In contrast to antimony(III) ethylenediaminetetraacetates, the analogous bismuth(III) compounds have high asymmetry parameters due to a significant distortion of the electron environment about the bismuth atoms.

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SYNTHESIS OF BIS(ISOCYANATOETHYL) DISULFIDE AND RELATED CARBAMIDE DERIVATIVES OF SEVERAL BIOGENIC AMINES

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A convenient method is described for the synthesis of bis(isocyanatoethyl) disulfide. The corresponding carbamide derivatives were obtained by the reaction of this disulfide with imidazole, tyramine, O-methyltyramine, and histamine.

Considerable data are available on biologically active cystamine derivatives [1, 2], but there is no information in the literature on carbamide derivatives of cystamine and other biogenic amines displaying specific biological activity. In this regard, we synthesized a number of such derivatives from bis(isocyanatoethyl) disulfide [3]. This disulfide was synthesized by our previously described method for the synthesis of isocyanates [4] by low-temperature phosgenation of N-trimethylsilyl (TMS) derivatives of the corresponding amines. This method is preferred for the preparation of isocyanates from labile amines, which do not survive the vigorous conditions of phosgenation by the usual method [5]. Bis-TMS-cystamine (I) was obtained directly by the reaction of a commercial sample of cystamine dihydrochloride with a small excess of N-TMS-diethylamine at 100-120°C and purified by vacuum distillation. This approach not only permits efficient purification of cystamine but also gives a cystamine derivative, which is stable in the absence of moisture, retains its characteristic reactivity, and is readily converted when necessary to the free, highly pure diamine by treatment with an equimolar amount of a low-molecular-weight alcohol (the corresponding trimethylalkoxysilane formed as a by-product is readily removed in vacuum). The subsequent phosgenation of (I) was carried out in ether in the absence of Et_3N at −20°C.

$$HCl\cdot H_2NCH_2CH_2SSCH_2CH_2NH_2\cdot HCl \xrightarrow{Me_3SiNEt_2} Me_3SiHNCH_2CH_2SSCH_2CH_2NHSiMe_3 \xrightarrow{COCl_2/NEt_3} -\left[\begin{array}{cc} ClCONCH_2CH_2SSCH_2CH_2NCOCl \\ | \qquad\qquad\qquad\quad | \\ SiMe_3 \qquad\qquad\quad SiMe_3 \end{array}\right] \xrightarrow{-2Me_3SiCl}$$

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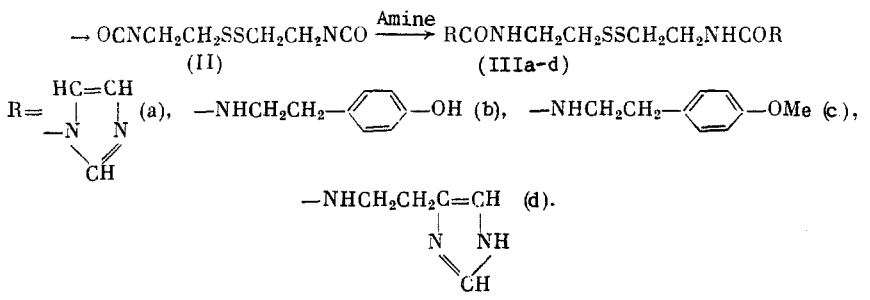

The desired product, bis(isocyanatoethyl) disulfide (II), was distilled in vacuum and identified by elemental analysis and IR spectroscopy. Bisisocyanate (II) was reacted with several biogenic amines and their derivatives, including imidazole, tyramine, O-methyltyramine, and histamine. The reaction was carried out with a stoichiometric ratio of the reagents in an inert organic solvent. The carbamide derivatives obtained (III) are given in Table 1.

EXPERIMENTAL

We used Fluka cystamine dihydrochloride, histamine, and tyramine and Serva imidazole. The sample of TMS–diethylamine was purified by distillation at 124-126°C. The solvents were purified according to standard procedures [6]. The IR spectra were taken on a Hitachi 260-10 spectrometer.

N,N-Bistrimethylsilylcystamine (I). A mixture of 10 g (44.44 mmoles) cystamine dihydrochloride and 32.2 g (222.0 mmoles) Me_3SiNEt_2 was heated upon stirring for 2 h at 120°C. The precipitate was filtered off and washed with ether. The filtrate was evaporated at 40°C (11 mm) and the residual oil was distilled in vacuum, taking the fraction with bp 180°C (1 mm) to give 11.35 g (86%) (I). Found: C 41.40; H 9.83; N 8.62; S 20.89; Si 19.26%. Calculated for $C_{10}H_{28}N_2S_2Si_2$: C 40.58; H 9.54; N 9.16; S 21.06; Si 18.98%. IR spectrum (neat, ν, cm^{-1}): 1258, 840 (Si–C).

