the methine proton adjacent to the oxygen atom of 4 in KOD–D_2O solution was found to be a doublet (J_1 = 1.8 Hz) of quartets (J_2 = 6.5 Hz). As a result of a decoupling experiment, J_1 was found to correspond to the vicinal coupling between the two methine groups in agreement with the assignment of β-adduct structure to **4**. Analogously to the case of **2**, the 3,5-dinitrobenzoate of **4** was obtained in 83% yield: mp 140–143° from methanol; ir (KBr) 1781 (s), 1721 (s), 1550 (s), 1347 (s), 1292 (s), 1179 (s), 1120 cm^{-1} (m); nmr ($CDCl_3$) δ 1.51 (d, 3 H), 1.73 (s, 6 H), 2.3–3.1 (m, 3 H), 4.80 (dq, J_1 = 6.6, J_2 = 2.8 Hz, 1 H), 9.0–9.3 (m, 3 H).

Anal. Calcd for $C_{15}H_{16}O_8N_2$: C, 51.14; H, 4.58; N, 7.95. Found: C, 51.12; H, 4.57; N, 8.09.

Isopropyl Alcohol Adducts of 5,6-Dihydro-6-methyl-2*H*-pyran-2-one. By the use of silica gel chromatography (eluent, benzene–ethyl acetate mixture in 1:1 ratio by v/v), two adducts were separated from the reaction mixture, **7b** (yield 36%) and **6a** (yield 16%). On the basis of both the spectroscopic and chemical evidences described below, **6a** and **7b** were concluded to be δ- and γ-lactone, respectively.

A. γ-Lactone 7b was a viscous liquid: ir (neat) 3440 (broad), 1760 (broad), 1273 cm^{-1} (broad); nmr (in benzene) δ 0.95 (s, 3 H), 1.22 (s, 3 H), 1.10 (d, J = 6.2 Hz, 3 H), 0.8–2.8 (m, 5 H), 2.99 (s, 1 H), 3.2–3.8 (m, 1 H); nmr ($CDCl_3$) δ 1.24 (d, J = 6.2 Hz, 3 H), 1.25 (s, 3 H), 1.45 (s, 3 H), 1.3–1.7 (m, 2 H), 1.7–3.0 (m, 3 H), 2.74 (s, 1 H), 3.5–4.1 (m, 1 H). The frequency of the carbonyl absorption band corresponds to those of saturated γ-lactones. As to the nmr spectra, we observe two singlet signals which correspond to three protons, respectively: the difference in chemical shifts between the two signals is as large as 0.2 ppm in both benzene and deuteriochloroform. It is suggested then that there are two highly nonequivalent methyl groups. In addition, the benzene-induced shifts for these singlets are much larger than that for the doublet (1.10 ppm in benzene) which is assigned to the methyl protons coupled to an adjacent methine proton. These facts are in good agreement with the proposed structure **7b**, but not with **6b**. Finally, the hydroxyl proton signal of **7b** splits into a doublet (J = 4.9 Hz), when the acetone solution is cooled down below −10°. Therefore, a secondary hydroxyl group must be involved in **7b**. The structure of **7b** is thus deduced. The corresponding 3,5-dinitrobenzoate was obtained by the usual method in 93% yield: mp 180–181° from methanol; ir (KBr) 1767 (s), 1756 (shoulder), 1726 (s), 1544 (s), 1347 (s), 1279 (s), 1173 (m), 1133 cm^{-1} (m); nmr ($CDCl_3$) δ 1.31 (s, 3 H), 1.48 (s, 3 H), 1.51 (d, J = 6.0 Hz, 3 H), 1.2–2.9 (m, 5 H), 5.0–5.5 (m, 1 H), 9.0–9.3 (m, 3 H).

Anal. Calcd for $C_{16}H_{18}O_8N_2$: C, 52.47; H, 4.95; N, 7.65. Found: C, 52.52; H, 4.94; N, 7.45.

