

The benzylthiuronium salt was prepared in 98% yield by hydrolyzing the adduct, acidifying, and adding benzylthiuronium chloride; m.p. 235° (dec.).

Anal. Calcd. for $C_{21}H_{20}O_5N_2S_2$: C, 54.73; H, 5.03; N, 9.12; S, 13.90. Found: C, 54.81; H, 5.20; N, 8.93; S, 12.99.

The *p*-toluidine salt was prepared in 97% yield from the hydrolysate; m.p. 217.5–219°.

Anal. Calcd. for $C_{20}H_{22}O_5N_2S$: C, 59.73; H, 5.51; N, 6.96; S, 7.97. Found: C, 60.03; H, 5.52; N, 6.83; S, 7.68.

2-*p*-Nitrophenyl-6-bromo[2,2,1]bicycloheptane-3,5-sultone.—When a once-recrystallized sample of adduct was hydrolyzed with dilute methanolic sodium hydroxide, followed by acid and potassium tribromide solution, the compound precipitated in 60–65% yield (crude). This was recrystallized several times from methanol–acetone; m.p. 206–208°.

Anal. Calcd. for $C_{15}H_{12}O_5NBrS$: C, 41.74; H, 3.23. Found: C, 42.11; H, 3.46.

It was also observed that the adduct, after hydrolysis, could be titrated quantitatively by bromate–bromide¹⁸; the yield of sultone remained 60–65%.

A sample of low-melting adduct was recrystallized fourteen times from methanol, petroleum ether, acetonitrile, nitromethane and acetone; it finally melted at 112–116°. This purer material gave a 93% yield of bromosultone.

2-Phenyl-6-bromo[2,2,1]bicycloheptane-3,5-sultone.—A mixture of 1.5 g. of methyl 2-phenylethene-1-sulfonate, 5 g. of cyclopentadiene, and 50 ml. of bromobenzene was refluxed for two hours. Volatile material was removed completely on the water-pump; the residue was taken up in methanolic sodium hydroxide and boiled for one hour. After adding water and extracting with ether, treatment with bromate–bromide and acid precipitated 0.223 g. (9%) of crude sultone, m.p. 103–113°. It was recrystallized from methanol for analysis; m.p. 114.5–116.5°.

Anal. Calcd. for $C_{13}H_{10}O_5BrS$: C, 47.43; H, 3.98. Found: C, 47.10; H, 4.00.

Unsuccessful Attempts to Form Adducts.—Combinations of reagents and conditions which did not yield an isolable adduct are tabulated.

Dienophile ^{a, d, e}	Diene ^b	Temp., °C.	Time, hr.
R ₁ Cl	B	150	10
R ₁ Cl	B	100	5
R ₁ NH ₂	B	150	9
R ₁ ONa	B	150	10
R ₁ OMe	B	100	18
R ₁ OMe	B ^c	c	c
R ₁ Cl	F	100	20
R ₁ OMe	C	100	36
R ₂ Cl	B	150	10
R ₂ Cl	C	100	11.5
R ₂ OMe	B	100	25
R ₂ NEt ₃	C	150	1.0

^a R₁ = C₆H₅CH = CHSO₂; R₂ = *p*-NO₂C₆H₄CH = CHSO₂. ^b B = butadiene; C = cyclopentadiene; F = furan. ^c A large excess of butadiene was used; the mixture was heated for 20 hours at 100°; then 34 hours at 80°. A large amount of polybutadiene was formed. ^d Solvents employed were benzene, toluene or bromobenzene; alcohol was used with the sodium salt. ^e Recovery of starting material usually exceeded 65% except with the sulfonyl chlorides.

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ANN ARBOR, MICHIGAN

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

Methylsulfur Trichloride¹

BY KAY ROBERT BROWER AND IRWIN B. DOUGLASS

Methyl disulfide reacts with chlorine at –10 to –20° to form crystalline methylsulfur trichloride, CH₃SCl₃, in nearly quantitative yield. The new compound is unstable and decomposes on standing at room temperature into chloromethane-sulfonyl chloride, ClCH₂SCl, as a principal product. It is hydrolyzed by water and weakly alkaline solutions into methane-sulfonic acid. Phenyl disulfide is chlorinated to the corresponding sulfonyl chloride by methylsulfur trichloride and the latter compound is reduced to methanesulfonyl chloride. The compound also reacts slowly with ethylene by a mechanism not yet fully established to yield a product believed to be methyl chlorovinyl sulfide.

