30 min under nitrogen, a solution of nitroethylene[10] (219 mg, 3 mmol) in dry xylene (1 mL) was added, and then the resultant mixture was heated at 100 °C for 4 h with stirring. The reaction mixture was worked up as usual to give an oil, which showed no formyl signals in the NMR spectrum. The crude product was purified by silica gel thick layer chromatography using ether–petroleum ether (2:1) as the eluent, giving an oil (245 mg, 82%): IR ($CHCl_3$) 1726, 1698, 1556, and 1378 cm^{-1}; NMR δ 1.42 (s, 3 H), 1.8–3.0 (m, 8 H), and 4.38 (t, 2 H, J = 7 Hz).

Anal. Calcd for $C_9H_{13}O_4N$: C, 54.26; H, 6.58; N, 7.03. Found: C, 54.48; H, 6.88; N, 6.89.

The oil slowly solidified on standing and gave low-melting crystals.

Attempted Conversion of the Nitrodione 2b into 3b. A mixture of the nitrodione **2b** (77 mg, 0.39 mmol), KF (27 mg, 0.46 mmol), and dry xylene (1 mL) was stirred at 100 °C for 38 h under nitrogen. The reaction mixture was worked up as usual to afford a brown oil. The oil was almost homogeneous as shown by GLC and TLC. A pale yellow, viscous oil (70 mg) obtained by passing through a silica gel column was identified as the starting material **2b** by IR and NMR.

Preparation of the Labeled 2-Methylcyclohexane-1,3-dione (1). A heterogeneous mixture of 2-methyl-3-(1-pyrrolidinyl)cyclohex-2-en-1-one (**8**,[5] 179 mg, 1 mmol) and $H_2{}^{18}O$-enriched water[12] (assay, over 20%; 1.0 mL) containing hydrogen chloride (55 mg) was stirred at reflux under nitrogen for 15 min. The reaction mixture was cooled to room temperature and the crystalline product was collected by filtration, washed with water, and dried in vacuo giving labeled **1** (91 mg, 72%). Recrystallization from ethanol gave crystals melting at 203.5–204.5 °C, IR (KBr) 1575 cm^{-1}.

A direct insertion probe was used for mass measurements. Relative intensities of peaks at m/e 128 to those at m/e 126 were 0.017 and 0.424 for the unlabeled and labeled diones **1**, respectively.[6]

Preparation of the Labeled 2-Methyl-2-acetonylcyclohexane-1,3-dione (3a). A heterogeneous mixture of the labeled dione **1** (252 mg, 2 mmol), 2-nitropropene (251 mg, 3 mmol), anhydrous KF (116 mg, 2 mmol), and dry xylene (3.5 mL) was stirred on a bath (115–120 °C) for 19 h. The resultant mixture was cooled to room temperature and separated by filtration. The filtrate was concentrated in vacuo giving an oil. Silica gel thick layer chromatography gave the labeled trione **3** (351 mg), which was purified further by distillation [110 °C (bath temperature)/(1–2 mm)]. The trione (298 mg, 82%) thus obtained crystallized on cooling (mp 54–57 °C). The IR and NMR spectra of the product were in agreement with those of the unlabeled trione. An exact mass determination gave m/e 184.0979 (calcd for $C_{10}H_{14}O_2{}^{18}O$, 184.0984).

In the mass spectra of the labeled trione, relative intensities of the molecular ion peak at m/e 184 to that at m/e 182 and of the fragment ion peak at m/e 141 to that at m/e 139 were 0.377 and 0.252, respectively. On the other hand, the corresponding relative values for the unlabeled trione were 0.009 and 0.029.[6] Exact masses of the fragment ion **9** were m/e 141.0822 (calcd for $C_8H_{11}O^{18}O$, 141.0801) and 139.0749 (calcd for $C_8H_{11}O_2$, 139.0758) for the labeled and unlabeled triones, respectively.

Acknowledgment. We thank Dr. K. Ogura for his helpful discussion in labeling experiments.

Registry No.—**1**, 1193-55-1; **1**-^{18}O, 62587-14-8; **2a**, 57822-04-5; **2b**, 57822-03-4; **3a**, 32561-57-2; **3a**-^{18}O, 62587-15-9; **7**, 62587-16-0; **8**, 53940-63-9; 2-nitropropene, 4749-28-0; 2-nitrooctane, 4609-91-0; nitroethylene, 3638-64-0.

