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Rearranged Products from the Reaction of Benzenesulfonic Acids with Caustic

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It has been demonstrated that the isomeric benzenedisulfonic acids and phenolsulfonic acids do not form rearranged, phenolic products when treated with molten caustic. These results are contrary to the generally accepted belief that molten caustic reacts with either benzene-1,2-disulfonic acid or benzene-1,4-disulfonic acid to form substantial amounts of the rearranged product, resorcinol. The most plausible explanation for this lack of agreement appears to be that the previous investigators incorrectly identified the sulfonic acids employed or employed sulfonic acids containing isomeric impurities.

A number of current organic chemistry books contain statements to the effect that a substantial amount of the rearranged product, resorcinol, is formed by the reaction of caustic with benzene-1,2-disulfonic acid and benzene-1,4-disulfonic acid. Statements relative to the formation of rearranged products from analogous reactions employing the phenolsulfonic acids are less common and no publications claiming the formation of catechol or hydroquinone by the reaction of caustic with benzene-1,3-disulfonic acid were found. It has been implied that the formation of rearranged products involves a benzyne intermediate[1] which would be consistent with the benzyne chemistry of substituted chlorobenzenes.[2]

Most of the experimental data relative to the formation of rearranged products by reactions of caustic with benzenedisulfonic acids or phenolsulfonic acids are very old and the reliability of these data has been questioned.[1] The literature contains numerous examples of lack of agreement between investigators, incorrect identification of reactants and products, and sketchy experimental details. Even in the case of the more recent literature, there are inconsistencies and the establishment of the isomeric purity of the sulfonic acids employed was not reported.

The conversion of benzenedisulfonic acids to dihydroxybenzenes involves the replacement of two sulfonate groups. It is thus possible that rearranged products are formed during the formation of the intermediate phenolsulfonic acids, during the conversion of the phenol sulfonic acid to the dihydroxybenzene, or during both reactions. The literature was reviewed in an attempt to determine at what stage rearrangement occurs.

Disulfonic Acids to Phenolsulfonic Acids.—Experimental details were not found for the conversion of benzene-1,2-disulfonic acid with molten caustic to a phenolsulfonic. Nearly a hundred years ago Barth and Senhofer[3] reported that both benzene-1,3-disulfonic acid and the 1,4 isomer produced nearly quantitative yields of phenol-3-sulfonic acid when allowed to react with caustic at intermediate temperatures. The conversion of benzene-1,3-disulfonic acid to phenol-3-sulfonic acid was verified by Willson and Meyer;[4] however, no subsequent report of the formation of phenol-3-sulfonic acid from benzene-1,4-disulfonic acid was found.

Phenolsulfonic Acids to Dihydroxybenzenes.—In 1867 Kekule[5] reported that the reaction of phenol-3-sulfonic acid with potassium hydroxide yielded the rearranged product, catechol, containing a substantial amount of resorcinol. Kekule's procedure for the preparation of what he reported to be phenol-3-sulfonic acid was later reported by Barth and Senhofer[3] as well as Degener[6] to yield phenol-2-sulfonic acid. Furthermore, these later investigators were unable to detect the presence of resorcinol in the product from the reaction of phenol-2-sulfonic acid with molten caustic. Other than the report by Kekule, no references claiming the formation of rearranged products by the reaction of phenol-3-sulfonic acid with caustic were found.

Kekule[5] also reported that the reaction of phenol-4-sulfonic acid with potassium hydroxide resulted in the formation of the rearranged product, resorcinol. A short time later Barth and Senhofer,[3] Degener,[6] and Lincke[7] all reported that neither resorcinol nor hydroquinone was formed by this reaction.