In continuing the study of the α -chloroalkane-sulfonyl chlorides² the preparation of chloromethanesulfonyl chloride was attempted by the method of Brintzinger and others.³ Methyl disulfide, diluted with methylene chloride, smoothly absorbed one mole of chlorine at –20° but when additional chlorine was passed in at this temperature a crystalline white solid began to separate. This solid was isolated and in elementary analysis corresponded to methylsulfur trichloride, CH₃SCl₃.

The diarylsulfur dichlorides, dibromides and diiodides are well known as are also certain dialkylsulfur dibromides and diiodides. The only dialkylsulfur dichloride to which reference has been found was prepared by Lawson and Dawson⁴ who treated mustard gas in carbon tetrachloride with chlorine at –5 to 0°, and obtained bis-(2-chloroethyl)-sulfur

dichloride, (ClCH₂CH₂)₂SCl₂. Methylsulfur trichloride is apparently the first monosubstituted organic derivative of sulfur tetrachloride to be reported.

Methylsulfur trichloride is unstable and decomposes spontaneously on standing at room temperature. The decomposition takes place chiefly according to the reaction



A 10-g. sample on decomposition gave the purest specimen of chloromethane-sulfonyl chloride, ClCH₂SCl II, yet obtained but when larger quantities were allowed to decompose products boiling lower and higher than II were also formed.

Methylsulfur trichloride is insoluble in non-polar solvents such as isopentane, and the chlorinated hydrocarbons. No evidence other than its solubility characteristics has been found for an ionic structure for the compound.

In cold water methylsulfur trichloride reacts instantly with the formation of water soluble color-

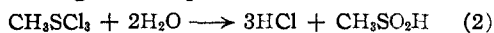
(1) This work was done on Project NR-055-165 under contract N8onr77000 with the Office of Naval Research, United States Navy.

(2) Douglass and Martin, *J. Org. Chem.*, **15**, 795 (1950).

(3) Brintzinger, Pfannstiel, Koddebusch and Kling, *Chem. Ber.*, **88**, 87 (1950).

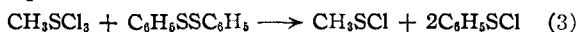
(4) Lawson and Dawson, *This Journal*, **49**, 3119 (1927).

less products. This reaction proceeds at least in part according to the equation

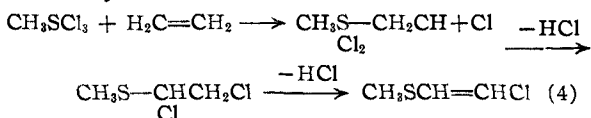


When the compound was added to a cold solution of sodium bicarbonate sodium methanesulfinate was formed which readily reacted with benzyl chloride to form methyl benzyl sulfone. In pure water the hydrolysis formed less than the four moles of acid indicated by equation (2), suggesting that the decomposition does not take place quantitatively in the direction indicated.

Methylsulfur trichloride dissolves in methyl disulfide with the formation of the reddish-yellow color characteristic of methanesulfenyl chloride. With phenyl disulfide it reacts according to the equation



Ethylene slowly reacts with methylsulfur trichloride to give a mixture of products. Their polar nature at one stage and the fact that a product corresponding in chlorine content and molar refractivity to methyl 2-chlorovinyl sulfide, $\text{CH}_3\text{SCH}=\text{CHCl}$, was isolated suggest that the following reactions may have occurred



The dehydrohalogenation shown would be analogous to the decomposition of bis-(2-chloroethyl)-sulfur dichloride observed by Lawson and Dawson.⁴

