

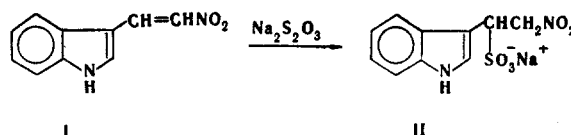
INDOLE DERIVATIVES. CV.* REACTION OF NITROVINYLINDOLE
WITH SODIUM THIOSULFATE

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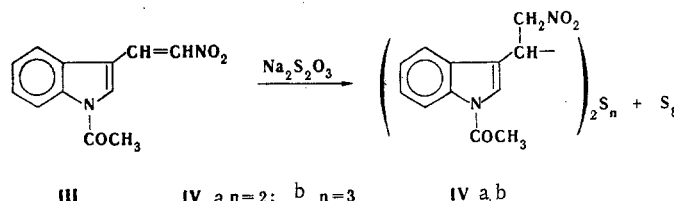
UDC 547.754

Depending on the presence of ring substituents, nitrovinylindole reacts with sodium thiosulfate to give nitro sulfides or nitro sulfonic acids.

The reaction of nitrovinyl compounds with thiosulfate has not been studied. 3-Nitrovinylindole (I) reacts with sodium thiosulfate in acetic acid to give a sulfonate (II) instead of the expected thiosulfonic acid or its salt.



Under similar conditions 1-acetyl-3-nitrovinylindole (III) also does not give a thiosulfonic acid, but the product in this case is bis[1-(1-acetyl-3-indolyl)-2-nitroethyl]disulfide (IVa) and trisulfide (IVb).



These transformations are somewhat unexpected, inasmuch as the addition of thiosulfates to unsaturated compounds in which the double bond is activated by ester [2], sulfone [3], or sulfo [4] groups usually leads to thiosulfates. In the first case, the reason should be sought in the fact that the electrophilicity of the vinyl group in I is somewhat weakened by the electron-donor indole system and is inadequate for the addition of a thiosulfate ion. However, the more nucleophilic bisulfite ion formed during the decomposition of the thiosulfate in acidic media is capable of addition. In the second case, the acetyl group lowers the electron-donor character of the indole system, and the vinyl bond becomes capable of adding the thiosulfate ion. However, the resulting thiosulfonic acid or its salt is insufficiently stable under the reaction conditions and is converted to disulfide and trisulfide, probably through the corresponding thiol.

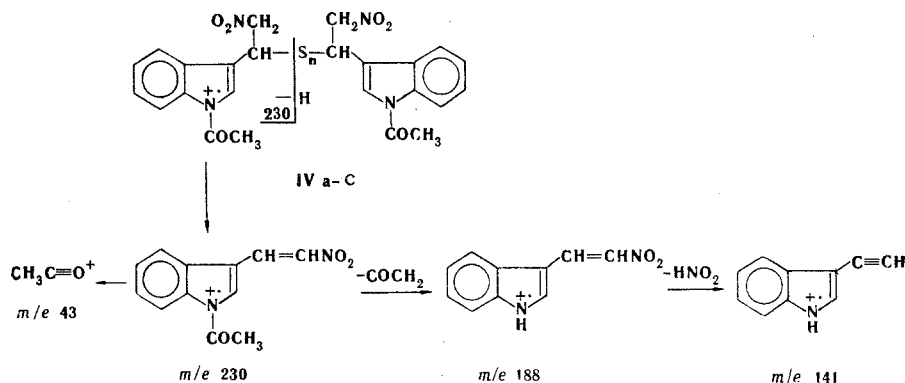
As one should have expected, the UV, IR, and PMR spectra of disulfide IVa, trisulfide IVb, and the previously obtained [5] monosulfide (IVc, $n = 1$) are extremely similar. However, the IR spectra contain characteristic bands at 773 and 762 cm^{-1} for the disulfide and 740 cm^{-1} for the trisulfide, and this makes it possible to differentiate them and even estimate their ratio when they are present together.

*See [1] for communication CIV.

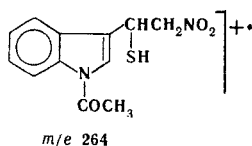
S. Ordzhonikidze All-Union Scientific-Research Pharmaceutical-Chemistry Institute, Moscow. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 6, pp. 792-794, June, 1975. Original article submitted July 10, 1974.

