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THERMAL RECYCLIZATION OF 5-R-2-ISOPROPENYLTETRAZOLES INTO 5-R-3-METHYLPYRAZOLES

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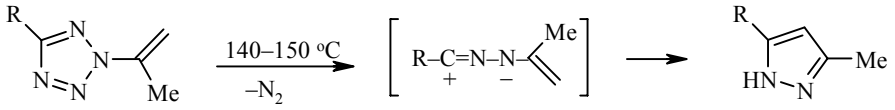
It is known that 2-alkenyl-5-phenyltetrazoles recyclize to 3-phenylpyrazine or its 4-alkyl(aryl)derivatives on heating or irradiation with UV light [1]. We have observed for the first time the thermally stimulated conversion of compounds of the given class, namely the formation of 5-substituted 3-methylpyrazoles **1** from 5-substituted 2-isopropenyltetrazoles **2**.



2a,**b** **3** **1a**,**b**

1-3 a R = Ph, **b** R = $Me_2NCH_2CH_2$

The mechanism of the thermolysis apparently includes opening of the tetrazole ring with the elimination of a molecule of nitrogen and the formation of an active nitrileimine **3**, which is characteristic of 2,5-substituted tetrazoles [2]. The nitrile imine **3** then undergoes an intramolecular cyclization into the pyrazole **1**. The observed transformation may provide a new method for the synthesis 3,5-disubstituted pyrazoles from the relatively available tetrazoles **2** [3]. The procedure includes the prolonged heating of tetrazole **2** in a high boiling organic solvent with subsequent removal of the solvent under vacuum. The yields of 5-R-3-methylpyrazoles **1** is 45% (boiling of compound **2a** in nonane for 8 h) and 88% (**2b**, DMF, 15 h). The spectroscopic data and the physico-chemical characteristics of 3-methyl-5-phenylpyrazole (**1a**) correspond with literature data [4]. Compound **1b** was identified by comparison of its spectroscopic characteristics with those of related 3,5-dialkylpyrazoles (^{1}H NMR [4] and ^{13}C NMR spectra [5]).

5-N,N-Dimethylaminoethyl)-2-isopropenyltetrazole (2b) was obtained by alkylation 5-(N,N-dimethylaminoethyl)tetrazole with allyl bromide with subsequent dehydrobromination of 2-(2-bromo-1-methylethyl)-5-(N,N-dimethylaminoethyl)tetrazole by a method described for the synthesis of **2a** [3]. A viscous oil, mp of the picrate 127-128°C (prepared by reaction of equimolar amounts tetrazole **2b** and picric acid in ethanol). ^{1}H NMR spectrum (CD_3CN, 100 MHz), δ, ppm: 5.93 (H, s, CH_{cis}=C–N); 5.20 (1H, s, CH_{trans}=C–N); 2.65-2.82 (2H, m, CH_2); 2.98-3.17 (2H, m, CH_2); 2.48 (3H, s, CH_3); 2.26 (6H, s, 2 CH_3). Found, %: C 52.83; H 8.03; N 38.25. $C_8H_{15}N_5$. Calculated, %: C 53.02; H 8.34; N 38.64.

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5-(N,N-Dimethylaminoethyl)-3-methylpyrazole (1b). Viscous oil, mp of picrate 162-163°C (prepared by interaction of equimolar amounts of pyrazole **1b** and picric acid in ethanol). ^{1}H NMR spectrum (DMSO-d_6, 100 MHz), δ, ppm: 5.80 (1H, s, HC=); 2.30-2.80 (4H, m, 2 CH_2); 2.16 (6H, s, 2 CH_3); 2.14 (3H, s, CH_3). ^{13}C NMR spectrum (DMSO-d_6, 25 MHz), δ, ppm: 147.2 (C-3), 143.4 (C-5), 104.6 (C-4), 62.3 (CH_2N), 48.6 (2 Me), 29.3 (CH_2), 16.4 (Me). Found, %: C 62.53; H 9.70; N 27.30. $C_8H_{15}N_3$. Calculated, %: C 62.71; H 9.87; N 27.42.

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