Experimental

Preparation of Methylsulfur Trichloride.—Methyl disulfide (31 g. or $\frac{1}{3}$ mole), diluted with 200 ml. of methylene chloride was placed in a three-neck flask fitted with sealed stirrer, thermometer and a gas inlet tube which terminated just above the surface of the liquid. The flask and contents were cooled to -25° by means of an acetone-Dry Ice-bath and a gentle stream of chlorine was admitted until 71 g. (one mole) of chlorine had been absorbed. The temperature was not allowed to rise above -20° . While adding the first half of the chlorine the solution acquired the reddish-orange color of methanesulfenyl chloride but the color decreased after the white methylsulfur trichloride began to precipitate. When the addition of chlorine was complete the mother liquor was drawn off by means of a filter stick, with care being taken to dry the air which replaced the liquid. The precipitate was then washed with isopentane (pract. grade) previously chilled to -20° . Three washings of 150 ml. each were usually sufficient to remove the color. The cold flask was connected through a cold trap to an aspirator and was evacuated with frequent shaking until the residual isopentane had evaporated. The product obtained in this way was quite pure and could be stored several days in a dry atmosphere below -10° . The yield was nearly quantitative. A small sample in a thin walled capillary tube decomposed at 31° when heated at the rate of about 1° per minute.

Anal. Calcd. for $\text{CH}_2\text{Cl}_2\text{S}$: C, 7.84; H, 1.97; Cl, 69.31; S, 20.90. Found: C, 7.85; H, 2.11; Cl, 69.02; S, 21.35.

The compound was usually prepared on a smaller scale in a test-tube fitted with an adjustable tube having a fritted glass end which served both as chlorine inlet tube and filter stick.

Solubility Characteristics and Conductivity.—Methylsulfur trichloride was not found to be appreciably soluble in chloroform, carbon tetrachloride, benzene, sulfur dichloride, sulfuryl chloride, chloropicrin, carbon disulfide, chlorobenzene, bromine, ethylene dichloride or ether. It proved to be slightly soluble in methanesulfenyl chloride and the solu-

tion had an equivalent conductance of less than 10^{-5} ohms⁻¹.

Decomposition.—A ten-gram sample of methylsulfur trichloride was allowed to decompose and the product was distilled. The principal fraction boiled $30\text{--}32^\circ$ (14 mm.) and had n_D^{20} 1.5404, d_4^{20} 1.519.⁵ The yield of chloromethanesulfenyl chloride was approximately 80%.

Anal. Calcd. for $\text{CH}_2\text{Cl}_2\text{S}$: Cl, 60.61. Found: Cl, 60.7.

When a larger quantity of methylsulfur trichloride was allowed to decompose there was obtained a small quantity of orange-red liquid boiling below 30° (14 mm.). In addition, approximately 35% of the material boiled higher than the boiling point of chloromethanesulfenyl chloride.

Hydrolysis.—Ten grams of methylsulfur trichloride was added in small increments to an intimate mixture of ice, 75 ml. of water and 25 g. of sodium bicarbonate. An instantaneous reaction occurred with carbon dioxide being liberated and resulting in a colorless solution. Only a fleeting yellow color developed in the solid at the instant of contact with the water. The solution was filtered from excess ice and sodium bicarbonate and was then refluxed with 10 g. of benzyl chloride for one hour. The resulting mixture was steam distilled until the odor of benzyl chloride was gone and, after boiling with decolorizing charcoal, filtering and allowing to crystallize, a few grams of benzyl methyl sulfone was obtained. The benzyl methyl sulfone melted at $125\text{--}126^\circ$ and a mixed melting point with an authentic sample was unchanged.

To about 20 ml. of ice-water contained in a test-tube 0.8424 g. of methylsulfur trichloride was added and the tube tightly stoppered and shaken. Titration of the resulting solution with 0.25 *N* sodium hydroxide required 60.0 ml. for neutralization indicating that 3.55 equivalents of acid per mole of methylsulfur trichloride had been liberated during hydrolysis.

Reaction with Disulfides.—In a preliminary test 1 g. of methylsulfur trichloride was added to 2–3 ml. of cold methyl disulfide. The solid dissolved and the color of methanesulfenyl chloride appeared.

Because in the above experiment no distinction could be made between the reduction and the chlorination products, 9 g. of methylsulfur trichloride was added to a solution of 11 g. of phenyl disulfide in 15 ml. of methylene chloride at -25° . The methylsulfur trichloride dissolved rapidly and a red solution resulted. This solution was distilled under reduced pressure and everything boiling below 15° was collected in a trap cooled in Dry Ice. The presence of methanesulfenyl chloride, in this distillate was demonstrated by aqueous chlorination to methanesulfonyl chloride which, in turn, was identified as the *p*-toluicide by a mixed melting point with an authentic sample.

