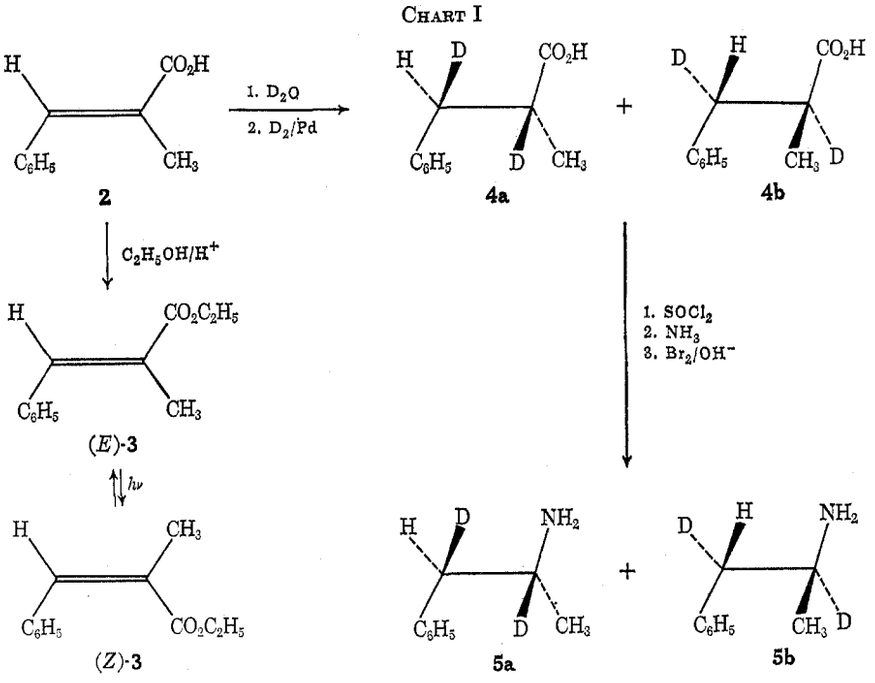
CHART I



c (Table I) should be the least populated, as is the case for amphetamine.[12a]

Experimental Section

Nmr spectra were recorded at 60 and 90 MHz as 0.5 *M* solutions in the indicated solvents. Coupling constants were determined from calculated spectra (LAOCN3).

(*E*)-2-Methylcinnamic acid (2) was prepared by silver oxide oxidation of 2-methylcinnamaldehyde (Aldrich) in 70% yield: mp 81–83° (lit.[4] mp 81°); nmr ($CDCl_3$) δ 2.04 (CH_3, d, J = 2.0 Hz), 7.59 (vinylic H, q, J = 2.0 Hz).

2,3-Dideuterio-2-methylcinnamic acid (4a and 4b) was prepared by exchanging the acidic proton of 15.0 g (0.093 mol) of **2** in 90 ml of ethyl acetate with three 15-ml portions of D_2O, with subsequent catalytic reduction (200 mg of 5% Pd on carbon) of **2**-d_1 in a deuterium atmosphere at 45 psi. Removal of catalyst and solvent afforded 12.3 g (80%) of **4**: mp 35–36°; bp 142° (2 mm)[13] [lit.[14] bp 174–176° (20 mm)]; nmr ($CDCl_3$) δ 1.10 (2-methyl, s), 2.55 (H_b, s).

2,3-Dideuterio-2-methylcinnamamide was prepared by the previously described sequence for the conversion of dihydro-2-methylcinnamic acid to dihydro-2-methylcinnamamide.[15] The product amide exhibited mp 108–110° (lit. mp 108°,[14] 110°[13]); nmr (DMSO-d_6) δ 0.97 (2-methyl, s), 2.44 (H_b, s).

(1*R*,2*R*)- and (1*S*,2*S*)-1,2-Dideuterio-1-phenyl-2-propylamine (5a and 5b) (dideuterioamphetamine) was prepared in a manner analogous to that described for the nondeuterated analog.[15] The product amine exhibited bp 200–201° (lit.[16] bp 205°); nmr ($CDCl_3$) δ 0.97 (2-methyl, s), 2.69 (H_b, s). Amphetamine (Aldrich) had nmr ($CDCl_3$) δ 0.97 (2-methyl, d, J = 6.0 Hz), 2.52 (H_a), 2.69 (H_b), 3.17 (H_x); J_{ab} = −14.29, J_{ax} = 8.31, J_{bx} = 5.84 Hz.

