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-$\Delta^2$-thiazoline and Related Compounds with Nitrous Acid[1a]

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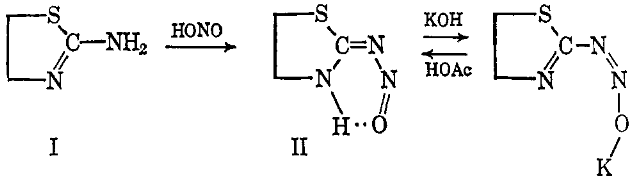
In order to confirm structural assignments made in a study of the reaction of 1(S),8(N)-*p*-menthyleneisothiourea and its N-methyl derivatives with nitrous acid,[2] 2-amino-$\Delta^2$-thiazoline (I) and its N-methyl derivatives, 2-imino-3-methylthiazolidine (IV), and 2-methylamino-$\Delta^2$-thiazoline (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.

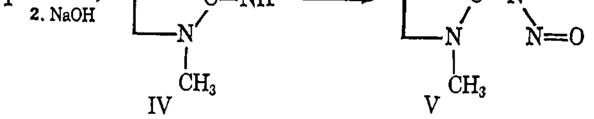
Reaction of I in cold glacial acetic acid with aqueous sodium nitrite resulted in the precipitation of a golden yellow solid, 2-nitrosoiminothiazolidine (II). This compound gave a positive Liebermann's nitrosoamine test and was decomposed by concentrated HCl to nitrous acid and the hydrochloride of I.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



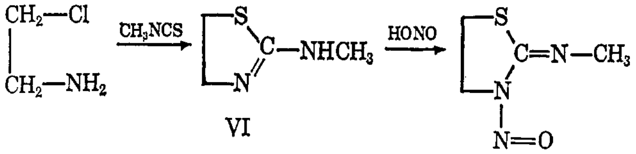
The structure of II, which is formulated as a primary rather than as a secondary nitrosoamine, was deduced from its intense color, its infrared spectrum, the reversibility of the reaction II $\rightleftarrows$ III, and from the colors and infrared spectra of the nitrosated N-methyl derivatives of I. 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 $\mu$ in the spectrum of I, assigned to C=N stretching,[3] is shifted to 6.30 $\mu$ in the spectrum of II, indicating conjugation.

The bands at 7.25 and 8.84 $\mu$ 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 $\mu$ 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 $\mu$ in the spectrum of I assigned to N–H stretching are shifted entirely to 3.29 $\mu$ 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 $\mu$) clearly show the consequences of such conjugation.



The other N-methyl derivative of I, 2-methylamino-$\Delta^2$-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 $\mu$) is unaltered in the spectrum of VII.



Compound VII was formulated as 2-methylimino-3-nitrosothiazolidine rather than as N-nitroso-2-methylamino-$\Delta^2$-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).

(3) N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).

(4) R. N. Haszeldine and J. Jander, *J. Chem. Soc.*, 695 (1954).

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 271.

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

(7) S. Gabriel, *Ber.*, **22**, 1139 (1889).

Corresponding behavior of the aminothiazoles has been reported,[8] although the compounds in this series were apparently less stable. Nitrosation of 2-aminothiazole and its directly methylated derivative resulted in the formation of highly colored products, while the isomeric N-methyl derivative prepared from dichloroethyl ether and methylthiourea yielded a yellowish white nitroso compound.

### Experimental[9]

**2-Nitrosoiminothiazolidine** (II).—A solution of 10 g. of I[10] in 50 ml. of glacial acetic acid was cooled in an ice bath, 60 ml. of ice-cold aqueous sodium nitrite was added, and the mixture was allowed to stand at ice temperature. After *ca.* 5 min., a yellow solid began to precipitate. After standing overnight, the solid was collected on a filter, washed with a little water, and recrystallized from absolute ethanol: decomposed explosively at 154–155°; infrared spectrum ($CHCl_3$), 3.29 (NH), 6.30 (C═N), 7.25, 8.84 μ (N═O).

*Anal.* Calcd. for $C_3H_5N_3OS$: N, 32.04. Found: N, 32.11.

The compound gave a positive Liebermann's nitrosoamine test. When II was treated with concentrated HCl, nitrous acid was formed. Subsequent evaporation of the solution yielded the hydrochloride of I, m.p. 198–200° (lit.[7] m.p. 198–199°).

**Potassium Δ²-Thiazoline-2-diazotate** (III).—Several pieces of potassium hydroxide were dissolved in absolute ethanol and some II was added to a small amount of the solution. The solution was cooled and dry ether was added until a white precipitate formed. The latter was collected on a suction filter and washed with chloroform and ether. The compound was pale yellow: dec. pt. 244–246°; infrared spectrum (KBr), 6.33 (C═N), 7.65–8.26 μ (diazotate.)

*Anal.* Calcd. for $C_3H_4KN_3OS$: ash (sulfate), 51.4. Found: ash, 49.8.

When reprecipitated from ethanol with ether, the compound was white but darkened again after being exposed to air for several minutes. Acidification with cold glacial acetic acid regenerated II.