The higher boiling residue was fractionally distilled and the fraction boiling $78\text{--}79^\circ$ (17 mm.), and having d_4^{20} 1.255 and n_D^{20} 1.6100 was identified as benzenesulfenyl chloride, a pure preparation of which has been found in this Laboratory to have d_4^{20} 1.253 and n_D^{20} 1.6108. The yield was 56%, based on phenyl disulfide.

Methanesulfenyl chloride was also identified as one product of the reaction between methylsulfur trichloride and benzyl disulfide.

Reaction with Ethylene.—Twenty-five grams of methylsulfur trichloride was added to 100 ml. of isopentane and ethylene gas was passed in at -20 to -10° . The solid gradually changed to a paste and finally to a separate liquid phase. A slight yellow color developed in the lower phase and gradually decreased as the passage of ethylene was continued. When no further decrease was apparent, the passage of ethylene was discontinued, the isopentane was evaporated and the residue was distilled through a 20-inch Vigreux column. The material boiled over the range of $35\text{--}86^\circ$ (17 mm.) with no homogeneous fraction being evident. The various fractions decomposed on standing and were not investigated further.

The experiment was repeated with the solid methylsulfur trichloride resulting from the chlorination of 31 g. of methyl disulfide. A flask containing the solid, without diluent, was kept in a bath maintained at -20° while ethylene was

(5) These values compare favorably with the extrapolated values for pure chloromethanesulfenyl chloride based on a comparison of the properties of its impure preparations and pure preparations of di- and trichloromethanesulfenyl chlorides; Douglass, Martin and Addor, *J. Org. Chem.*, **16**, 1297 (1951).

passed in for 90 minutes until the solid had liquefied and no further change in color occurred. A small amount of hydrogen chloride was liberated during this period. On distilling the liquid product (60 g.) much hydrogen chloride was liberated and 30 g. of product boiling 75–87° (17 mm.) was obtained. On redistillation, 7 g. of product was obtained boiling 82–84° (15 mm.) and having n_D^{20} 1.5410, d_4^{20} 1.190. The molar refractivity and chlorine content of this fraction corresponded to methyl 2-chlorovinyl sulfide,

$\text{CH}_3\text{SCH}=\text{CHCl}$. The yield of purified product, based on methyl disulfide, was only 10%.

Anal. Calcd. for $\text{C}_3\text{H}_5\text{SCl}$: Cl, 32.65; MR_D , 28.2.⁶
Found: Cl, 32.91; MR_D , 28.4.

(6) Atomic and group refractivities are taken from Vogel, *J. Chem. Soc.*, 1833 (1948).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Electric Moments of Some Azo Dyes

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The electric dipole moments of a series of azo dyes $\text{X}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{N}(\text{CH}_3)_2$ (with $\text{X} = \text{H}, \text{CH}_3, \text{t}-\text{C}_6\text{H}_5, -\text{OCH}_3, \text{Cl}, \text{I}, -\text{SCN}, -\text{SeCN}, \text{NO}_2$) have been measured in benzene solution at 25°. The observed moments have been compared with values calculated from bond moments; it is found that when the group X is a strong electron acceptor ($-\text{NO}_2, -\text{SCN}$ or $-\text{SeCN}$) or a halogen (Cl, I) the observed moment is larger than the expected value. The results have been interpreted in terms of resonance theory.

The electric moments of azobenzene and a number of para-substituted derivatives have been reported.^{1–3} The moment of azobenzene is zero⁴ and the moments of para-substituted compounds are close to those of the corresponding benzene derivatives (within experimental error in most cases); hence, it has been concluded that these compounds as ordinarily prepared have the *trans* configuration.

The observed⁵ dipole moments of *p*-aminoazobenzene (2.71) and *p*-dimethylaminoazobenzene (3.68) are exceptions since they are much larger than aniline (1.53) and dimethylaniline (1.58). The value reported⁵ for *p*-nitro-*p'*-dimethylaminoazobenzene (8.1) is larger than the sum of the moments of *p*-dimethylaminoazobenzene and nitrobenzene indicating an enhancement of resonance similar to that observed⁶ with *p*-nitrodimethylaniline and, to a lesser extent, with other para-substituted dimethylanilines measured.

