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SYNTHESIS OF NEW TYPES OF ORGANOSULFUR NITRO COMPOUNDS

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We have synthesized for the first time analogs of sulfoxides and sulfones of the I-III type in which the oxygen atoms are replaced by N-nitroimido groups: $R_2\overset{+}{S}-\overset{-}{N}-NO_2$ (I), $R_2\overset{+}{S}(O)\overset{-}{N}-NO_2$ (II), and $R\overset{++}{S}(\overset{-}{N}-NO_2)_2$ (III).

N-Nitrosulfylimides I were obtained by direct replacement of the oxygen atom by a nitroimido group by reaction of the sulfoxides with nitroamide in the presence of acetic anhydride or by an exchange reaction of iodonium N-nitroimides with dialkyl sulfides:

$$R^1R^2S \rightarrow O + H_2N-NO_2 \xrightarrow{(CH_3CO)_2O} \underset{(I)}{R^1R^2\overset{+}{S}-\overset{-}{N}-NO_2}$$

$$R^1 = R^2 = Me\ (Ia),\ R^1 = R^2 = Et\ (Ib),\ R^1 = Me,\ R^2 = Ph\ (Ic),\ R^1 = R^2 = Ph\ (Id).$$

$$o\text{-}NO_2C_6H_4IO + NH_2NO_2 \rightarrow o\text{-}NO_2C_6H_4\overset{+}{I}-\overset{-}{N}-NO_2 \xrightarrow{(CH_3)_2S} o\text{-}NO_2C_6H_4I + (CH_3)_2\overset{+}{S}-\overset{-}{N}-NO_2.$$

N-Nitrosulfoximides II were synthesized by oxidation of I with $KMnO_4$ or H_2O_2:

$$R^1R^2\overset{+}{S}-\overset{-}{N}-NO_2 \xrightarrow{KMnO_4\ \text{or}\ H_2O_2)} \underset{(II)}{R^1R^2\overset{+}{S}(O)\overset{-}{N}-NO_2}$$

$$R^1 = R^2 = Me\ (IIa),\ R^1 = Me,\ R^2 = Ph(IIb),\ R^1 = R^2 = Ph(IIc).$$

N,N'-Dinitrosulfodiimides III were obtained by nitration of unsubstituted sulfodiimides or their N,N'-bis(trimethylsilyl) derivatives with nitronium tetrafluoroborate or dinitrogen pentoxide in acetonitrile:

$$R^1R^2S(NR')_2 + NO_2X \rightarrow R^1R^2\overset{++}{S}(\overset{-}{N} - NO_2)_2 + RX$$

$$R^1 = R^2 = Me\ (IIIa),\ R^1 = R^2 = Ph\ (IIIb);\ R' = H,\ Si(CH_3)_3;\ X = BF_4,\ NO_3.$$

Compounds I-III are stable crystalline substances, the structures of which were confirmed by the results of elemental analysis and data from the IR, UV, and PMR spectra and x-ray diffraction analysis.

N-Nitro-S,S-dimethylsulfylimide (Ia). This compound was obtained in 64.8% yield and had mp 56°C. PMR spectrum (CH_2Cl_2, δ, ppm): 2.82 (6H, CH_3). IR spectrum (ν, cm^{-1}): 1402, 1273 ($N-NO_2$). UV spectrum (CH_3OH, λ, nm, log ε): 255/3.99.

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N-Nitro-S,S-diethylsulfylimide (Ib). This compound was obtained in 15% yield and had mp 16°C. PMR spectrum ($CHCl_3$, δ, ppm): 1.42 (6H, CH_3), 3.18 (4H, CH_2). IR spectrum (ν, cm^{-1}): 1408, 1268 ($N-NO_2$). UV spectrum (CH_3OH, λ, nm, log ε): 254/3.93.

N-Nitro-S,S-methylphenylsulfylimide (Ic). This compound was obtained in 35% yield and had mp 110°C. IR spectrum (ν, cm^{-1}): 1398, 1274 ($N-NO_2$). UV spectrum (CH_3OH, λ, nm, log ε): 254/3.97.

N-Nitro-S,S-diphenylsulfylimide (Id). This compound was obtained in 15% yield and had mp 98°C. IR spectrum (ν, cm^{-1}): 1420, 1260 ($N-NO_2$). UV spectrum (CH_3OH, λ, nm, log ε): 264/4.04.

N-Nitro-S,S-dimethylsulfoximide (IIa). This compound was obtained in 70% yield and had mp 96°C. PMR spectrum (d_6-acetone, δ, ppm): 3.49 (6H, CH_3). IR spectrum (ν, cm^{-1}): 1482, 1273 ($N-NO_2$). UV spectrum (H_2O, λ, nm): 238.

N-Nitro-S,S-methylphenylsulfoximide (IIb). This compound was obtained in 69% yield and had mp 91°C. IR spectrum (ν, cm^{-1}): 1490, 1282 ($N-NO_2$).

N-Nitro-S,S-diphenylsulfoximide (IIc). This compound was obtained in 46% yield and had mp 100-101°C. IR spectrum (ν, cm^{-1}): 1500, 1282 ($N-NO_2$). UV spectrum (CH_3, λ, nm): 242.

N,N'-Dinitro-S,S-dimethylsulfodiimide (IIIa). This compound was obtained in 71.3% yield and had mp 142-144°C. IR spectrum (ν, cm^{-1}): 1502-1515 ($N-NO_2$). UV spectrum (H_2O, λ, nm): 245.

N,N'-Dinitro-S,S-diphenylsulfodiimide (IIIb). This compound was obtained in 90% yield and had mp 170.5-172°C. IR spectrum (ν, cm^{-1}): 1502-1512, 1272 ($N-NO_2$). UV spectrum (C_2H_5OH, λ, nm): 253.

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SYNTHESIS OF SALTS OF HETEROCYCLIC N- AND C-NITRAMINO-N-NITROIMIDES

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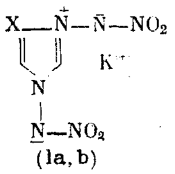
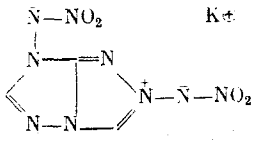
547.821

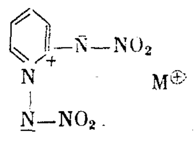
We have developed a general method for the synthesis of salts I-III of heterocyclic N- and C-nitramino-N-nitroimides.



(Ia,b)
X = CH (Ia), N (Ib).



(II)



(IIIa,b)
M = H (IIIa), K (IIIb)

The introduction simultaneously of two nitramino fragments into a nitrogen-containing heterocycle (imidazole, 1,2,4-triazole, s-triazolo[4,3-c]-s-triazole, and pyridine) was accomplished by amination of the amino derivatives of the corresponding heterocycles with O-picrylhydroxylamine or hydroxylamine-O-sulfonic acid with subsequent nitration of the resulting quaternary N-amino salts with nitronium tetrafluoroborate and treatment of the reaction mixture with a base.

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