small column of silicic acid prepared in chloroform. Ether elution yielded 26 mg. (96%) of material whose infrared spectrum (dioxane) possessed all major bands present in the spectrum of the material obtained from the reaction of 2-acetamidoanthracene with maleic anhydride except one at 10.70 μ. The material was crystallized to a constant melting point from an acetone–benzene mixture by slowly boiling off the acetone. The white plates obtained changed at 146°, became amorphous at 160°, and liquid at 166°. Ultraviolet spectrum (methanol): $\lambda_{\max}$ 253 mμ, ε 16,000; $\lambda_{\max}$ 287 mμ, ε 1500.

*Anal.* Calcd. for $C_{20}H_{15}O_4N$: C, 72.06; H, 4.54; N, 4.20. Found: C, 71.85; H, 4.62; N, 4.26.

Reductive acetylation of the *syn* adduct yielded material which possessed in its infrared spectrum all bands present in the spectrum of the material obtained from the reaction of 2-acetamidoanthracene with maleic anhydride except one at 10.80 μ. Crystallizations from acetone–benzene gave white needles, m.p. 149–150°. Ultraviolet spectrum (methanol): $\lambda_{\max}$ 253 mμ, ε 16,000; $\lambda_{\max}$ 287 mμ, ε 1500.

*Anal.* Calcd. for $C_{20}H_{15}O_4N$: C, 72.06; H, 4.54; N, 4.20. Found: C, 72.53; H, 4.73; N, 4.01.

**Reductive Methylation of *syn*- and *anti*-2-Nitro-9,10-dihydroanthracene-9,10-*endo*-α,β-succinic Anhydrides (Ia and IIa) to *syn*- and *anti*-2-Dimethylamino-9,10-dihydroanthracene-9,10-*endo*-α,β-succinic Anhydrides (Ic and IIc).**—A solution of 128 mg. (0.4 mmole) of the *anti*-2-nitroanthracene–maleic anhydride adduct in 5 cc. of 95% ethanol, 0.5 cc. of glacial acetic acid, and 0.4 cc. of 36% formaldehyde solution was hydrogenated in the presence of 15 mg. of Adam's catalyst. An uptake of 55 cc. of hydrogen (expected for $-NO_2$ to $-N(CH_3)_2$, 49 cc.) occurred over a period of 24 hr. The solution was evaporated to dryness after removal of the catalyst. The material was extracted with aqueous ether. The ethereal extract, after drying over anhydrous sodium sulfate and evaporation, yielded 107 mg. of material. The white solid was refluxed in 30 cc. of benzene for 20 min. After evaporation of the solvent, 105 mg. (82%) of material was obtained whose infrared spectrum was almost identical with that of the material obtained from the reaction of 2-dimethylaminoanthracene with maleic anhydride. Crystallizations from a methylene chloride–petroleum ether mixture afforded off-white plates, m.p. 208–209°. Ultraviolet spectrum (methanol): $\lambda_{\max}$ 270 mμ, ε 12,000; $\lambda_{\max}$ 310 mμ, ε 24,000.

Reductive methylation of the *syn* adduct required a longer period of time. The infrared spectrum of the material obtained (79%) was similar but not identical with that of the *anti* adduct. No major difference existed.

**Reaction Mixture Analysis.**—The ratio of adducts obtained from reaction mixtures of 2-nitroanthracene and 2-acetamidoanthracene with maleic anhydride were determined by quantitative infrared analysis. A variation of the "cell in-cell out" method[24] was used. A constant incident intensity (100% transmission) and zero reading (0% transmission) were obtained in the 10.5- to 11.0-μ region for all samples. Beer's law for a two-component system was used to calculate the composition of the mixture.

The 2-nitroanthracene-maleic anhydride reaction mixture was found to be composed of 39.2% of the *syn* adduct and 60.8% of the *anti* adduct. The 10.57- and 10.87-μ bands of the *anti* adduct and the 10.70 μ band of the *syn* adduct were utilized for the analysis. The 2-acetamidoanthracene–maleic anhydride reaction mixture contained 52.0% of the *syn* adduct absorbing at 10.70 μ and 48.0% of the *anti* adduct absorbing at 10.80 μ. Analyses were performed on solutions of known concentration similar to those of the unknowns using the same technique. The analyses were in good agreement and accurate to 0.3%.

The composition of the reaction mixture of 2-dimethylaminoanthracene and maleic anhydride was determined by analysis of its nuclear magnetic resonance spectrum in benzene solution. The *N*-methyl peaks of the *syn*- and *anti*-dimethylamino adducts appeared at 141 and 149 c.p.s., respectively. The relative areas of the two peaks were determined. The mixture was composed of 45% of the *anti* adduct and 55% of the *syn* adduct. The method of analysis was accurate to 2%.

**Attempted Equilibration of *syn*- and *anti*-Adducts.**—The infrared spectrum of 5 mg. of pure *syn*- or *anti*- adduct in 0.5 cc. of benzene was recorded. The infrared spectrum of the solution after refluxing for 1 week was identical with that of starting material. To this solution was added 10 mg. of maleic anhydride. After refluxing the solution for 24 hr., no change was observed in the spectrum. No change occurred in the nuclear magnetic resonance spectra of the 2-dimethylaminoanthracene adducts.

