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THE REACTIONS OF ORGANOBORANES WITH N-CHLORO-N-SODIOCARBAMATES: A NOVEL SYNTHESIS OF N-ALKYLCARBAMATES.

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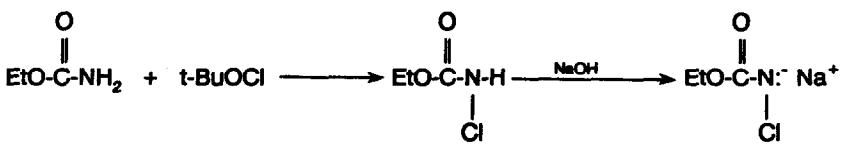
Abstract: Trialkylboranes react with N-chloro-N-sodiocarbamates to form N-alkylcarbamates in yields ranging from 50-88%. The reaction is best carried out without intermediate isolation of the N-chlorocarbamate salt. Only one of the alkyl groups of the trialkylborane is utilized.

Organoboranes react with the *N*-chlorinated derivatives of primary amines and aromatic sulfonamides to form secondary amines and *N*-alkyl sulfonamides, respectively.[1-4] Similarly, organoboranes react with *N*-(paranitrobenzenesulfonoxy)urethane under two-phase alkaline conditions to yield the corresponding *N*-alkyl urethane.[5] We introduce here the *N*-alkylation of carbamic acid esters by reacting the conveniently synthesized *N*-chloro-*N*-sodiocarbamates with trialkylboranes.

Simple carbamic acid esters are easily obtained and stable to storage over long periods.[6] Most industrial methods currently employed in the synthesis of more complex forms of carbamates involve hazardous volatile chemicals.[7] Less common methods of synthesis involve unstable intermediates.[5] *N*-Chloro-*N*-sodiocarbamates can be conveniently synthesized from commercially available carbamic acid esters.[6] They are reported to be relatively stable to storage in either the anhydrous or hydrated forms.[8,9]

N-Chlorocarbamates are readily produced when the carbamate, dissolved in methanol, is reacted with an equivalent of *tert*-butyl hypochlorite. Addition of alcoholic sodium hydroxide generates the metallic salt (Equation 1).[9]

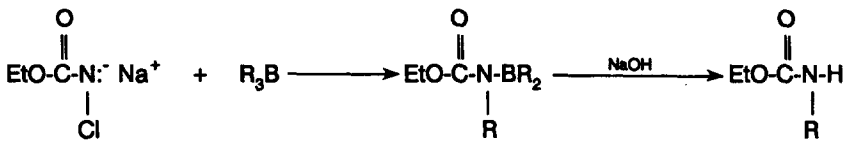


(1)

In the initial stages of this work *N*-chloro-*N*-sodioethylcarbamate was isolated and dried in a vacuum dessicator. CAUTION: on several occasions the dry salt decomposed violently shattering

the dessicator. Thereafter, the concentration of the *N*-chlorocarbamate salts in methanol were determined by iodometric methods and reacted without prior isolation with an equivalent of the organoborane. Yields of *N*-alkylcarbamates did not vary significantly whether the *N*-chlorocarbamate salts were isolated or not.

Reaction of the *N*-chlorocarbamate salt in methanol with an equivalent of a trialkylborane in THF for 4-6 hours at 65-70 °C followed by hydrolysis gives the corresponding *N*-alkylcarbamate (Equation 2 and Table I).



(2)

The organoboranes were either commercially available in one molar solutions in THF or were synthesized from three equivalents of the corresponding alkene with a one molar solution of borane in THF.

Table 1. Yields of Alkylcarbamic Acid Esters.

Carbamate salt	Trialkylborane	Product	% Yield
EtO_2CNH_2	Et_3B	EtO_2C-NHEt	80-88
EtO_2CNH_2	$(n\text{-}C_6H_{13})_3B$	EtO_2C-NH-$(n\text{-}C_6H_{13})$	50-56
EtO_2CNH_2	$(C_6H_{11})_3B$	EtO_2C-NH-C_6H_{11}	46
$n\text{-}BuO_2CNH_2$	Et_3B	$n\text{-}BuO_2C$-NH-Et	68-74

When three equivalents of the *N*-chloro-*N*-sodiocarbamate were reacted with an equivalent of a trialkylborane, only one equivalent of the corresponding *N*-alkylcarbamate was recovered. This suggested that only one of the alkyl groups initially attached to the boron was transferred during the course of the reaction. This observation is consistent with those obtained for similar reactions between organoboranes and threefold excesses of chloramines or *N*-chlorosulfonamides.[1-4] The

trialkylborane with the bulkiest alkyl group (cyclohexyl) gave the lowest product yield.