Registry No.—**1**, 300-62-9; **2**, 1895-97-2; **4**, 39949-56-9; **5**, 39949-57-0.

(12a) NOTE ADDED IN PROOF.—The assignments of protons H_A and H_B of amphetamine have recently been made [G. E. Wright, *Tetrahedron Lett.*, 1097 (1973)]; although the assignments are correct by comparison with this work, the claim that the assignments confirm the work of Bailey, *et al.* [K. Bailey, A. W. By, K. C. Graham, and D. Verner, *Can. J. Chem.*, **49**, 3143 (1971)] is incorrect since the assignments of conformer population by Wright are reversed.

(13) I. Shahak, *J. Chem. Soc.*, 3160 (1961).

(14) V. Franzen, *Justus Liebigs Ann. Chem.*, **602**, 199 (1957).

(15) E. S. Wallis and S. C. Nagel, *J. Amer. Chem. Soc.*, **53**, 2787 (1931).

(16) D. H. Hey, *J. Chem. Soc.*, 18 (1930).

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Preparation of Methyl and Ethyl *N*-Monochlorocarbamates by Disproportionation[1]

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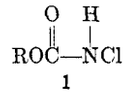
N-Monochlorocarbamate esters (**1**) are versatile pseudohalogens. They add predominantly in cis fashion to olefins in the presence of ultraviolet to yield vicinal chlorocarbamates,[3] they react rapidly with thioethers to form iminosulfonium salts,[4] and they form interesting isolable salts on reaction with base.[5,6]



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(1) Pseudohalogens. XIX. Paper XVIII: *J. Org. Chem.*, **37**, 3004 (1972). Work supported in part by U. S. Public Health Service Grants CA-12227 and CA-07803 of the National Cancer Institute, and the Samuel S. Fels Fund.

(2) Participants in the Chemistry Honors Undergraduate Research Program, Temple University.

(3) K. Schrage, *Tetrahedron Lett.*, 5795 (1966); *Tetrahedron*, **23**, 3033, 3039 (1967).

(4) G. F. Whitfield, H. S. Beilan, D. Saika, and D. Swern, *Tetrahedron Lett.*, 3543 (1970).

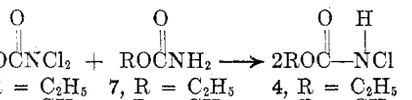
(5) D. Saika and D. Swern, *J. Org. Chem.*, **33**, 4548 (1968).

(6) P. Chabrier, *Ann. Chim. (Paris)*, **17**, 353 (1942), and references therein to older literature.

The usual method of preparation of **1** is reaction of equimolar quantities of chlorine with carbamate esters (**2**).[5-7] It was recognized only recently, however, that the reaction product is a mixture of **1** (major component), *N*,*N*-dichlorocarbamates (**3**) and unreacted **2**.[5] Analysis of reaction products solely for positive halogen is an insufficient criterion of product purity. Assay of composition requires iodometric analysis for positive halogen and determination of acid value (compounds **1** are relatively strong acids), and nmr to determine unreacted **2**. To obtain pure **1** from such mixtures vacuum distillation is required, but it is essential that distillation temperatures be below about 100° as disproportionation of **1** to **2** and **3** occurs at elevated temperatures, a fact not recognized by early investigators. In our earlier work,[5] we isolated ethyl *N*-monochlorocarbamate (**4**), purity >99%, by distillation at 45° (0.2 Torr), but yields are only 40–50% at best.

Earlier investigators had stated that **1** can be prepared in virtually quantitative yield by reaction of equimolar quantities of neat **2** and **3** at room temperature in a disproportionation reaction,[6,8] but details are lacking in the older literature and criteria of purity are not reported. Since pure **3** can be easily prepared in 80–90% yield from **2** and 2 mol of chlorine,[9] we have reinvestigated the disproportionation reaction for the preparation of **4** and methyl *N*-chlorocarbamate (**5**). We report here the explicit experimental details and determination of purity of **1**.

Reaction of equimolar quantities of ethyl *N*,*N*-dichlorocarbamate (**6**) with ethyl carbamate (**7**) at room temperature in the dark for 24 hr (reaction monitored by refractive index and neutralization analysis[5]) gave virtually a quantitative yield of **4**, purity of undistilled product >97%. Increased purity can be obtained by vacuum distillation but considerable reduction in yield is experienced; the crude reaction product is satisfactory for the usual reactions of **4**. Identical results are obtained in the preparation of **5** from methyl *N*,*N*-dichlorocarbamate (**8**) and methyl carbamate (**9**), but the reaction is complete in 3.5–4.5 hr. Because of the high positive halogen content of **8** (*ca.* 50%), its purification by vacuum distillation should be conducted at low pressures in the dark [bp 50–70° (12–20 Torr)] and in all-glass apparatus to avoid overheating and possible vigorous decomposition.