**Kinetic Data.**—Benzene solutions of known concentration (0.00469 *M* anthracene, 0.000158 *M* 2-dimethylaminoanthracene, 0.000184 *M* 2-nitroanthracene—all with 1.2806 *M* maleic anhydride) were placed in a 1-cm. quartz spectrophotometric cell. Five minutes were allowed for complete mixing to occur before initial readings were taken. Measurements of optical density were made with a Beckman DU spectrophotometer at 420 mμ. Only starting material was found to absorb at this wave length. The values of the rate constants, $k$, were determined from the first-order rate expression $k = 2.303 \log (ODi/ODt)/(MA)t$.

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[24] *Perkin-Elmer Instrument News*, **II**, **3**, 6 (1951).

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# Reactions of Ethylene Diisothiocyanate with Primary and Secondary Amines[1]

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Ethylene diisothiocyanate (I) reacts with an excess of aqueous methylamine and ethylamine to give 1-methyl- and 1-ethylthiocarbamylimidazolidine-2-thione (Va, b). The phenyl analog (Vc) has been obtained upon addition of aniline to I in acetone solution, whereas the reverse mode of addition yielded the substituted ethylenedithiourea (II). Structures Va, b, and c have been prepared by independent syntheses. Reaction of I with excess aqueous dimethylamine and pyrrolidine gave almost exclusively the ethylenedithioureas; with excess of aqueous piperidine, a mixture of bis- and monoadduct was formed. The monoadducts could be conveniently obtained from all the secondary amines studied, by adding them to I in acetone solution. The properties of these monoadducts are consistent with the structures 1-dialkyl- and 1-alkylenethiocarbamylimidazolidine-2-thione, similar to those of Va, b, and c.

Ethylene diisothiocyanate (I) has been reported to react with aqueous ammonia forming ethylenedithiourea (II. R = R′ = H) and a monoadduct for which structure III has been formulated.[2] Alkylene dithioureas had been obtained previously by treating I with aniline,[3] as well as by treating the homolog $(CH_2)_4(NCS)_2$ with ammonia, methylamine, and aniline,[4] and $(CH_2)_6(NCS)_2$ with aziridine.[5]

The structure of the monoadduct formed by the reaction of I with ammonia currently is being elucidated in our laboratories by X-ray diffraction.[6] In this

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[1] Part of this work has been treated in a preliminary communication: F. D'Angeli and A. Bandel, *Tetrahedron Letters*, **1**, 5 (1961).

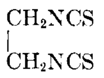
[2] G. D. Thorn and R. A. Ludwig, *Can. J. Chem.*, **32**, 872 (1954).

[3] A. Ya. Yakubovic and V. A. Klimova, *J. Gen. Chem. USSR* (Eng. Transl.), **9**, 1777 (1939); *Chem. Abstr.*, **34**, 3685 (1940).

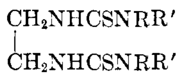
[4] J. v. Braun and G. Lemke, *Ber.*, **55**, 3552 (1922).

[5] A. G. Bayer, British Patent 753, 247; *Chem. Abstr.*, **51**, 9681 (1957).

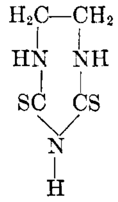
[6] Unpublished work.



I



II



III

paper we report the chemical behavior of I toward primary and secondary amines.

Ethylene diisothiocyanate (I) reacts with these amines at room temperature, giving two different types of compounds whose relative yields depend upon structural factors and experimental conditions. This is shown in Table I.

TABLE I

FORMATION OF MONO- AND BISADDUCTS IN REACTIONS OF ETHYLENE DIISOTHIOCYANATE (I) WITH PRIMARY AND SECONDARY AMINES

| Amine | Moles of amine per mole of I | Medium | Order of addition of reagents | % Yield of products Monoadduct | Bisadduct |
|---|---|---|---|---|---|
| $CH_3NH_2$ | 5 | $H_2O$ | | 52 | 10 |
| $C_2H_5NH_2$ | 5 | $H_2O$ | | 63 | 10 |
| $C_6H_5NH_2$ | 5 | acetone | *a* | Traces | 46 |
| | 1 | acetone | *b* | 42 | Traces |
| $(CH_3)_2NH$ | 5 | $H_2O$ | | Traces | 72 |
| | 5 | acetone | *a* | – | 46 |
| | 1 | acetone | *b* | 42 | Traces |
| $(CH_2)_4NH$ | 5 | $H_2O$ | | Traces | 66 |
| | 5 | acetone | *a* | – | 60 |
| | 1 | acetone | *b* | 42 | Traces |
| $(CH_2)_5NH$ | 5 | $H_2O$ | | 30 | 30 |
| | 5 | acetone | *a* | – | 97 |
| | 1 | acetone | *b* | 75 | Traces |

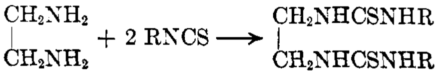
[a] I was added to the amine. [b] The amine was added to I.

