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LETTERS TO THE EDITOR

N-Methylmorpholinium 6-Amino-4-(4-bromophenyl)-3,5-dicyano-1,4-dihydropyridine-2-selenolate

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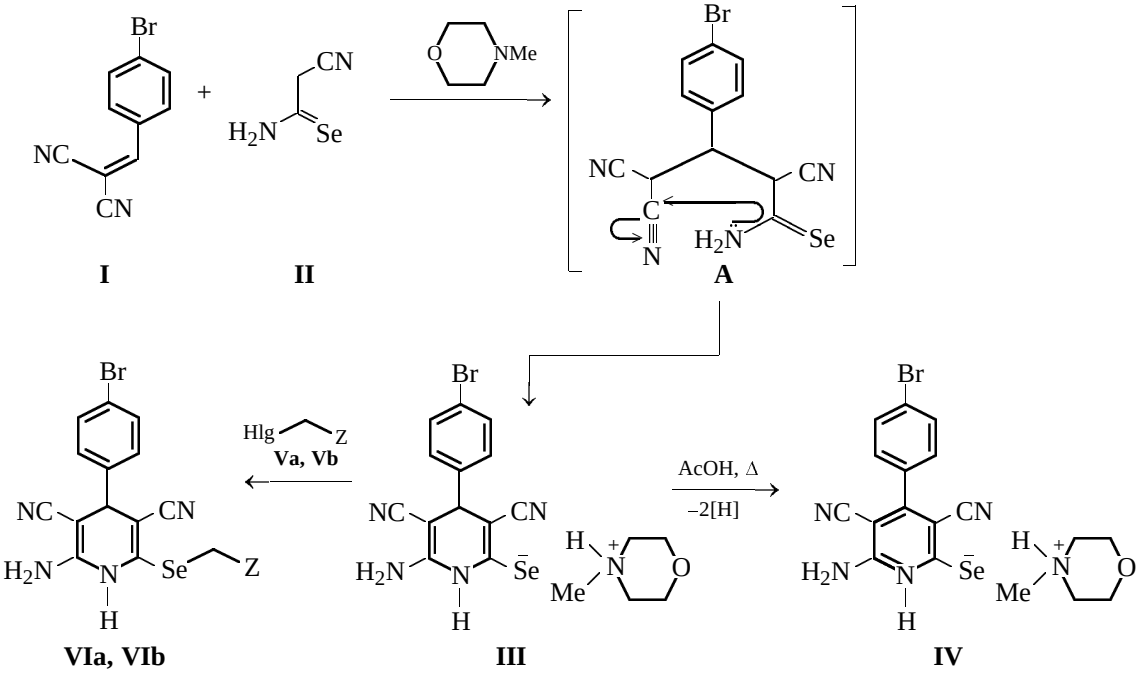
Benzylidenemalonodinitrile [1, 2] and (pyridin-3-ylmethylene)malonodinitrile [3, 4] react with cyanoselenoacetamide under conditions of the Michael reaction to form 2,6-diamino-4-phenyl(pyridin-3-yl)-3,5-dicyano-4*H*-selenopyrans, recyclizing in refluxing absolute ethanol in the presence of *N*-methylmorpholine into the corresponding *N*-methylmorpholinium 6-amino-4-phenyl(pyridin-3-yl)-3,5-dicyanopyridine-2-selenolates.

We found that the reaction of (4-bromophenylmethylene)malonodinitrile **I** with cyanoselenoacetamide **II** in absolute ethanol under argon at 20°C in the presence of *N*-methylmorpholine yields *N*-methylmorpholinium 6-amino-4-(4-bromophenyl)-3,5-dicyano-1,4-dihydropyridine-2-selenolate **III**. Refluxing of **III** in glacial acetic acid in air results in aromatization of the dihydropyridine core and formation of compound **IV**, which was also prepared by independent synthesis from 4-bromobenzaldehyde, malonodinitrile, cyanoselenoacetamide, and *N*-methylmorpholine [2].

Compound **III** is formed, apparently, via Michael adduct **A**. The structure of substituted *N*-methylmorpholinium 1,4-dihydropyridine-2-selenolate was confirmed by its dehydrogenation to known compound **IV** [2] and by alkylation with alkyl halides **V** to obtain organic selenides **VIa** and **VIb**.

The applicability limits of the reaction and the biological properties of the dihydropyridines synthesized are under investigation.



V, Hlg = Cl (**a**), Br (**b**); **V, VI**, Z = CN (**a**), PhCO (**b**).

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***N*-Methylmorpholinium 6-amino-4-(4-bromophenyl)-3,5-dicyano-1,4-dihydropyridine-2-selenolate III.** Yield 72%, mp 180–183°C. IR spectrum, ν, cm^{-1}: 1650 [ν(NH_2)], 2192 [ν(C≡N)], 3200, 3313, 3405 [ν(NH_2)]. ^{1}H NMR spectrum, δ, ppm: 2.75 s (3H, Me), 3.12 t (4H, CH_2NCH_2), 3.76 t (4H, $CH_2O\cdot CH_2$, ^3J 4.41 Hz), 3.97 s (1H, C^4H), 5.65 br.s (2H, NH_2), 7.09 d and 7.49 d (2H each, C_6H_4, ^3J 7.52 Hz), 8.26 br.s (1H, N^1H). The N^+H proton is not manifested, probably because of deuterium exchange. Found, %: C 44.85; H 4.16; N 14.30. $C_{18}H_{20}BrN_5\cdot$ OSe. Calculated, %: C 44.92; H 4.19; N 14.55.

6-Amino-4-(4-bromophenyl)-3,5-dicyano-2-cyanomethylseleno-1,4-dihydropyridine VIa. Yield 78%, mp 158–160°C (from MeOH). IR spectrum, ν, cm^{-1}: 1647 [ν(NH_2)], 2196, 2254 [ν(C≡N)], 3200, 3331, 3418 [ν(NH_2)]. ^{1}H NMR spectrum, δ, ppm: 4.21 s (2H, CH_2), 4.44 s (1H, C^4H), 7.26 d and 7.60 d (2H each, C_6H_4, ^3J 7.47 Hz), 8.38 br.s (2H, NH_2), 9.94 br.s (1H, NH). Found, %: C 43.11; H 2.24; N 16.65. $C_{15}H_{10}BrN_5Se$. Calculated, %: C 42.98; H 2.41; N 16.71.

6-Amino-2-benzoylmethylseleno-4-(4-bromphenyl)-3,5-dicyano-1,4-dihydropyridine VIb. Yield 85%, mp 234–236°C (from EtOH). IR spectrum, ν, cm^{-1}: 1643 [ν(NH_2)], 1714 [ν(C=O)], 2198 [ν(C≡N)], 3184, 3300, 3396 [ν(NH_2)]. ^{1}H NMR spectrum, δ, ppm: 4.30 s (1H, C^4H), 4.59 s (2H, CH_2), 5.91 br.s (2H, NH_2), 7.20 d and 8.01 d (2H each, C_6H_4, ^3J 7.48 Hz), 9.26 br.s (1H, NH), 7.42–7.79 m (5H, Ph). Found, %: C 50.49; H 2.91; N 11.07. $C_{21}H_{15}BrN_4\cdot$ OSe. Calculated, %: C 50.63; H 3.04; N 11.25.

The IR spectra were taken on a UR-20 spectrometer (KBr pellets), and the ^{1}H NMR spectra, on a Bruker WP-100SY spectrometer (100 MHz) in DMSO-d_6, internal reference TMS.

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