Our experience with the disproportionation reaction for the preparation of **4** and **5** suggests that the reaction is of general applicability for the preparation of other homologous esters in high purity.

Experimental Section

Ethyl *N*-Monochlorocarbamate (4).—In a three-neck flask equipped with a thermometer and a calcium sulfate drying tube, **6** (8.17 g, 0.052 mol) (obtained either from Aldrich Chemical Co. or prepared in our laboratory[9]) and **7** (4.56 g, 0.051 mol) were stirred slowly with a Teflon-coated magnetic stirrer at room temperature in the dark. Samples were removed periodically and monitored by change in refractive index and by the combined neutralization and iodometric methods.[5] No exotherm was noted and reaction was complete in about 24 hr: purity 96.7% (iodometric), 98.9% (neutralization); nmr (neat) δ 1.29 (t, 3, CH_3, J = 7 cps), 4.24 (q, 2, CH_2, J = 7 cps), and 7.53 (broad s, 1, NH). A small broad signal at δ 5.7 suggested that the impurity was **7**.

Methyl *N*-Monochlorocarbamate (5).—As described above, **5** was prepared from **8** (14.64 g, 0.100 mol, 98.3% purity) and **9** (7.507 g, 0.100 mol) (Baker Chemical Co.). The reaction mixture became homogeneous within about 20 min. Reaction was usually complete within 3.5–4.5 hr: purity 99.3% (iodometric), 98.3% (neutralization); nmr ($CDCl_3$ with TMS as internal standard) δ 3.80 (s, 3, CH_3O–), 6.98 (broad s, 1, NH_2) [nmr (neat) shows same shift for methoxyl protons but δ 7.52 (broad s, 1, NH) for associated (hydrogen bonded) amide proton]; mp 23–24° (lit.[8] 32°).

Compound **8** was prepared from **9** and chlorine as described for the preparation of **6**[9] but special precautions (shields, all-glass apparatus, avoidance of light) should be taken owing to the high positive halogen content.

Registry No.—**4**, 16844-21-6; **5**, 39982-28-0; **6**, 13698-16-3; **7**, 51-79-6; **8**, 16487-46-0; **9**, 598-55-0.

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(8) Fabriques de Produits de Chimie Organique de Laire, French Patent 974,085 (1951).
(9) T. A. Foglia and D. Swern, *J. Org. Chem.*, **31**, 3325 (1966).

Wolff–Kishner Reduction of 8,9-Dehydro-2-adamantanone

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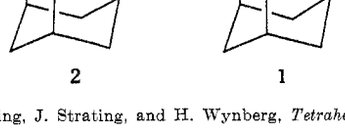
As the cyclopropane ring in 2,4-dehydroadamantane (**1**) can readily be opened by a variety of electrophilic reagents, **1** has proven to be a useful precursor for the synthesis of a variety of 2-substituted and 2,4-disubstituted adamantane derivatives.[1] Three syntheses of **1** have been reported:[2] (1) pyrolysis of the lithium salt of the *p*-tosylhydrazone of adamantanone provides **1** in 65% yield and a 5% yield of adamantane,[3] (2) lithium aluminum hydride reduction of 2,4-diiodoadamantane gives **1** and adamantane in *ca.* 50–55 and 20–25% yields, respectively,[1] and (3) pyrolysis of 2-adamantyl methane- or toluene-*p*-sulfonate affords a mixture (3:2) of **1** and protoadamantene in 95% yield overall.[4] In each case, preparative glpc separation is required to obtain pure **1**.

In principle, **1** should be accessible by the Wolff–Kishner reduction of 8,9-dehydro-2-adamantanone (**2**).



2 **1**

(1) A. C. Udding, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 1345 (1968).
(2) 2,4-Dehydroadamantane has also been detected in the reaction mixture obtained in the deamination of 2-aminoadamantane by the phenyltriazine method: M. L. Sinnott, H. J. Storesund, and M. C. Whiting, *Chem. Commun.*, 1000 (1969).
(3) A. C. Udding, J. Strating, and H. Wynberg, *Chem. Commun.*, 657 (1966).
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