**Aqueous Medium.**—Excess aqueous methylamine and ethylamine transformed I for the most part into monoadducts. In addition, minor amounts of bisadducts, namely the ethylenedithioureas (II) were formed. The pattern was reversed with secondary amines, which yielded largely (as with piperidine) or almost exclusively (as with dimethylamine and pyrrolidine) the bisadducts II.

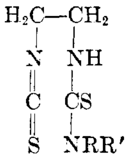
**Acetone Solution.**—In acetone solution, the products which were obtained depended upon the order of addition, and possibly upon molar ratio.

In this paper no distinction is drawn between these two variables, since the purpose of the research was to elucidate the structure of the monoadducts from the reactions of I with primary aliphatic amines and to find suitable conditions favoring monoadduct formation, rather than bisadduct formation with secondary amines. Addition of I to an excess of the secondary amines and aniline resulted in the formation of the dithioureas. On the contrary, the addition of these amines to an equimolecular quantity of I yielded mostly the monoadducts.

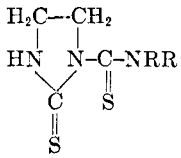
The structures of some of the bisadducts II which had been described incompletely in the literature were proven by independent synthesis, using reaction 1.[7] None of the monoadducts of I with the various amines showed the characteristic infrared absorption of the –NCS group in the 2100-cm.$^{-1}$ region. This rules out structure IV for all the monoadducts.



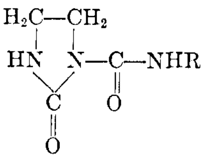
$$\begin{matrix} CH_2NH_2 \\ | \\ CH_2NH_2 \end{matrix} + 2\,RNCS \longrightarrow \begin{matrix} CH_2NHCSNHR \\ | \\ CH_2NHCSNHR \end{matrix} \qquad (1)$$



IV

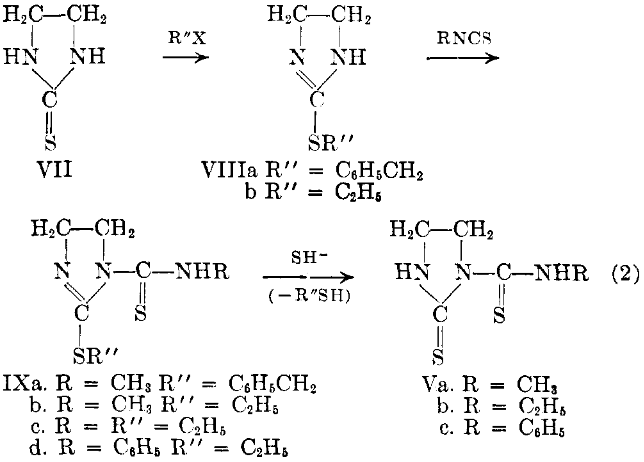


V



VI

Because of the well known tendency of bifunctional ethylenic systems to form imidazole derivatives,[8] the possibility of the formation of structure V was first investigated. The monoadducts obtained from I with primary amines are identical with the 1-alkyl-, and 1-phenylthiocarbamylimidazolidine-2-thiones obtained by the independent synthesis shown in reaction 2.[9]



VII

VIIIa R″ = $C_6H_5CH_2$
b R″ = $C_2H_5$

IXa. R = $CH_3$ R″ = $C_6H_5CH_2$
b. R = $CH_3$ R″ = $C_2H_5$
c. R = R″ = $C_2H_5$
d. R = $C_6H_5$ R″ = $C_2H_5$

Va. R = $CH_3$
b. R = $C_2H_5$
c. R = $C_6H_5$

Reaction 2 is an application of synthesis[10] of 1,5-dialkyl-2,4-dithiobiurets, RNHCSNHCSNHR, which are open chain analogs of structure V. It seems unlikely that under the mild conditions in which the last two steps were performed (0° or room temperature), the five-atom ring of 2-alkyl- and 2-benzylmercapto-2-imidazoline (VIIIa, VIIIb) would undergo any transformation besides the expected thiocarbamylation and subsequent thiohydrolysis.[11]

All monoadducts behaved in the same way upon acid and alkaline treatment. Thus they were stable to dilute acid, whereas all yielded imidazolidine-2-thione (VII) on alkaline hydrolysis.

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[7] Ethylendiamine reacts with isothiocyanates also in equimolecular ratio; the produced amino-ethylthioureas have been transformed into 2-amino-imidazolines. L. Helgen, O. Stoutland and C. L. Agre, *J. Org. Chem.*, **24**, 818, 884 (1959). German Patent 842, 065; *Chem. Abstr.*, **52**, 10208 (1958).

[8] L. K. Hofmann, "Imidazole and its derivatives, Part 1," Interscience Publishers, Inc., New York, N. Y., 1953.

[9] The isosteric structure VI has been attributed, apparently with no experimental evidence, to the compound obtained from $(-CH_2NCO)_2$ and $NH_3$. W. Nusshag, *Inaug. Diss. zur Erlang. d.W. eines Dr. Med. Vet.*, Berlin, 1913. O. Nitsche, *Centr. Bl.*, **2**, 60 (1914). *Cf.* G. Schroeter and C. Seidler, *J. prakt. Chem.*, **105**, 165 (1922); Th. Curtius and W. Hechtenberg, *ibid.*, **106**, 289 (1923).