B. δ-Lactone 6a was a viscous liquid: ir (neat) 3510 (broad), 1729 (s), 1254 cm^{-1} (broad); nmr (in benzene) δ 0.98 (s, 6 H), 1.09 (d, J = 6.2 Hz, 3 H), 0.9–2.5 (m, 5 H), 2.46 (s, 1 H), 3.5–4.2 (m, 1 H). The proton signals of **6a** in $CDCl_3$ gradually disappear and new sets of signals arise in return. Then a benzene solution of **6a** was prepared and a very small amount of dry hydrogen chloride was bubbled into the solution. This treatment completed the transformation from **6a** into the new compound **7a**, which was easily recovered by purging the solvent with a nitrogen stream.

C. γ-Lactone 7a was recrystallized from *n*-hexane–benzene mixture: mp 122.5–123.5°; ir (KBr) 3250 (shoulder), 3400 (broad), 1761 (s), 1747 (shoulder), 1275 (m), 1262 (s), 1122 (s), 1103 cm^{-1} (s); nmr ($CDCl_3$) δ 1.23 (d, J = 6.3 Hz, 3 H), 1.25 (s, 3 H), 1.45 (s, 3 H), 1.3–1.7 (m, 2 H), 1.7–2.9 (m, 3 H), 2.68 (s, 1 H), 3.38 (tq, J_1 = J_2 = 6.3 Hz, 1 H). The structure of multiplets with a pair of prominent peaks around 2.5 ppm is clearly different from the corresponding multiplets of **7b** in which a single, sharp peak is observed at 2.5 ppm. The hydroxyl proton signal of **7a** also splits into a doublet (J = 4.8 Hz) when the acetone solution is cooled down. In vpc analyses, there is a small but clear difference in retention time between **7a** and **7b** so that a pair of slightly overlapping peaks are observed when both of the compounds are injected into the column at the same time.

Anal. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.37. Found: C, 62.88; H, 9.66.

Registry No. **1**, 497-23-4; **2**, 42867-48-1; **2 3,5-dinitrobenzoate**, 42867-49-2; **3**, 591-11-7; **4**, 42867-50-5; **4 3,5-dinitrobenzoate**, 42867-51-6; **5**, 108-54-3; **6a**, 42867-52-7; **6b**, 42867-53-8; **7a**, 42867-54-9; **7b**, 42867-55-0; **7** 3,5-dinitrobenzoate, 42867-56-1; isopropyl alcohol, 67-63-0; 3,5-dinitrobenzoyl chloride, 99-33-2.

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Synthesis of Hydroxycitronellal. Hydration and Subsequent Hydrolysis of Imines, Enamines, or Oxazolidines Prepared from Citronellal and Amines

Ritsuko Ishino* and Ju Kumanotani*

Engineering Research Institute, Faculty of Engineering, University of Tokyo, Yayoi, Bunkyo-ku, Tokyo, Japan

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Hydroxycitronellal (**4**), one of the most widely used synthetic perfumery materials, has been prepared from citronellal (**1**) by the hydration of citronellal bisulfite (**2**) in sulfuric acid and the subsequent hydrolysis with alkali (course A in Scheme I).[1] The process, however, is accompanied by the liberation of **1** from the adduct **2** and the cyclization of **1** to isopulegol (**5**), which is further hydrated to menthoglycol (**6**), as shown in Scheme I (course B).[2] Consequently, the yield of **4** is very poor.

The hydration of olefinic compounds to alcohols generally proceeds very fast in strong acidic media,[3] whereas the hydrolyses of some aldehyde–amine adducts, *i.e.*, imines,[4] oxazolidines,[5] and enamines,[6] have been reported to be relatively slow in strong acidic media and fast in weak alkaline solutions or in water. Imines and enamines have been used for protecting aldehyde grouping in the related citral system where sulfuric acid has been used for generating a carbonium ion to induce cyclization.[7] Thus, these amine adducts should be useful intermediates for protecting the aldehyde group of **1** in strong acid in order to prevent the side reaction shown in Scheme I (course B).

