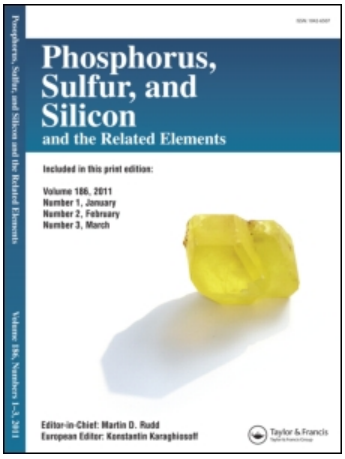

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COMMUNICATION. B-THIOACYLTHIO-9-BBN AS A THIOACYLATING REAGENT

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Communication

B-THIOACYLTHIO-9-BBN AS A THIOACYLATING REAGENT

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Convenient syntheses of S-aryldithioesters and thioamides are described: thus, thiols and amines are readily thioacylated with the S-borondithioester formed *in situ*, by the mild reaction of a dithioacid with 9-BBN.

Key words: Dithioacids; 9-BBN; thioacylation.

We have recently developed some functional transformations of dithioacids, by means of catecholborane (CB).[1] Namely, dithioacids were reacted with CB in refluxing toluene; the resulting S-borondithioesters showed enhanced reactivity towards nucleophilic attack on the functional carbon atom: their reaction with an amine or a thiol led to the corresponding thioamide or dithioester. This method suffers limitations due to an incomplete first step: 75 to 80% yield based on the measurement of hydrogen evolved.

Dithioesters bearing a good leaving group on the sulphur atom are of special interest for thioacylation procedures, as exemplified by the preparation of S-aryldithioesters. The first general method to synthesize these compounds, described by Beslin *et al.*,[2] involves the reaction of S-phenylcarbonochlorodithioate with halomagnesium or sodium salts of dithioacids. Very recently, Kato *et al.*,[3] have prepared new thioacylating reagents, the 1-methyl-2-thioacylpyridinium salts, leading particularly to S-aryldithioesters with thiolates.

This prompted us to report that 9-borabicyclo [3.3.1] nonane (9-BBN) reacted with dithioacids under mild conditions, allowing increased yields of these functional transformations.

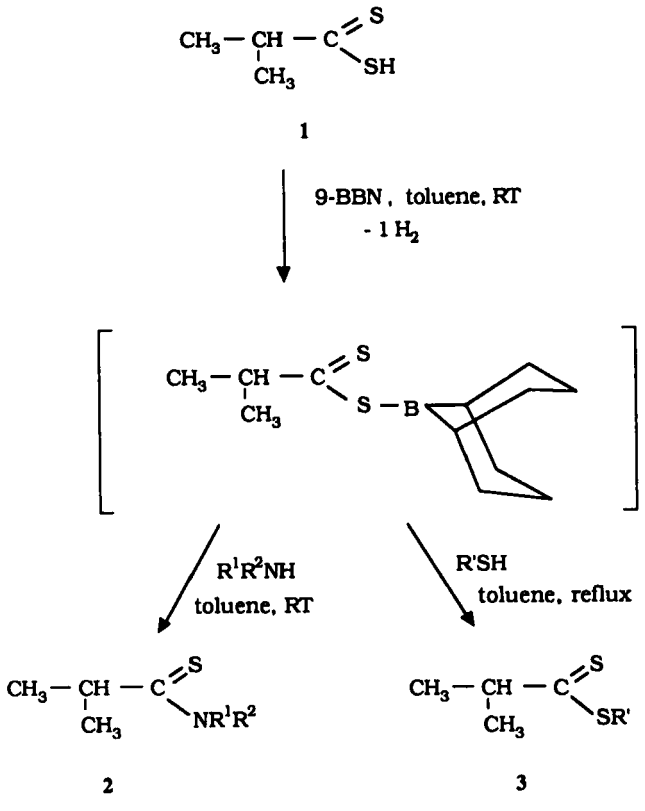
9-BBN reacted readily in toluene with 2-methylpropandithioic acid (**1**); one equivalent of hydrogen was rapidly evolved at room temperature. Treatment of the resulting S-borondithioester (not isolated), with amines at room temperature, afforded the corresponding thioamides (**2**) in good yield. Nucleophilic displacement with less reactive aromatic or aliphatic thiols required higher temperatures (110°C for several hours); the dithioesters (**3**) were obtained in quite good yields. These results are listed in Table I.