[10] (a) F. H. S. Curd, D. G. Davey, D. N. Richardson, and R. de B. Ashworth, *J. Chem. Soc.*, 1739 (1949); (b) A. E. S. Fairfull and D. Peak, *J. Chem. Soc.*, 796, (1955).

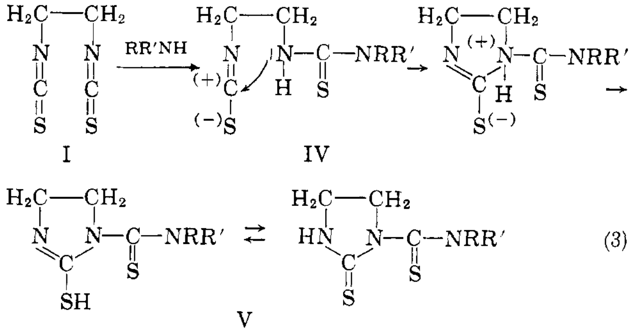
[11] It has been known for many years that N-thiocarbamylaziridines rearrange to thiazoles. More recently, it has been reported that N-thiocarbamylazetidines rearrange to thiazines. N-Thiocarbamylpyrrolidines do not rearrange under comparable conditions. M. Tisler, *Arch. Pharm.*, **291**, 467 (1958); **293**, 621 (1960); *cf.* H. W. Heine, W. G. Kenyon, and E. M. Johnson, *J. Am. Chem. Soc.*, **83**, 2570 (1961).

On the grounds of spectroscopic and chemical data, we also assign structure V to the monoadducts obtained from the reactions of I with secondary amines. Additional evidence from independent synthesis and/or from physical studies will be reported in a subsequent paper.

## Discussion

While in suitable conditions monoadducts were obtained both from primary and secondary amines, further research is needed to understand why, in aqueous medium, ring closure occurs preferentially with the former.

Compound IV was never observed to appear and, if it is formed at all in the course of the various reactions, it might act as an intermediate in the formation of the imidazole ring—possibly through scheme 3—because of a particularly favorable steric situation.



(3)

It has been reported, in fact, that acyclic dithiobiurets are not formed from alkyl or aryl isothiocyanates and thioureas.[10a] Research in progress on reactions of homologs of I with ammonia and amines confirms the importance of steric requirements in the formation of the imidazole derivatives V described here.[12]

## Experimental[13]

**Ethylene diisothiocyanate** (I) was obtained by decomposing $(\text{—}CH_2NHCSSCOOC_2H_5)_2$ (X) at 110–120° *in vacuo* until a constant weight was reached; each sample was prepared at the time of use and this procedure yielded I in a pure state. X in turn was prepared from sodium ethylene dithiocarbamate (XI) and ethyl chloroformate.[3,14]

**Chromatography.**—Descending technique, Whatman no. 1 paper sheets, and a *n*-butyl alcohol–acetic acid–water (4:1:5) solvent mixture were used throughout. Grote's reagent[15] gave (i) blue spots with all ethylenedithioureas (as well as with ethylenethiourea VII); (ii) rose spots with monoadducts obtained from primary amines; (iii) yellow spots with monoadducts obtained from secondary amines. Silver nitrate (1% in ethanol) gave, respectively, dark yellow, ochre, and rose to gray-rose spots; furthermore it gave a rose spot with VII, $R_f$ 0.65.[16] $R_f$ values are reported in the following paragraphs for most of the compounds obtained.

**Reaction of Ethylene Diisothiocyanate (I) with Methylamine.**—To 9.4 g. (0.065 mole) of I was added carefully with stirring 32.5 ml. of aqueous solution of $CH_3NH_2$ (11.4 g., 0.365 mole). An exothermic reaction took place, and a solid was gradually formed: stirring was continued occasionally for 1 hr., I being completely transformed into a white powder. This was filtered, first washed with water, then with ethanol; the crude compound (5.45 g.) was recrystallized four times from about 700 parts of water, yielding small, colorless prisms, m.p. 202–203°, $R_f$ 0.87. It is slightly soluble in cold, more in warm ethanol, soluble in acetone and pyridine, slightly soluble in chloroform and benzene, almost insoluble in petroleum ether and carbon disulfide. It was identical with the compound obtained through reaction 2 ($R = CH_3$) with regard to melting point, mixture melting point, infrared spectrum, and chromatographic behavior.

*Anal.* Calcd. for $C_5H_9N_3S_2$ (Va): C, 34.28; H, 5.18; N, 23.99; S, 36.54. Found: C, 34.10; H, 5.37; N, 23.96; S, 36.30.

By gradual concentration at room temperature of the mother liquor, a green heavy oil separated, followed by several crops of colorless crystals melting at 120–130°; despite the low melting points, paper chromatography of these fractions revealed only the presence of N,N'-dimethylethylenedithiourea (IIa). When the original mother liquor was evaporated to a sirup and this was taken up with ethanol, IIa was obtained in about 10% yield. No depression was observed in mixture melting point with a sample prepared as follows.