We have found a synthetic route to **4** which is superior in yield as well as in simplicity to the conventional method (Scheme II).[8]

Reactions of **1** with five primary amines gave the imines **7–10** and **18** (Table I). In the crude products prepared from **1** and ethanolamine, the presence of an oxazolidine derivative[9] as well as **8** was noticed from the newly observed νC–O–C band at 1020 cm^{-1} and the decreased absorption at 1060 cm^{-1} attributable to primary OH. The relatively great value (1669 cm^{-1}) of νC=N absorption in **9** suggests that the tautomerism described below does not take place.

$$C_6H_5CH_2N{=}CH{\sim} \rightleftharpoons C_6H_5CH{=}NCH_2{\sim}$$

The isolation of **10** and **18** by means of distillation resulted in the formation of undesirable resinous materials. Therefore, the crude adduct **18** was used for the synthesis of **4**.

Five enamines, **11–15**, were derived from aliphatic secondary amines (Table II). From two aliphatic secondary amines substituted with one or two 2-hydroxyethyl

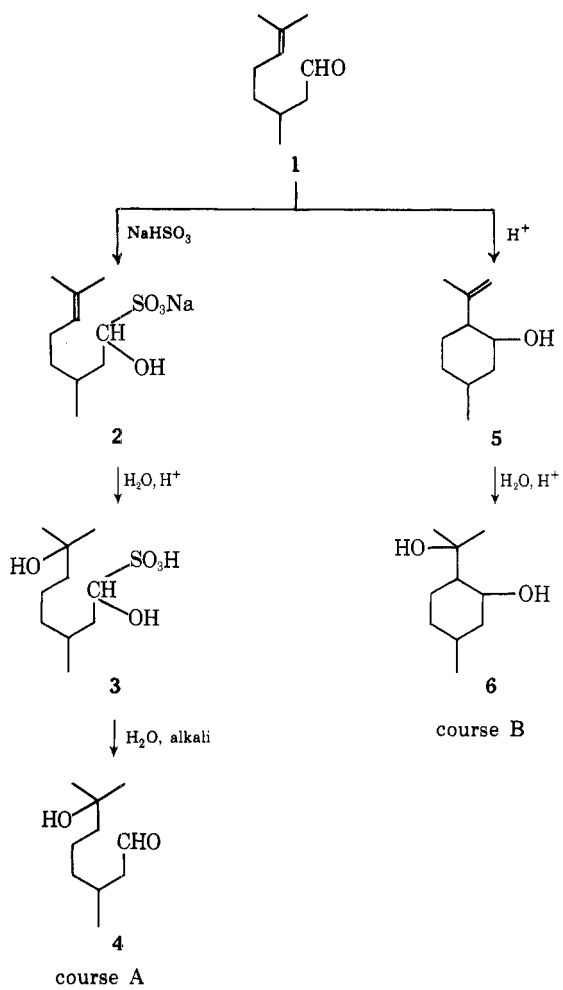
* Address correspondence to Institute of Industrial Science, University of Tokyo, Roppongi, Minato-ku, Tokyo.