In 1942 Fierz-David and Stamm[8] stated "it is known that considerable amounts of hydroquinone are formed by treatment of phenol-4-sulfonic acid with aqueous alkali particularly in the presence of copper or a copper salt." These authors further stated that this reaction produced resorcinol in up to 9.5% yield. A search of the literature failed to uncover any experiments in which copper or its salts were used to catalyze the reaction of sulfonic acids with caustic or any experimental evidence for the formation of hydroquinone from phenol-4-sulfonic acid. The reliability of the report by Fierz-David and Stamm is rendered more questionable by their own statement in a later portion of this paper that "phenol-4-sulfonic acid yields practically no resorcinol when treated with molten caustic."

Benzenedisulfonic Acids to Dihydroxybenzenes.—Statements can be found in books and journal articles to the effect that the rearranged product, resorcinol, is formed by the reaction of caustic with benzene-1,2-disulfonic acid; however, published experimental

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(1) R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).

(2) See ref 1 for leading references.

(3) L. Barth and C. Senhofer, *Ber.*, **8**, 1477 (1875); **9**, 969 (1876).

(4) F. Willson and K. H. Meyer, *ibid.*, **47**, 3162 (1914).

(5) A. Kekule, *Z. Chem.*, **10**, 641 (1867).

(6) P. Degener, *J. Prakt. Chem.*, **128**, 300 (1879).

(7) E. Lincke, *ibid.*, **116**, 43 (1873).

(8) H. E. Fierz-David and G. Stamm, *Helv. Chim. Acta*, **25**, 364 (1942).

support for these statements was not found. Also, no report was found which claimed that the rearranged products, catechol or hydroquinone, were formed by a reaction of caustic with benzene-1,3-disulfonic acid.

During less than a 10-year period, both Garrick[9] as well as Barth and Senhofer[3] reported a nearly quantitative yield of resorcinol from the reaction of benzene-1,4-disulfonic acid with molten potassium hydroxide. The structures of the disulfonic acids employed by these investigators were apparently established by the reaction of these sulfonic acids with potassium cyanide. Dinitriles which were hydrolyzed to terephthalic acid were reported to be the product of these reactions for which experimental details and yields were not given. Barth and Senhofer,[3] however, felt that Garrick's sulfonation procedure produced primarily the *meta* isomer and that Garrick had mistaken isophthalic acid to be terephthalic acid.

In 1942 Fierz-David and Stamm[8] strongly refuted the Barth and Senhofer[3] claim that a nearly quantitative yield of resorcinol is obtained by the reaction of benzene-1,4-disulfonic acid with molten potassium hydroxide. Fierz-David and Stamm[8] reported that they were able to obtain, at most, only a 5% yield of resorcinol from this reaction.

Discussion of Experimental Results

In view of the conflicting and inconsistent literature reports, an investigation was undertaken to determine if rearranged products are, indeed, formed by reactions of the isomeric benzenedisulfonic acids or phenolsulfonic acids with caustic. To ensure that apparent rearranged products were not products formed from isomeric impurities in the reactants employed, the reactants were carefully prepared, purified, and analyzed. The salts of the benzenedisulfonic acids were prepared from the corresponding acid chlorides which were hydrolyzed to the acids, then converted to the sodium or potassium salts. The identity and purity of the acid chlorides were established by melting points and infrared spectra. Infrared spectra also established that no detectable amount of isomerization occurred during conversion of the acid chlorides to sodium and potassium salts. The sodium phenol-4-sulfonate employed was recovered from reactions of sodium benzene-1,4-disulfonate with sodium hydroxide which were carried out under relatively mild reaction conditions. Infrared spectra confirmed the absence of isomeric impurities in the sodium phenol-4-sulfonate thus obtained.

A reaction of potassium benzene-1,4-disulfonate with potassium hydroxide was carried out under mild conditions (170–180°) so that only one of the sulfonate groups was replaced. The reaction was modeled after a reaction reported by Barth and Senhofer,[3] which was implied to produce the rearranged product, phenol-3-sulfonic acid, in a nearly quantitative yield. Since Barth and Senhofer used a silver reactor and since the potassium hydroxide was reported to contain chloride ion, catalytic amounts of silver chloride (silver metal plated on the surface of the reactor) and sodium chloride were added to the reaction mixture. The product of this reaction was found to contain an 87.5% yield of potassium phenol-4-sulfonate which was free of isomeric impurities. Potassium phenol-4-sulfonate was also found to be the major (70% yield) product from a reaction of the disulfonate with potassium hydroxide at a high reaction temperature (330–340°). In addition, a 15% yield of phenol but none of the isomeric dihydroxybenzenes and none of the other isomeric phenolsulfonates were obtained.