**N,N'-Dimethylethylenedithiourea** (IIa).—To a solution of anhydrous ethylenediamine (0.3 g., 0.005 mole) in 1 ml. of ethanol, methyl isothiocyanate (0.8 g., 0.011 mole) was added. After an exothermic reaction, colorless prisms were obtained (0.93 g., 90%); crystallization from ethanol yielded m.p. 163–164°[17]; $R_f$ 0.76.

*Anal.* Calcd. for $C_6H_{14}N_4S_2$ (IIa): N, 27.17; S, 31.04: Found: N, 27.01; S, 31.11.

**Reaction of Ethylene Diisothiocyanate (I) with Ethylamine.**—An aqueous 33% solution of ethylamine (50 ml., 0.36 mole) was cautiously added with stirring to I (9.4 g., 0.065 mole). I gradually turned red and a heterogeneous mass was formed, which was vigorously stirred for 1 hr. The colorless, crystalline powder obtained (7.8 g., 62%) gave, on recrystallization from water, bunches of fine colorless needles, m.p. 166–167°; $R_f$ 0.90.

*Anal.* Calcd. for $C_6H_{11}N_3S_2$ (Vb): C, 38.09; H, 5.86; N, 22.21; S, 33.83. Found: C, 38.19; H, 6.16; N, 22.42; S, 33.80.

The infrared spectrum, chromatographic behavior, etc., proved the identity of this compound with that obtained through equation 2. Evaporation of the mother liquor gave a semisolid mass (1.9 g.), which was shown by chromatography to be a mixture of Vb and of N,N'-diethylethylenedithiourea (IIb). The latter could be identified conclusively by chromatographic comparison with a specimen obtained through equation 1 ($R = C_2H_5$); m.p. 130–132°[18]; $R_f$ 0.89.

**Reactions of Ethylene Diisothiocyanate (I) with Aniline. A.**—The solution of I (1.62 g., 0.0112 mole) in 5 ml. of acetone was added dropwise during 10 min. with stirring, to a solution of aniline (5.35 g., 0.056 mole) in 7 ml. of acetone. There was a mild exothermic reaction; the solution gradually yielded a yellow powder (1.7 g., 46%). Washing with acetone and then with hot ethanol produced a colorless solid melting near 190°, as reported for N,N'-diphenylethylenedithiourea (IIc)[19]; $R_f$ 0.94.

B.—The solution of I (4.75 g., 0.033 mole) in 5 ml. of acetone was carefully added during 10 min. with a solution of aniline (3.1 g., 0.033 mole) in 5 ml. of acetone. A yellow solution was obtained which turned red in 20–30 min. and gave a yellow powder by scratching or seeding (3.28 g., 42%). This was washed with acetone and repeatedly crystallized from ethanol, yielding small colorless prisms, m.p. 175–177°; $R_f$ 0.96.

*Anal.* Calcd. for $C_{10}H_{11}N_3S_2$ (Vc): C, 50.63; H, 4.67; N, 17.72; S, 26.98. Found: C, 50.45; H, 4.59; N, 17.82; S, 26.72.

This compound was identical with the one obtained according to reaction 2. The mother liquor gave, on evaporation, a solid compound which appeared, by chromatography, to consist of

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[12] F. D'Angeli and V. Giormani, *Proc. Israel Chem. soc.*, **11A**, 5 (1962).

[13] Melting points were taken in capillary tubes and are uncorrected. Infrared spectra were obtained with a Perkin-Elmer Model 21 spectrometer equipped with sodium chloride optics. Solid compounds were examined in potassium bromide disks. We are indebted to Dr. C. Pecile and to the Institute of Physical Chemistry of the University of Padova for the infrared spectra and to Dr. Eloisa Celon for the microanalyses.

[14] Transformation of XI into X is favored by using a slight defficiency of $ClCOOC_2H_5$ at 0 – 5°. Crude X is best washed with cold ethanol till a recrystallization from warm ethanol becomes possible, without formation of $(\text{—}CH_2NHCSOC_2H_5)_2$.

[15] I. W. Grote, *J. Biol. Chem.*, **93**, 25 (1931).

[16] R. A. Ludwig and G. D. Thorn, *Rec. trav. chim. Pays Bas*, **79**, 160 (1960).

[17] Structure IIa had been assigned previously to a compound of m.p. 85–86°; T. N. Gosh, *J. Indian Chem. Soc.*, **10**, 583 (1933).

[18] H. Nagele, *Monatsh. Chem.*, **33**, 958 (1912); P. W. Preisler, *J. Am. Chem. Soc.*, **71**, 2849 (1949); O. Stoutland, L. Helgen, and C. L. Agre, *J. Org. Chem.*, **24**, 818 (1959).

[19] E. Lellmann and E. Wurthner, *Liebigs Ann.*, **228**, 234 (1885); K. N. Campbell, B. K. Campbell and S. J. Patelsky, *Proc. Indiana Acad. Sci.*, **53**, 119 (1943); *Chem. Abstr.*, **39**, 881 (1945).

Vc along with several other compounds, one of which was probably IIc (traces).

