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SHORT COMMUNICATIONS

Controlled Cyclization of 1,3-Dilithiopropargylbenzene Adduct with Phenyl Isothiocyanate: Highly Selective Synthesis of Iminothietane and Iminocyclobutene

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We recently discovered an unconventional approach to the synthesis of rare and inaccessible iminocyclobutenes and iminothietanes, promising monomers, synthons and building blocks for fine organic synthesis, potential ligands for transition metals and biologically active compounds. The synthesis consists in reaction of 1,3-dilithiopropargylbenzene with isothiocyanates that we have already reported in short (without experimental details) [1]. We established that at similar experimental conditions, namely at successive addition to a solution of 1,3-dilithiopropargylbenzene in THF–hexane mixture of isothio-cyanate (–90...–55°C), *t*-BuOH (–55...–40°C), of *t*-BuOK solution in DMSO (–40°C), warming the reaction mixture to room temperature and intermediates alkylation with MeI the results of reaction (yield and ratio of cyclic products) depended fundamentally on the structure of isothiocyanate. For instance, the reaction with methyl isothiocyanate afforded a mixture of three structural isomers: the expected *N,N*-dimethyl-3-phenyl-2-thiophenamine, *N*-(3-methyl-4-methylene-3-phenyl-thietanylidene)methanamine, and *N*-[3-(methylthio)-2-phenyl-2-cyclobutenylidene)methanamine in ~1 : 1 : 4 ratio [1], with *tert*-butyl isothiocyanate formed the corresponding iminocyclobutene (yield ~65%), and with phenyl isothiocyanate was obtained exclusively iminothietane **I**.

In continuation of this research we obtained by an example of dilithiopropargylbenzenea and phenyl isothiocyanate a compelling evidence that the reaction proceeded through primary formation of thietanyl anion (**II**) that proved to be stable up to ~25°C. Its alkylation with methyl iodide furnished N-(3-methyl-4-methylene-3-phenyl-2-thietanylidene)aniline (**I**) in a high yield (77%). At increasing temperature (>25°C) thietanyl anion (**II**) rearranged (recyclized) into a cyclobutenyl sulfide anion (**III**). Analysis of the reaction mixture (by ^{1}H NMR spectroscopy) after 10 min of heating to 45–50°C revealed the presence alongside of expected iminocyclobutene **IV** also of ~10% of iminothietane **I**. The rearrangement completed at this temperature within ~30 min. Methylation of intermediate **III** afforded previously unknown *N*-[3-(methylthio)-2-phenyl-2-cyclobutenylidene]aniline (**IV**) in a preparative yield (76%).

Hence the observed rigorous dependence of the reaction path on temperature provides a possibility to perform easily a highly selective synthesis of the target iminothietane and isomeric iminocyclobutene from the same precursor.

Reaction of 1,3-dilithiopropargylbenzene with phenyl isothiocyanate and MeI. To a solution of 5.8 g (50 mmol) of propargylbenzene in 110 ml of THF at –100°C in a flow of argon was added 110 mmol of BuLi (68 ml of 1.6 M.solution in hexane) within ~1 min. After stirring for 10 min at 10–12°C the reaction mixture was cooled to –90°C, 6.75 g (50 mmol) of PhNCS in 5 ml of THF was added in one portion, and the stirring at –65... –60°C was carried out for 5 min. Then the cooling was removed, at –55°C was added 4 g (54 mmol) of *t*-BuOH with ~2 ml of ether, and at –40°C was added a solution of 6 g (54 mmol) of *t*-BuOK in 40 g of DMSO (here the temperature sharply grew to –20°C). To obtain thietane **I** the reaction mixture was quickly (within 2–3 min) heated from –20°C to 25°C, then immediately cooled to 10°C, and 22 g (150 mmol) of MeI was added. To obtain cyclobutene **IV** the reaction mixture was quickly heated from –20 to 50°C and then stirred at 45–50°C for 30 min, then it was cooled to 10°C, and 22 g (150 mmol) of MeI was added. After adding MeI the stirring at 25–40°C continued for 1.5 h, then to the reaction mixture was added

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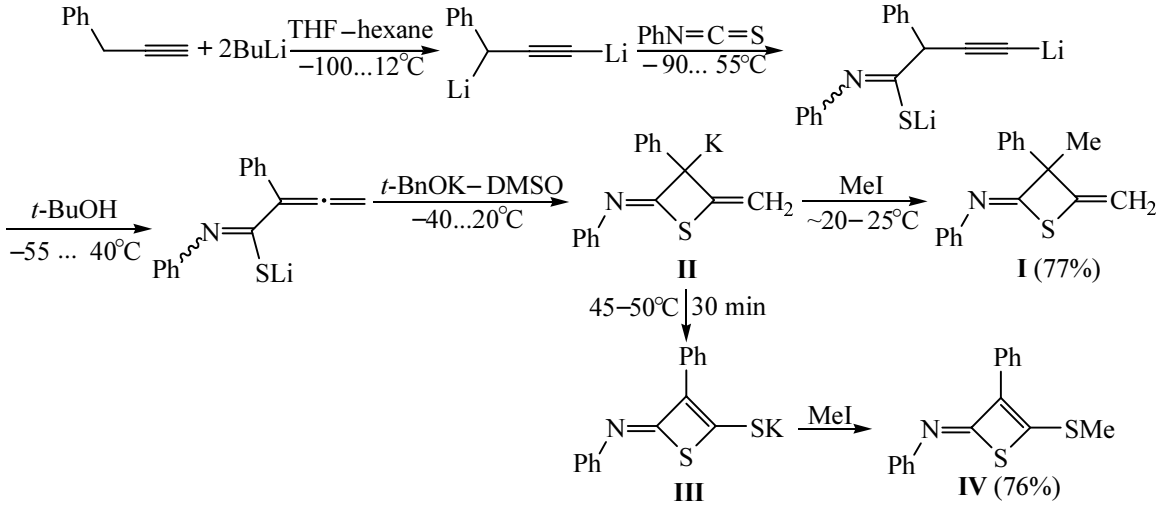