Sodium phenol-4-sulfonate was treated with sodium hydroxide at 340–380° and at 400–440°. At the lower temperature no reaction occurred and a nearly quantitative recovery of the sulfonate was obtained. The high-temperature reaction produced a small amount of phenol and a high-boiling residue, but no resorcinol, hydroquinone, or catechol. The stability of hydroquinone in molten sodium hydroxide was checked and it was found that 85% of the charged hydroquinone was recovered. It thus appears that the absence of significant hydroquinone in the reaction is not due to its instability in molten caustic.

The reaction of sodium benzene-1,2-disulfonate with sodium hydroxide was carried out under conditions that would result in only partial replacement of both sulfonate groups. This allowed an examination of both the phenolsulfonates and the dihydroxybenzenes produced. Since no evidence for rearranged products was found, this reaction demonstrates that neither benzene-1,2-disulfonic acid nor phenol-2-sulfonic acid yields rearranged products when treated with caustic.

The reaction of sodium benzene-1,3-disulfonic acid with sodium hydroxide formed resorcinol in 84% yield. The product was found to contain a small amount of phenol but no catechol or hydroquinone. The reaction of phenol-3-sulfonic acid with caustic was not investigated since no report was found which claimed the formation of rearranged products.

Experimental Section

Analyses.—The identity of reaction products and the absence of isomeric impurities in the products, reactants, and the reactant intermediates (the benzenedisulfonyl chlorides) were established primarily by infrared spectra. The samples were analyzed as mineral oil mulls using a Perkin-Elmer, Model 21 spectrometer. An examination of the spectra of several known mixtures demonstrated that the compounds listed in Table I could be detected in the presence of their isomers at or above the listed concentrations. Wavelengths employed to detect each compound are also listed.

Since minor amounts of hydroquinone cannot be detected in the presence of resorcinol by infrared analysis, a chemical method was used to establish the absence of hydroquinone in the resorcinol formed by the reaction of sodium benzene-1,3-disulfonate with sodium hydroxide. A 1.5-g sample of the resorcinol in 5 ml of ethanol was added to 20 g of ferric sulfate in 40 ml of water. About 50 ml of steam distillate was collected which failed to have the yellow color of benzoquinone. It was established that this procedure could readily detect the presence of 1% hydroquinone in a known sample.

Preparation of Sodium Benzene-1,2-disulfonate.—Orthanilic acid was prepared from 2-nitrochlorobenzene according to directions by Wertheim[10] and was converted to crude sodium benzene-1,2-disulfonate by applying the method reported by Meerwein[11] for converting sulfanilic acid to sodium benzene-1,4-disulfonate except for the omission of the purification steps. The crude sodium benzene-1,2-disulfonate was purified by converting it to the disulfonyl chloride according to the method

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[9] A. R. Garrick, *Z. Chem.*, **12**, 549 (1869).

[10] E. Wertheim, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 48.

[11] H. Meerwein, *et al.*, *Ber.*, **90**, 841 (1957).