The facile reaction of 9-BBN with dithioacids afforded useful reagents for thioacylations under mild conditions, allowing especially convenient syntheses of S-aryldithioesters.

TABLE I

List of prepared compounds and yields

Compound	R^1	R^2	R'	Yield % (9-BBN)	Yield % $(CB)^{Ref}$
2a	CH_3	CH_3		92	67[1]
2b	$(CH_2)_4$			73	55
3a			C_6H_5	65	35[1]
3b			$(CH_3)_2CH—CH_2$	60	30[1]



EXPERIMENTAL

The flash liquid chromatographies were performed on a column of silicagel Merck 60 M (63 to 200 microns); crude compounds were injected at atmospheric pressure, and eluted under *ca.* 1.5 Bars. The ^1H NMR spectra were recorded with a "Varian EM 360" spectrometer at 60 MHz using TMS as internal standard. The ^{13}C NMR spectra were recorded with a "Bruker WP 80 SY" spectrometer, at 20.15 MHz, using TMS as internal standard. Mass spectra were recorded with a "Nermag R 10 10 H" spectrometer at 70 eV.

General procedure for the reaction of a dithioacid with 9-BBN. Under nitrogen, 2-methylpropandithioic acid (**1**) (0.01 mole) was dissolved in toluene (10 ml). With stirring, one equivalent of 9-BBN (0.5 M solution in *n*-hexane) was added. The reaction mixture was stirred at RT for 4 hours. Evolution of 1 equivalent of hydrogen was measured.

Preparation of thioamides (**2**). The solution of the S-borondithioester, prepared as above in toluene, was saturated with gaseous dimethylamine (20 min), or liquid pyrrolidine (0.02 mole) was added to the preceding solution; the reaction mixture was stirred at RT for 15 hours. Then petroleum ether was added; the organic layer was washed with NaOH 1N, then with water, dried over Na_2SO_4, filtered, and the mixed organic solvents were evaporated under reduced pressure. The thioamide was separated by flash liquid chromatography on silicagel (eluent: petroleum ether/ethyl acetate 95/5). Pure thioamide (**2**) was isolated as a pale yellow liquid. Analysis and spectroscopic data for compound (**2a**) were described.[1]

Compound (**2b**): Analysis: $C_8H_{15}NS$: Calc.%: S 20.39; Obs.%: S 20.50. ^1H NMR (CCl_4): δ (ppm): 1.18 (*d*, J = 7 Hz, 6H); 1.80 to 2.30 (*m*, 4H); 2.95 (sept, J = 7 Hz, 1H); 3.55 to 3.95 (*m*, 4H). ^{13}C NMR (CCl_4): δ (ppm): 22.63 CH_3; 24.02 CH_2—*CH_2*—CH_2; 26.28 CH_2—*CH_2*—CH_2; 38.58 CH; 50.04 NCH_2; 53.83 NCH_2; 207 C=S. Masse: m/z: $157^+\cdot$(100%); 142 $M^+\cdot$-(CH_3); 129 $M^+\cdot$-(C_2H_4); 124 $M^+\cdot$-(SH); 72 $C_3H_4S^+\cdot$; 70 $C_4H_8N^+$; 55 $C_4H_7^+$.

Preparation of dithioesters (**3**). To the solution of the S-borondithioester previously prepared in toluene, the thiol (0.02 mole) was added at RT. The reaction mixture was refluxed for 48 hours. After cooling, pentane was added; the organic layer was washed with NaOH 1N, then with water, dried over Na_2SO_4, and filtered. The mixed organic solvents were eliminated at RT under reduced pressure. The dithioester was separated by flash liquid chromatography on silicagel (eluent: pentane). The dithioester was obtained as an orange-coloured liquid. Analyses and spectroscopic data of compounds (**3a**) and (**3b**) were previously reported.[1]

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