(35 Torr). Compound **4** (347 mg, 83.5%) was obtained as a white downy powder with m.p. 157—158 °C. Found (%): C, 49.63; H, 8.83; N, 19.39. $C_6H_{12}N_2O_2$. Calculated (%): C, 49.98; H, 8.39; N, 19.43. IR (Vaseline oil), ν/cm^{-1}: 3236 (NH); 2700—2500 (OH); 1720, 1704 (C=O). ^1H NMR (200 MHz, CD_3OD), δ: 1.35 (d, 3 H, C(5)Me, ^3J = 7.0 Hz); 1.37, 1.47 (both s, 6 H, 2 C(2)Me); 3.54 (q, 1 H, H(5), ^3J = 7.0 Hz). ^{13}C NMR (50 MHz, CD_3OD), δ: 17.5 (MeC(5)); 24.0, 26.8 (2 MeC(2)); 52.7 (C(5)); 77.7 (C(2)); 173.6 (C=O).

The sample for X-ray analysis was obtained by the crystallization of powder **4** from acetone. Crystals **4** are monoclinic, m.p. 159—160 °C, M = 144.173, a = 17.178(3) Å, b = 9.410(2) Å, c = 10.270(2) Å, β = 107.32(3)°, V = 1584.8(5) Å^3, d_{calc} = 1.209 g cm^{-3}, space group $P2_1/c$, Z = 8. (Detailed X-ray analysis data will be published elsewhere.)

It is assumed that *N*-alkylation is the predominant direction of the reaction of α-amino HA with ketones because it corresponds to the preferential *NH*-deprotonation of HA.[1] At the same time, the selective formation of HA **4** (see Scheme 1) can be due to the position of tautomeric equilibrium of imidazolidinone **4**, the *O*-alkylated derivative of type **1**, and the corresponding Schiff's base.[3]

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Nitrile cleavage of heterocycle in the electrochemical reduction of 1-chloro-4-(isopropylthio)phthalazine

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We have recently found[1] the previously unknown electron transfer-induced disclosure of the pyridazine cycle in 1-Cl-4-X-phthalazines (X = Cl, OAr, and OAlk) with elimination of the Cl^- and X^- anions, resulting in the formation of phthalonitrile. It was of interest to reveal the possibility of a similar reaction for other phthalazine derivatives containing two nucleophilic groups in positions 1 and 4. Therefore, we studied the electrochemical reduction (ECR) of 1-chloro-4-(isopropylthio)phthalazine (**1**) and 1,4-di(isopropylthio)phthalazine (**2**) in the DMF—Bu_4NI system (0.1 mol L^{-1} Bu_4NI) by voltammetry and electrolysis, which was carried out directly in the cavity of an ESR spectrometer.

The character of the voltammograms and the direction of reduction of phthalazine **1** are completely similar to the ECR of 1,4-dichlorophthalazine. The transfer of two electrons of the first irreversible wave ($E_{1/2}^1$ = −1.04 V relative to Hg/I^-, n = 2) results in the nitrile cleavage of the pyridazine cycle with elimination of chloride and isopropyl thiolate ions and formation of phthalonitrile. The reduction of the latter at potentials of the subsequent two waves is accompanied by the generation of phthalonitrile ($E_{1/2}^2$ = −1.15 V, n = 1) and benzonitrile ($E_{1/2}^3$ = −2.15 V, n = 2, 4) radical anions, respectively (Scheme 1). The one-electron level of the second reversible reduction wave, whose potential coincides with that of the reduction wave of

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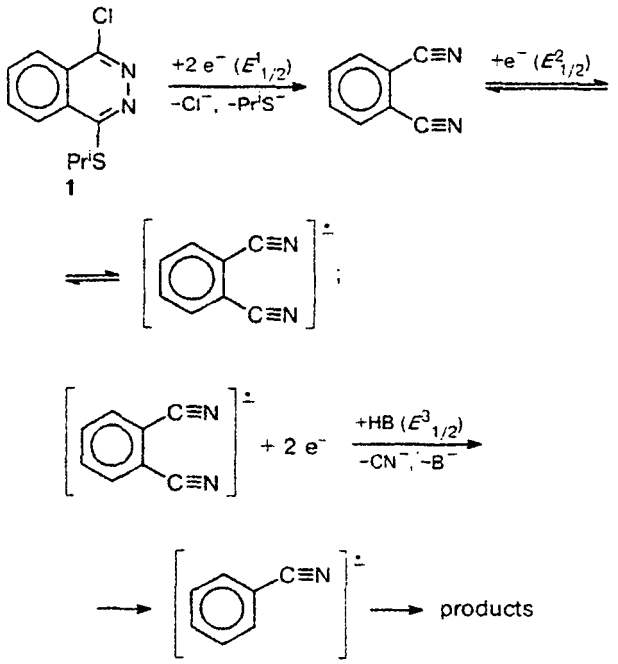
Scheme 1



phthalonitrile, indicates that nitrile cleavage occurs quantitatively under voltammetric conditions in an aprotic medium.

The metastable at room temperature primary radical anions ($E_{1/2}^{1} = -1.31$ V) undergoing further transformation without heterocycle disclosure are formed by ECR of phthalazine **2**. All radical anions were detected and reliably identified by commutator polarography, cyclic voltammetry, and ESR spectroscopy. The different directions of reduction of phthalazines **1** and **2** are due to a high nucleophilicity of chlorine as compared to that of the PriS group. It is most likely that the presence of at least one easily leaving group is the necessary requirement for nitrile cleavage of the heterocycle.

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