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LETTERS TO THE EDITOR

Thermal Addition of Pyrazoles to But-3-enenitrile

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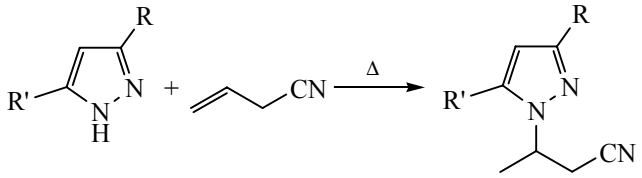
In the present work, we investigated the reactivity of pyrazoles **I–III** in reactions with but-3-enenitrile, where the double bond was not directly connected to the electron-withdrawing nitrile group.

The general prerequisite for the successful usage of ethylene compounds in nucleophilic addition reactions is the presence of electron-withdrawing groups at the double bond, which are activating them towards the nucleophilic attack [1–10].

As should be expected, pyrazoles **I–III** do not react with but-3-enenitriles even at prolonged heating. However, the reaction proceeded at an elevated pressure at 200–220°C to form the corresponding adducts **IV–VI** with 60–80% yields.



I–III **IV–VI**

$R^1 = R^2 = H$ (**I, IV**), $R^1 = CH_3$, $R^2 = CH_3$ (**IIa, Va**), $R^1 = H$, $R^2 = CH_3$ (**IIb, Vb**), $R^1 = R^2 = CH_3$ (**III, VI**).

Probably, at 200–220°C in the presence of azoles the isomerization of but-3-enenitriles into but-2-enenitrile occurs, which further facilitates the attachment of a nucleophilic reagent to the β-carbon atom of the conjugated double bond.

The structure of obtained compounds was confirmed by IR and NMR spectroscopy methods. Thus, the IR spectra of compounds **IV–VI** contains absorption bands of the nitrile group (2250 cm^{-1}) and the pyrazole ring (1500–1510 cm^{-1}). The ^1H NMR spectra of compounds **IV–VI** contain a multiplet signal of the NCH group in the range of 4.50–4.79 ppm.

But-3-enenitrile was produced by ARIAC (Armenia).

3-(1*H*-Pyrazol-1-yl)butanenitrile (IV). A mixture of 1.7 g (0.025 mol) of pyrazole **I** and 2 g (0.03 mol) of but-3-enenitrile was heated for 24 h in a pressure reactor at a temperature of 200–220°C. After cooling, the reaction mixture was distilled in a vacuum. Yield 2.1 g (60%), bp 116°C (1 mmHg), n_D^{20} 1.4862. IR spectrum, ν, cm^{-1}: 1500 (ring), 2250 (CN). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.60 d (3H, $C\underline{H}_3CH$, *J* 6.7), 2.94 d.d (1H, CH_2, *J* 16.8, 6.2), 3.00 d.d (1H, CH_2, *J* 16.8, 6.8), 4.63–4.79 m (1H, $CH_3C\underline{H}$), 6.19 d.d (1H, H^4, *J* 2.4, 1.7), 7.41 d.d (1H, H^5, *J* 1.7, 0.5), 7.65 d.d (1H, H^3, *J* 2.4, 0.5). Found, %: C 62.58; H 6.32; N 31.44. $C_7H_9N_3$. Calculated, %:C 62.20; H 6.71; N 31.09.

3-[3(5)-Methyl-1*H*-pyrazol-1-yl]butanenitrile (Va, Vb) (mixture of isomers) was prepared similarly from 2 g (0.025 mol) of 3(5)-methylpyrazole **IIa**, **IIb**. Yield 2.4 g (65%), bp 120°C (1 mmHg), n_D^{20} 1.4831. IR spectrum, ν, cm^{-1}: 1500 (ring), 2250 (CN). ^1H NMR spectrum, δ, ppm, (*J*, Hz): 1.57 d (**a**) and 1.50 d (**b**) (3H,$C\underline{H}_3CH$), 2.21 s (**a**) and 2.33 s (**b**) (3H, 3-CH_3), 2.85–3.00 m (2H, CH_2), 4.55–4.73 m (1H, $CH_3C\underline{H}$), 5.92–5.94 m (1H, H^4), 7.48 d [1H, $H^{5(3)}$, *J* 2.2 (**a**), *J* 1.6 (**b**)]. Found, %: C 64.75; H 7.29; N 28.55. $C_8H_{11}N_3$. Calculated, %: C 64.40; H 7.73; N 28.16.

3-(3,5-Dimethyl-1*H*-pyrazol-1-yl)butanenitrile (VI) was prepared similarly from 3,5-dimethylpyrazole **III**.

Yield 4.1 g (80%), bp 123°C (1 mmHg), n_D^{20} 1.4810. IR spectrum, ν, cm^{-1}: 1500 (ring), 2250 (CN). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.49 d (3H, $C\underline{H}_3CH$, *J* 6.7), 2.22 s (3H, 5-CH_3), 2.34 s (3H, 3-CH_3), 2.85–2.90 m (2H, CH_2), 4.50–4.70 m (1H, $CH_3C\underline{H}$), 5.82 s (1H, H^4). Found, %:C 66.58; H 8.91; N 25.38. $C_9H_{13}N_3$. Calculated, %: C 66.23; H 8.03; N 25.74.

IR spectra were obtained on a Nexus spectrometer (Thermo Nicolet Corporation, USA). ^1H NMR spectra were recorded on a Varian Mercury instrument (300 MHz) in DMSO–CCl_4, 1 : 3. Elemental analysis was performed on a Korshun–Klimov apparatus.

REFERENCES

1. Teret'ev, A.P. and Kost, A.N., *Reaktsii i metody issledovaniya organicheskikh soedinenii* (Reactions and Methods for Studying of Organic Compounds), Moscow: Goskhimizdat, 1952, vol. 2, p. 47.
2. Bruson, H.A., *Organic Reactions*, New York; London: John Wiley & Sons, 1949, no. 5, p. 79.
3. Srivastava, N. and Bimal, K.B., *J. Org. Chem*., 2003, vol. 68, no. 6, p. 2109. DOI: 10.1021/jo026550s.
4. Jing-ping, K., Yu-juan, L., Xu-yang, L., and Ji-zhen, L., *Chem. Res. Chinese Univ*., 2009, vol. 25, no. 4, p. 461.
5. Ranu, B.C. and Banerjee, S., *Tetrahedron Lett*., 2007, vol. 48, no. 1, p. 141. DOI: 10.1016/j.tetlet.2006.10.142.
6. Surendra, K., Srilakshmi Krishnaveni, N., Sridhar, R., and Rama Rao, K., *Tetrahedron Lett*., vol. 47, no. 13, 2006, p. 2125. DOI: 10.1016/j.tetlet.2006.01.124.
7. Attaryan, O.S., Baltayan, A.O., and Matsoyan, S.G., *Khim. Zh. Armenii*, 2005, vol. 58, no. 4, p. 68.
8. Attaryan, O.S., Eliazyan, G.A., Asratyan, G.V., Panosyan, G.A., Darbinyan, E.G., and Matsoayn, S.G., *Arm. Khim. Zh.*, 1986, vol. 39, no. 8, p. 511.
9. Attaryan, O.S., Baltayan, A.O., Badalyan, K.S., Minasyan, G.G., and Matsoyan, S.G., *Russ. J. Gen. Chem*., 2006, vol. 76, no. 7, p. 1131. DOI: 10.1134/S1070363206070218.
10. Khachatryan, H.N, Hayotsyan, S.S., and Attaryan, H.S., Book of Abstracts, *4th Int. Conf. Young Scientists Chemistry Today*, Yerevan, 2014, p. 136.