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Synthesis of 1-(*N*-alkylnitraminomethyl)-3-nitroureas using *N*-alkylsulfamates

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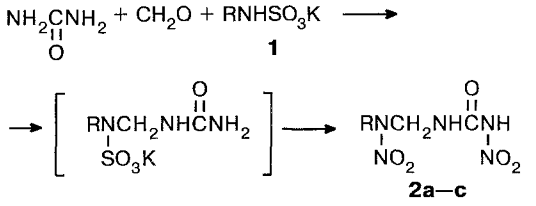
1-(*N*-alkylnitraminomethyl)-3-nitroureas were prepared by nitration of condensation products of urea with formaldehyde and *N*-alkylsulfamate.

Key words: 1-(*N*-alkylnitraminomethyl)-3-nitroureas, N-alkylsulfamates, condensation, nitration.

Previously[1] we demonstrated that the reaction of substitutive nitration of *N*-alkylsulfamates is a convenient method for the synthesis of cyclic nitramine derivatives. In the present work this reaction was used for the preparation of acyclic nitramines: 1-(*N*-alkylnitroaminomethyl)-3-nitroureas.

The literature contains spotty reports about condensation of urea with formaldehyde and sulfaminic acid derivatives[2,3]. The reaction products were not analyzed properly, and the physico-chemical properties were the basis for assigning a polymer structure for these compounds.

We carried out condensation reaction of urea with formaldehyde and primary *N*-alkylderivatives of sulfaminic acid in the form of potassium salts (**1**) in an aqueous medium, with simultaneous distillation of solvent *in vacuo*. The crystalline products do not have definite melting points. The attempts to isolate these products in pure state were unsuccessful. Therefore the product obtained was immediatly nitrated according to the technique we developed earlier.[1]



$$NH_2\underset{\underset{O}{\|}}{C}NH_2 + CH_2O + \underset{\mathbf{1}}{RNHSO_3K} \longrightarrow \left[\underset{\underset{SO_3K}{|}}{R N}CH_2NH\overset{\overset{O}{\|}}{C}NH_2\right] \longrightarrow \underset{\underset{NO_2}{|}}{RN}CH_2NH\overset{\overset{O}{\|}}{C}\underset{\underset{NO_2}{|}}{NH}$$

2a—c

R = CH_3 (**2a**), Et (**2b**), Pr^i (**2c**)

The nitration products, (1-(*N*-alkylnitraminomethyl)-3-nitroureas (**2**)), were obtained in moderate yields. Their structure was confirmed by spectral data and by elemental analysis. In the case of **2a**, nitration of the terminal NH_2 group of urea is supported by the presence of characteristic coupling constant $^3J_{HCNH}$ = 5.7 Hz.

It is interesting to note that the condensation carried out in similar conditions, but at a different molar ratio of starting compounds (urea : formaldehyde : **1** = 1 : 2 : 2), followed by nitration also gives 1-(*N*-alkylnitraminomethyl)-3-nitroureas **2a—c**.

Experimental

NMR spectra were measured on Bruker AM-300 and Tesla BS-467 spectrophotometers (60 MHz) relative to TMS (^{13}C, ^1H) and CH_3NO_2 (^{14}N). IR spectra were measured in KBr pellets on UR-20 instrument.

General methods of synthesis of 1-(*N*-alkylnitraminomethyl)-3-nitroureas (2). To the solution of 10 mmol of urea in 10 mL water, 10 mmol of the corresponding *N*-alkylsulphamate 1 and 0.9 mL of 33%-formaline were added, pH was adjusted to 6.5 and the mixture was evaporated by a rotating evaporator at the temperature of boiling water. The residue thus obtained (2 g) was added to the mixture of 6 mL

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of 98 % HNO_3 and 5 mL of 20 % oleum at −20÷−25° C. The mixture was stirred at the same temperature for 2 h, then poured on 50 g ice. The product was extracted by ethyl acetate (3×30 mL); the extract was washed with water (2×20 mL), dried over $MgSO_4$ and evoporated *in vacuo*. The residue was recrystallizated from an isopropanol : water mixture (5 : 1) to give compound **2**.

2a, yield 42 %, m.p. 152—154 °C. IR (ν/cm^{-1}): 3410, 3170 (NH), 1700 (C=O), 1622, 1546, 1522, 1296 (N—NO_2). ^{1}H NMR (DMSO-d_6, δ, ppm): 3.34 (s, 3 H, Me), 5.13 (d, 2 H, CH_2, ^3J = 5.4 Hz), 7.8 (br. s, 1 H, NH—NO_2), 8.56 (t, 1 H, C—NH—C). ^{13}C NMR (CD_3COCD_3, δ, ppm): 38.8 (CH_3), 56.9 (CH_2), 151.2 (C=O). ^{14}N NMR (DMSO-d_6, δ, ppm): −35.0 ($\underline{N}O_2$—NH), -28.2 ($\underline{N}O_2$—N—CH_3).

2b, yield 44 %, m.p. 126—127 °C. IR (ν/cm^{-1}): 3420, 3180 (NH), 1698 (C=O), 1632, 1520, 1288 (N—NO_2). ^{1}H NMR (CD_3COCD_3, δ, ppm): 1.14 (t, 3 H, Me), 3.9 (q., 2 H, CH_2—C), 5.23 (d, 2 H, N—CH_2—N).

2c, yield 28 %, m.p. 113—115 °C. IR (ν/cm^{-1}): 3400, 3160 (NH), 1706 (C=O), 1624, 1550, 13 (N—NO_2). ^{1}H NMR (CD_3COCD_3, δ, ppm): 1.20 (d, 6 H, 2 Me), 4.57 (m, 1 H, CH), 5.20 (d, 2 H, CH_2).

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X-Ray photoelectron spectra and electronic structure of pyrazolanthrone and its derivatives

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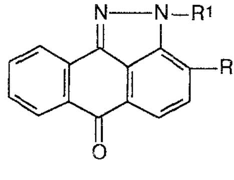
X-ray photoelectron spectroscopy (XPS) was used to investigate the electronic structures of pyrazolanthrone and its derivatives on the basis of quantum-chemical data. The high mobility of hydrogen atoms adjacent to the pyrrole atom as well as the existence of an intermolecular hydrogen bond were hypothesized. The considerable influence of the carbonyl group on redistribution of electronic density in a pyrazole fragment was observed.

Key words: pyrazolanthrone, X-ray photoelectron spectroscopy, N1s level, binding energy, electronic density.

Pyrazolanthrone and its derivatives are of practical significance and used as vat dyes. However, the chemical properties and electronic structure of this class of compounds have not been adequately investigated.

In this work the electronic structures of pyrazolanthrone and its derivatives were studied by X-ray photoelectron spectroscopy (XPS) using data from quantum-chemical calculations. The class of pyrazolanthrone derivatives under consideration consists of compounds with the following structures:



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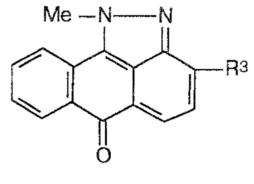

8—9

1: $R^1 = R^2$ = H; **2**: R^1 = H, R^2 = Me; **3**: R^1 = H, R^2 = Bu^t;
4: R^1 = Me , R^2 = H; **5**: $R^1 = R^2$ = Me;
6: R^1 = C(O)Ph, R^2 = H; **7**: R^1 = $CH_3C_6H_4SO_2$, R^2 = H;
8: R^3 = H; **9**: R^3 = Me.

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