5-MERCAPTO DERIVATIVES OF 1,3-DIMETHYLBENZIMIDAZOLINE

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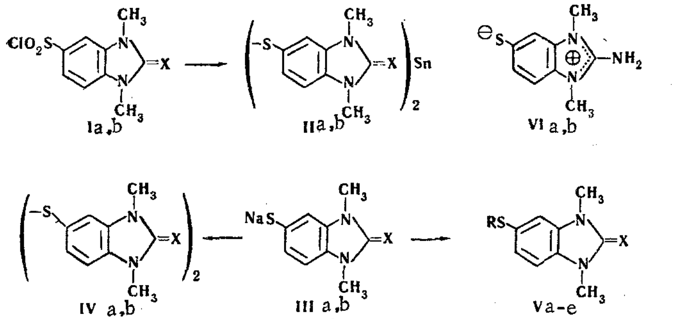
The preparation of tin and sodium 1,3-dimethylbenzimidazolone- and 2-imino-1,3-dimethylbenzimidazoline-5-thiolates and their S-methyl and S-benzoyl derivatives is described. The hydrolysis of sodium 2-imino-1,3-dimethylbenzimidazoline-5-thiolate forms the fairly stable thiol.

No 5-mercapto derivatives of the benzimidazoline series have been described hitherto. In order to obtain such thiols, we have subjected the 5-sulfonyl chlorides of 1,3-dimethylbenzimidazolone (Ia) and of 2-imino-1,3-dimethylbenzimidazoline (Ib) to reduction with tin in hydrochloric acid [1]. The reduction products – thiols – were isolated from the reaction medium in the form of their tin salts (II). The action of caustic soda converts them into the sodium salts of the mercaptobenzimidazolines (III). The thiolate IIIb is insoluble in concentrated alkali, which enables it to be isolated from the reaction mixture. The reaction of IIIa,b with dimethyl sulfate leads to the S-methyl derivatives Va and Vd. The action of benzoyl chloride on IIIa forms the S-benzoyl derivative Vb, while the same treatment converts IIIb into the N,S-dibenzoyl derivative Ve. Acidification of solutions of the Na salts III gives the disulfides IV, in addition to the expected 5-mercapto derivatives.



I-IVa $X=O$, b $X=NH$; V a $X=O$, $R=CH_3$; b $X=O$, $R=C_6H_5CO$; c $X=NH$, $R=H$; d $X=NH$, $R=CH_3$; e $X=NCOC_6H_5$, $R=C_6H_5CO$

5-Mercapto-1,3-dimethylbenzimidazolone, obtained by the electrolysis of the tin salt IIa and isolated by extraction with benzene, is unstable; it oxidizes immediately to the disulfide. Conversely, 2-imino-1,3-dimethylbenzimidazoline-5-thiol (IVc), formed by the hydrolysis of the sodium salt during the prolonged standing of its aqueous solution, can be stored at the ordinary temperature and oxidizes only slowly; however, on heating IVc is rapidly converted into the disulfide.

The IR spectrum of Vc, like that of the disulfide IVb, lacks absorption in the 2850-2000 cm^{-1} region, while the spectrum of its hydrochloride has a weak, but very distinct, band at 2400 cm^{-1}; this can apparently be ascribed to the vibrations of the SH group. The shift of the band as compared with its usual position [2,3] is obviously due to the formation of hydrogen bonds. The absence of vibrations of a SH group in the spectrum of Vc is probably explained by the fact that the compound has the bipolar structure VI.

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EXPERIMENTAL

Tin 1,3-Dimethylbenzimidazolone-5-thiolate (IIa). A suspension of 2 g of powdered tin in 5 ml of conc. HCl was heated in the boiling water bath and stirred while 1.30 g (5 mmoles) of Ia [1] was added over 20 min, and heating was continued until the tin had dissolved completely. After cooling, the IIa was filtered off and dried in a desiccator over $CaCl_2$. Yield 1.95 g (78%). Colorless needles (from conc. HCl) with a diffuse melting point (160-170°C), yellowing in the air. Found, %: C 42.4; H 3.9; N 11.5; S 12.3. Calculated for $C_{18}H_{18}N_4O_2S_2Sn$, %: C 42.8; H 3.6; N 11.1; S 12.7.

