Scheme I

$$\underset{(\underline{1})}{\text{R-COOR'}} \xrightarrow[\text{PEG 400}]{\text{NaBH}_4} \underset{(\underline{2})}{\text{R-CH}_2\text{OH}}$$

a. $R=C_6H_5$	$R'=CH_3$	g. $R=C_9H_{19}$	$R'=C_2H_5$
b. $R=pCH_3-C_6H_4$	$R'=C_2H_5$	h. $R=C_5H_{11}$	$R'=C_2H_5$
c. $R=pNO_2-C_6H_4$	$R'=C_2H_5$	i. $R=C_6H_5-CH=CH$	$R'=C_2H_5$
d. $R=pOCH_3-C_6H_4$	$R'=CH_3$	l. $R=pBr-C_6H_4$	$R'=CH_3$
e. $R=CH_3-(CH_2)_3-CH(OH)-$	$R'=C_2H_5$	m. $R=CH_3-(CH_2)_{11}-CHBr-$	$R'=C_2H_5$
f. $R=pOH-C_6H_4$	$R'=C_2H_5$	n. $R=pNH_2-C_6H_4$	$R'=C_2H_5$

o. $R=(4-OH,3-OCH_3)-C_6H_3$ $R'=CH_3$

hydroxybenzoates as well as methyl vanillate (3-methoxy-4-hydroxybenzoate) (**1f,n,o**) were not reduced to any extent after prolonged heating of the reaction mixture. Furthermore, whereas the 4-bromobenzoate **1l** was reduced to alcohol **2l**, the 2-bromo ester **1m** afforded at first a mixture of the bromo alcohol **2m** and the product of complete reduction, tetradecanol. After a prolonged time of reaction (24 h), excellent yields of the fully reduced, saturated alcohol, $C_{14}H_{43}OH$, were obtained as the sole product. During the reaction, a vigorous evolution of gas was noticed, and we have also observed that addition of $NaBH_4$ to pure PEG 400 at 65 °C results in the evolution of 1 molar equiv of hydrogen in 15 min and of 2 molar equiv in 1 h. Moreover, this solution is still capable of reducing esters in good yields and is more reluctant to undergo acidic hydrolysis after the evolution of 2 molar equiv of hydrogen at the end of the reaction. At higher temperatures (120 °C) an extremely viscous liquid is formed, and in every case, addition of solvent leads to precipitation of white amorphous material, which is soluble only in PEG itself. All these preliminary observations led us to postulate the formation of alkoxy-borohydrides of a general formula $[BH_n(OR)_{4-n}]^-$, whose molecular formula and degree of substitution of the active hydrogens can be dependent on the temperature. Species such as that above may be able to reduce esters, since it is known that sodium alkoxyborohydrides can effect such a reduction.[14] On the other hand, the dramatic difference of reactivity of $NaBH_4$ in PEG 400 with respect to the cited nonhydroxylic polyethers[10,11] cannot be explained only in terms of a different degree of complexation in the cation. It is conceivable that at 65 °C stable polymeric dialkoxyborohydrides $[BH_2(OR)_2]^-$ where $(OR)_2 = -OCH_2CH_2(OCH_2CH_2)_6CH_2CH_2O-$ are formed, which may show an higher reactivity than $NaBH_4$ itself.

Experimental Section

IR spectra were recorded on a Perkin-Elmer 157 spectrometer. ^1H NMR spectra (60 MHz) were recorded in deuteriochloroform solutions (tetramethylsilane as internal standard) on a Hitachi Perkin-Elmer R-24 spectrometer. The progress of reactions was monitored on silica gel microplates (benzene–ethyl acetate, 8:2). Column chromatographies were performed on silic gel (Kieselgel 60, 70–230 mesh, Merck). GC analyses were done on a 2-m silanized column of 1% SE-30 on Gas Chrom Q, operating at 70–200 °C.

Esters. The esters were either purchased (Fluka, Buchs) or prepared by standard methods of esterification from the appropriate acid and methanol or ethanol in the presence of catalytic amounts of sulfuric acid.

General Procedure of the Reductions. To the appropriate ester (5 mmol) in PEG 400 (30 mL) was added sodium borohydride (0.6 g, 15 mmol) portionwise. Under stirring, the solution was slowly brought to 65 °C (evolution of hydrogen) and kept at this temperature for 10 h. During this time the reaction was generally complete. Diluted HCl (10%) was added to the reaction mixture dropwise, and the products were extracted (3 × 30 mL) with diethyl ether. Drying of the extracts on sodium sulfate and evaporation afforded the products listed in Table I. Yields were of isolated products, which were bulb-to-bulb distilled in Büchi GKR-50 apparatus and in some cases purified on column chromatography.

