The Synthesis of Trichloronitrosomethane

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Trichloronitrosomethane was prepared first by Prandtl and Sennewald in 1929 by the oxidation of trichloromethylsulfinic acid with nitric acid.[1] This synthesis was later improved by reacting a solution of sodium trichloromethylsulfinate, sodium nitrite, and sodium nitrate with hot 20% sulfuric acid and distilling off the nitroso compound as formed.[2] These methods suffer from the disadvantage that the high temperature of the reaction brings about some decomposition of the nitroso compound, and the product so produced is wet.

Other syntheses reported in the literature are the thermal decomposition of trichloroacethydroxamic

$$\mathrm{CCl_3CONHOH} \longrightarrow \mathrm{CCl_3NO} + \mathrm{CH_2O}$$

acid[3] and a radiochemical method which involves bubbling nitric oxide through γ-irradiated carbon tetrachloride.[4]

The present work reports a synthesis of trichloronitrosomethane which is a rapid, low-temperature process and gives a 65–70% yield of trichloronitrosomethane. Nitrosyl chloride reacts rapidly below 0° with sodium trichloromethylsulfinate to yield trichloronitrosomethane, sulfur dioxide, and sodium chloride.

$$\mathrm{CCl_3SO_2Na} + \mathrm{NOCl} \longrightarrow \mathrm{CCl_3NO} + \mathrm{SO_2} + \mathrm{NaCl}$$

Reaction begins when the nitrosyl chloride melts and is complete when the reactants have warmed to 0°.

No reaction is observed between sodium trichloromethylsulfinate and nitrosyl chloride in sulfur dioxide solution.

The reaction probably proceeds by a radical-chain mechanism initiated by chlorine atom attack on sodium trichloromethylsulfinate.

$$\mathrm{NOCl} \rightleftharpoons \mathrm{NO} + \mathrm{Cl} \tag{1}$$

$$\mathrm{CCl_3SO_2Na} + \mathrm{Cl}\cdot \longrightarrow \mathrm{CCl_3SO_2}\cdot + \mathrm{NaCl} \tag{2}$$

$$\mathrm{CCl_3SO_2}\cdot + \mathrm{NOCl} \longrightarrow \mathrm{CCl_3SO_2NO} + \mathrm{Cl}\cdot \tag{3}$$

$$\mathrm{CCl_3SO_2NO} \longrightarrow \mathrm{CCl_3NO} + \mathrm{SO_2} \tag{4}$$

Nitrosyl chloride no doubt dissociates to a small extent into chlorine atoms, a large concentration of which need not be postulated since, once initiated, the reaction is self-propagating by steps 2 and 3.

Although an ionic mechanism can be readily envisaged followed by reaction 4, this is considered un-

$$\mathrm{CCl_3SO_2^-\,Na^+} + \mathrm{NO^+Cl^-} \longrightarrow \mathrm{CCl_3SO_2NO} + \mathrm{NaCl}$$

likely since it has been shown that no trichloronitrosomethane is formed in sulfur dioxide solution.

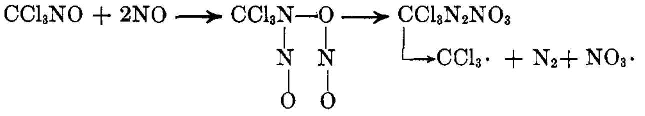
An attempt to prepare trichloronitrosomethane by the reaction of silver trichloroacetate with nitrosyl chloride resulted in an explosive reaction. An explosion also occurred when a mixture of sodium trichloroacetate and nitrosyl chloride was irradiated with ultraviolet light. A possible cause of this explosion could be the intermediate formation of a diazonium nitrate from trichloronitrosomethane and nitric oxide, followed by the rapid decomposition of the diazonium compound according to the following scheme.

$$\mathrm{NOCl} \rightleftharpoons \mathrm{NO}\cdot + \mathrm{Cl}\cdot$$

$$\mathrm{CCl_3COONa} + \mathrm{Cl}\cdot \longrightarrow \mathrm{CCl_3COO}\cdot + \mathrm{NaCl}$$

$$\mathrm{CCl_3COO}\cdot + \mathrm{NOCl} \longrightarrow \mathrm{CCl_3COONO} + \mathrm{Cl}\cdot$$

$$\mathrm{CCl_3COONO} \longrightarrow \mathrm{CCl_3NO} + \mathrm{CO_2}$$



$$\mathrm{CCl_3NO} + 2\mathrm{NO} \longrightarrow \mathrm{CCl_3}\underset{\substack{|\\ \mathrm{N}\\ |\\ \mathrm{O}}}{\mathrm{N}}\text{—}\underset{\substack{|\\ \mathrm{N}\\ |\\ \mathrm{O}}}{\mathrm{O}} \longrightarrow \mathrm{CCl_3N_2NO_3} \;\llcorner\!\!\longrightarrow \mathrm{CCl_3}\cdot + \mathrm{N_2} + \mathrm{NO_3}\cdot$$