Table I
Imines Derived from Citronellal and Amines

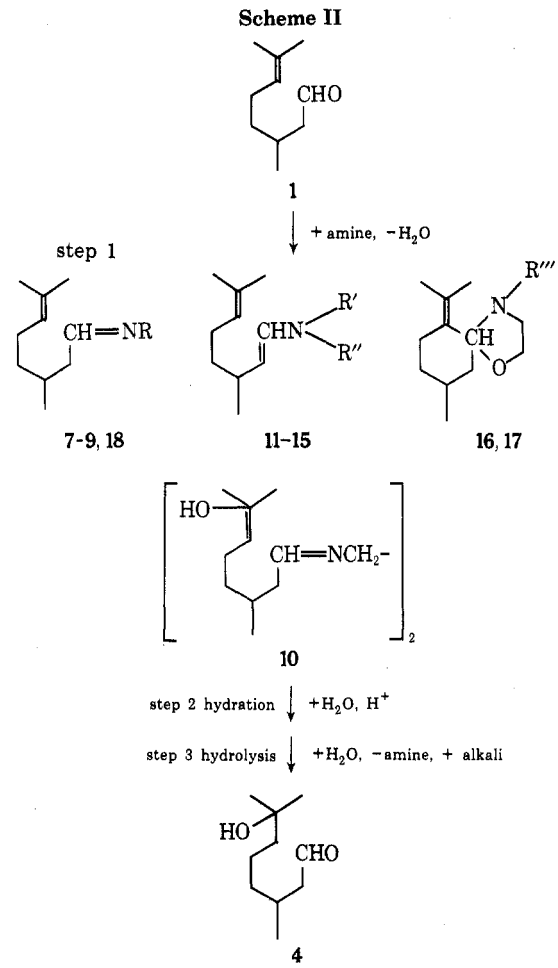
Compd	Applied amine	Yield, %	Bp, °C (mm)	Ir (film), cm^{-1} C=N	Ir (film), cm^{-1} Primary OH	Uv (C_6H_{12}), nm (ε)	Mass (80 eV), m/e M+	Mass (80 eV), m/e Others[d]
7	Methylamine	93	61 (1.5)	1677		231 (3.9 × 10^2) (–CH=NCH_3)[b]	167	
8	Ethanolamine	58	94 (1.5)	1670	3300, 1060		197	166, 87, 69
9	Benzylamine	84	139 (3.0)	1669			243	
10	Ethylenediamine	60	170 (1.5)	1670			332	166, 69
18[a]	Aniline			1650		235 (6.1 × 10^3) (–CH=NC_6H_5)[c]		

[a] A mixture of **18** and **1** (*ca.* 90 and *ca.* 10% by glpc) was employed for spectral analyses. [b] R. Bonnett, *J. Chem. Soc.*, 2313 (1965). [c] R. Bonnett in "The Chemistry of the Carbon–Nitrogen Double Bond," S. Patai, Ed., Interscience, New York, N. Y., 1970, p 49. [d] $(CH_3)_2C$=$CHCH_2$⦚$CH_2CH(CH_3)CH_2CH$=NCH_2⦚CH_2OH. (69⦚ ⦚166)

Scheme I



Scheme II



7, R = CH_3
8, R = $(CH_2)_2OH$
9, R = $CH_2C_6H_5$
18, R = C_6H_5

11, R′ = R″ = CH_3
12, R′ = R″ = $(CH_2)_3CH_3$
13, R′, R″ = $-(CH_2)_5-$
14, R′, R″ = $-(CH_2)_2O(CH_2)_2-$
15, R′ = CH_3; R″ = $-(CH_2)_3NH_2$
16, R‴ = $(CH_2)_2OH$
17, R‴ = CH_3

groups, however, oxazolidines **16** and **17** were obtained (Table III). When *N*-methylaminopropylamine was allowed to react with **1**, not the primary but the secondary amino group was found to react.

The citronellal–amine adducts **7–18**, crude or isolated, were hydrated[10] and the subsequent hydrolysis at neutral pH gave excellent yields of **4** from any of the isolated compounds **11–17**, although accompanied by minor amounts of **5** and **6** (Table IV). This proves that the enamines and oxazolidines are excellent intermediates in protecting the aldehyde group of **1** in strong acidic media. The imines **7–10** are also effective for preventing the cyclization of **1** in the same media; however, only Schiff base **18** gave a large amount of resinous materials. It is noticeable that the yield of **4** from the crude ethanolamine adduct (72%) was found to be greater than that from the isolated **8** (50%). This is attributable to the presence of some oxazolidine derivative as well as **8** in the crude adduct.

From (+)-**1** ($[\alpha]^{20}D$, +8.1°), (+)-**4** ($[\alpha]^{20}D$ +9.8°), which has been recognized as the enantiomer having the desired olfactory properties,[11] was produced by the present practical method.