TABLE I

INFRARED ANALYSES. LIMITS OF DETECTABILITY AND WAVELENGTHS EMPLOYED

Compound	Wt % detectable	Wavelength, μ
o-$C_6H_4(SO_2Cl)_2$	0.5	13.0
m-$C_6H_4(SO_2Cl)_2$	0.5	12.5
p-$C_6H_4(CO_2Cl)_2$	0.5	11.9
o-$C_6H_4(SO_3Na)_2$	0.5	12.9
m-$C_6H_4(SO_3Na)_2$	0.5	12.3
p-$C_6H_4(SO_3Na)_2$	0.5	11.9
p-$C_6H_4(SO_3K)_2$	0.5	11.9
o-$C_6H_4(OH)SO_3Na$	1.0	13.2
m-$C_6H_4(OH)SO_3Na$	1.0	11.5 and 12.4
p-$C_6H_4(OH)SO_3Na$	1.0	11.9
p-$C_6H_4(OH)SO_3K$	1.0	11.8
o-$C_6H_4(OH)_2$	1.0	9.1 and 11.7
m-$C_6H_4(OH)_2$	0.5	10.4 and 14.7
p-$C_6H_4(OH)_2$ (in absence of resorcinol)	0.5	12.0
p-$C_6H_4(OH)_2$ (in presence of resorcinol)	5.0	12.0

reported by Bosshard[12] (excess thionyl chloride and a catalytic amount of dimethylformamide). The disulfonyl chloride thus obtained (mp 136–140°) was recrystallized twice from chloroform then recrystallized from benzene yielding benzene-1,2-disulfonyl chloride, mp 143.5–144° (lit.[13] mp 142°), which did not contain a detectable amount of isomeric impurities.

A 97.3-g (0.354 mole) sample of purified benzene-1,2-disulfonyl chloride was refluxed in 2 l. of water for 2 hr yielding a homogeneous solution containing the theoretical acidity. The product was distilled to dryness by heating to 75° at 0.1 mm yielding 98.5 g of solid which was dissolved in 200 ml of water and neutralized to pH 8–9 with a solution of sodium hydroxide. Sodium benzene-1,2-disulfonate, which did not contain a detectable amount of isomeric impurities, was recovered (88% yield) from the solution by distilling the water at reduced pressure and drying the ground product at 150–175° and 0.1 mm.

Preparation of Salts of Benzene-1,4-disulfonic Acid.—The procedure of Meerwein[11] was employed to convert sulfanilic acid to crude sodium benzene-1,4-disulfonate which was converted, without purification, to the disulfonyl chloride by use of the method of the preceding experiment. Benzene-1,4-disulfonyl chloride (mp 140–141° found, lit.[14] mp 140.8°) containing no detectable amount of isomeric impurities was obtained.

By employing the method of the preceding synthesis, the disulfonyl chloride (126 g, 0.47 mole) was hydrolyzed, and the acid was recovered and divided into two portions which were converted to the sodium and potassium salts. These salts did not contain a detectable amount of isomeric impurities.

Purification of Sodium Benzene-1,3-disulfonate.—Technical grade sodium benzene-1,3-disulfonate was converted to the disulfonyl chloride as described for the other isomers. The disulfonyl chloride was recrystallized twice from each diethyl ether and di-*n*-butyl ether then sublimed yielding benzene-1,3-disulfonyl chloride (mp 61–62° found, lit.[15] mp 63°). This product, which did not contain a detectable amount of isomeric impurities was hydrolyzed, and the acid was recovered and converted to the sodium salt as described for the other isomers. Detectable amounts of isomeric impurities were not found in this product.

Caustic Fusion Apparatus.—The reactor consisted of a 7-in. length of 2-in. carbon steel pipe with a cap welded on one end. A thermocouple well, which was also used as a stirring rod, was made from a piece of $^1/_8$-in. pipe closed on one end. The reactor was heated with a gas burner and a nitrogen purge was maintained into the open end of the reactor during operation.

Stability of Hydroquinone in Molten Sodium Hydroxide.—The fusion reactor, charged with 85 g (2.1 moles) of sodium hydroxide and 10 ml of water was heated to 160–170° where a melt was obtained. A 19.5-g (0.177 mole) portion of hydroquinone was added over a 10-min period, after which the charge was heated to 400°, in 60 min then held at about 400° for 15 min. The cooled reaction mixture was diluted to about 150 ml with water and then acidified with 200 ml (2.4 moles) of concentrated hydrochloric acid. The ether extract (three 150-ml portions) was distilled (final conditions 40–50° (0.1 mm)) yielding 16.6 g (85% recovery) of hydroquinone (mp 169–171° found, lit.[16] mp 172.3°).

