All procedures were carried out in an atmosphere of N_2. 1-(Methylthio)propyne and isopropyl isocyanate were synthesized by the known methods.[5,6] Tetrahydrofuran was purified using mechanically dispersed KOH (~50 g L^{-1}) and by distillation over $LiAlH_4$ in the presence of benzophenone in an N_2 atmosphere. *n*-Butyllithium (1.6 *M* solution in hexane) was presented by Chemetall (Germany).

Reaction of lithiated 1-(methylthio)propyne with isopropyl isocyanate and methyl iodide. 1-(Methylthio)propyne (9.1 g, 0.10 mol) was added to a solution of Bu^nLi (0.10 mol) in anhydrous THF (80 mL) and hexane (65 mL) cooled to −60 °C. When the temperature increased to 0 °C, it was decreased to −95 °C, then isopropyl isothiocyanate (10.97 g, 0.11 mmol) was rapidly added. The reaction mixture, whose temperature had increased again to −35 °C, was again cooled to −60 °C, and methyl iodide (22 g, 0.15 mol) was added. The mixture was stirred for 10—15 min at 10—15 °C and diluted with cold water (~60 mL) with intense stirring. The organic layer was separated, the aqueous layer was extracted with pentane (three times) and ether, and the combined organic fractions were dried over K_2CO_3. After the solvent was evaporated on a rotary evaporator, 2-methyl-4,5-di(methylthio)-3-azahepta-2,4,6-triene (**4**) was obtained (19.34 g, 96.2%) (^{1}H NMR, δ: 6.10 (d d, 1 H, CH); 5.40 and 4.85 (dd, 2 H, CH_2); 2.27 (s, 3 H, SMe); 2.17 (s, 3 H, SMe); 2.03 (s, 3 H, Me); 1.85 (s, 3 H, Me)) with a minor admixture of azatriene **3** (^{1}H NMR: 5.14 (s, CH_2)).

After short heating of compound **4**, the exothermic reaction of heterocyclization began (the temperature of self-warming was ~200 °C). 2,3-Bis(methylthio)-6,6-dimethyl-5,6-dihydropyridine (**5**) (14.1 g, 70.1%) with 96.4% purity (GLC) (b.p. 143—145 °C (15 Torr), n_D^{20} 1.5682) was isolated by distillation *in vacuo*. IR, ν/cm^{-1}: 600, 670, 800, 810, 870, 880 sh, 940, 950 sh, 990, 1010, 1080, 1130, 1170, 1220, 1250, 1280, 1300, 1350, 1360, 1410, 1440 sh, 1460 sh, 1550, 1590, 2800, 2860, 2910, 2950, 3050, 3100. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 5.92 (t, 1 H, H-4); 2.13 (d, 2 H, H-5); 2.14 (s, 3 H, SMe); 2.19 (s, 3 H, SMe); 1.10 (s, 6 H, 2 Me). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 158.52 (C-2); 129.02 (C-3); 128.75 (C-4), 35.80 (C-5); 54.09 (C-6); 16.34 (3-SMe); 12.41 (2-SMe); 28.01 (Me). Found (%): C, 53.63; H, 7.99; N, 6.95; S, 31.52. $C_9H_{15}NS_2$. Calculated (%): C, 53.73; H, 7.46; 6.96; S, 31.84.

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Nickel acetate-promoted reaction of benzoylcyanamide with 1-aryl-3-methyl-2-pyrazolin-5-ones

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It has been found previously[1,2] that nickel salts and complexes promote the addition of methylene-active β-diketones and esters of β-oxocarboxylic acids to cyanamides. However, similar transformations involving monocarbonyl compounds were unknown. We have established that 3-methyl-2-pyrazolin-5-ones (**1a,b**), which have a phenyl group with electron-withdrawing substituents at position 1, are also capable of adding to the C≡N bond of cyanamides. For example, the corresponding adducts **3a,b**, which are new representatives of ketene aminals of the heterocyclic series, were obtained from compounds **1a,b** and benzoylcyanamide (**2**).

The reaction does not occur in the absence of $Ni(OAc)_2$. Probably, the nickel enolates, forming from compounds **1a,b** as intermediates, participate in the formation of ketene aminals **3a,b**.