Experimental Section

Infrared spectra were run with a Nihonbunko ir spectrophotometer, Model IR-S. Nuclear magnetic resonance spectra were taken at 60 MHz with a Nihondenshi nmr spectrometer, JMN C-60, using tetramethylsilane as an internal standard. Ultraviolet spectra were determined at 25° in cyclohexane with a Hitachi spectro-

Table II
Enamines Derived from Citronellal and Amines

Compd	Applied amine	Yield, %	Bp, °C (mm)	Ir (film), cm⁻¹ –CH=CH–, trans	Ir (film), cm⁻¹ C–N	Ir (film), cm⁻¹ –NH₂	Uv (C_6H_{12}), nm (ε) –CH=CHN< [a]	Nmr (CCl_4), δ H_a [b]	Nmr (CCl_4), δ H_b [b]	Mol wt (C_6H_6) (calcd)
11	Dimethylamine	80	117 (27)	1655, 935	1070		229 (6.0 × 10³)	5.77	3.99	188 (181.3)
12	Dibutylamine	66	126 (3.5)	1650, 935	1100			5.75	4.23	
13	Piperidine	90	126 (5.5)	1653, 935	1100		228 (8.3 × 10³)	5.65	4.23	226 (221.4)
14	Morpholine	90	132 (5.5)	1653, 935	1120		225 (7.6 × 10³)	5.88	4.41	207 (223.4)
15	*N*-Methylamino-propylamine	54	110 (2.0)	1655, 935	1100	735				217 [c] (224.4)

[a] N. J. Leonard and D. M. Locke, *J. Amer. Chem. Soc.*, **77**, 437 (1955). [b] >CHCH$_b$=CH$_a$N< (trans); signals of H_a and H_b appeared as d, 1, J = 14 Hz, and q, 1, J = 8.3 and 14 Hz, respectively. [c] Solvent was methyl ethyl ketone.

Table III
Oxazolidines Derived from Citronellal and Amines

Compd	Applied amine	Yield, %	Bp, °C (mm)	Ir (film), cm⁻¹ C–O–C	Ir (film), cm⁻¹ Primary OH	Nmr (CCl_4), [a] δ
16 [b,d]	Diethanolamine	95	161 (5)	1020	3400, 1050	3.40–2.90 (m, 1, H_a) [c] 2.85–2.40 (m, 3, H_b and H_e) [c] 3.97–3.70 (t, 2, J = 6.8 Hz, H_c) 3.75–3.50 (q, 2, H_f) 4.24–4.05 (t, 1, J = 5 Hz, H_d) 3.04 (21°) or 2.14 (100°) (s, 1, H_g)
17 [b]	*N*-Methylethanolamine	95	96 (4)	1020		3.33–2.88 (m, 1, H_a) [c] 2.74–2.33 (m, 1, H_b) [c] 3.95–3.71 (m, 2, H_c) 3.95–3.85 (t, 1, H_d) 2.31 (s, 3, H_h)

[a] R''' = $-CH_{e2}CH_{f2}OH_g$ or $-CH_{h3}$. See i. [b] Uv (C_6H_{12}) no absorption at 210–360 nm. [c] J. B. Lambert and R. G. Keske, *J. Amer. Chem. Soc.*, **88**, 620 (1966). [d] Mol wt (C_6H_6) 238 (calcd, 241.4).