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(1) Tohoku University.
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(4) Similar transformations with other 1,3-dicarbonylic substrates will be published elsewhere.
(5) J. J. Panouse and C. Sannié, *Bull. Soc. Chim. Fr.*, 1374 (1956).
(6) Multi-ion detection techniques were utilized for all quantitative analyses of the mass spectra.
(7) Regarding the calculation, for example, see K. Biemann, "Mass Spectrometry. Organic Chemical Applications", McGraw-Hill, New York, N.Y., 1962, p 204.
(8) Designating the isotopic contents of the labeled trione **3a** and its fragment ions (labeled **9** and **10**) as a, b, and c, the migration ratio of oxygen (x) based on the labeled ion **9** or **10** may be given by eq 1 or 2, respectively.

$$b = a(1 - x/2) \quad (1)$$

$$c = ax/2 \quad (2)$$

(9) For example, see G. W. Wheland and J. Farr, *J. Am. Chem. Soc.*, **65**, 1433 (1943).
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(12) Supplied by the British Oxygen Co., Ltd.

Trichlorosilane-Induced Cleavage. A Mild Method for Retrieving Carbinols from Carbamates

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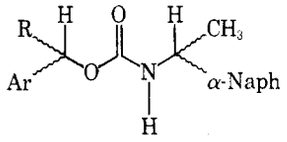
To complement our recent reports[1,2] utilizing type 1 diastereomeric carbamate derivatives to chromatographically resolve a variety of chiral carbinols, we now report a mild, high-yield method for retrieving the optically active carbinol moieties from these diastereomeric carbamates. Beyond this somewhat specialized application, the presently described retrieval method promises to have wide applicability as part of a hydroxyl blocking–unblocking sequence in organic synthesis.



R = alkyl or fluoroalkyl

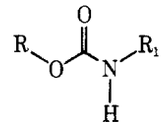
1

Carbamates are generally hydrolyzed by means of either strong base or strong acid. However, such harsh conditions do not always furnish the desired products. For example, ethoxide treatment of either of the diastereomeric carbamates derived from 1-(1-naphthyl)ethyl isocyanate and 2,2,2-tribromophenylethanol affords decomposition products rather than retrieval of carbinol. Moreover, hydrolysis of carbamates derived from allylic alcohols could conceivably occur by an S_N2' process with attendant rearrangement or racemization, and thermal reactions of such carbamates have been noted[3] (albeit at somewhat higher temperatures than might normally be used during hydrolysis).

Several chlorosilanes have been used to prepare isocyanates from carbamates.[2,4] We have explored modifications of the "silanolysis" reaction as an alternate means for retrieving alcohols from carbamates.

Treatment of carbamates **2–16** with trichlorosilane–triethylamine in any of several dry solvents[5] followed by aqueous workup affords the liberated carbinol in high yield. Table I contains representative examples of carbamates which have been successfully cleaved as well as the reaction conditions utilized. Note that, in all cases, the silane retrieval sequence is essentially independent of the structure of the alcohol and works equally well for primary, secondary, tertiary, or allylic, propargylic, and benzylic alcohols. Most importantly, no racemization or rearrangement of the carbinols has been observed. Further evidence of the mildness of the overall sequence was obtained by applying it to a cyclic hemiacetal. Reduction of γ-valerolactone with diisobutylaluminum hydride at −78 °C in hexane affords a 70:30 mixture of the dia-

Table I. A Representative List of Carbamates which Undergo Trichlorosilane Cleavage



No.	R	R_1	Reaction time, h	Reaction temp, °C	% yield[c]
2	2,2,2-Tribromo-1-phenylethyl	*a*	12	40	85
3	2,2,2-Trifluoro-1-phenylethyl	*a*	12	80	95
4	2,2,2-Trifluoro-1-(1-naphthyl)ethyl	*a*	12	80	90
5	1-Ethynylethyl	*a*	24–48	25	90
6	1-Ethynylpropyl	*a*	24–48	25	83
7	1-Ethynylpentyl	*a*	24–48	25	89
8	2,2,3,3,4,4,4-Heptafluoro-1-phenylbutyl	*a*	3	40	95
9	2,2,3,3,4,4,4-Heptafluoro-1-(1-naphthyl)butyl	*a*	8	40	95
10	2-Octyl	*a*	4	40	90
11	*l*-Menthyl	*a*	4	40	93
12	1-Cyclopentyl	*b*	4	40	85
13	1-Methyl-1-cyclopentyl	*b*	4	40	82
14	Allyl	*b*	24	25	75
15	Benzyl	*b*	4	40	91
16	Cyclohex-2-enyl	*b*	12	40	70

[a] R_1 = 1-(1-naphthyl)ethyl. [b] R_1 = phenyl. [c] Optical purities of chiral carbinols were determined by polarimetry. Each was found to be optically pure.

stereomeric lactols **17a,b** in 70% yield. The lactol mixture was converted into a 70:30 mixture of diastereomeric carbamates (via the chloroformates) and retrieved in high yield without alteration of the original 70:30 ratio. Cyclic hemiacetals such as **17a,b** are readily epimerized by acid- or base-catalyzed ring opening–reclosure. Indeed, treatment of **17a,b** with acid results in a 55:45 equilibrium composition. Since cyclic hemiacetals often occur in nature or as synthetic intermediates, the ability to mask–unmask the hydroxyl group of a cyclic (and presumably acyclic) hemiacetal without epimerization or racemization should be of synthetic utility.