**1-Methylthiocarbamyl-2-benzylthioimidazoline (IXa).**—2-Benzylthio-2-imidazoline hydrochloride (VIIIa)[20] (11.4 g., 0.05 mole) was dissolved in 15 ml. of water and treated with methyl isothiocyanate (3.65 g., 0.05 mole), followed by ethanol to produce a clear solution (13 ml.). Twenty milliliters of 2.5 *N* sodium hydroxide was added dropwise in 40 min. with stirring; a solid substance separated and the suspension was stirred for an additional hour, then left overnight at 0°. The solid was filtered, washed with water, then with dilute ethanol (1:3), and dried (12.6 g., 94%). On crystallization from ethanol, colorless shiny prisms were obtained; m.p. 117–122°.

*Anal.* Calcd. for $C_{12}H_{15}N_3S_2$ (IXa): N, 15.83; S, 24.16. Found: N, 15.9; S, 24.36.

**Picrate.**—To 0.8 g. (0.003 mole) of IXa dissolved at 40° in 45 ml. of ethanol, 16 ml. of 5% ethanolic picric acid was added. Yellow prisms separated which were washed with ethanol, then with ether, and recrystallized from dimethylformamide and water; m.p. 160–164°; insoluble in the common solvents at room temperature; on warming there was evidence of decomposition (odor of $C_6H_5CH_2SH$).

*Anal.* Calcd. for $C_{12}H_{15}N_3S_2\cdot C_6H_3N_3O_7$: N, 17.00; S, 12.94. Found: N, 17.02; S, 12.84.

**1-Methylthiocarbamyl-2-ethylthioimidazoline (IXb).**—2-Ethylthio-2-imidazoline hydroiodide (VIIIb)[20] (5.16 g., 0.02 mole) was dissolved in water (2.5 ml.) and treated with methyl isothiocyanate (1.46 g., 0.02 mole) then with ethanol (5.5 ml.). The solution was cooled to 0° and 2.5 *M* sodium hydroxide (8 ml., 0.02 equivalent) was added during 30 min. with stirring. After 2 hr. of additional stirring, water was added and colorless crystals were obtained (2.9 g., 71%): the m.p. varied between 40 and 80° and the crystals effloresced when kept *in vacuo*.

*Anal.* Calcd. for $C_7H_{13}N_3S_2\cdot 2H_2O$: N, 17.56; S, 26.79. Found: N, 17.40; S, 26.57.

**Picrate.**—Two tenths of a gram of base, dissolved in ethanol (4 ml.), was treated with 4 ml. of 5% ethanolic picric acid; yellow crystals were recrystallized by dissolving them in acetone and diluting with water; m.p. 147–148°.

*Anal.* Calcd. for $C_7H_{13}N_3S_2\cdot C_6H_3N_3O_7$: N, 19.44; S, 14.83. Found: N, 19.57; S, 14.79.

**1-Ethylthiocarbamyl-2-ethylthioimidazoline (IXc).**—IXc has been obtained as was IXb, from VIIIb, ethyl isothiocyanate, and sodium hydroxide. It separated from the aqueous alcoholic solution as a heavy oil; water was added to complete precipitation and the oil was taken up in ether. The extract, washed (water), dried (sodium sulfate), and evaporated, left a colorless oil (65–70%). For the identification, a sample was converted into the *picrate*; prisms from acetone and water; m.p. 136°.

*Anal.* Calcd. for $C_8H_{15}N_3S_2\cdot C_6H_3N_3O_7$; N, 18.82; S, 14.37. Found: N, 18.60; S, 14.24.

**1-Phenylthiocarbamyl-2-ethylthioimidazoline (IXd).**—This compound was obtained like IXb, using phenyl isothiocyanate; during and after the addition of sodium hydroxide, a solid separated which was filtered after 4 hr., thoroughly washed with water, dried, then washed with ether leaving a colorless powder (66%); m.p. 83–85°. It was analyzed as the *picrate*; m.p. 128–130°, alteration above 110°.

*Anal.* Calcd. for $C_{12}H_{15}N_3S_2\cdot C_6H_3N_3O_7$: N, 16.99; S, 12.97. Found: N, 17.10; S, 13.01.

**Thiohydrolysis of IXa and IXb; IXc; IXd.**—Each thioether has been treated either without a solvent (IXa) or in a saturated alcoholic solution (IXb, IXc, and IXd) with an ethanolic solution of equimolecular sodium hydrosulfide, obtained by passing dry hydrogen sulfide into a 5% solution of sodium in ethanol. In one case (IXd), bubbling of hydrogen sulfide was continued after mixing of the reagents, for an additional hour. In all cases the reaction mixture was kept with occasional stirring at room temperature from 30 min. to a few hours, till no more changes could be noted. The resulting colorless solids were washed first with water and then with ethanol, and recrystallized from an appropriate solvent. No care was taken to secure highest yields; the following have been obtained in the indicated times: Va, 68% in 21 hr., from IXa; 65% in 30 min. from IXb; Vb, 73% in 30 min. from IXc; Vc, 22% in 2 hr. from IXd. They were identical with the compounds described previously with respect to melting point, mixture melting point, infrared spectra, and chromatographic behavior.