$$\mathrm{NO_3}\cdot + \mathrm{NOCl} \longrightarrow 2\mathrm{NO_2} + \mathrm{Cl}\cdot$$

$$\mathrm{CCl_3}\cdot + \mathrm{NO_2} \longrightarrow \mathrm{CCl_3NO_2}$$

$$2\mathrm{CCl_3}\cdot \longrightarrow \mathrm{C_2Cl_6}$$

Diazonium nitrates have been postulated previously as intermediates in the decomposition of nitroso compounds.[5–11]

Experimental

Infrared spectra were recorded on a Perkin–Elmer Model 221 infrared spectrophotometer. Molecular weight measurements were taken by Regnaults method and elemental analyses were carried out by Messrs. Wiele and Strauss, Cambridge, England.

Reagents.—Trichloromethylsulfonyl chloride was a technical grade of Eastman Kodak and was used without further purification. Nitrosyl chloride was prepared by a standard procedure[12] and purified by distillation using a 16 cm. × 7–8 mm. i.d. column packed with 3-mm. Fenske glass helices. The purity was checked by infrared analysis and molecular weight measurement.

Sodium trichloromethylsulfinate was prepared from trichloromethylsulfonyl chloride by the procedure of Prandtl and Sennewald.[1]

The Preparation of Trichloronitrosomethane.—The following procedure is typical. A 300-ml. capacity heavy-walled (3–4 mm.) Pyrex glass Carius tube was charged with finely powdered sodium trichloromethylsulfinate (33.5 g., 0.163 mole) and evacuated, and nitrosyl chloride (21.0 g., 0.321 mole) was condensed in. The tube was sealed off at the neck and placed in an ice bath. Reaction was complete when the tube and contents had warmed to 0°. The volatile materials were removed *in vacuo* to leave an involatile solid (10.77 g.) which consisted of sodium chloride (7.77 g.), unchanged sodium trichloromethylsulfinate, and some unidentified material. The volatile materials were fractionated by trap-to-trap condensation *in vacuo*. The bulk of the trichloronitrosomethane (17.2 g., 0.115 mole) collected in a −63° trap although a small amount passed through to the liquid nitrogen trap where the sulfur dioxide and excess nitrosyl chloride condensed (27.1 g.).

The trichloronitrosomethane so produced was a deep blue liquid, b.p. 55–56° dec. (lit.[1] b.p. 57–58°), which decomposed slowly at room temperature. The infrared spectrum exhibits a band at 6.18 μ typical of the —N═O stretching frequency.

Anal. Calcd. for $\mathrm{CCl_3ON}$: C, 8.09; Cl, 73.1; N, 9.44; mol. wt., 148.5. Found: C, 8.58; H, 0.17; Cl, 75.26; N, 9.64; mol. wt., 149.

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(1) W. Prandtl and K. Sennewald, *Ber.*, **62**, 1754 (1929).

(2) W. Prandtl and W. Dolfus, *ibid.*, **65**, 754 (1932).

(3) I. L. Knunyants and G. A. Sokol'sku, *Dokl. Akad. Nauk SSSR*, **132**, 602 (1960).

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(12) J. R. Morton and H. W. Wilcox, *Inorg. Syn.*, **4**, 48 (1953).

The discrepancy between the calculated and the experimental figures was probably due to some decomposition taking place after the sample was dispatched to the analyst.

When a similar experiment was carried out in sulfur dioxide solution no reaction took place.

The Reaction of 2-Amino-Δ^2-thiazoline and Related Compounds with Nitrous Acid[1a]

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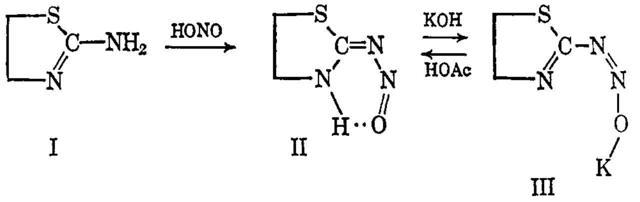
In order to confirm structural assignments made in a study of the reaction of 1(S),8(N)-*p*-menthyleneisothiourea and its N-methyl derivatives with nitrous acid,[2] 2-amino-Δ^2-thiazoline (I) and its N-methyl derivatives, 2-imino-3-methylthiazolidine (IV), and 2-methylamino-Δ^2-thiazoline (VI) were prepared and nitrosated. Reactions observed in this series were completely analogous to those observed for the 1(S),-8(N)-*p*-menthyleneisothioureas, supporting the assignments made as well as indicating the functional similarity of the two ring systems.

