Anal. Calcd. for $C_{16}H_{19}O_3NS_2$: C, 56.97; H, 5.68; N, 4.15; S, 19.0; mol. wt., 337. Calcd. for $C_{16}H_{19}O_4NS_2$: C, 54.36; H, 5.38; N, 3.97; S, 18.1; mol. wt., 353. Found: C, 57.16, 57.39; H, 5.52, 5.50; N, 4.07; S, 19.6; mol. wt. (cryoscopically in benzene), 344, 351.

In other experiments to establish the most likely route for formation of A and N: (1) a solution of 1.00 g. of III in 25 ml. of absolute ethanol was refluxed for 40 hours. Unreacted III, 0.85 g., m.p. 43–45°, was recovered. (2) Sodium *p*-toluenesulfonate dihydrate (0.0125 mole), prepared by exact neutralization of the acid and dried *in vacuo* for 12 hours, was refluxed for 40 hours with 2.87 g. (0.0125 mole) of III in 50 ml. of absolute alcohol. Only 2.27 g. of III was recovered.

LOS ANGELES, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Derivatives of Sulfenic Acids. IX. Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with Some Symmetrical Alkynes

BY NORMAN KHARASCH AND STEVEN J. ASSONY

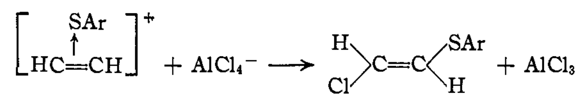
RECEIVED JULY 23, 1952

2,4-Dinitrobenzenesulfenyl chloride reacts with acetylene, 2-butyne, 3-hexyne and diphenylacetylene in accord with the equation: $RC{\equiv}CR + ArSCl \rightarrow RC(Cl){=}CR(SAr)$, Ar = 2,4-dinitrophenyl. The reaction suggests a practical method for characterizing such alkynes. Aluminum chloride catalysis was required in the case of acetylene. Addition to butynedioic acid or diethyl butynedioate could not, however, be effected.

The addition of 2-chloroethanesulfenyl chloride ($ClCH_2CH_2SCl$) to acetylene, to yield 2-chloroethyl 2-chlorovinyl sulfide,[1] appears to be the only recorded instance of reaction of a sulfenyl halide with an alkyne. The purpose of the present work was to determine whether 2,4-dinitrobenzenesulfenyl chloride (I) could participate in this type of reaction.[2]

It was found that I does react with acetylene, 2-butyne, 3-hexyne and diphenylacetylene to give sharp-melting, excellently crystalline 1:1 adducts, in yields ranging from 76–93%. The results suggest a new approach to the characterization of symmetrical alkynes. Procedures for obtaining maximum yields of products are recorded in the Experimental section.

In contrast to the reaction of I with ethylene,[2b] as well as with the higher alkynes now reported, the reaction of I with acetylene failed in the absence of a catalyst. Formation of the 1:1 adduct was, however, facilitated by catalytic amounts of aluminum chloride. The catalyst presumably functions as shown (Ar = 2,4-dinitrophenyl):



Evidence for the existence of 2,4-dinitrobenzenesulfenium ion, generated as above—or in sulfuric acid solutions of I—will be presented in a following paper. There is as yet, however, no decisive evidence that the addition occurs in the *trans* manner shown above.

While several attempts were made to add I to butynedioic acid, or to diethyl butynedioate, the reactions could not be effected. This failure is not unexpected, since the carboxyl or carbethoxy groups strongly deactivate the acetylenic bond toward addition of electrophilic reagents.

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Experimental[3]

Starting Materials.—2,4-Dinitrobenzenesulfenyl chloride (I), m.p. 95–96°, was obtained by catalytic chlorinolysis of 2,4-dinitrophenyl disulfide.[4] Commercial acetylene (Prest-O-Lite) was purified by passage through concentrated sulfuric acid. 3-Hexyne (b.p. 80.8–81.1°), from Farchan Laboratories, Cleveland, Ohio, tested negatively for peroxides, and was used without further purification. 2-Butyne,[5] diphenylacetylene,[6] butynedioic acid[7] and diethyl butynedioate[8] were prepared by recorded procedures. Other reagents and solvents were C.P. grade or were purified by standard methods.