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Registry No. 1a, 93-58-3; **1b**, 94-08-6; **1c**, 99-77-4; **1d**, 121-98-2; **1e**, 52089-55-1; **1f**, 120-47-8; **1g**, 110-38-3; **1h**, 123-66-0; **1i**, 103-36-6; **1l**, 619-42-1; **1m**, 14980-92-8; **1n**, 94-09-7; **1o**, 3943-74-6; **2a**, 100-51-6; **2b**, 589-18-4; **2c**, 619-73-8; **2d**, 105-13-5; **2e**, 6920-22-5; **2g**, 112-30-1; **2h**, 111-27-3; **2l**, 873-75-6; tetradecanol, 112-72-1; $NaBH_4$, 16940-66-2.

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[14] See ref 4, p 220.

Vinyl Carbamates via Interaction of Alkylidenecarbenes with Isocyanates

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Vinyl carbamates, a novel member of the family of enol esters, are virtually unknown. To date they have only been prepared indirectly via dehydrohalogenation of α-chloroalkyl carbamates[1] or by reaction of vinyloxycarbonyl chloride with amines.[2] The latter method has been used for the introduction of the vinyloxycarbonyl group for the amino protection in peptide synthesis.[2] Hence in this note we report a simple, general, and new method for the preparation of vinyl carbamates.

To a solution of excess isocyanate in glyme, maintained at −20 ± 3 °C and containing 1.1 equiv of n-Bu_4NF, is added 1.0 equiv of silylvinyl triflate[3] (**1**), all at once, and the mixture stirred for 2 min. The reaction is quenched

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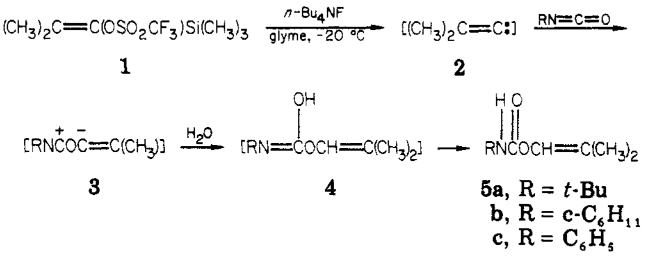
Table I. Summary of Physical and Spectral Data for Vinyl Carbamates 5

compd	% yield	mp, °C	mass spec (70 eV), m/z (%)	IR (CCl_4) ν_{max}, cm^{-1}	^{1}H NMR (CCl_4, Me_4Si), ppm
5a	72	oil	171 (1.8, M$^+$), 72 (100), 70 (14.4), 57 (66)	3442 (NH), 3090 (HC=C), 1742 (C=O), 1695 (C=C), 1491, 1455, 1395, 1368, 1260, 1197, 1140	1.28 (s, 9 H, t-Bu), 1.54^a (s, 6 H, 2CH$_3$), 4.64 (s, 1 H, NH), 6.78 (s, 1 H, C=CH)
5b	23	54–55	197 (2.1, M$^+$), 83 (8.5), 72 (100), 57 (14), 55 (21)	3442 (NH), 3092 (HC=C), 1730 (C=O), 1697 (C=C), 1489, 1450, 1379, 1319, 1167, 1150, 1092, 1045	0.9–2.2 (m, 10 H), 1.7^a (s, 6 H), 3.3–3.8 (m, 1 H), 4.6–5.0 (br s, 1 H), 6.91 (s, 1 H)
5c	58	88–89	192 (15.5), 191 (85.7, M$^+$), 120 (65.6), 119 (100)	3442 (NH), 1759 (C=O), 1520, 1441, 1380, 1326, 1313, 1250, 1201, 1130, 1002	1.71^a (s, 6 H, 2CH$_3$), 6.66 (br s, 1 H, NH), 6.98 (s, 1 H, C=CH), 7.2–7.8 (m, 5 H, C$_6$H$_5$)

^{a} Split into two sharp singlets each 3 H in C_6H_6.

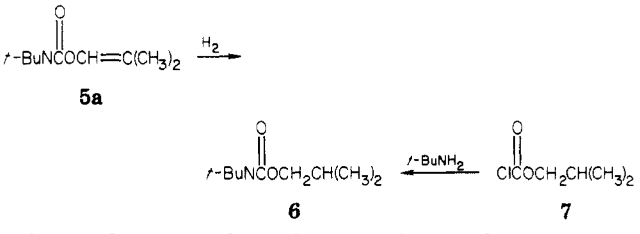
Scheme I



with *wet* hexane, and the solvent and unreacted isocyanate are removed by a rotary evaporator. The residue is washed with several fractions of pentane and the combined concentrated pentane solution chromatographed on a silica column with 90/10 hexane/THF as eluant. The products and their spectral properties are given in Table I.

