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LETTERS TO THE EDITOR

Extrusion of Formaldehyde from Bis(pyrazolylmethyl) Ethers on Heating

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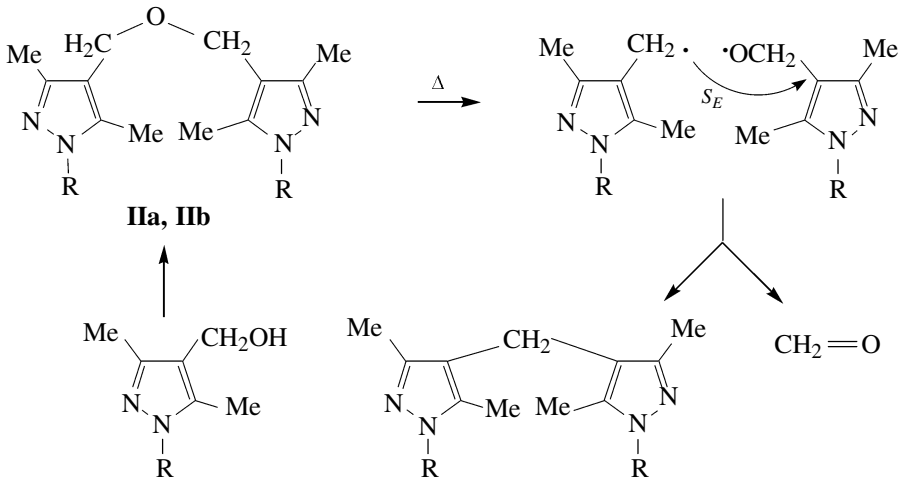
We recently showed that 1-substituted 3,5-dimethylpyrazolylmethanols **I** on heating to 200°C (2 h) are converted into bis(pyrazolylmethyl) ethers **II** [1]. While studying the behavior of ethers **II** we revealed an unusual transformation. It was found that on heating to 250°C ethers **II** lose formaldehyde molecule with formation of dipyrazolylmethanes **III** which are usually obtained from pyrazoles and formaldehyde in the presence of acids [2, 3]. The structure of compound **III** was confirmed by independent synthesis according to the scheme described in [2]. We also found that formaldehyde does not react with initial 1-substituted 3,5-dimethylpyrazoles on heating.



R = Me (**a**), $PhCH_2$ (**b**).

No cross-coupling products were formed when the transformation was carried out in the presence of pyrazoles (R = Me, $PhCH_2$). These data suggest that the observed fragmentation of compounds **II** follows intramolecular mechanism with intermediate formation of electrophilic carbon-centered radical species which are stabilized via intramolecular electron transfer. Presumably, the presence of nitrogen atoms in molecules **II** hinders heterolytic dissociation of the C–O bond but favors formation of radical species and facilitates electron density redistribution according to single-electron transfer mechanism. Such assistance was substantiated by us previously [4].

Bis(1,3,5-trimethyl-1*H*-pyrazol-4-yl)methane (IIIa). Bis(1,3,5-trimethyl-1*H*-pyrazol-4-ylmethyl)

ether (**IIa**), 0.01 mol, was heated for 5 h at 250°C in a flask equipped with a reflux condenser. Yield of **IIIa** 72%, mp 87–88°C (from petroleum ether). IR spectrum: ν 1550 cm^{-1} (pyrazole ring). ^1H NMR spectrum, δ, ppm: 1.98 s (6H, 3-CH_3), 2.06 s (6H, 5-CH_3), 3.31 s (2H, CH_2), 3.64 s (3H, 1-CH_3). Found, %: C 67.11; H 8.59; N 23.78. $C_{13}H_{20}N_4$. Calculated, %: C 67.24; H 8.62; N 24.14.

Bis(1-benzyl-3,5-dimethyl-1*H*-pyrazol-4-yl)-methane (IIIb) was obtained in a similar way from bis(1-benzyl-3,5-dimethyl-1*H*-pyrazol-4-ylmethyl) ether (**IIb**). Yield 67%, mp 110°C (from petroleum ether). IR spectrum: ν 1550 cm^{-1} (pyrazole ring). ^1H NMR spectrum, δ, ppm: 1.99 s (12H, 3-CH_3, 5-CH_3), 3.29 s (2H, CH_2), 5.18 s (4H, C$H_2C_6H_5$), 7–7.25 m (10H, C_6H_5). Found, %: C 77.98; H 7.02; N 14.12. $C_{25}H_{28}N_4$. Calculated, %: C 78.13; H 7.29; N 14.58.

The ^1H NMR spectra were recorded on a Varian Mercury-300 spectrometer (300 MHz) from solutions in DMSO-d_6–CCl_4 (1 : 3). The IR spectra were measured on a Specord 75-IR instrument from samples prepared as thin films.

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