Because of the absence of epimerization, racemization, or rearrangement during silanolysis, we infer that the carbon–oxygen bond is not broken. Presumably, the reaction involves nitrogen[4] or oxygen silylation followed by an elimination akin to that of the Wittig or Pederson reactions. Under the conditions employed, N,N-disubstituted carbamates afford negligible reaction.[6]

The carbinol and isocyanate cleavage products do not appear to recombine during the course of reaction; however, the subsequent aqueous work-up does convert some of the isocyanate to urea. The trichlorosilane cleavages described in Table I were performed on millimole quantities. On large-scale reactions, a white silicon-containing solid sometimes persists after addition of aqueous ammonium chloride. To avoid possible loss of product through entrainment, the aqueous slurry was extracted continuously with ether.

Experimental

Melting points were taken on a Buchi apparatus and are uncorrected. Infrared spectra were obtained with Beckman IR-12 or Perkin-Elmer 237B spectrophotometers. Proton NMR spectra were obtained with Varian Associates A60A, EM-390, HA-100, or HR-220 instruments at 44, 41, 28, and 27 °C, respectively. Mass spectra were determined using a Varian MAT CH-5 spectrometer. Microanalyses were performed by J. Nemeth and his colleagues.

Carbamates. All carbamates were prepared by a previously described procedure[1] and **2–12** as well as **14–16** have been previously reported. The mixed carbamates of **17a,b** were characterized by NMR and by mass spectrometry.

1-Methyl-1-cyclopentyl *N*-phenylcarbamate (13) is a colorless solid: mp 86–88 °C; NMR ($CDCl_3$) δ 1.63–1.80 (m, C_6H_9), 2.20 [doublet of doublet of doublets, O–C(C_2H_2)], 6.86 (br s, N–H), 6.98–7.43 ppm (m, C_6H_5); IR (KBr) 3330 (NH), 2990, 1701 (C=O), 1600, 1540, 1470, 1440, 1380, 1325, 1240, 1170, 1120, 1050, 1030 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 219 (10.5, M^+), 138 (14.2), 137 (88.2), 120 (4.2), 119 (10.3), 100 (4.8), 94 (6.2), 93 (89.3), 92 (5.1), 85 (5.4), 84 (6.5), 83 (100.0), 82 (4.2), 81 (6.5), 77 (9.2), 71 (23.0), 67 (11.3), 65 (8.4), 58 (17.0), 55 (65.7), 43 (15.1), 41 (19.9).

Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.82; N, 6.39. Found: C, 71.06; H, 7.82; N, 6.53.

Trichlorosilane Cleavage. The following procedure is representative. To a solution of carbamate (10 mmol) and triethylamine (1.11 g, 11 mmol) in 25 mL of dry solvent under N_2 was added dropwise (10 min) a solution of trichlorosilane (1.49 g, 11 mmol) in 10 mL of dry solvent. Solvents (usually benzene) were selected to be more volatile than the liberated carbinol. After silane addition, the stirred solution was heated to reflux for 4 h. Alternatively, the reaction may be conducted at room temperature for longer periods (24–48 h). Reactions were worked up by washing the organic layer with two 50-mL portions of saturated aqueous NH_4Cl and drying it over anhydrous $MgSO_4$. Carbinols were isolated by distillation or by liquid chromatography.

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Registry No.—**2**, 62509-64-2; **3**, 62532-81-4; **4**, 62509-65-3; **5**, 62509-66-4; **6**, 62509-67-5; **7**, 62509-68-6; **8**, 62509-69-7; **9**, 62509-70-0; **10**, 62509-71-1; **11**, 62509-72-2; **12**, 3422-04-6; **13**, 3976-79-2; **14**, 18992-89-7; **15**, 3422-02-4; **16**, 62509-73-3; 2,2,2-tribromo-1-phenylethanol, 38158-81-5; 2,2,2-trifluoro-1-phenylethanol, 340-04-5; 2,2,2-trifluoro-1-(1-naphthyl)ethanol, 62509-74-4; 1-ethynylethanol, 2028-63-9; 1-ethynylpropanol, 4187-86-4; 1-ethynylpentanol, 7383-19-9; 2,2,3,3,4,4,4-heptafluoro-1-phenylbutanol, 785-93-3; 2,2,3,3,4,4,4-heptafluoro-1-(1-naphthyl)butanol, 62509-75-5; 2-octanol, 123-96-6; *l*-menthol, 3858-43-3; cyclopentanol, 96-41-3; 1-methylcyclopentanol, 1462-03-9; allyl alcohol, 107-18-6; benzyl alcohol, 100-51-6; cyclohex-2-enol, 822-67-3; trichlorosilane, 10025-78-2.

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(6) Trichlorosilane has been reported[7] to react with N,N-disubstituted amides at higher temperatures to afford reduction products and to afford unknown products upon reaction with N-monosubstituted amides.
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