Sodium 2-Imino-1,3-dimethylbenzimidazoline-5-thiolate (IIIb). The tin thiolate (IIb) obtained as in in the preceding experiment from 1.48 g (5 mmoles) of Ib · HCl was carefully triturated with 15 ml of 40% sodium hydroxide. The precipitate was filtered off and dried in the air. Yield 0.80 g (75%). The compound, which is insoluble in the usual organic solvents, was purified by reprecipitation from aqueuos solution with ethanol. Colorless powder not melting below 400°C. Found, %: C 49.8; H 4.5; N 19.2; S 14.4. Calculated for $C_9H_{10}N_3NaS$, %: C 50.2; H 4.7; N 19.5; S 14.9.

Di(1,3-dimethylbenzimidazolon-5-yl) Disulfide (IVa). Compound IIa was treated with 10% caustic soda solution, the precipitate was filtered off, and the filtrate was acidified to pH 3-4. Compound IVa precipitated. Yellow crystals, mp 250°C (from acetic acid). Found, %: C 55.6; H 5.1; N 14.7; S 16.1. Calculated for $C_{18}H_{18}N_4O_2S_2$, %: C 55.9; H 4.7; N 14.5; S 16.6.

Di(2-imino-1,3-dimethylbenzimidazolin-5-yl) disulfide (IVb) was formed by the addition of conc. HCl to an aqueous solution of IIIb. Yellow-green crystals insoluble in water and the usual organic solvents other than acetic acid. It decomposed at about 360°C. Found, %: C 56.4; H 5.1; N 21.5; S 16.3. Calculated for $C_{18}H_{20}N_6S_2$, %: C 56.2; H 5.2; N 21.9; S 16.7.

1,3-Dimethyl-5-methylthiobenzimidazolone (Va). 0.5 g (1 mmole) of IIa was dissolved in 7 ml of 10% caustic soda, and the solution was filtered from the insoluble residue and treated with 0.38 g (3 mmoles) of dimethyl sulfate with shaking. A precipitate of Va was formed. Yield 0.33 g (78%), Colorless needles (from water) with mp 113°C. Found, %: C 57.8; H 5.8; N 13.4; S 15.4. Calculated for $C_{10}H_{12}N_2OS$, %: C 57.6; H 5.8; N 13.4; S 15.4.

5-Benzoylthio-1,3-dimethylbenzimidazolone (Vb). To the Na salt obtained as in the preceding experiment from 0.5 g of IIa 0.31 g (2.2 mmoles) of benzoyl chloride was gradually added with shaking, and the mixture was shaken for another 30 min. Then the precipitate was filtered off. Colorless needles, mp 140°C (from ethanol). Yield 0.36 g (60%). Found, %: C 64.4; H 4.8; N 9.5; S 10.5. Calculated for $C_{16}H_{14}N_2OS$, %: C 64.4; H 4.7; N 9.4; S 10.7.

2-Imino-1,3-dimethyl-5-methylthiobenzimidazoline (Vd). A solution of 0.43 g (2 mmoles) of IIIb in 10 ml of water was treated with 1 ml of 10% NaOH solution, and then, with shaking, 0.3 g (2.4 mmoles) of dimethyl sulfate was added and the mixture was shaken for another 20 min. The oil that had separated out crystallized on standing. Colorless needles with mp 98°C (from benzene with petroleum ether). Yield 0.37 g (89%). Found, %: S 58.1; H 6.3; N 20.5; S 15.1. Calculated for $C_{10}H_{13}N_3S$, %: C 57.9; H 6.3; N 20.3; S 15.5.

2-Benzoylimino-5-benzoylthio-1,3-dimethylbenzimidazoline (Ve) was obtained similarly by the action of benzoyl chloride on a solution of IIIb. Small colorless needles with mp 204-205°C (from ethanol). Yield 85%. Found, %: C 69.0; H 5.0; N 10.5; S 7.9. Calculated for $C_{23}H_{19}N_3O_2S$, %; C 68.8; H 4.8; N 10.5; S 8.0.

2-Imino-5-mercapto-1,3-dimethylbenzimidazoline (Vc). A solution of 0.43 g (2 mmoles) of IIIb in 20 ml of water was left for two days, and the precipitate that had deposited was filtered off, washed with water and dried in the air. Yield 0.34 g (81%). Colorless needles with mp 183-184°C (from 90% ethanol). Found, %: C 51.0; H 6.1; N 20.2; S 15.0. Calculated for $C_9H_{11}N_3S \cdot H_2O$, %: C 51.2; H 6.2; N 19.9; S 15.2.

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