**2-Imino-3-methylthiazolidine** (IV).—A quantity of I was dissolved in dry ether, an equivalent amount of methyl iodide was added, and the mixture was warmed on the steam bath for several minutes. White crystals precipitated immediately. After standing overnight, the precipitate was collected on a filter; m.p. 157–158° (lit.[7] m.p. 159–160°).

The hydriodide was treated with 33% KOH. The oil which separated was extracted with benzene, the extract was dried and evaporated, and the oily residue was used directly in the following experiment.

**2-Nitrosoimino-3-methylthiazolidine** (V).—Compound IV was dissolved in cold glacial acetic acid and treated with excess cold 10% aqueous $NaNO_2$. The mixture was allowed to stand overnight at ice temperature. It was then extracted with ether. The bright orange extract was dried over anhydrous $Na_2SO_4$, and the solvent was evaporated. An orange residue remained which, on crystallization from benzene–hexane, decomposed at 124–125°; infrared spectrum ($CHCl_3$), 6.31 (C═N), 7.32, 9.17 μ (N═O).

*Anal.* Calcd. for $C_4H_7N_3OS$: N, 28.94. Found: N, 29.18.

The compound gave a positive Liebermann's test.

**2-Methylimino-3-nitrosothiazolidine** (VII).—A solution of 5 g. of VI[11] in 25 ml. of glacial acetic acid was cooled on ice and treated with excess cold 10% aqueous $NaNO_2$. A white precipitate formed after about 10 min. The mixture was allowed to stand at ice temperature for several hours, after which time 3.8 g. of a yellowish white solid was collected on a filter. Recrystallization from hexane gave crystals: m.p. 40–41°; infrared spectrum ($CHCl_3$), 6.19 (C═N), 7.41, 9.60 μ (N═O).

*Anal.* Calcd. for $C_4H_7N_3OS$: N, 28.94. Found: N, 29.32.

The compound gave a positive Liebermann's test and evolved nitrous acid when treated with concentrated HCl.

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[8] E. Näf, *Ann.*, **265**, 108 (1891).

[9] All melting points were taken on a Fisher-Johns block. Analyses are by H. Beck, J. Sorenson, and C. White.

[10] Prepared according to G. W. Raiziss and L. W. Clemmence, *J. Am. Chem. Soc.*, **63**, 3124 (1941).

[11] Prepared according to directions in ref. 7.

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## 1,1-Dicyano-2,2,2-trialkoxyethane Salts

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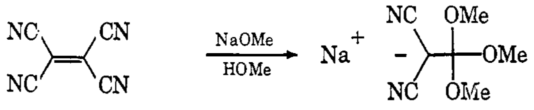
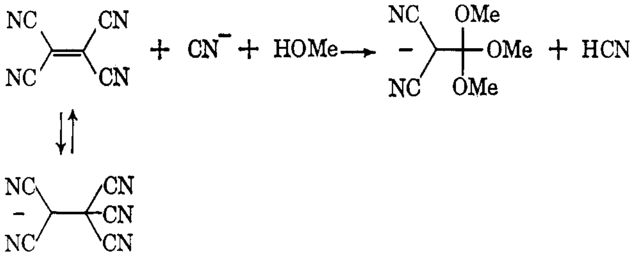
*Contribution No. 1084 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898*

*Received April 9, 1965*

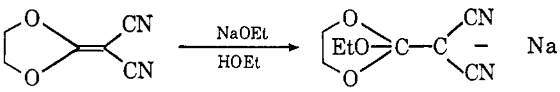
Tetracyanoethylene reacts with methanolic sodium methoxide to give sodium 1,1-dicyano-2,2,2-trimethoxyethanide, a stable white salt. The corresponding potassium salt is produced from methanolic potassium hydroxide and tetracyanoethylene. This result points out the presence of potassium methoxide in "methanolic potassium hydroxide" as well as a greater rate of reaction for the methoxide since tetracyanoethylene reacts with hydroxide ion to give mainly pentacyanopropenide.[1] Surprisingly, methanolic potassium cyanide and tetracyanoethylene also give the trimethoxy compound. In contrast, potassium cyanide, in acetonitrile, adds to tetracyanoethylene to form potassium pentacyanoethanide.[2] Possibly the pentacyanoethanide is formed to some extent in the methanol solution in equilibrium with TCNE and cyanide ion, but is removed by the irreversible formation of the trimethoxide.





The products can be accounted for by the stepwise addition of methoxide ion and elimination of cyanide ion.

The addition of potassium methoxide to dicyanoketene dimethyl acetal,[3] of sodium ethoxide to dicyanoketene diethyl acetal,[3] and of sodium ethoxide to dicyanoketene ethylene acetal[3] supports the last step of the proposed reaction sequence and confirms the structural assignments. In addition, the last example indicates that an equilibrium is not established in the final addition of alkoxide, for then the product would be sodium dicyanotriethoxyethanide.



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[1] W. J. Middleton, E. L. Little, D. D. Coffman, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).

[2] O. W. Webster, W. Mahler, and R. E. Benson, *ibid.*, **84**, 3678 (1962).

[3] W. J. Middleton and V. A. Engelhardt, *ibid.*, **80**, 2788 (1958).