100 ml of saturated water solution of NH_4Cl, the organic phase was separated, and the water layer was extracted with ether (2×50 ml). The combined organic solution was washed with water (4 times), and dried on $MgSO_4$. The solvent was removed on a rotary evaporator, the residue was dried in a vacuum at 2 mm Hg. Then in the case of thietane **I** synthesis it was distilled in a vacuum at 0.1 mm Hg, and at cyclobutene **IV** preparation it was recrystallized from hexane.

***N*-(3-Methyl-4-methylene-3-phenyl-2-thietanylidene)aniline (I)**. Yield 77%, n_D^{22} 1.6370 (yellow viscous fliud), bp 160°C (0.8 mm Hg). IR spectrum, cm^{-1}: 494, 519, 623 w, 647, 658, 695 s, 763 s, 778 s, 835, 863, 914, 955 s, 1028, 1072, 1156 w, 1170 w, 1182 w, 1220, 1286 w, 1369 w, 1445, 1488 s, 1593 s, 1634 s [ν(C=C)], 1702 s [ν(C=N)], 2868 w, 2930, 2972, 3031, 3059, 3083. ^1H NMR spectrum, δ, ppm: 1.93 s (3H, Me), 5.18 d and 5.34 d (2H, $=CH_2$, $^2J_{HH}$ 2.9 Hz), 7.01 d (2H^o), 7.13 t (H^p), 7.36 t (2H^m), signals of protons N–Ph; 7.27 t (H^p), 7.31 t (2H^m), 7.66 d (2H^o), signals of protons C–Ph. ^{13}C NMR spectrum, δ, ppm: 25.34 (Me), 75.68 (C^3), 104.96 ($=CH_2$), 145.88 (C^4), 163.77 (C^2), 120.36 (2C^o), 125.54 (C^p), 129.27 (2C^m), 147.67 (C^i), signals of carbons N–Ph; 125.81 (2C^o), 127.58 (C^p), 128.61 (2C^m), 140.39 (C^i), signals of carbons C–Ph. Found, %: C 76.82; H 5.48; N 5.18; S 12.60. $M^{+\cdot}$ 265 (I_{rel} 4%), [$M^{+\cdot}$ – PhNCS] 130 (I_{rel} 100%). $C_{17}H_{15}NS$. Calculated, %: C 76.94; H 5.70; N 5.28; S 12.08. *M* 265.37.

***N*-[3-(Methylthio)-2-phenyl-2-cyclobutenylidene]-aniline (IV)**. Yield 76%, mp 75°C. IR spectrum, cm^{-1}: 494, 532 w, 546, 630, 663, 694 s, 710 sh, 754 sh, 768 s, 783 sh, 838 w, 879, 903, 913, 976 s, 999 w, 1024, 1071, 1085, 1151 s, 1181 w, 1221 s, 1275 s, 1291 s, 1317, 1341 s, 1362 w, 1431, 1445, 1484 s, 1560 s, 1575 s, 1592 s, 1634 w, 1674–1686 v.s [ν(C=N)], 2815 w, 2864 w, 2926, 2953 w, 3028, 3056, 3079. ^1H NMR spectrum, δ, ppm: 2.38 s (3H, SMe), 3.37 s (2H, CH_2), 6.97 d (2H^o), 7.06 t (H^p), 7.26 t (2H^m), signals of protons N–Ph; 7.23 t (H^p), 7.35 t (2H^m), 7.84 d (2H^o), signals of protons C–Ph. ^{13}C NMR spectrum, δ, ppm: 15.20 (SMe), 41.74 (CH_2), 121.60 (2C^o), 123.56 (C^p), 128.44 (2C^m), 149.45 (C^i), signals of carbons N–Ph; 126.85 (2C^o), 127.20 (C^p), 128.23 (2C^m), 131.18 (C^i), signals of carbons C–Ph; 136.85 (C^2), 154.47 (C^3), 157.47 (C^1).Found, %: C 77.38; H 5.89; N 5.29; S 12.25. $M^{+\cdot}$ 265 (I_{rel} 73%). $C_{17}H_{15}NS$. Calculated, %: C 76.94; H 5.70; N 5.28; S 12.08. *M* 265.37.

Assignment of signals in the NMR spectra of compounds **I** and **IV** was done with the help of two-dimensional homo- and heteronuclear correlation spectra: NOESY, HMQC and HMBC, COSY-45, CHCOR COLOC.

^1H and ^{13}C NMR spectra were registered on spectrometer Bruker DPX-400 (operating frequencies 400.13 MHz for ^1H and 100.69 MHz for ^{13}C) in $CDCl_3$, internal reference HMDS. IR spectra were recorded on spectrometer Bruker IFS 25 in thin film for thietane **I** in KBr pellet for cyclobutene **IV**. Mass spectra were measured on GC-MS instrument LKB-2091 with direct admission of the sample into the ion source, ion source temperature 240°C.

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