Enhancement of resonance⁶ has so far only been demonstrated with a few aromatic nitro compounds but might be expected to be more general, especially when an electron-donating and an electron-receiving group are para to one another in a conjugated system. Such an effect should be magnified in *p,p'*-disubstituted azobenzenes, since the expected charge separation would be through nearly three times the distance in corresponding disubstituted benzenes. We have, therefore, measured the dipole moments of *p*-dimethylaminoazobenzene and eight *p'*-substituted derivatives of it in order to obtain information concerning the effects of substituents on resonance in azo dyes.

(1) E. Bergmann, L. Engel and S. Sandor, *Ber.*, **63**, 2572 (1930).

(2) E. Bergmann and A. Weizmann, *Trans. Faraday Soc.*, **32**, 1318 (1936).

(3) A. Weizmann, *ibid.*, **36**, 978 (1940).

(4) G. S. Hartley and R. J. W. LeFevre, *J. Chem. Soc.*, 531 (1939); the relatively unstable *cis* modification has a dipole moment of 3.0. It has been shown that the *cis* forms of some of these azo compounds are formed under certain conditions.

(5) R. J. W. LeFevre and J. W. Smith, *J. Chem. Soc.*, 2239 (1932).

(6) (a) For a discussion, see Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944; (b) T. W. Campbell and M. T. Rogers, *THIS JOURNAL*, **76**, 1029 (1948).

Experimental Part

Materials. Benzene.—Baker C.P. benzene was purified by freezing out about three-fourths of the liquid and collecting the crystals. This is repeated and the product of the second purification is distilled and dried over sodium: d_4^{20} , 0.87355, n_D^{20} 1.4980.

Azo Dyes.—The dyes of the type $\text{X}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{N}(\text{CH}_3)_2$ employed were made by conventional methods from a sodium acetate-buffered solution of the appropriate diazonium salt and an acetic acid solution of dimethylaniline. The crude product was recrystallized several times from *n*-propanol (boiling toluene when X was the nitro group). The following uncorrected melting points, in general slightly higher than those recorded in the literature, were observed: $\text{X} = \text{H}$,⁷ m.p. 117.5–118°; $-\text{CH}_3$,⁷ m.p. 171°; $-\text{C}(\text{CH}_3)_3$,⁸ m.p. 142°; $-\text{Cl}$,⁹ m.p. 159°; $-\text{I}$,¹⁰ m.p. 163.5–164°; $-\text{OCH}_3$,⁷ m.p. 163.5–164°; $-\text{NO}_2$,⁷ m.p. 229–230°; $-\text{SCN}$, m.p. 154°; $-\text{SeCN}$, m.p. 180°.

Apparatus and Method.—The electric moments were determined in benzene at 25° by the dilute solution method. Dielectric constants were measured using a heterodyne-beat apparatus similar to that described by Chien.¹¹ Densities were determined with a modified Ostwald pycnometer.

The experimental data and molar polarizations are shown in Table I, and the derived values of P_2^∞ (the molar polarization of the solute at infinite dilution), MR_D (calculated value of molar refraction), and μ (the dipole moment) for each compound are shown in Table II. The molar polarizations were obtained using the method of calculation suggested by Halverstadt and Kumler,¹² as well as by the conventional method.¹³

Table II also includes predicted values of the moments of the dyes calculated from the group moments and angles.¹³ The group moments used, except for $-\text{N}(\text{CH}_3)_2$, are those derived from benzene derivatives^{6b}; the $-\text{N}(\text{CH}_3)_2$ group moment and angle are derived from the measured dipole moments of dimethylaminoazobenzene and *p,p'*-didimethyl-

(7) Cf. Beilstein's "Handbuch," **16**, 321, *et seq.*

(8) *Anal.* carbon found 76.71, theory 76.83; hydrogen found 8.35, theory 8.24.

(9) *Anal.* carbon found 64.57, theory 64.74; hydrogen found 5.51, theory 5.43.

(10) *Anal.* carbon found 47.74, theory 47.88; hydrogen found 4.13, theory 4.02.

(11) J. Chien, *J. Chem. Educ.*, **24**, 494 (1947).

(12) I. F. Halverstadt and W. D. Kumler, *THIS JOURNAL*, **64**, 2988 (1942).

(13) See, for example, C. P. Smyth, in Weissberger, "Physical Methods of Organic Chemistry," Volume I, Part II, Second edition, Chapter XXIV, Interscience Publishers, Inc., New York, N. Y., 1949.