**Reactions of Ethylene Diisothiocyanate (I) with Dimethylamine. A.**—To 0.86 g. (0.006 mole) of I was carefully added under stirring 6 ml. of aqueous 22% dimethylamine (0.03 mole). An exothermic reaction took place and a solid was gradually formed which was thoroughly stirred during 40 min. The colorless microcrystalline powder was filtered, washed with water, and dried (1 g., 72%). It was recrystallized from water, yielding colorless opaque needles, soluble in acetone and chloroform, less so in ethanol, ether, benzene, and petroleum ether; m.p. 179–181°; $R_f$ 0.87.

*Anal.* Calcd. for $C_8H_{18}N_4S_2$ (IId): N, 23.92; S, 27.32. Found: N, 23.72; S, 27.39.

**B.**—A solution of I (1.68 g., 0.0116 mole) in 5 ml. of anhydrous acetone was added dropwise with stirring during 10 min. into 13.2 ml. of an acetone solution of dimethylamine (2.8 g., 0.062 mole). The reaction was slightly exothermic at the beginning; after 3 hr. of stirring, small colorless prisms of IId were gradually formed (1.26 g., 46%).

**C.**—To the solution of I (4.75 g., 0.033 mole) in 14 ml. of acetone, was added dropwise for 10 min., under stirring, 10 ml. of an acetone solution of dimethylamine (1.49 g., 0.033 mole). The dark solution obtained was left overnight with continued stirring; a pink-yellow powder separated. It was filtered, washed with acetone, and then with hot ethanol to remove trace of IId, and crystallized from ethanol in the presence of charcoal. Small colorless prisms were obtained, soluble in acetone and chloroform, less so in ether and cold water or ethanol, more in the warm; m.p. 186–187°; $R_f$ 0.81.

*Anal.* Calcd. for $C_6H_{11}N_3S_2$ (Vd): C, 38.09; H, 5.86; N, 22.21; S, 33.83. Found: C, 38.13; H, 6.08; N, 22.35; S, 34.32.

**Reactions of Ethylene Diisothiocyanate (I) with Pyrrolidine. A.**—I (1.67 g., 0.0116 mole) was carefully treated with pyrrolidine (4.1 g., 0.059 mole) diluted with water to give a 30% solution. A pink-yellow mass was obtained which was left overnight, then homogenized in a mortar and filtered. The powder was washed with water and ethanol and dried (2 g., 66%); by several crystallizations from ethanol, in presence of charcoal, colorless platelets assembled in stars were obtained; m.p. 223–224°; $R_f$ 0.91.

*Anal.* Calcd. for $C_{12}H_{22}N_4S_2$ (IIe): N, 19.56; S, 22.38. Found: N, 19.12; S, 22.37.

**B.**—A sample of I (3.3 g., 0.023 mole), dissolved in 10 ml. of acetone was added dropwise during 20 min. with stirring, to 8.2 g. (0.115 mole) of pyrrolidine diluted with 10 ml. of acetone. Stirring was continued 2 hr. and 3.9 g. (60%) IIe was obtained.

**C.**—Another sample of I (4.5 g., 0.031 mole) dissolved in 13 ml. of acetone, was treated dropwise (15 min.) with pyrrolidine (2.23 g., 0.031 mole) diluted with 13 ml. of acetone. Stirring was continued for 3 hr., then the orange powder was filtered, washed (acetone and benzene), and dried (1.43 g.); evaporation of the acetone mother liquor gave an additional 1.4 g. (total 42%). After extraction with boiling ethanol, to remove trace amounts of IIe, it was recrystallized from the same solvent, yielding colorless shiny needles, melting at 196–197°; $R_f$ 0.87.

*Anal.* Calcd. for $C_8H_{13}N_3S_2$ (Ve): C, 44.62; H, 6.08; N, 19.52; S, 29.78. Found: C, 44.46; H, 6.15; N, 19.73; S, 29.52.

**Reactions of Ethylenediisothiocyanate (I) with Piperidine. A.**—The suspension of I (1.7 g., 0.0118 mole) in 15.2 ml. of 33% aqueous solution of piperidine (0.055 mole) was stirred 20 min., then left overnight. The solid which formed was filtered, washed with ethanol and water, and dried (2.13 g.). Mono- and bidimensional chromatography (second run in water) indicated that a mixture of IIf and Vf had been obtained. The two compounds were separated using ethanol in which Vf gave supersaturated solutions; their identification is described.

**B.**—A solution of I (1.4 g., 0.01 mole) in 5 ml. of acetone was added dropwise during 20 min. with stirring, to piperidine (4.15 g., 0.05 mole) diluted with 5 ml. of acetone. A colorless crystalline powder gradually separated, which was washed with acetone and dried (2.95 g., 97%). On crystallization from ethanol, colorless prisms were obtained, very slightly soluble in water, ethanol and benzene, more so in dioxane; m.p. 207–209°; $R_f$ 0.91; in water, $R_f$ 0.56.

*Anal.* Calcd. for $C_{14}H_{26}N_4S_2$ (IIf): N, 17.82; S, 20.36. Found: N, 17.95; S, 20.44.