Bis(isocyanatoethyl) Disulfide (II). A solution of 8.8 g (29.75 mmoles) (I) and 6.0 g (59.50 mmoles) Et_3N in 50 ml ether was added with stirring to a solution of 23.1 g (233.33 mmoles) phosgene in 100 ml dry ether cooled to −40°C. The mixture was warmed to about 20°C and stirred for 2 h. The precipitate was filtered off and washed with ether. The filtrate was evaporated. The residue was distilled at 1 mm, taking the fraction with bp 143°C to give 3.5 g (57%) (II). Found: C 35.19; H 3.72; N 13.84; S 31.25%. Calculated for $C_6H_8N_2S_2O_2$: C 35.28; H 3.95; N 13.71; S 31.40%. IR spectrum (ν, cm^{-1}): 2260 (NCO).

Diimidazolylcarbamidoethyl Disulfide (IIIa) A sample of 1 g (4.88 mmoles) (II) was added to 0.66 g (9.75 mmoles) imidazole in 5 ml dioxane. The precipitate was filtered off, washed with ether, and dried in vacuum to give 1.63 g (IIIa). IR spectrum (ν, cm^{-1}): 3240 (NH), 1730 (C=O, Amide I); δ 1555 (NH, Amide II).

Bis-β-(4-hydroxyphenyl)ethylcarbamidoethyl Disulfide (IIIb). A sample of 0.75 g (3.67 mmoles) (II) was added to 1 g (7.34 mmoles) tyramine in 7 ml DMF. After 24 h, the solvent was distilled off at 45°C (1 mm). The residue was triturated with ether. The precipitate was filtered off, washed with ether, and dried in vacuum to give 1.65 g (IIIb). IR spectrum: ν 3350 (NH), 1630 (C=O) cm^{-1}; δ 1590 (NH) cm^{-1}.

Bis-β-(4-methoxyphenyl)ethylcarbamidoethyl Disulfide (IIIc). A sample of 0.70 g (3.43 mmoles) (II) was added to 1.04 g (6.85 mmoles) O-methyltyramine in 4 ml dioxane. The precipitate formed was washed with ether and dried in vacuum to give 1.14 g (IIIc). IR spectrum: ν 3345 (NH), 1635 (C=O) cm^{-1}; δ 1590 (NH) cm^{-1}.

Bis-2-(4-imidazolyl)ethylcarbamidoethyl Disulfide (IIId). A sample of 0.94 g (8.18 mmoles) (II) was added to 0.84 g (4.09 mmoles) histamine in 7 ml DMF. After 24 h, the solvent was distilled off at 45°C (1 mm). The residue was triturated in ether, washed with ether, and dried in vacuum to give 1.84 g (IIId). IR spectrum: ν 3340 (NH), 1625 (C=O) cm^{-1}; δ 1585 (NH) cm^{-1}.

TABLE 1

Carbamide derivatives	Mp, °C	Yield, %	Found, %				Chemical formula	Calculated, %			
			C	H	N	S		C	H	N	S
(IIIa)	147–149	98	42.66	5.00	24.84	18.85	$C_{12}H_{16}N_6S_2O_2$	42.34	4.74	24.69	18.80
(IIIb)	92–94	94	54.28	6.22	11.82	13.19	$C_{22}H_{30}N_4S_2O_4$	55.21	6.32	11.71	13.19
(IIIc)	167–169	66	56.47	6.77	11.32	12.85	$C_{24}H_{34}N_4S_2O_4$	56.89	6.76	11.06	12.63
(IIId)	155–157	99	–	–	–	14.63	$C_{16}H_{26}N_8S_2O_2$	–	–	–	15.00

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STEREOSELECTIVE HYDROGENATION OF A MENTHONE–ISOMENTHONE MIXTURE ON HETEROGENEOUS NICKEL, NICKEL–COBALT, AND COBALT CATALYSTS

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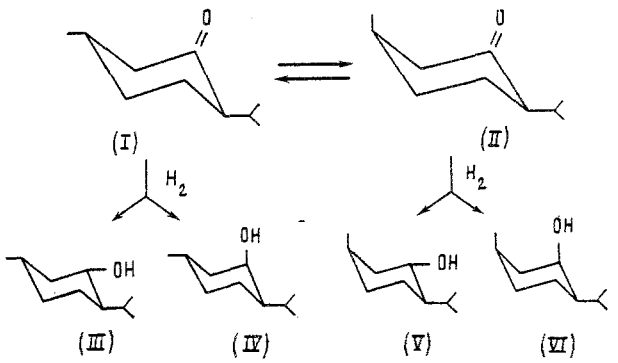
A study was carried out on the effect of the nature of the catalysts, additives, and solvents on the stereoselectivity of the liquid-phase hydrogenation of an equilibrium menthone–isomenthone mixture to give menthols. Neoisomenthol, which is the least stable of all the menthol isomers, was predominantly formed on a cobalt catalyst modified by (+)-tartaric acid in ethyl acetate at 130°C and 10 MPa.

The catalytic reduction of mixtures of menthone (I) and isomenthone (II) holds interest since a valuable product, menthol (III), is formed in addition to other stereoisomers, including neomenthol (IV), isomenthol (V), and neoisomenthol (VI)



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