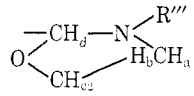


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Table IV
Products of Hydration and Subsequent Hydrolysis of Citronellal–Amine Adducts

Substrate Citronellal–amine adduct	Yield, % (mol/100 mol substrate) Hydroxycitronellal	Citronellal and isopulegol	*cis*- and *trans*-Menthoglycol
7	72	2	10
8	87 [a] (72) [b]	2 (3) [b]	3 (8) [b]
9	50	3	10
10	80	6	20
11	85 (77) [b]	2 (2) [b]	5 (14) [b]
12	85	2	5
13	90	2	0
14	95	2	0
15	95	2	0
16	95 (88) [b]	3 (3) [b]	0 (11) [b]
17	85	2	0
18	(0) [b]	(15) [b]	(10) [b]

[a] The yield based upon citronellal employed is 50%. [b] Crude citronellal–amine adducts were used and yields (mol/100 mol citronellal) are listed.

photometer, Model EPS-2. Mass spectra were measured with a Hitachi mass spectrometer, Model RMS-4. Molecular weights were determined in benzene or methyl ethyl ketone with a vapor pressure osmometer, Model 301-A, Mechrolab, Inc. Gas chromatography was carried out with a Kotaki Super Fractioner, Model GU-21, equipped with a column containing 15% Reoplex on Celite 545 SK (40–60 mesh) at 180°.

Materials. Citronellal [bp 64° (5.5 mm)], citronellol [bp 104° (10 mm)], and hydroxycitronellal [bp 110° (5.5 mm)] (given by Ogawa Koryo Co., Ltd.) were more than 99% pure (by glpc). *cis*- and *trans*-Menthoglycols were prepared from citronellal in 5% sulfuric acid according to the method of Zimmerman.[12] All amines (G.R. grade) were used as received.

Preparation of Citronellal–Amine Adducts. An amine (0.1 mol) was added to **1** (15.4 g, 0.1 mol) over a period of 3 min with stirring. The temperature was kept between 15 and 25° on a water–ice bath and additional stirring was continued for 30 min. Centrifuging yielded an oily layer, which was distilled, and the fraction of imine, enamine, or oxazolidine (**7**–**18**) was obtained.

Hydration of Citronellal–Amine Adducts and the Subsequent Hydrolysis to Hydroxycitronellal (4). To 50% (v/v) sulfuric acid (34 ml) cooled at 7° on a water–ice bath, a citronellal–amine adduct (0.1 mol) was added drop by drop over a period of 2 min below 30° with vigorous stirring. Further stirring was continued for 2 min at 25–30°. Then the sulfuric acid solution was poured into a mixture of a saturated aqueous NaCl solution (500 ml), benzene (50 ml), NaOH (24 g), and crushed ice (200 g) below 15°. Then the pH of the solution was adjusted to the range 6.5–7.0 with dilute aqueous $NaHCO_3$ or H_2SO_4. The benzene layer was separated and the aqueous portion was extracted twice with benzene (50 ml). The combined benzene extracts were washed with a saturated NaCl solution (3 × 20 ml) and the benzene was distilled off at 40° *in vacuo*. The oil obtained was analyzed by glpc using 1,3-propanediol as an internal standard, and the amounts of hydroxycitronellal (**4**), citronellal (**1**), isopulegol (**5**), and *cis*- and *trans*-menthoglycols (**6**) were determined.

Acknowledgment. We wish to thank Ogawa Koryo Co., Ltd., for supplying citronellal, hydroxycitronellal, and citronellol and determinations of optical rotation.

Registry No. **1**, 106-23-0; **4**, 107-75-5; **5**, 89-79-2; **6**, 42822-86-6; **7**, 42822-87-7; **8**, 42822-88-8; **9**, 42822-89-9; **10**, 42822-90-2; **11**, 42822-91-3; **12**, 42822-92-4; **13**, 1723-79-1; **14**, 42822-94-6; **15**, 42822-95-7; **16**, 42822-96-8; **17**, 42822-97-9; **18**, 42822-98-0.

