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LETTERS TO THE EDITOR

Dehydrochlorination of 1-(2-Chloroethyl)azoles in Aqueous Solution of *N*-Methylmorpholine *N*-Oxide

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Synthesis of 1-vinylazoles and development of the relevant, available and easily simulated technological processes are one of actual issues in organic chemistry in view of the propensity of the 1-vinylazoles for polymerization under conditions of radical initiation and special properties of the thus produced polymers [1–10].

Dehydrochlorination of 1-(2-chloroethyl)azoles **1–4**, **9**, and **11** in alcoholic solutions of KOH is among the methods of preparation of 1-vinylazoles **5–8**, **10**, and **12**. However, this method does not afford high yields of the target compounds and can be hardly implemented in industry [11–14]. Dehydrochlorination under conditions of the phase-transfer catalysis is the alternative to the homogeneous process; however, the product yield is still low [15–18].

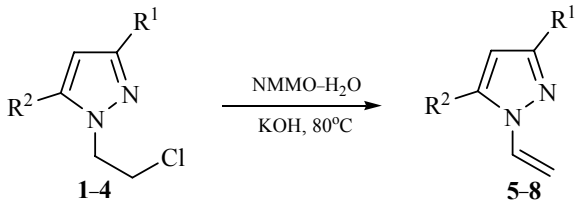
Based on the data of mild alkylation of pyrazoles and 3-nitro-1,2,4-triazole with bromopropyne in aqueous solution of *N*-methylmorpholine *N*-oxide (NMMO) in the presence of KOH reported in [19], we studied the dehydrochlorination of 1-(2-chloroethyl) pyrazoles **1–4**, **9**, and **11** in an aqueous NMMO solution in order to investigate the application scopes of mentioned system. We found that the dehydrochlorination of the mentioned compounds occurrs in this conditions without any phase-transfer catalyst (Scheme 1).

The patterns revealed in the study of dehydrochlorination of 1-(2-chloroethyl)pyrazoles **1–4** for the phase-transfer catalysis [16] were retained for the NMMO–water system.

In contrast to the cases of 1-(2-chloroethyl)pyrazoles **1–4**, dehydrochlorination of 2-chloroethyltriazole **9** and 2-chloroethyltetrazole **11** in an aqueous MMO solution occurrs under much milder conditions, at 20–25°C (Scheme 2).

By the easiness of the dehydrochlorination, the studied azoles can be arranged in the **11 > 9 > 1 > 2 > 3 > 4** series, which corresponds with the data in [20]

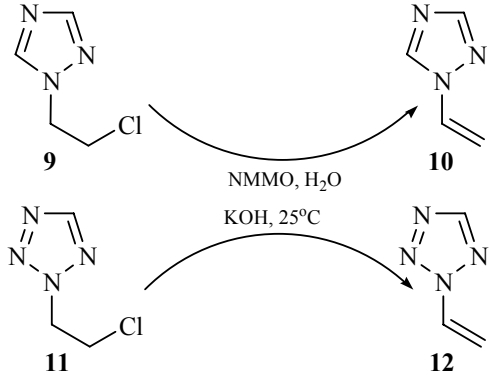
Scheme 1.



1–4 **5–8**

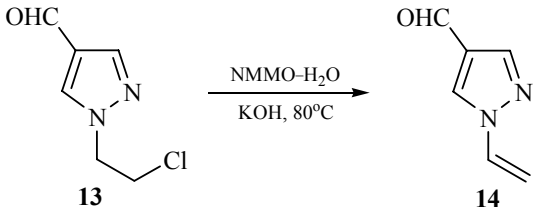
$R^1 = R^2 = H$ (**1**, **5**); $R^1 = CH_3$, $R^2 = H$ (**2**, **6**); $R^1 = H$, $R^2 = CH_3$ (**3**, **7**); $R^1 = R^2 = CH_3$ (**4**, **8**).

Scheme 2.



9 **10** **11** **12**

Scheme 3.



13 **14**

on the increasing of the acceptor inductive effect of the hetero-ring by the increasing of the number of heteroatoms in the last. The effect leads to the facilitation of deprotonation on the N-substituent.

Dehydrochlorination is further facilitated by the presence of the formyl group at position 4 of the pyrazole cycle: dehydrochlorination of 4-formylpyrazole **13** was complete within 15 min at 80°C. For comparison, dehydrochlorination at room temperature occurred similarly to the case of 1-(2-chloroethyl)triazole **9**, being complete within 5 h (Scheme 3).

In summary, 50 wt % aqueous solution of MMO can serve as the alternative reaction medium foe dehydrochlorination of a series of 1-(2-chloroethyl)azoles.

1-Vinylpyrazole (5). A mixture of 13.02 g (0.1 mol) of 1-(2-chloroethyl)pyrazole **1**, 11.2 g (0.2 mol) of KOH, and 50 mL of 50 wt% aqueous solution of MMO was vigorously stirred during 2 h at 80°C. After cooling to ambient, the reaction mixture was extracted with chloroform. The solvent was removed, and the residue was distilled in vacuum. Yield 7.0 g (75%), bp 63°C (50 mmHg), n_D^{20} 1.5160 [16]. IR spectrum, ν, cm^{-1}: 1520 (ring), 1640 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.00 d.d (1H, $=CH_2$, *J* = 9.0, 1.5), 5.52 d.d (1H, $=CH_2$, *J* = 15.8, 1.5), 6.26 t (1H, 4-H, *J* = 2.2), 7.12 d.d (1H, NC=H, *J* = 15.8, 9.0), 7.50 d (1H, 3-H, *J* = 2.4), 7.58 d (1H, 5-H, *J* = 2.0).