Reaction of Benzene-1,4-disulfonates with Potassium Hydroxide. Run 1.[17]—A mixture containing 36.5 g (0.116 mole) of potassium benzene-1,4-disulfonate, 250 g (3.78 moles) of potassium hydroxide, 2 g of silver chloride, 2 g of sodium chloride, and 70 ml of water was heated in the fusion reactor at 170–180° for 1.5 hr. After cooling to 120° the reaction mixture was diluted with 100 ml of water. The reaction mixture was neutralized at room temperature with about 110 ml (3.9 equiv) of sulfuric acid then extracted with ether (two 200-ml portions). Distillation of the ether extract failed to yield any residue. The aqueous phase was distilled to dryness (heated to 150–200° (0.1 mm)) and the residue was slurried in methanol (five 200-ml portions), filtered, and washed (five 20-ml portions) with hot methanol. Distillation of the methanol solution (final conditions 150–200° (0.1 mm)) yielded 21.5 g (87.5% conversion) of potassium phenol-4-sulfonate. This material did not contain a detectable amount of unreacted disulfonate or other phenolsulfonates.

Run 2.—The fusion reactor was charged with a solution of 50 g (0.18 mole) of sodium benzene-1,4-disulfonate in 150 ml of water and 340 g (5.15 moles) of 85% potassium hydroxide. The mixture was heated at 170–180° for 3 hr. Throughout this period it was difficult to prevent the mixture from foaming out of the reactor and impossible to further elevate the reaction temperature. About half of the reaction mixture was discharged and the remaining portion was heated to 250° over 50 min. The discharged portion of the reaction mixture was recharged to the reactor in two equal portions. After the addition of the first portion the mixture was heated to 275° in 50 min and after the second addition the mixture was heated to 340° in 160 min. The reaction mixture was then held at 330–340° for 30 min. The cooled product was acidified with an excess of concentrated hydrochloric acid (625 ml) and the resulting solution (about 1200 ml) was extracted with ether (five 150-ml portions). Distillation of the ether extract (final conditions 25° (0.1 mm)) yielded 5 g of residue which was sublimed at 0.1 mm and temperatures up to 230°. The sublimate was found to contain about 2.5 g of phenol (15% conversion) and no detectable amount of resorcinol or hydroquinone. It appeared (infrared spectra and boiling point) that the remainder of this ether-soluble product was a mixture of complex, phenolic compounds. The aqueous phase was neutralized to pH 7–8 and distilled to dryness (final conditions 150–200° (0.1 mm)) yielding 440 g of solids. The ground solid was slurried with hot methanol (three 500-ml portions), filtered, and washed with methanol (three 100-ml portions). After the methanol extract was distilled (final conditions 150–200° (0.1 mm)), 23.5 g (63% theory) of the potassium salt of phenol-4-sulfonic acid was obtained which did not contain a detectable amount of the corresponding *ortho* or *meta* isomers.

Reaction of Sodium Phenol-4-sulfonate with Sodium Hydroxide. Run 1.—The fusion reactor, charged with 85 g (2.1 moles) of sodium hydroxide and 15 ml of water, was heated to 160° where a melt was obtained. A 34.8-g (0.177 mole) portion of sodium phenol-4-sulfonate was added over 8 min while the temperature was held at 160–165°. The reaction mixture was then heated to 340° over 50 min. (The foamy nature of the reaction mixture limited the heating rate.) After the reaction mixture was held at 340–380° for 15 min, the product was cooled, acidified to pH 1–2 with concentrated hydrochloric acid (190 ml), diluted with water to about 1 l., and filtered yielding 13 g of solid 1. Five 100-ml ether extractions removed less than 0.5 g from the aqueous phase. The aqueous phase was distilled to dryness (final conditions 150–200° (0.1 mm)) and the resulting solids were extracted and washed with hot methanol (extraction two 200-ml portions, wash two 50-ml portions). The methanol solution was distilled (final conditions 150–200° (0.1 mm)) yielding 20.5 g of solid 2. Solids 1 and 2 were found to be the

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[12] H. H. Bosshard, R. Mory, M. Schmid, and H. Zollinger, *Helv. Chim. Acta*, **42**, 1653 (1959).