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C.—A solution of I (3.29 g., 0.022 mole) in acetone (10 ml.) was treated dropwise during 10 min. with piperidine (1.9 g., 0.022 mole) in acetone (10 ml.) and stirring was continued 3.5 hr. The yellow powder (3.55 g., 70%) was extracted with hot ethanol to remove traces of IIf, then crystallized from ethanol; colorless prisms, m.p. 180–181°; $R_f$ 0.88; in water, $R_f$ 0.75.

*Anal.* Calcd. for $C_9H_{15}N_3S_2$ (Vf): C, 47.15; H, 6.70; N, 18.33; S, 27.92. Found: C, 46.80; H, 6.69; N, 18.28; S, 27.70.

**Reactions of Ethylene Diisothiocyanate (I) with Diethylamine.**—I was treated with diethylamine in water and in acetone according to runs A to B. The presence of both mono- and bisadducts was ascertained by chromatography ($R_f$ values: 0.90 and 0.87, respectively). The products were not investigated further.

**Hydrolysis.**—All mono- and bisadducts were stable towards dilute acid. The substituted ethylenedithioureas were also stable towards alkali. The monoadducts, on the contrary, were hydrolyzed by dilute sodium hydroxide with formation of the known imidazolidine-2-thione (VII). This was collected in minute amount after refluxing 30 min. on the water bath Vf (100 mg.) with normal sodium hydroxide (10 ml.); in the other cases, VII was identified by chromatography of the alkaline solutions by comparison with a standard sample. In most cases, additional spots due to unidentified compounds appeared in the chromatograms. Acidification of the alkaline solution caused evolution of hydrogen sulfide.

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# Interaction of Phenyl Isocyanate and Related Compounds with Sodium Borohydride[1]

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Catalytic trimerization of phenyl, *p*-tolyl, and *p*-methoxyphenyl isocyanates has been observed with several complex metal hydrides, with and without solvent. Excess sodium borohydride in refluxing diglyme (diethylene glycol dimethyl ether) transforms phenyl isocyanate, its dimer and trimer, and *N*-formyl-*N,N'*-diphenylurea into a mixture of aniline, *N*-methylaniline, tris(*N*-methylanilino)borine, and formanilide. The latter compound is itself converted into aniline, *N*-methylaniline, and the aminoborine under the same conditions. Phenyl isothiocyanate yields only *N*-methylaniline and traces of the aminoborine at high temperature, but at lower temperatures thioformanilide is formed. A mechanism for the formation of the observed products is proposed.

The reaction of phenyl isocyanate with lithium aluminum hydride in refluxing ether has been reported by several workers[3,4] to give *N*-methylaniline in high yield. In a careful quantitative study Finholt and coworkers[5] reported the following stoichiometry for the following reaction.

$$4PhNCO + 3LiAlH_4 \rightarrow (PhNCH_3)_4AlLi + 2LiAlO_2$$

Hydrolysis of the intermediate complex then gave *N*-methylaniline.

In addition, other reports[6,7] have appeared on the reduction to substituted methylamines of other isocyanates with lithium aluminum hydride.

Formanilide[3] and phenyl isothiocyanate[4,5] also yield *N*-methylaniline with lithium aluminum hydride while *sym*-diphenylurea[4] was recovered unchanged after thirty hours in contact with lithium aluminum hydride.

This investigation extends complex metal hydride reactions with aryl isocyanates to sodium borohydride.

## Results and Discussion

In the presence of catalytic amounts of sodium borohydride phenyl, *p*-tolyl, and *p*-methoxyphenyl isocyanates are converted into the corresponding trimers (isocyanurates) in high yield. Identity of the products was established by mixture melting points and comparison of their infrared curves with those of authentic samples. The formation of trimers was exothermic in either dioxane or diglyme without external heating when as little as 0.01 mole of sodium borohydride per mole of isocyanate was present. When the catalyst concentration was one tenth this value moderate heating was required to initiate reaction. Treatment of phenyl isocyanate with a catalytic amount of lithium aluminum hydride in ether also afforded the trimer.

Bulk polymerization of phenyl isocyanate by a catalytic amount of sodium borohydride also afforded triphenyl isocyanurate, although in this case moderate heating was required. Lithium aluminum hydride, lithium tri-*t*-butoxyaluminohydride, and potassium borohydride are also effective catalysts in the bulk polymerization of phenyl isocyanate. The two lithium hydrides gave exothermic reactions while potassium borohydride, like sodium borohydride, required moderate heating to initiate a reaction.

The catalytic bulk or solution trimerization of phenyl isocyanate by lithium aluminum hydride is noteworthy in view of the several reports of the formation of *N*-methylaniline from the isocyanate and equivalent quantities of this hydride. An explanation may be that, in the presence of excess hydride, reduction is the predominant reaction. Alternatively, an equilibrium may exist between the isocyanate monomer and the initially formed trimer, with gradual catalytic detrimerization to the monomer as reduction of the latter proceeds. Purely thermal displacement of the equilibrium in favor of the monomer is an unsatisfactory explanation for the failure to isolate trimer in refluxing ether since triphenyl isocyanurate represents a structure which is very stable to thermal attack.

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