4-(*N*-Benzoyl)diaminomethylene-3-methyl-1-(4-nitrophenyl)pyrazolin-5-one (3a). A mixture of pyrazolinone **1a** (0.219 g, 1 mmol), cyanamide **2** (0.160 g, 1.1 mmol), and $Ni(OAc)_2$ (0.089 g, 0.5 mmol) in DMF (3 mL) was refluxed

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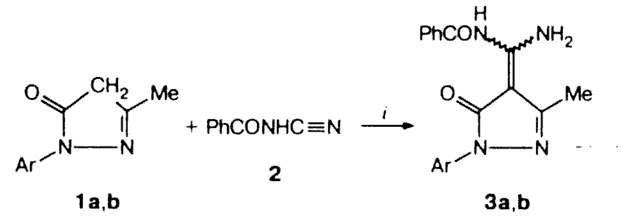

Ar = p-$NO_2C_6H_4$ (**a**), C_6F_5 (**b**)
Reagents and conditions: *i*. $Ni(OAc)_2$, DMF, Δ, 2 h.

for 2 h. The precipitate that formed during cooling was filtered off and recrystallized (DMF). Ketene aminal **3a** (0.24 g, 65%) was obtained (m.p. 336—338 °C).

MS (IE, 70 eV), *m/z*: 365 $[M]^+$. IR (KBr), ν/cm^{-1}: 3460, 3290 br, 3120—2800 (NH), 1698 sh, 1675, 1650, 1595. ^1H NMR (DMSO-d_6), δ: 2.40 (s, 3 H, Me), 7.60—8.10 (m, 5 H, Ph); 8.29 (br.s, 5 H, $C_6H_4NO_2$ + NH); 9.63 (br.s, 1 H, NH), 13.60 (br.s, 1 H, NH).

4-(*N*-Benzoyl)diaminomethylene-1-pentafluorophenyl-3-methylpyrazolin-5-one (3b) was obtained from pyrazolinone **1b** and cyanamide **2** similarly to the preparation of compound **3a**. After the mixture was refluxed, the solvent was distilled off, and water was added to the residue, which was filtered off and recrystallized from MeCN. The yield of **3b** was 54%, m.p. 254—256 °C. MS (IE, 70 eV), *m/z*: 410 $[M]^+$. ^1H NMR (DMSO-d_6), δ: 2.40 (s, 3 H, Me), 7.60—8.10 (m, 5 H, Ph), 8.32 (br.s, 1 H, NH), 9.65 (s, 1 H, NH), 13.65 (br.s, 1 H, NH).

The data of elemental analysis of compounds **3a,b** correspond to the calculated values.

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One-step synthesis of 4,5-dichloroanthrone from 1,8-dichloroanthraquinone

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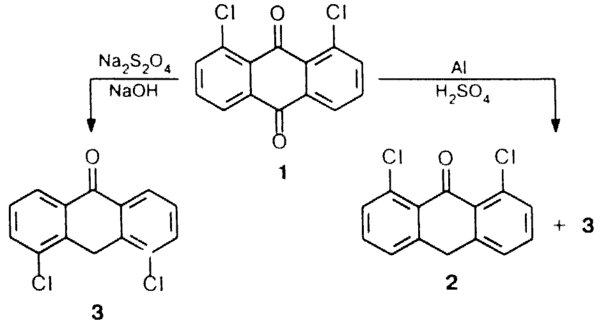
When 1,8-dichloroanthraquinone (**1**) reacts with reducing agents, the formation of both 1,8-dichloro- (**2**) and 4,5-dichloroanthrones (**3**) is possible. It is known[1] that reduction by powdered Al and conc. H_2SO_4 leads to anthrone **2**, while anthrone **3** can be obtained from 1,8-dichloroanthracene[2] in six stages or from 1,8-dichloro-9-methoxy-10-(dimethoxyphosphoryloxy)anthracene synthesized from quinone **1** and trimethyl phosphite in three stages.[3]

We found that anthrone **3** can by obtained with high regioselectivity by the reduction of quinone **1** by sodium dithionite in an alkaline medium. Small amounts of anthrone **3** are also formed when **1** is reduced in the Al—H_2SO_4 system. According to the data of ^1H NMR spectroscopy, the ratio of anthrones **2** and **3** formed is equal to ~ 4 : 1.



The results obtained indicate that the dependence of the direction of reduction of quinone **1** on the nature of the reducing agent is similar to that for 1-chloroanthraquinone.[4]

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