Russian Journal of Organic Chemistry, Vol. 37, No. 12, 2001, pp. 1795–1796. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 12, 2001, p. 1876.
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SHORT COMMUNICATIONS

Dedicated to Academician M.G.Voronkov on occasion of his 80th birthday

Synthesis of Pyrazole Derivatives from 1,1-Dimethylhydrazine and Chlorovinyl Ketones

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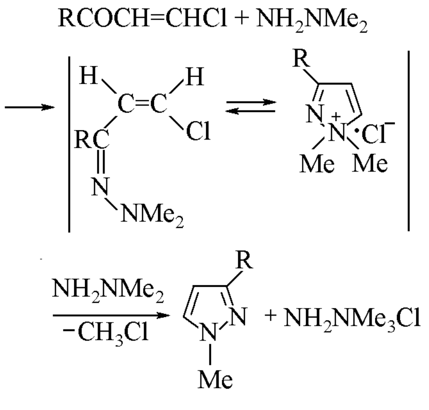
Received October 27, 2000

We previously showed [1] that 2,2-dichlorovinyl ketones react with 1,1-dimethylhydrazine to give the corresponding 3-substituted 5-chloro-1-methylpyrazoles. We now report on a new way to pyrazole derivatives which can be obtained in up to 70% yield from accessible 2-chlorovinyl methyl ketone and 2-chlorovinyl chloromethyl ketone [2, 3] and 1,1-dimethylhydrazine.



R = Me, CH_2Cl.

The reactions were carried out at a reactant ratio of 1 : 2 in an organic solvent and were accompanied by heat evolution. The second product was 1,1,1-trimethylhydrazinium chloride which was isolated in 90% yield. When the reaction was performed with equimolar amounts of the reactants, we also obtained the corresponding pyrazole and trimethylhydrazinium chloride, but the conversion of the initial chlorovinyl ketone was smaller. The scheme of the process is likely to include initial formation of 2-chlorovinyl ketone dimethylhydrazone, followed by intramolecular attack by the nucleophilic dimethylamino group on the β-carbon atom of the vinyl group. *N*,*N*-Dimethylpyrazolium chloride thus formed undergoes transquaternization by the action of the second dimethylhydrazine molecule.

3-Chloromethyl-1-methylpyrazole. To a solution of 1.2 g of 1,1-dimethylhydrazine in 50–100 ml of dry diethyl ether we slowly added 1.39 g of 1,4-dichloro-3-buten-2-one at such a rate that the mixture did not boil. When the exothermic reaction was complete, the mixture was stirred for 0.5–2 h. The yield of trimethylhydrazinium chloride (which precipitated from the mixture) was 0.96 g (88%). mp 261–262°C {published data [4]: mp 245°C with decomposition (from EtOH–EtOAc)}. The filtrate was evaporated, and the product was purified by column chromatography on silica gel or by distillation. Yield 0.91 g (70%). bp 146–148°C, n_D^{20} 1.5275. ^1H NMR spectrum, δ, ppm: 7.324, 7.319 (4-H), 6.278 and 6.274 (5-H), 4.58 (CH_2Cl), 3.86 (CH_3N). ^{13}C NMR spectrum, δ_C, ppm: 148.37 (C^3), 130.97 (C^5), 105.08 (C^4), 76.83 (CH_2Cl), 38.62 (CH_3N). Found, %: C 45.78; H 5.24; N 21.47. $C_5H_7ClN_2$. Calculated, %: C 45.99; H 5.40; N 21.45.

1,3-Dimethylpyrazole. Following the above procedure, from 1.2 g of 1,1-dimethylhydrazine and 1.04 g of 4-chloro-3-buten-2-one in 50–100 ml of dry hexane we obtained 0.9 g of trimethylhydrazinium chloride and 0.84 g (64%) of 1,3-dimethylpyrazole. bp 136–138°C, n_D^{20} 1.4674 [5], d_4^{20} 0.9626 [5].

The NMR spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$ using tetramethylsilane as internal reference.

1070-4280/01/3712-1795 $25.00 ©2001 MAIK “Nauka / Interperiodica”

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