Chemistry of Heterocyclic Compounds, Vol. 38, No. 10, 2002

UNUSUAL THERMAL REARRANGEMENTS OF N-CYCLOHEXYLIDENE-4-METHYL-1-(METHYLTHIO)PENTA-1,3-DIEN-1-AMINE*

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We have observed unusual thermal rearrangements of N-cyclohexylidene-4-methyl-1-(methylthio)penta-1,3-dien-1-amine to 4,4-dimethyl-2-(methylthio)-3,3a,4,4a,5,6,7,8-octahydrobenzo[4,1]cyclobuta-[1,2-b]pyrrole and 1-cyclohexyl-5-methylpyridine-2(1H)-thione.

Keywords: 1,1-dimethylallene, 4,4-dimethyl-2-(methylthio)-3,3a,4,4a,5,6,7,8-octahydrobenzo[4,1]-cyclobuta[1,2-*b*]pyrrole, 1-cyclohexyl-5-methylpyridine-2(1H)-thione, cyclohexylisothiocyanate, alkylation, lithiation, rearrangement.

As we showed for the first time in [2-4], electrocyclization of the reaction products of S-alkylated adducts of deprotonated 1,1-dimethylallene (**1**) with methyl-, ethyl-, and 2-(vinyloxy)ethylisothiocyanates of penta-2,3-dienimidothioates **2** leads to difficultly accessible 2,3-dihydropyridines **3**.

Recently [5] we observed an unusual thermal (~230°C, 10-15 min) rearrangement of N-cyclohexylidene-4-methyl-1-(methylthio)penta-1,3-dien-1-amine (**5**), easily obtained by addition of lithiated allene **1** to cyclohexylisothiocyanate followed by S-alkylation of the adduct and [1,5]-prototropic isomerization of the penta-2,3-dienimidothioate **4** formed, to the previously unknown 4,4-dimethyl-2-(methylthio)-3,3a,4,4a,5,6,7,8-octahydrobenzo[4,1]cyclobuta[1,2-*b*]pyrrole (**6**) (yield ~75%). We also obtained the corresponding cyclobuta[1,2-*b*]pyrroles from penta-2,3-dienimidothioates **2**, when R = *i*-Pr or *cyclo*-C_5H_9 [2,6].

However, heating amine **5** at higher temperature (~280°C-285°C, ~10-15 min) unexpectedly also led to another heterocyclic product: 1-cyclohexyl-5-methylpyridine-2(1H)-thione (**7**) (yield ~30%). A possible reaction route includes rearrangement of penta-1,3-dien-1-amine **5** to penta-2,4-dienimidothioate followed by electrocyclization to 1,2-dihydropyridine, accompanied by elimination of methane (see Scheme 1).

Amine **5** [5], cyclobuta[1,2-*b*]pyrrole **6** [5] and pyridine-2(1H)-thione **7** were isolated by distillation; their composition and structure were confirmed by elemental analysis, IR, ^{1}H and ^{13}C NMR, and mass spectra.

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* Communication 6 in the series "Reactions of isothiocyanates with organometallic reagents"; for Communication 5, see [1].

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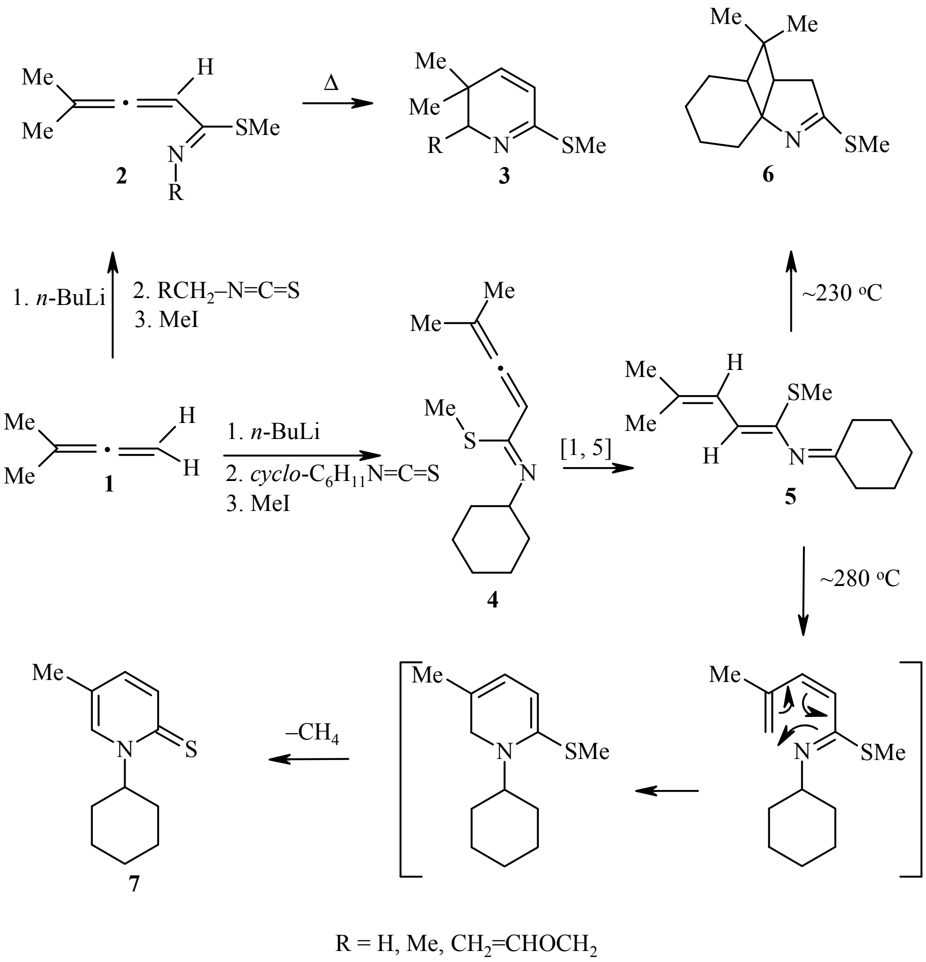
Scheme 1



EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 spectrometer in KBr disks. The ^{1}H and ^{13}NMR spectra were obtained on Varian EM-390 (90 MHz, ~20% solutions in CCl_4, TMS as internal standard) and Jeol FX-90Q (^{1}H - 90 MHz, ^{13}C - 22 MHz, ~10% solutions in $CDCl_3$ and acetone-d_6, HMDS as internal standard) spectrometers at room temperature. The mass spectra were recorded on a Jeol AX-505 spectrometer (accelerating potential 3 kV, emission current 100 mA, ionization energy 70 eV, helium as carrier gas).

All the reactions were carried out under a nitrogen atmosphere. The THF was purified with mechanically dispersed KOH (~50 g/l) and distilled over $LiAlH_4$ in the presence of benzophenone under a nitrogen atmosphere. Butyllithium (1.6 M solution in hexane) was the commercial product.

Cyclohexylisothiocyanate and 1,1-dimethylallene (**1**) were obtained by the procedures we developed in [4, 7]. N-Cyclohexylidene-4-methyl-1-(methylthio)penta-1,3-dien-1-amine (**5**) was synthesized as described previously in [5].

1-Cyclohexyl-5-methylpyridine-2(1H)-thione (7). Amine **5** (7.2 g, 0.03 mol) were heated under a nitrogen atmosphere at ~280-285°C for ~10-15 min. Vacuum distillation resulted in isolation of 4.2 g (~63%) cyclobuta[1,2-*b*]pyrrole **6** (bp 95-100°C (1 torr), n_D^{20} 1.5360, ^{1}H NMR spectrum identical to what we described previously in [5]) and pyridinethione **7** (2.1 g, ~34%) in the form of a viscous liquid with bp ~160-170°C (1 torr), which upon cooling completely recrystallized; mp 135-139°C (ethanol). IR spectrum (KBr), ν, cm^{-1}: 470, 525, 630, 650, 700, 745, 800, 850, 875, 920, 1000, 1020, 1045, 1065, 1100, 1145, 1170, 1200, 1240, 1255, 1335, 1360, 1400, 1440, 1460, 1520, 1635, 2850, 2930, 3030. Mass spectrum: *m*/*z* (I_{rel}, %) 207 (45.64 $[M]^+$), 126 (46.91, $[M\ C_6H_9]^{+\cdot}$, 125 (100, $[M\ C_6H_{10}]^{+\cdot}$), 81 (27, $[C_6H_9]^{+\cdot}$). ^{1}H NMR spectrum, δ, ppm, *J* (Hz), (CCl_4): 7.48 (1H, s, 4-CH=); 7.40 (1H, d, 3-CH=); 6.85 (1H, dd, 6-CH=); 5.85 (1H, m, NCH); 2.20 (3H, s, Me); 2.05-1.35 (10H, m, $(CH_2)_5$); ($CDCl_3$): 7.64 (1H, d, *J* = 8.9, 4-CH=); 7.49 (1H, narrow m, 3-CH=); 6.97 (1H, dd, *J* = 2.1, 6-CH=); 5.95 (1H, m, NCH); 2.16 (3H, s, Me); 1.81 and 1.45 (10H, m and m, $(CH_2)_5$); (acetone-d_6): 7.83 (1H, narrow m, 4-CH=); 7.46 (1H, d, ^3J = 8.7, 3-CH=); 7.02 (1H, dd, ^4J = 2.1, 6-CH=); 5.90 (1H, m, NCH); 2.14 (3H, s, Me); 2.06-0.98 (10H, m, $(CH_2)_5$). ^{13}C NMR spectrum, δ, ppm ($CDCl_3$): 176.66 (C=S), 135.30 ($C_{(4,6)}$), 134.52 ($C_{(3)}$), 123.66 ($C_{(5)}$), 61.49 (NCH), 32.10 (cyclohexyl, $C_{(2,6)}$), 25.47 (cyclohexyl, $C_{(3,5)}$), 25.14 (cyclohexyl, $C_{(4)}$), 17.60 (Me); (acetone-d_6): 179.39 (C=S), 136.66 ($C_{(6)}$), 136.47 ($C_{(4)}$), 136.27 ($C_{(3)}$), 124.50 ($C_{(5)}$), 62.53 (NCH), 33.00, 30.40, 27.15 (cyclohexyl), 17.98 (Me). Found, %: C 69.75; H 8.19; N 6.69; S 15.37. $C_{12}H_{17}NS$. Calculated, %: C 69.51; H 8.26; N 6.76; S 15.47.

This research was conducted with the financial support of the Russian Foundation for Basic Research grant No. 98-03-32941a). We would like to thank A. I. Albanov (Candidate of Chemical Sciences) for recording the NMR spectra.

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