[13] A. H. Holleman and J. J. Polak, *Rec. Trav. Chim.*, **29**, 427 (1910).

[14] A. H. Holleman and J. J. Polak, *ibid.*, **29**, 429 (1910).

[15] R. Otto, *Ber.*, **19**, 2422 (1886).

[16] D. H. Andrews, G. Lynn, and J. Johnston, *J. Am. Chem. Soc.*, **48**, 1286 (1926).

[17] Procedure modeled after that reported by Barth and Senhofer.[3]

same salt of phenol-4-sulfonic acid. It thus appears that no reaction occurred since a nearly quantitative recovery (95%) of starting material was realized.

Run 2.—The fusion reactor was charged with 85 g (2.1 moles) of sodium hydroxide and heated to 425°. Over a period of 90 min, 34.8 g (0.177 mole) of sodium phenol-4-sulfonate was added while the reaction temperature was held at 400–440°. After the addition was complete, the mixture was held at 420–440° for 5 min. The cooled reaction mixture was dissolved in water and added to 190 ml (2.3 moles) of concentrated hydrochloric acid, then extracted with ether. The ether extract was distilled at reduced pressure (final conditions 25° (0.1 mm)) yielding 15.3 g. Sublimation of this material at 0.1 mm yielded sublimate 1, 2.0 g. by heating to 170°; sublimate 2, 2.6 g by heating to 250°; and residue, 6.9 g. Analyses of the above products showed that the reaction produced at most 0.5 g of phenol (3% conversion) and demonstrated the absence of detectable amounts of hydroquinone, resorcinol, and catechol. With the exception of phenol, infrared spectra indicated the above products to be a mixture of complex phenolic compounds.

The aqueous phase, which was distilled to dryness then extracted with methanol as in the preceding experiments, failed to yield any salts of the phenolsulfonic acids.

Reaction of Benzene-1,3-disulfonate with Sodium Hydroxide.—The fusion reactor, charged with 28 g (0.7 mole) of sodium hydroxide and 5 ml of water, was heated to 180° where a melt was obtained. Sodium benzene-1,3-disulfonate (50 g, 0.18 mole) was added over 6 min at 180–195°. An additional 57 g (2.1 moles total) of sodium hydroxide was added after the mixture had been held at 195–220° for 20 min. The mixture was heated to 350° over 45 min (heating rate limited by foamy nature of reaction) and held at 350–360° for 10 min. The diluted product was neutralized to pH 7 with about 140 ml (1.7 moles) of concentrated hydrochloric acid, and the resulting solution (about 750 ml) was extracted with ether (one 50-ml portion, three 75-ml portions, two 100-ml portions). The ether extract was distilled (final conditions, 40° (0.1 mm)) yielding 16.44 g (83.4% conversion) of resorcinol (mp 102–107° found, lit.[16] mp 110°) which contained some phenol but no detectable amount of catechol or hydroquinone.

Reaction of Sodium Benzene-1,2-disulfonate with Sodium Hydroxide.—A 50-g (0.18 mole) sample of sodium benzene-1,2-disulfonate was added to 85 g (2.1 moles) of molten sodium hydroxde at 340–360°. The addition was completed in 35 min after which the reaction mixture was held at 350–370° for 30 min. The cooled product was diluted with water to a volume of about 300 ml, strongly acidified with excess hydrochloric acid, and extracted with ether (five 200-ml portions). The ether extract was distilled yielding 8.61 g of residue which was identified as catechol containing some phenol but no detectable amount of resorcinol or hydroquinone. The aqueous phase was distilled to dryness at reduced pressure and the solids extracted with hot methanol (six 200-ml portions). The methanol solution was distilled to dryness yielding 24.2 g of a mixture of phenol-2-sulfonic acid and its sodium salt contaminated with sodium chloride. This mixture was found to be free of detectable amounts of the other isomeric phenolsulfonic acids or their sodium salts.

