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Ambident isothiocyanatomethanide anion for regioselective synthesis of thiazoles

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Under the action of methyl isothiocyanate, the ambident isothiocyanatomethanide anion, which was generated by deprotonation of methyl isothiocyanate with lithium diisopropylamide, was readily and selectively transformed to 5-methylaminothiazole-2-thiolate.

Key words: methyl isothiocyanate, lithium diisopropylamide, deprotonation, isothiocyanatomethanide anion, heterocyclization, alkylation, thiazoles.

Recently,[1] we reported the reaction of isothiocyanatomethanide anion (**2**), which was generated by *in situ* deprotonation of methyl isothiocyanate (**1**) with lithium diisopropylamide (LDA), with trimethylchlorosilane. This reaction is a new simple route for the synthesis of mono-, bis-, and tris(trimethylsilyl)methyl isothiocyanates. We have also found[2] that the reaction of methyl isothiocyanate with the superbasic potassium diisopropylamide—lithium *tert*-butoxide system opens an unexpectedly simple route to difficultly accessible derivatives of imidazole.

In this work, we report briefly the results of our continuing studies of deprotonation of nonactivated isothiocyanates with superbases. We found that changes in the nature of the counter-ion in diisopropylamide and in isothiocyanatomethanide anion **2**, the reaction temperature, and the rate and order in which the reagents are introduced into the reaction allow one to change fundamentally the pathway of this reaction. Thus, when the K^+ counter-ion was replaced by the Li^+ cation and the reaction was carried out at low temperature (−100 to −50 °C) in a THF—hexane mixture, ambident anion **3** underwent rapid quantitative cyclization to 5-methylaminothiazole-2-thiolate (**4**). Derivatives of thiazole, for example, 5-dimethylamino-2-methylthiothiazole (**6**), were readily and selectively synthesized by lithiation of compound **4** and alkylation of the resulting dianion **5** with alkyl halide or dialkyl sulfate. Compound **6** was obtained in one preparative stage in high yield. The possible pathway of the reaction is shown in Scheme 1.

The structure of thiazole **6** was confirmed by IR and ^{1}H NMR spectra. The composition corresponds to the molecular formula $C_6H_{10}N_2S_2$.

Experimental

The IR spectra were recorded on a Specord IR-75 spectrophotometer in thin films. The ^{1}H NMR spectra were recorded on a Varian EM-390 spectrometer (90 MHz; ~20% solution in

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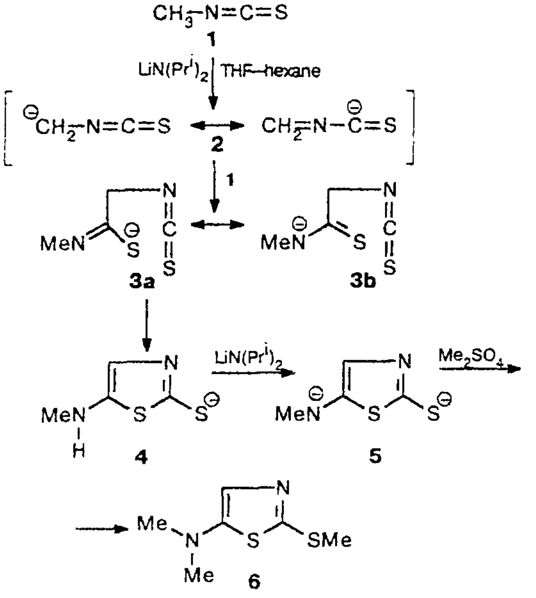
Scheme 1



CCl$_4$; Me$_4$Si as the internal standard). A GLC analysis was carried out on a Varian 3400 gas chromatograph (flame ionization detector; 15 m×0.53-mm capillary column; the thickness of the DB-5 stationary phase was 1.5 μm; nitrogen was the carrier gas).

All operations were carried out in an atmosphere of nitrogen. Tetrahydrofuran was purified with dispersed KOH (~50 g L^{-1}) and by distillation over LiAlH$_4$ in the presence of benzophenone in an atmosphere of nitrogen. Butyllithium (1.6 *M* solution in hexane) and the other reagents used in the work were commercial products.

Reaction of methyl isothiocyanate (1) with lithium diisopropylamide and dimethyl sulfate. A solution of methyl isothiocyanate (0.10 mol) in THF (10 mL) was added portionwise (within ~1 min) to a solution of lithium diisopropylamide (which was prepared from diisopropylamine (0.12 mol) and Bu^{n}Li (0.12 mol)) in a mixture of hexane (70 mL) and THF (70 mL) at temperatures from −100 to −50 °C. The temperature of the reaction mixture was decreased to −80 °C. Then dimethyl sulfate (0.13 mol) was added, the cooling bath was removed, and the reaction mixture was stirred until the temperature increased to 10 °C. The reaction mixture was treated with water (100 mL) with vigorous stirring. The organic layer was separated. The aqueous layer was extracted with pentane and ether. The combined extracts were dried with K$_2$CO$_3$. The solvents were evaporated under reduced pressure. The residue was distilled *in vacuo*. 5-Dimethylamino-2-methylthiothiazole (**6**) was obtained in a yield of 7.0 g (77.3%); the purity was 94.3% (GLC); b.p. ~110 °C (0.8 Torr). $n^{20}{}_D$ 1.6110. Found (%): C, 42.06; H, 6.20; N, 15.41; S, 36.69. $C_6H_{10}N_2S_2$. Calculated (%): C, 41.38; H, 5.75; N, 16.09; S, 36.78.

IR, ν/cm^{-1}: 720, 740, 900, 950, 1000, 1040 sh, 1100, 1200, 1300, 1400, 1430 sh, 1500, 2770, 2850, 2900, 2930 sh, 2960 sh, 3070. ^{1}H NMR, δ: 2.55 (s, 3 H, SMe), 2.80 (s, 6 H, NMe$_2$), 6.55 (s, 1 H, CH=).

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Synthesis of (*m*-carboran-9-yl)ferrocene and (*m*-carboran-9-yl)cymantrene

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Cross-coupling reactions of 9-iodo-*m*-carborane with ferrocenylzinc chloride or cymantrenylzinc chloride catalyzed by $(Ph_3P)_2PdCl_2$ result in the formation of (*m*-carboran-9-yl)ferrocene and (*m*-carboran-9-yl)cymantrene, respectively.

Key words: cross-coupling reaction, 9-iodo-*m*-carborane, ferrocenylzinc chloride, cymantrenylzinc chloride.

Carboranylmetallocenes, in which the metallocenyl group is bonded to the boron atom of the carborane polyhedron by the C—B σ-bond, have been little studied. (*o*-Carboran-3-yl)ferrocene, the first and only metallocene derivative, in which the carbon atom is bonded to the carborane boron atom, was obtained in

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