Reaction of I in cold glacial acetic acid with aqueous sodium nitrite resulted in the precipitation of a golden yellow solid, 2-nitrosoiminothiazolidine (II). This compound gave a positive Liebermann's nitrosoamine test and was decomposed by concentrated HCl to nitrous acid and the hydrochloride of I. Treatment of II with ethanolic KOH resulted in the formation of colorless potassium Δ^2-thiazoline-2-diazotate (III). Compound III regenerated II on acidification with cold glacial acetic acid.

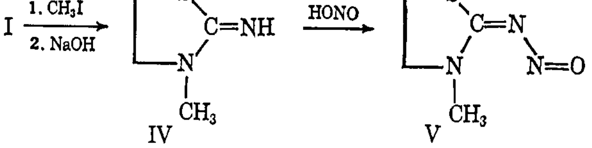


I II III

The structure of II, which is formulated as a primary rather than as a secondary nitrosoamine, was deduced from its intense color, its infrared spectrum, the reversibility of the reaction II ⇄ III, and from the colors and infrared spectra of the nitrosated N-methyl derivatives of I. Thus, if the yellow compound were 2-imino-3-nitrosothiazolidine, the nitroso group would not be in conjugation with the C=N group, and the color of the compound would be expected to be more like that of most secondary nitrosoamines. Further support for the assigned structure comes from a comparison of the infrared spectra of I and II. The absorption band at 6.18 μ in the spectrum of I, assigned to C=N stretching,[3] is shifted to 6.30 μ in the spectrum of II, indicating conjugation.

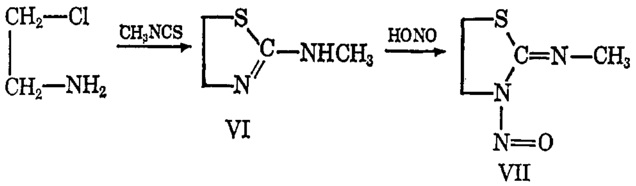
The bands at 7.25 and 8.84 μ in the spectrum of II are assigned to the N=O group.[4] These bands are absent in the spectrum of III and are replaced by a large, poorly resolved absorption in the region 7.65–8.26 μ which is assigned to the diazotate group. While this lies somewhat outside the region where absorptions characteristic of the N=N group are expected to occur,[5] a similar broad band has been found in the spectra of the *cis*- and *trans*-potassium benzenediazotates.[6] Bands at 2.92 and 3.01 μ in the spectrum of I assigned to N-H stretching are shifted entirely to 3.29 μ in the spectrum of II, consistent with hydrogen bonding to the nitroso group as shown.

Additional evidence for the correctness of structure II was obtained by examining the nitrosated N-methyl derivatives of I. Treatment of 2-imino-3-methylthiazolidine (IV), prepared from I and methyl iodide,[7] with nitrous acid gave rise to an orange compound, 2-nitrosoimino-3-methylthiazolidine (V). In this case, conjugation of the C=N groups is unavoidable, and the intense color of V as well as the position of the C=N absorption band in the infrared spectrum (6.31 μ) clearly show the consequences of such conjugation.



IV V

The other N-methyl derivative of I, 2-methylamino-Δ^2-thiazoline (VI), cannot be prepared directly from I but was prepared from 2-chloroethylamine and methyl isothiocyanate.[7] Nitrosation of either nitrogen cannot lead to conjugation, and consequently, the nitroso compound obtained (VII) on treating VI in cold glacial acetic acid with aqueous $NaNO_2$ is a faintly yellowish white. As expected, the position of the C=N band in the infrared spectrum of VI (6.19 μ) is unaltered in the spectrum of VII.



VI VII

Compound VII was formulated as 2-methylimino-3-nitrosothiazolidine rather than as N-nitroso-2-methylamino-Δ^2-thiazoline (VIII) since electrophilic attack on systems of the type represented by VI appears to occur preferentially on the imino nitrogen. Thus, as mentioned previously, direct methylation of I produces only IV and not a mixture of IV and VI. The apparently anomalous formation of II from I must therefore be attributed to enhanced stability provided in conjugation.

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[1] (a) From the Ph.D. thesis of E. W. Stern, 1954. (b) The M. W. Kellogg Co., Division of Pullman, Inc., New Market, N. J.

[2] L. C. King and E. W. Stern, *J. Org. Chem.*, **23**, 1928 (1958).

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[6] R. J. W. Lefevre, M. F. O'Dwyer, and R. L. Werner, *Australian J. Chem.*, **6**, 341 (1953).

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