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LETTERS TO THE EDITOR

Synthesis and Properties of *N,N'*-Sulfinylbis[alkyl 2-hydroxy-2-methylpropanimidates]

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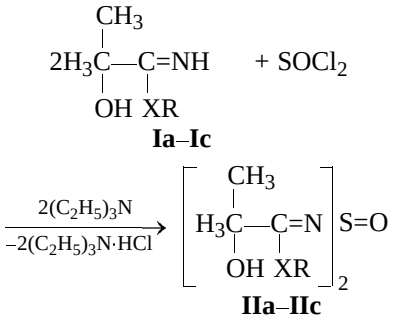
Mednikov [1] reported that the reactions of phosphorylated imidates with thionyl chloride yielded the corresponding substitution products which exhibited the fungicidal activity. With the aim to prepare *N,N'*-sulfinyl derivatives of hydroxy imidates, we performed the reactions of hydroxy imidates with thionyl chloride. The products of such reactions are of practical interest in the context of searching for promising biologically active compounds of low toxicity.

The reaction was carried out in anhydrous diethyl ether at 2:1:2 molar ratio of the hydroxy imidate (hydroxy thioimidate), thionyl chloride, and triethylamine. The initial reaction temperature was from –8 to –11°C. The reaction was accompanied by heat evolution and was complete in 1.5–2 h.



Ia–**Ic**

IIa–**IIc**

R = *i*-C_3H_7 (**a**), *i*-C_4H_9 (**b**), C_4H_9 (**c**); X = O (**a, b**), S (**c**).

The presence of a hydrogen chloride acceptor prevents the formation of hydroxy imidate hydrochlorides and favors the substitution of hydrogen at the nitrogen atom. Low reaction temperature also favors the substitution in the more nucleophilic imino group.

To isolate the products (**IIa**–**IIc**), triethylamine hydrochloride was filtered off, and the solvent was distilled off. The residue was purified by column chromatography on silica gel of KSK grade, elution with 1:3 (vol/vol) methanol– chloroform. The product purity was checked by TLC on Silufol plates [2]. The compositions and chemical structures of the products were determined by IR and ^{1}H NMR spectroscopy and mass spectrometry [3, 4]. The IR spectra contain the following characteristic absorption bands (ν, cm^{-1}): 1640–1690 [ν(C=N)], 1120–1180 [ν(C–O–C)], 1370–1380 {ν[$C(CH_3)_2$]}, 3320–3455 [ν(OH)], 1050, 1360 [δ(OH)], 1020–1070 [ν(S=O)]. The NH absorption band, present in the spectra of the starting hydroxy imidates, disappears. The molecular ion and characteristic fragmentation peaks in the mass spectra of **IIa** and **IIc** confirm the suggested structure. Compounds **IIa**–**IIc** are viscous light yellow liquids readily soluble in diethyl ether, dioxane, alcohols, and water and poorly soluble in lower paraffins. The starting hydroxy imidates were prepared by Pinner's method from acetone cyanohydrine.

***N,N'*-Sulfinylbis(isopropyl 2-hydroxy-2-methylpropanimidate) IIa.** A solution of 0.014 mol of thionyl chloride in 50 ml of anhydrous ether was slowly added dropwise at –8°C to a solution of 0.028 mol of isopropyl 2-hydroxy-2-methylpropanimidate and 0.028 mol of triethylamine in 90 ml of diethyl ether. The reaction was complete in 1.5 h. After that, triethylamine hydrochloride was filtered off and diethyl ether was distilled off from the filtrate. The target product was purified by column chromatography on a silica gel of KSK grade, elution with 1:3 (vol/vol) methanol–chloroform. Yield 64%, d_4^{20} 1.1773, n_D^{20} 1.4597, MR_D 83.90, calc. 84.40, R_f 0.32. IR spectrum, ν, cm^{-1}: 3450, 1300 (OH), 1375 [$C(CH_3)_2$], 1685 (C=N), 1180 (C–O–C), 1060 (S=O). Mass spectrum, *m/z* (I_{rel}, %): 336 (5.1) $[M]^+$, 321 (7) $[M - CH_3]^+$, 250 (2.1) $[M - C_6H_{14}]^+$, 234 (6.3) $[M - C_6H_{14}O]^+$. ^{1}H NMR spectrum (CCl_4), δ, ppm: 1.23 s (12H, $4CH_3$), 1.06–1.08 d (12H, $4CH_3$), 4.88–4.94 m (2H, 2CH), 5.24 s (2H, 2OH).

***N,N'*-Sulfinylbis(isobutyl 2-hydroxy-2-methylpropanimidate) IIb.** Thionyl chloride, 0.02 mol, was

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added dropwise with stirring at –10°C over a period of 2 h to a solution of 0.04 mol of isobutyl-(2-hydroxy-2-methyl)propanimidate and 0.041 mol of triethylamine in anhydrous diethyl ether. Yield 62%, d_4^{20} 1.1889, n_D^{20} 1.4612, MR_D 89.01, calc. 88.71, R_f 0.27. IR spectrum, ν, cm^{-1}: 3420, 1315 (OH), 1365 [$C(CH_3)_2$], 1685 (C=N), 1180 (C–O–C), 1055 (S=O).

***N,N'*-Sulfinylbis(butyl 2-hydroxy-2-methylpropanimidothioate) IIc.** Thionyl chloride, 0.17 mol, was added dropwise with stirring at –11°C over a period of 2 h to a solution of 0.034 mol of butyl 2-hydroxy-2-methylpropanimidothioate. The target product was isolated and purified as described above. Yield 69%, d_4^{20} 1.1804, n_D^{20} 1.4516, MR_D 90.07, calc. 90.57, R_f 0.30. IR spectrum, ν, cm^{-1}: 3400, 1300 (OH), 1365 [$C(CH_3)_2$], 1685 (C=N), 1045 (S=O). Mass spectrum, *m/z* (I_{rel}, %): 367 (4.9) $[M]^+$, 308 (7.5) $[M - C_3H_7O]^+$, 294 (12.8) $[M - C_4H_9O]^+$, 209 (18.2) $[M - C_8H_{16}O_2N]^+$.

The IR spectra of **IIa**–**IIc** were recorded in thin films on a Specord-82 spectrometer, KBr prism. The mass spectra of **IIa** and **IIc** were taken on a Varian MAT-11 gas chromatograph–mass spectrometer with the direct sample inlet. The ionizing electron energy was 70 eV. The ^1H NMR spectra were measured on a Mercury-Plus-300 NMR spectrometer (300 MHz).

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