which did not take place in a similar preparation of 1,3-butadiene from 1,4-dibromo-2-butene and zinc. The mixture of volatile products when treated with excess bromine in carbon tetrachloride gave a crystalline mush which, though no longer unsaturated to bromine, readily reduced potassium permanganate. Apparently 1,2,3,4-tetrabromo-2-butene was present. On recrystallization, the crude bromination product gave fairly

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[1] Supported in part by a Cottrell Grant of the Research Corporation.

[2] W. M. Schubert, W. A. Lanka and T. H. Liddicoet, *Science*, **116**, 124 (1952).

[3] J. Thiele, *Ann.*, **308**, 333 (1899).

[4] A. Lüttringhaus, G. V. Saaf and K. Hauschild, *Ber.*, **71**, 1673 (1938).

[5] G. N. Khitrik, *J. Gen. Chem.* (*U.S.S.R*), **10**, 2098 (1940).

[6] E. B. Reid and J. F. Yost, THIS JOURNAL, **72**, 1807 (1950).

[7] E. M. Schantz, *ibid.*, **68**, 2552 (1946).

[8] E. H. Farmer, B. Das Laroia, T. M. Switz and J. F. Thorpe, *J. Chem. Soc.*, 2937 (1927).

[9] R. Kuhn and H. Zahn, *Chem. Ber.*, **84**, 566 (1951).

[10] After this work was completed, C. Troyanowsky, *Compt. rend.*, **236**, 618 (1953), reported that 1,4-dibromo-2-butyne when treated with zinc and ethanol gave only 1,3-butadiene.