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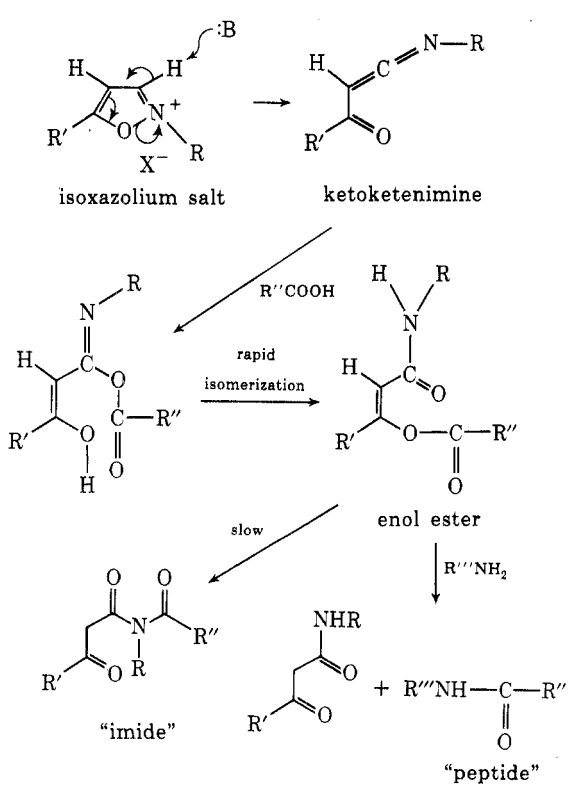
Communications

A Facile Conversion of Carboxylic Acids to Carbinols under Mild Conditions[1]

Summary: Enol ester derivatives, produced upon treatment of carboxylic acids with *N*-ethyl-5-phenylisoxazolium 3′-sulfonate, afford carbinols upon reduction with sodium borohydride in aqueous solution.

Sir: In a reinvestigation of isoxazolium salts, originally reported by Otto Mumm,[2] Woodward and coworkers[3-5] showed that a number of 3-substituted isoxazolium salts react with carboxylic acids in the presence of a base to yield enol ester derivatives which are useful acylating agents, especially in peptide synthesis. The principal features of this chemistry are indicated in Scheme I.

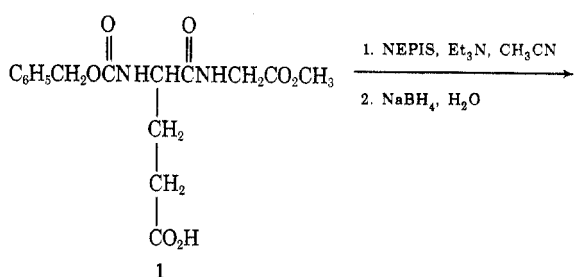
Scheme I



In conjunction with our studies on the catalytic roles of carboxyl groups in the active sites of enzymes, we required a means by which such carboxyl groups could be reduced to carbinol groups. Clearly, the conventional methods employing lithium aluminum hydride or sodium borohydride–aluminum chloride could not be employed for protein modification in aqueous solution. However, recent reports on the use of Woodward's isoxazolium salts in aqueous solution to activate carboxyl groups in enzymes toward attack by various nucleophilic reagents[6-8] suggested that perhaps activation of such carboxyl groups toward reduction by aqueous sodium borohydride might be similarly achieved. The preliminary investigations reported here show that such is indeed the case.

Enol ester derivatives of the acids in Table I were prepared essentially as described by Woodward, *et al.*,[5] using *N*-ethyl-5-phenylisoxazolium 3′-sulfonate[9] (NEPIS) with triethylamine as the derivatizing agent in acetonitrile solution at room temperature. The crude enol esters were then freed of solvent *in vacuo*, dissolved in water, and treated with a 10-fold molar excess of sodium borohydride.[10] Carbinol yields (Table I) varied from 40 to 100%.

The peptide derivative **1** (*O*-methyl *N*-benzyloxycarbonyl-α-L-glutamylglycinate) was prepared as a model substrate to test the applicability of our reduction proce-



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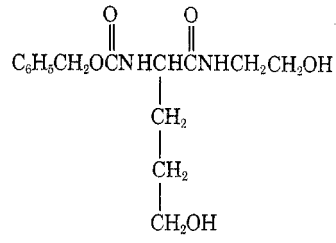

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