1-Vinyl-3-methylpyrazole (6) was prepared similarly from 14.4 g (0.1 mol) of 1-(2-chloroethyl)-3-methylpyrazole **2**; reaction duration was of 3 h. Yield 8.6 g (80%), bp 50°C (10 mmHg), n_D^{20} 1.5150 [21]. IR spectrum, ν, cm^{-1}: 1530 (ring), 1640 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.16 s (3H, 3-CH_3), 4.76 d.d (1H, $=CH_2$, *J* = 9.2, 1.5), 5.42 d.d (1H, $=CH_2$, *J* = 15.7, 1.5), 5.85 d (1H, 4-H, *J* = 2.0), 6.92 d.d (1H, NC=H, *J* = 15.7, 9.3), 7.42 d (1H, 5-H, *J* = 2.3).

1-Vinyl-5-methylpyrazole (7) was prepared similarly from 14.4 g (0.1 mol) of 1-(2-chloroethyl)-5-methylpyrazole **3**; reaction duration was of 2.5 h. Yield 8.0 g (74%), bp 55°C (10 mmHg), n_D^{20} 1.5200 [21]. IR spectrum, ν, cm^{-1}: 1530 (ring), 1640 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.20 s (3H, 5-CH_3), 4.80 d.d (1H, $=CH_2$, *J* = 9.3, 1.5), 5.45 d.d (1H, $=CH_2$, *J* = 15.7, 1.5), 5.95 d (1H, 4-H, *J* = 2.0), 6.90 d.d (1H, NC=H, *J* = 15.7, 9.3), 7.28 d (1H, 3-H, *J* = 2.2).

1-Vinyl-3,5-dimethylpyrazole (8) was prepared similarly from 15.8 g (0.1 mol) of 1-(2-chloroethyl)-3,5-dimethylpyrazole **4**; reaction duration was of 4 h. Yield 7.9 g (65%), bp 70°C (10 mmHg), n_D^{20} 1.5180 [16]. IR spectrum, ν, cm^{-1}: 1540 (ring), 1640 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.11 s (3H, 3-CH_3), 2.33 s (3H, 5-CH_3), 4.42 d.d (1H, $=CH_2$, *J* = 9.5, 1.5), 5.22 d.d (1H, $=CH_2$, *J* = 15.3, 1.5), 5.67 s (1H, 4-H), 6.33 d.d (1H, NC=H, *J* = 15.3, 9.5).

1-Vinyl-1,2,4-triazole (10). A mixture of 13.1 g (0.1 mol) of 1-(2-chloroethyl)-1,2,4-triazole **9**, 11.2 g (0.2 mol) of KOH, and 50 mL of 50 wt% of aqueous MMO solution was vigorously stirred during 5 h at 20–25°C and then extracted with chloroform. After removal of chloroform, the residue was distilled in vacuum. Yield 6.6 g (70%), bp 58°C (1 mmHg), n_D^{20} 1.5200 [15]. IR spectrum, ν, cm^{-1}: 1500 (ring), 1640 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.00 d.d (1H, $=CH_2$, *J* = 9.0, 1.5), 5.78 d.d (1H, $=CH_2$, *J* = 15.8, 1.5), 7.12 d.d (1H, NC=H, *J* = 15.8, 9.0), 7.92 s (1H, 3-H), 8.38 s (1H, 5-H).

2-Vinyltetrazole (12) was prepared similarly from 13.2 g (0.1 mol) of 2-(2-chloroethyl)tetrazole **11**; reaction duration was of 2 h. Yield 8.2 g (85%), bp 63°C (60 mmHg), n_D^{20} 1.4830 [18]. IR spectrum, ν, cm^{-1}: 1490 (ring), 1640 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.43 d.d (1H, $=CH_2$, *J* = 8.7, 1.3), 6.22 d.d (1H, $=CH_2$, *J* = 15.6, 1.3), 7.62 d.d (1H, NC=H, *J* = 15.6, 8.7), 8.70 br. s (1H, 5-H).

1-Vinyl-4-formylpyrazole (14) was prepared similarly to pyrazole **5** from 15.8 g (0.1 mol) of 1-(2-chloroethyl)-4-formylpyrazole **13**; reaction duration was of 15 min. Yield 8.7 g (72%), bp 90°C (3 mmHg), n_D^{20} 1.5640 [22]. IR spectrum, ν, cm^{-1}: 1520 (ring), 1640 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.98 d.d (1H, $=CH_2$, *J* = 9.0, 1.0), 5.77 d.d (1H, $=CH_2$, *J* = 15.5, 1.0), 7.19 d.d (1H, =CH, *J* = 15.5, 9.0), 7.96 s (1H, 3-H), 8.56 s (1H, 5-H), 8.83 s (1H, CHO).

^{1}H NMR spectra were recorded using a Varian Mercury-300VX (300.05 Hz) instrument at 300 K in the solutions in DMSO-d_6–CCl_4 (1 : 3) with TMS as

internal reference. IR spectra were recorded using a Specord 75 IR instrument (suspension in Vaseline oil or thin film).

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