The mechanism for the reactions of trialkylboranes with chloramines and *N*-chlorosulfonamides presumably involves anionotropic migration of an alkyl group from the boron to the nitrogen with simultaneous departure of a chloride ion.[2,4] Alternatively, α-elimination of chloride would yield a carbalkoxynitrene which would react with the organoborane.[5,10] The following procedure for preparation of *N*-ethyl ethylcarbamate is representative. *N*-Chloro-*N*-sodioethylcarbamate was prepared[9] by reacting 100 mmol of ethylcarbamate dissolved in 50 mL of methanol with 100 mmol of *tert*-butyl hypochlorite in an ice bath. A methanolic solution of sodium hydroxide (110 mmol) was then added dropwise over a period of several minutes with continuous stirring. The salt solution was allowed to come to room temperature and diluted to 100 mL in a volumetric flask. A 2.00 mL aliquot was removed and added to 100 mL of Milli-Q® water containing 1 g of potassium iodide and 5 mL of glacial acetic acid. The aqueous solution was immediately titrated with a standardized (0.100 N) solution of sodium thiosulfate. One equivalent of *N*-chlorocarbamate was assumed to oxidize iodide to one equivalent of iodine.

A 100-mL three-necked round-bottom flask containing 20 mL of a 1.0 M solution of triethylborane in THF (20 mmol triethylborane) under a nitrogen atmosphere was equipped with a reflux condenser, a rubber stopple, a nitrogen inlet tube, and a magnetic stirring bar. A standardized solution of *N*-chloro-*N*-sodioethylcarbamate (20 mmol) in methanol was slowly added to the flask via syringe. After an initial exothermic reaction during which the solution became milky white, the mixture was heated to ca. 65 °C and maintained 4-6 hours with stirring. During the course of the reaction the solution was concentrated by slowly distilling off approximately 20 mL of solvent. The mixture was cooled to 20 °C and 10 mL of 4 M $NaOH_{(aq)}$ was added to the thick, white solution. The precipitate dissolved within five minutes. The product mixture was extracted with diethyl ether, dried, and the product was obtained by simple distillation. The purity was checked by gas chromatography (DB 5 fused silica capillary column, 0.32 mm i.d. x 30 m, 0.25 μm film thickness) with mass spectrometric detection. In all cases the purity was greater than 90-95%.

N-Ethyl Ethylcarbamate bp 82 °C/20 mmHg; lit.[11] bp 75 °C/14 mmHg. Anal. Calcd for $C_5H_{11}NO_2$: C, 51.26; H, 9.46; N, 11.96 %. Found: C, 51.30; H, 9.50; N, 11.94%.

N-Ethyl Butylcarbamate bp 67-68 °C/3 mmHg; lit.[11] bp 66 °C/3 mmHg. Anal. Calcd for $C_7H_{15}NO_2$: C, 57.90; H, 10.41; N, 9.65 %. Found: C, 57.84; H, 10.45; N, 9.69 %.

N-Hexyl Ethylcarbamate bp 91-93 °C/3 mmHg. ^{1}H-NMR: δ (d-acetone) 6.1 (br, 1, NH); 4.2 - 3.9 (q, 2, CO_2-CH_2); 3.2 - 3.0 (m, 2, NH-CH_2); 1.4 - 1.1 (m, 8, $NHCH_2(CH_2)_4$); 1.0 - 0.9 (m, 6, CH_3's). ^{13}C-NMR: δ (d-acetone) 157 (s, CO); 61 (t, CO_2-CH_2); 42 (t, NH-CH_2); 33, 31, 27($(CH_2)_3$); 23 (t, $NH(CH_2)_4$-CH_2); 15 and 14 (q, CH_3's). MS m/e (relative intensity): (M^+) 173 (5), 144 (7), 131 (5), 102 (100), 99 (13), 90 (21), 84 (18). Anal. Calcd for $C_9H_{19}NO_2$: C, 62.39; H, 11.05; N, 8.08 %. Found: C, 62.47; H, 11.10; N, 7.99 %.

N-Cyclohexyl Ethylcarbamate mp 54-55 °C; lit.[12] mp 56 °C. Anal. Calcd for $C_9H_{17}NO_2$: C, 63.13; H, 10.01; N, 8.18 %. Found: C, 63.26; H, 10.05; N, 8.10 %.

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