There is little doubt that reaction proceeds via alkylidenecarbenes[4] 2 that are trapped by the presence of isocyanate to give ylides 3 as shown in Scheme I. Subsequent quenching with water results in 4 that upon tautomerization gives the observed products 5. The reaction is general vis-à-vis a variety of isocyanates and presumably unsaturated carbenes[4] as well. However, since isocyanates are sensitive to strong bases, such as *t*-BuOK, the alkylidenecarbene must be generated by the fluoride method.[3] Similar ylide-type intermediates have been observed in the reaction of $(CH_3)_2N\ddot{C}OCH_3$ with isocyanates.[5]

The identity of the products follow from their spectral data as well as chemical confirmation. Hydrogenation of vinyl carbamate **5a** in methanol over Pd/C gave isobutyl carbamate **6** identical in all respects with authentic material prepared by reaction of isobutyl chloroformate **7** with *t*-butylamine.



In conclusion, we have discovered a novel, general procedure for the ready preparation of vinyl carbamates, in moderate isolated yields, via the interaction of alkylidenecarbenes with commercially available isocyanates.

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 298 spectrometer. Proton NMR spectra were recorded on a Varian EM-360 or EM-390 spectrometer. Mass spectra were recorded on a Varian MAT 112 GC mass spectrometer. All solvents and reagents (isocyanates, isobutyl chloroformate (7), and *tert*-butylamine) were commercial ACS reagent grade products and were purified and dried prior to use.

General Procedure for Reaction of Alkylidenecarbenes with Isocyanates. Formation of Vinyl Carbamate 5a. Into a 10-mL round-bottom flask, flame-dried and flushed with dry N_2 and fitted with a magnetic stirrer and a nitrogen inlet and outlet, were added 0.34 g (3.5 mmol) of *tert*-butyl isocyanate, 0.45 mL of a 0.80 M glyme (0.36 mmol) solution of *n*-Bu_4NF, and 1 mL of glyme. The solution was cooled to −20 ± 3 °C by means of a CCl_4/dry ice slush bath, and 0.1 g (0.36 mmol) of silylvinyl triflate[3] (1) in 1 mL of glyme was added all at once. Reaction was monitored for unreacted starting triflate by means of GC (10% UCW 982 on Chrom W, 100 °C) and none was found after 2 min. The reaction was quenched by 1 mL of *wet* hexane, and the solvent and unreacted isocyanate were removed by rotary evaporator. The residue was washed with several 5-mL fractions of pentane. The combined pentane fraction was concentrated and chromatographed on a silica column with 90/10 hexane/THF as eluant. Evaporation of the eluant gave 44 mg (72%) of pure **5a** as an oil. Spectral properties of all adducts appear in Table I.

Vinyl Carbamate 5b. In a similar manner, reaction of 0.1 g (0.36 mmol) of triflate **1** with 0.45 g (3.6 mmol) of cyclohexyl isocyanate gave after workup 160 mg (23%) of crystalline **5b**.

Vinyl Carbamate 5c. Reaction of 0.1 g (0.36 mmol) of triflate 1 with 0.43 g (3.6 mmol) of the phenyl isocyanate gave after workup 390 mg (58%) of crystalline **5c**.

Preparation of Isobutyl *N*-*tert*-Butylcarbamate 6. Reaction of 5.32 g (72.8 mmol) of *tert*-butylamine with 10 g (73.5 mmol) of isobutyl chloroformate according to ref 6 gave 12 g (94%) of carbamate **6** as a colorless oil: bp 74 °C (4.5 torr) [lit.[7] bp 93 °C (16 torr)]; IR (CCl_4) 3442, 2960, 2878, 1725, 1469, 1452, 1390, 1367, 1270, 1194, 1090 cm^{-1}; NMR (CCl_4, internal Me_4Si) δ 0.94 (d, J = 11.5 Hz, 6 H), 1.36 (s, 9 H), 1.7–2.0 (m, 1 H), 3.86 (d, J = 11.5 Hz, 2 H), 4.87 (br s, 1 H).

Hydrogenation of Vinyl Carbamate 5a to 6. A solution of 20 mg (0.11 mmol) of vinyl carbamate **5** in 1 mL of methanol containing 5 mg of 10% Pd/C was placed in a Parr hydrogenation apparatus at 60 psi for 1.5 h. The solution was filtered and washed with methanol. The methanol was evaporated on a rotary evaporator, yielding 18 mg (94.5%) of carbamate **6**, which was identical in all respects with the above prepared authentic material.

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Registry No. 1, 73876-87-6; **5a**, 78837-38-4; **5b**, 78837-39-5; **5c**, 78837-40-8; **6**, 6952-02-9; **7**, 543-27-1; *tert*-butyl isocyanate, 1609-86-5; cyclohexyl isocyanate, 3173-53-3; phenyl isocyanate, 103-71-9; *tert*-butylamine, 75-64-9.

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