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In view of the instability of the compounds, molecular-ion peaks are not observed in the mass spectra of the investigated sulfides, but the character of the fragmentation is in satisfactory agreement with the proposed structures. An intense ion peak with mass number 230, which results from the cleavage of the C-S bond in the molecular ion, and ion peaks that are the products of its subsequent fragmentation are observed in all of these spectra.



Peaks of fragments with m/e 185, 143, and 115 are also observed. A distinguishing feature of the spectra of monosulfide IVc and disulfide IVa is the presence of the peak of a sulfur-containing fragment, probably



Peaks of S^+ (m/e 32) and H_2S^+ (m/e 34) ions are characteristic for the spectra of all of the investigated sulfides. Intense S_2^+ ion peaks (m/e 64), which are absent in the spectrum of monosulfide IVc, are observed in the spectra of the disulfide and trisulfide. In addition, the spectrum of trisulfide IVb contains an ion peak with mass number 96 (S_3^+), which confirms its structure.

EXPERIMENTAL METHOD

The PMR spectra of the compounds were recorded with a JNM 4H-100 spectrometer with tetramethylsilane as the internal standard. The IR and UV spectra were recorded with Perkin-Elmer and EPS-3 spectrometers. The mass spectra were obtained with an MKh-1303 spectrometer with direct introduction of the samples into the ion source at an ionizing-electron energy of 50 eV. Thin-layer chromatography (TLC) was carried out on Silufol with benzene-acetone (9:1); the spots were detected by spraying with 10% phosphomolybdic acid in alcohol and subsequent heating at 110°.

Reaction of 1-Acetyl-3-(2-nitrovinyl)indole with Sodium Thiosulfate. A hot solution of 11.5 g (0.05 mole) of nitro compound III in 210 ml of glacial acetic acid was added in portions with stirring to a solution of 74.4 g (0.3 mmole) of sodium thiosulfate in 280 ml of water in such a way that the temperature did not exceed 40°. The bright-yellow suspension was heated at 40° for 5 h until the precipitate became completely colorless. The precipitate was then removed by filtration, washed with water and dilute acetic acid, and air dried to give 11.8 g of a mixture of compounds. Crystallization from chloroform gave 4.1 g (28%) of colorless crystals of a stable solvate of bis[1-(1-acetyl-3-indolyl)-2-nitroethyl]disulfite (IVa) with chloroform with mp 141° (after vacuum drying over calcium chloride at 30°) and R_f 0.41. Found: C 50.1; H 4.0; Cl 9.0; N 9.4; S 10.7%. $2C_{24}H_{22}N_4O_6S_2 \cdot CHCl_3$. Calculated: C 50.2; H 3.9; Cl 9.1; N 9.5; S 10.9%. The mother liquor was evaporated to a small volume to give 2.3 g (17%) of colorless crystals of bis[1-(1-acetyl-3-indolyl)-2-nitroethyl]trisulfide (IVb) with mp 179° and R_f 0.43. Found: C 51.3; H 3.9; N 9.7; S 17.0%. $C_{24}H_{22}N_4O_6S_3$. Calculated: C 51.1; H 3.9; N 9.8; S 17.1%. UV spectrum ($CHCl_3$) λ_{max} (log ϵ): 301 (4.17) and 293 nm (4.16). IR spectrum ($CHCl_3$): 1712 (C=O), 1566, 1334 cm^{-1} (NO_2); (mineral oil): 1722 (C=O); 1552, 1326 (NO_2); 740 cm^{-1} (aromatic CH). PMR spectrum ($CDCl_3$), δ : 2.53 (s, 6H, COCH₃), 4.85 (m, 6H, CHCH₂), 6.9–8.4 ppm (m, 10H, aromatic protons).*

*Abbreviations: s is singlet and m is multiplet.

Reaction of 3-(2-Nitrovinyl)indole with Sodium Thiosulfate. A hot solution of 7.9 g (0.04 mole) of I in 110 ml of glacial acetic acid was added in portions to a solution of 63.3 g (0.26 mole) of sodium thiosulfate in 110 ml of water, after which the suspension was heated at 40° for 2 h until the precipitate had become completely colorless. The sulfur was removed by filtration, the filtrate was evaporated, and the residue was extracted with absolute alcohol. The extract was evaporated, the residue was dissolved in water, and an aqueous solution of 6 g (0.04 mole) of p-toluidine hydrochloride was added to the resulting solution of sodium 1-(3-indolyl)-2-nitroethanesulfonate (II). As a result of this exchange reaction, 5.2 g of easily crystallized p-toluidine salt of II, with physical constants identical to those described in [6], was obtained.

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