2-Chloro-1-(2′,4′-dinitrophenylthio)-ethene.—To 35 ml. of ethylene chloride, was added 2.35 g. (0.01 mole) of I and 0.1 g. of aluminum chloride. The solution was stirred magnetically and kept under an atmosphere of purified acetylene (initial pressure, 1.70 atm.) for 5 days, in an apparatus similar to the quantitative hydrogenator described by Joshel.[9] During this time, the acetylene pressure dropped to 1.35 atm. The reaction mixture was then washed with 50 ml. of 1 *N* hydrochloric acid and extracted with 150 ml. of benzene. The extract was washed twice more with 50-ml. portions of water and dried over anhydrous calcium chloride. Solvent was removed by distillation and the residue crystallized (with the aid of charcoal) from carbon tetrachloride; orange prisms, m.p. 128–129°, 1.99 g. (76%). Excellent orange needles could also be obtained from 95% alcohol. The analytical sample was recrystallized from carbon tetrachloride to m.p. 130–130.5°.

Anal. Calcd. for $C_8H_5N_2O_4SCl$: C, 36.86; H, 1.98; S, 12.30. Found: C, 36.85; H, 1.93; S, 12.22.

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(1) R. C. Fuson, C. C. Price and D. M. Burness, *J. Org. Chem.*, **11**, 470 (1946).

(2) Previous work on the reaction of I with olefins is recorded in other papers of this series: (a) N. Kharasch, H. L. Wehrmeister and H. Tigerman, THIS JOURNAL, **69**, 1612 (1947); (b) N. Kharasch and C. M. Buess, *ibid.*, **71**, 2724 (1949); (c) N. Kharasch, C. M. Buess and S. I. Strashun, *ibid.*, **74**, 3422 (1952).

(3) Microanalyses were performed by Mr. J. Pirie of this Laboratory. Melting points are not corrected.

(4) N. Kharasch, G. I. Gleason and C. M. Buess, THIS JOURNAL, **72**, 1796 (1950).

(5) J. B. Conn, G. B. Kistiakowsky and E. A. Smith, *ibid.*, **61**, 1868 (1939).

(6) L. I. Smith and M. M. Falkoff, *Org. Syntheses*, **22**, 50 (1942).

(7) T. W. Abbott, R. T. Arnold and R. B. Thompson, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 10.

(8) A. Michael, *J. prakt. Chem.*, [2] **46**, 224 (1892).

(9) L. M. Joshel, *Ind. Eng. Chem., Anal. Ed.*, **15**, 590 (1943).

If aluminum chloride was not added to the reaction mixture, the acetylene pressure remained constant during eight days and I was recovered in high yield.

3-Chloro-2-(2′,4′-dinitrophenylthio)-2-butene.—To a solution of 1.60 g. (0.007 mole) of I in 15 ml. of ethylene chloride at 0°, was added 3 ml. of ice-cold 2-butyne. The mixture was kept at 0° for two hours, the solvent removed by aspiration and the clear yellow oil refrigerated for two days. The crude crystals were dissolved in 25 ml. of absolute ethanol, and the solution was decolorized by charcoal and filtered. The filtrate yielded plate-like crystals (1.35 g., 69%), m.p. 68–70°; and, from the mother liquor, 0.33 g. more of product, m.p. 67–70°, was obtained; total yield 85%. Three recrystallizations raised the melting point to 75–76°.

Anal. Calcd. for $C_{10}H_9O_4N_2SCl$: C, 41.60; H, 3.14; N, 9.71. Found: C, 41.89; H, 3.36; N, 9.49.

4-Chloro-3-(2′,4′-dinitrophenylthio)-3-hexene.—3-Hexyne (2.0 g., 0.025 mole) was added to 4.7 g. (0.02 mole) of I in a mixture of 40 ml. ethylene chloride and 10 ml. of glacial acetic acid, and the mixture let stand two hours at room temperature. The solvents were removed by aspiration and the residual oil crystallized from absolute alcohol, giving 5.12 g. of product, m.p. 65–66°, and a second crop, 0.77 g., m.p. 62–65°; total yield 93%. The analytical sample, m.p. 65–66°, was prepared by three recrystallizations from absolute alcohol.

Anal. Calcd. for $C_{12}H_{13}O_4N_2SCl$: C, 45.50; H, 4.14; S, 10.12. Found: C, 45.73; H, 4.30; S, 10.38.

2-Chloro-1-(2′,4′-dinitrophenylthio)-1,2-diphenylethene.—Diphenylacetylene (2.13 g., 0.12 mole) was refluxed with 2.35 g. (0.01 mole) of I, in 25 ml. of glacial acetic acid for 8 hours. On cooling to room temperature, 3.82 g. (92.5%) of yellow prisms, m.p. 196–201°, was obtained. Three recrystallizations from glacial acetic acid gave cubic crystals, m.p. 205.5–207°, raised to 206–207° by recrystallizing from nitromethane.

Anal. Calcd. for $C_{20}H_{13}O_4N_2SCl$: C, 58.18; H, 3.17. Found: C, 58.29; H, 3.14.

