treated with ozone until the blue color persisted. The solvent was then removed and the oily residue was dissolved in acetone and added over 1 h to 485 mL of Jones reagent maintained at -5 °C. After addition was complete, the reaction mixture was maintained at -5 °C for an additional hour and allowed to warm to room temperature (~3 h). The reaction mixture was then recooled to -5 °C and 30 mL of 2-propanol was added. After 1 h the cooling bath was removed and following an additional hour of stirring the organic phase of the reaction mixture was separated. Water (400 mL) was added to the aqueous phase, which was then extracted 4 times with 200-mL portions of ethyl acetate. The combined organic extract was dried and the solvent removed. Esterification with CH_2N_2 (Et_2O) furnished after removal of the solvent a colorless syrupy residue which was chromatographed over silica gel with 5% ethyl acetate in dichloromethane to yield 16.4 (80%) of methyl 5,6-dicyanohexanoate (**8b**).

Method C. A solution of 19.6 g of 6,7-dicyanohept-1-yne (**7c**) in 650 mL of dichloromethane was ozonized in three portions at -78 °C until the blue color persisted. Methanol (100 mL) cooled to -78 °C was then added and the reaction mixture was allowed to warm slowly to -10 °C during 24 h. (More rapid warming results in a vigorous exothermic reaction with no adverse effect on product yield.) The solvent was then removed and the resulting oil was dissolved in methanol and heated on a steam bath for 20 min. Carbon tetrachloride was then added to the reaction mixture, and solvents were distilled under reduced pressure to ensure that residual formic acid was removed. The residual oil dissolved in ethyl acetate was treated with ethereal diazomethane and chromatographed as described to yield 18.9 g (78%) of methyl 5,6-dicyanohexanoate (**8b**).

7-Amino-5-(aminomethyl)heptanoic Acid (4). A mixture of 9.2 g of methyl 5,6-dicyanohexanoate (**8b**) in 300 mL of ethanol-concentrated hydrochloric acid (1:1) and 1 g of platinum oxide was shaken under 2 atm of hydrogen until uptake of hydrogen ceased. The catalyst was removed, and the solvents were distilled to afford a semicrystalline solid, which was triturated first with acetone and then with cold ether–ethanol (1:4) to yield 7 g (55%) of 7-amino-5-(aminomethyl)heptanoic acid dihydrochloride: mp 196–198 °C; ^{1}H NMR (D_2O) δ 1.4–2.2 (m, 7 H), 2.62 (t, 2 H), 3.22 (m, 4 H); ^{13}C NMR δ 20.97, 28.55, 29.42, 33.80, 34.08, 37.60, 42.64, 178.50; mass spectrum, *m/e* 175 (MH^+), 156.

Evaporation from the ether–ethanol solvent yielded 2.2 g (21%) of 4-(pyrrolidin-3-yl)butyric acid (**9**): ^{13}C NMR (D_2O) δ 23.30, 30.18, 31.64, 34.13, 37.60, 45.78, 50.49, 178.34; mass spectrum, *m/e* 157 ($M^{+\cdot}$).

Acknowledgment. Financial support was provided by a grant from the National Cancer Institute (CA 16328). We thank Drs. Robert A. Campbell, Dagmar Bartos, and Frantisek Bartos for encouragement and useful discussions concerning hapten design.

Registry No. 4, 78790-58-6; 4·2HCl, 78790-59-7; **5a**, 52244-70-9; **5b**, 821-41-0; **5c**, 928-90-5; **6a**, 56047-51-9; **6b**, 764-59-0; **6c**, 29329-03-1; **7a**, 78790-60-0; **7b**, 78790-61-1; **7c**, 78790-62-2; **8b**, 78790-63-3; **9**, 78790-64-4; ethyl cyanoacetate, 105-56-6.

Reduction of Esters to Alcohols by means of Sodium Borohydride in Polyethylene Glycols

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Received December 23, 1980

It is well-known that esters are essentially inert toward reduction by sodium borohydride,[2] although in some instances a few exceptions are reported. In fact, esters containing participating neighboring groups[3] as well as some heterocyclic aromatic esters[4] can be converted into the corresponding alcohols. The above reaction can be also performed by use of reagents which are added to $NaBH_4$, thus enhancing its reducing power by deeply changing the reacting species.[5,6] In addition, the nature of the solvent plays a very important role in the rate and kind of reduction, as it has been pointed out also very recently.[7]

We have previously suggested that polyethylene glycols (PEG) could be used as complexing solvents of inorganic salts, in order to enhance the reactivity of the anion with the organic substrate.[8,9] In the first report,[8] we had observed that $NaBH_4$ in PEG 400 was able to reduce carbonyl compounds, the reaction being in contrast with the behavior of $NaBH_4$ in crown ethers[10] and polyethylene glycol ethers.[11] In these systems, where the anion could be brought into solution, a lowered reactivity was observed. As extension of our observation, we have studied the reduction of esters in PEG 400 by $NaBH_4$ (see Scheme I), which is unable to accomplish such a reaction itself. The reaction was successfully carried out with several substrates, the yields generally good (Table I).

Table I. Reduction of Esters to Alcohols by $NaBH_4$ in PEG 400[a]

substrate	product	yield, %[b]
1a	2a	80
1b	2b	82
1c	2c	73[c]
1d	2d	75
1e	2e	65
1g	2g	90
1h	2h	80
1i	*d*	86
1l	2l	80
1m	$C_{14}H_{43}OH$	90

[a] Molar ratio of $NaBH_4$/ester of 3:1, unless otherwise stated, temperature 65 °C, time 10 h. [b] Yields refer to isolated products. Purity and identity of compounds were established by usual spectroscopic methods as well as by TLC and GC. [c] 10% of 4-aminobenzyl alcohol was present. [d] 3-Phenylpropanol was the only detectable product of the reaction. [e] 24 h at 65 °C, $NaBH_4$/ester molar ratio of 9:1.

As a comment to our results, no substantial difference has been noticed between ethyl and methyl esters, and, unless otherwise stated, an average 10-h reaction time has been established as optimum. Only a small amount of reduction of the nitro group of **1c** was noticed (10% of the products), and **1i** was not reduced to **2i** but to 3-phenylpropanol, as in the sodium borohydride reduction of α,β-unsaturated ketones to saturated alcohols.[12] In agreement with results of Maki and co-workers,[13] *p*-amino- and *p*-

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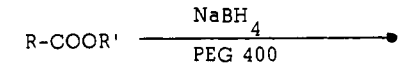
Scheme I



(1) (2)

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

Acknowledgment. We thank C.N.R. (Rome) for financial support and Professors A. Fiecchi and M. Farina for helpful discussions.

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.

(14) See ref 4, p 220.

Vinyl Carbamates via Interaction of Alkylidenecarbenes with Isocyanates

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Received May 27, 1981

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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