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Oxidative Coupling of 3,3,3-Trifluoropropyne

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Cupric chloride and the zinc derivative of 1,1,1-trifluoropropyne in dimethylformamide give 1,1,1,6,6,6-hexafluorohexa-2,4-diyne (III), along with various amounts of 1-chloro-3,3,3-trifluoropropyne (IV), *cis*- and *trans*-2,3-dichloro-1,1,1,6,6,6-hexafluorohexa-2-ene-4-yne, and 2-chloro-3(3,3,3-trifluoropropynyl)-1,1,1,6,6,6-hexafluorohexa-2-ene-4-yne (VI). Chlorination of III by cupric chloride in the reaction mixture leads to *trans*-2,3-dichloro-1,1,1,6,6,6-hexafluoro-2-ene-4-yne, and addition of a chloro group and a 3,3,3-trifluoropropynyl group (*via* the cupric salts) to III gives VI. 1,1,1,6,6,6-Hexafluorohexa-2,4-diyne is a low-boiling liquid (33°) which polymerizes at 25° but is stable at −78°. It reacts with 2 moles of organic azide to give bitriazolyl derivatives.

In this paper we wish to report our work on the oxidative coupling of the 3,3,3-trifluoropropyne derivative, $CF_3C{\equiv}CZnX$ (I,[1] where $X = Cl$ or $CF_3C{\equiv}C$).

An initial attempt to couple 3,3,3-trifluoropropyne through oxidation of its cuprous salt with oxygen in aqueous solution gave no 1,1,1,6,6,6-hexafluorohexa-2,4-diyne (III). The diyne (III) was synthesized successfully by treating I with cupric chloride in dimethylformamide at reduced pressure.[2] This method is particularly convenient since I is prepared with dimethylformamide as solvent.[1] In addition to III there is produced 1-chloro-3,3,3-trifluoropropyne (IV), 2,3-dichloro-1,1,1,6,6,6-hexafluorohexa-2-ene-4-yne, 2-chloro-3-(3,3,3-trifluoropropynyl)-1,1,1,6,6,6-hexafluorohexa-2-ene-4-yne (VI), and a compound which is probably 2- or 3-chloro-1,1,1,6,6,6-hexafluorohexa-2-ene-4-yne (VII).

The composition and yield of the product mixture are strongly dependent upon the reaction conditions. It is necessary to run the reaction under reduced pressure in order to remove the products as quickly as possible. Most of them are consumed by undetermined processes if left in contact with the reaction mixture. Another important factor is the manner of mixing the solutions of I and cupric chloride. When I is added to an excess of cupric chloride in dimethylformamide the recovery of fluorinated products is low and consists chiefly of *cis*- and *trans*-2,3-dichloro-1,1,1,6,6,6-hexafluorohexa-2-ene-4-yne (V) with lesser amounts of III, IV, VI, and VII. When the order of addition is reversed the total yield of products is even lower but now the major component is III and no VI or VII is detected. Simultaneous mixing of approximately equimolar solutions of I and of cupric chloride in a simple flow reactor gives the best yield of III. Using this method III can be prepared in 46% yield along with lesser amounts of IV, V, and VI.

The first step (1) in the reaction must be the formation of the cupric derivative, II. The details of step

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[1] W. G. Finnegan and W. P. Norris, *J. Org. Chem.*, **28**, 1139 (1963).

[2] Alkynylmagnesium halides and cupric halides in ether give coupled products: (a) J. P. Danehy and J. A. Nieuwland, *J. Am. Chem. Soc.*, **58**, 1609 (1936); (b) J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 2014 (1952); (c) H. H. Schlubach and V. Franzen, *Ann.*, **572**, 116 (1951). In one case (ref a) a 1-bromoalkyne also was isolated.