When the reaction of I and diphenylacetylene was conducted as above, but at room temperature, reaction was incomplete even after several weeks—as indicated by a positive starch–iodide test for unreacted I. The major product which first precipitated from the reaction mixture was identical with the one recorded above; but from the remaining reaction mixture (after two weeks) there was isolated a lesser quantity of perfectly-formed, clear orange, diamond crystals, m.p. 167–192°. Recrystallization of the diamonds from hot glacial acetic acid, however, partially converted them to the yellow cubes melting at 206–207°. The diamond shaped crystals were not encountered at all when the reaction was carried out at reflux, as above. This alternate material was not further investigated.

Attempted Additions of I to Butynedioic Acid and to Diethyl Butynedioate.—Attempts to add I to this acid or the diethyl ester included variations, such as: refluxing equimolar quantities of the reactants in ethylene chloride solutions for periods up to 95 hours; attempted reactions in concentrated acetic acid solutions at room temperature for 4 months; attempted additions at room temperature, with aluminum chloride, in catalytic quantities (up to 0.1 mole $AlCl_3$/mole I) for extended periods; and refluxing in ethylene chloride, with 0.1 mole $AlCl_3$/mole I for 22 hours. In all of the non-catalyzed reactions with the ester, I was recovered in good yields; while with the acid some I could be recovered, but other complex products were indicated. With the catalyst present, dark colored, possibly polymeric products resulted. In no cases were any products encountered which could be identified as the desired adducts.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DEPAUW UNIVERSITY]

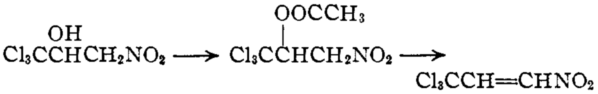
1,1,1-Trichloro-2-arylamino-3-nitropropanes

BY FRANK BROWER AND HOWARD BURKETT

RECEIVED SEPTEMBER 29, 1952

Evidence is presented which indicates that the previously reported 1,1,1,2-tetrachloro-3-nitropropane was probably 1,1,1-trichloro-3-nitropropene. Thirteen 1,1,1-trichloro-2-arylamino-3-nitropropanes have been prepared. Reduction of the nitro group of the 1,1,1-trichloro-2-arylamino-3-nitropropane to the corresponding amine was successful in only one case.

The preparation of 1,1,1,2-tetrachloro-3-nitropropane (I) by the reaction of phosphorus pentachloride with 1,1,1-trichloro-3-nitropropanol-2[1] was reported in 1897 by Henry[2] and in 1936 by Irving.[3] Upon repeating this preparation the authors obtained a product (II) which had physical properties nearly identical with those reported previously but which did not react as had been anticipated. Analyses and molecular refractivity of II correspond more nearly to 1,1,1-trichloro-3-nitropropene (III) than to I. Moreover, the physical and chemical properties of II are the same as for III prepared by the treatment of 1,1,1-trichloro-2-acetoxy-3-nitropropane[4] (IV) with sodium carbonate



$$\overset{OH}{Cl_3CCHCH_2NO_2} \longrightarrow \overset{OOCCH_3}{Cl_3C\overset{|}{C}HCH_2NO_2} \longrightarrow Cl_3CCH{=}CHNO_2$$

The use of this procedure for the preparation of nitroölefins has been reported[5,6] but has not been used for this compound. From the above data it is doubtful that earlier workers actually prepared 1,1,1,2-tetrachloro-3-nitropropane.

The authors had planned to synthesize 1,1,1-trichloro-2-arylamino-3-nitropropanes by the reaction of I with various amines. Since the latter could not be prepared, it became necessary to seek other methods. Chattaway and co-workers[7,8] reported the replacement of the acetoxyl group of IV with certain basic groups and Irving[9] described the addition of amines to III. We have prepared twelve 1,1,1-trichloro-2-arylamino-3-nitropropanes by the reaction of IV with two equivalents of amine in alcoholic solution. Three of the above nitroamines and an additional one were prepared by the addition of amines to III. The ease of this latter reaction

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[2] L. Henry, *Bull. acad. roy. med. Belg.*, **34**, 568 (1897).

[3] H. Irving, *J. Chem. Soc.*, **138**, 797 (1936).

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[5] H. B. Hass, A. G. Susie and R. L. Heider, *J. Org. Chem.*, **15**, 8 (1950).

[6] E. Schmidt and G. Rutz, *Ber.*, **61**, 2142 (1928).

[7] F. D. Chattaway, *J. Chem. Soc.*, **138**, 355 (1936).

[8] F. D. Chattaway, J. G. N. Drewitt and G. D. Parks, *ibid.*, **138**, 1530 (1936).

[9] H. Irving, *ibid.*, **150**, 1989 (1948).