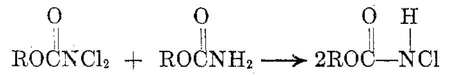
The usual method of preparation of **1** is reaction of equimolar quantities of chlorine with carbamate esters (**2**).[5–7] It was recognized only recently, however, that the reaction product is a mixture of **1** (major component), *N*,*N*-dichlorocarbamates (**3**) and unreacted **2**.[5] Analysis 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.



$$\mathrm{RO\overset{O}{\overset{\|}{C}}NCl_2 + RO\overset{O}{\overset{\|}{C}}NH_2 \longrightarrow 2RO\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}Cl}$$

6, R = C_2H_5 **7**, R = C_2H_5 **4**, R = C_2H_5
8, R = CH_3 **9**, R = CH_3 **5**, R = CH_3

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,) [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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[7] W. Traube and H. Gockel, *Chem. Ber.*, **56B**, 384 (1923).

[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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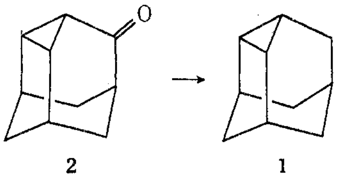
As the cyclopropane ring in 2,4-dehydroadamantane (**1**) can readily be opened by a variety of electrophilic reagents, **1** has proven to be a useful precursor for the synthesis of a variety of 2-substituted and 2,4-disubstituted adamantane derivatives.[1] Three syntheses of **1** have been reported:[2] (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**

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[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).

[4] J. Boyd and K. H. Overton, *J. Chem. Soc., Perkin Trans. 1*, 2533 (1972).

Although ring cleavage has been found to occur in the Wolff–Kishner reduction of one cyclopropyl ketone,[5] a number of strained cyclopropyl ketones have been successfully reduced to the corresponding hydrocarbons by this technique.[6] In contrast to these results, Baldwin and Foglesong have reported that attempts to convert **2** to **1** by Wolff–Kishner reduction were unsuccessful.[7] We have repeated this study and have found that treatment of **2** under the conditions of the normal Huang-Minlon modification of the Wolff–Kishner reduction[8] provides **1** as the only detectable product in 75% yield. In particular, it is to be noted that by glpc analysis neither protoadamantane nor adamantane could be detected in the material isolated from the reaction mixture.

Experimental Section

2,4-Dehydroadamantane (1).—A solution of 1.0 g of potassium hydroxide, 0.75 g of 95% hydrazine, and 188 mg (1.27×10^{-3} mol) of **2**[7] in 3 ml of diethylene glycol was heated with stirring at 110° for 30 min, and then for 3 hr at 180°. During this time, a white solid appeared on the water-cooled condenser. The system was cooled and the material on the condenser was dissolved in cyclohexane,[9] which was then dried over anhydrous magnesium sulfate and concentrated. Analysis by gas chromatography indicated the presence of a single product and no remaining starting material. Chromatography of this material on silica gel with heptane provided 128 mg (75%) of **1** which was identical in its physical (melting point and glpc retention time) and spectral (ir and pmr) properties with an authentic sample of 2,4-dehydroadamantane.[3]

Registry No.—**1,** 10501-16-3; **2,** 10497-56-0.

Acknowledgment.—This work was supported by grants from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Delaware Research Foundation.

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[5] S. M. Kupchan, E. Abushanab, K. T. Shamasundar, and A. W. By, *J. Amer. Chem. Soc.*, **89**, 6327 (1967).

[6] For examples see N. A. LeBel and R. N. Liesemer, *J. Amer. Chem. Soc.*, **87**, 4301 (1965); U. Biethan, U. v. Gizycki, and H. Musso, *Tetrahedron Lett.*, 1477 (1965); W. v. E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, 3943 (1967); S. A. Monti, *J. Org. Chem.*, **35**, 380 (1970).

[7] J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4303 (1968).

[8] R. L. Augustine, Ed., "Reduction Techniques and Applications in Organic Synthesis," Marcel Dekker, New York, N. Y., 1968, pp 171–185, and references cited therein.

[9] Extraction of the pot residue with cyclohexane provided negligible organic material.

4-Isocyanatophthalic Anhydride. A Novel Difunctional Monomer

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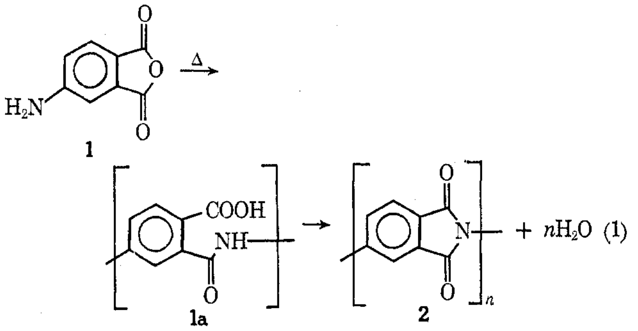
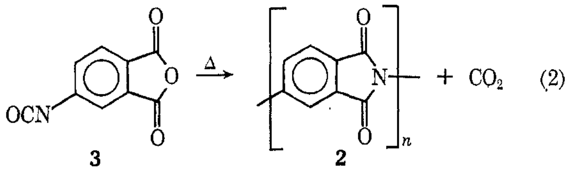
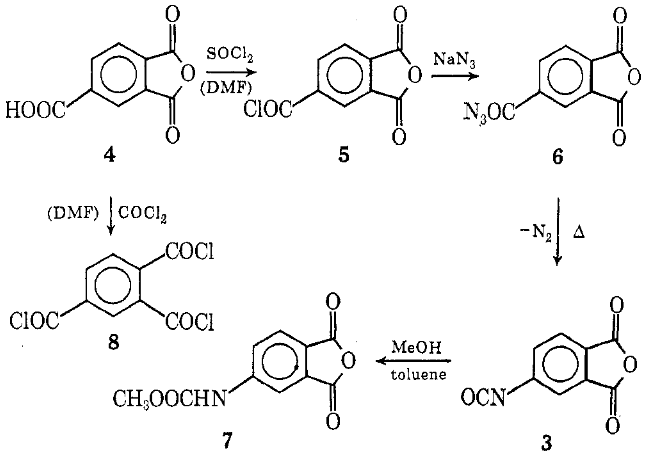
The incorporation of two different polymerizable groups into one molecule capable of undergoing a polycondensation reaction is an interesting concept because only one monomer is required to construct the macromolecule. Stoichiometric problems are eliminated and the purity of the monomers and possible side reactions determine the degree of polymerization achievable. For example, the polyimide **2** was prepared from 4-aminophthalic anhydride **1**[1] (eq 1).



Our interest in isocyanate chemistry prompted us to synthesize 4-isocyanatophthalic anhydride (**3**) a novel monomer having the isocyanato group as well as the anhydride group attached to the benzene ring. It has been previously shown that the reaction of a diisocyanate with a dianhydride produces polyimides with elimination of carbon dioxide.[2] This one-step method (eq 2) has advantages over the amine anhydride route (eq 1) because the complex[3] water elimination step from the intermediate polyamide acid **1a** is not required. The synthesis of **3** (Scheme I)



Scheme I



started with trimellitic anhydride (**4**) or the corresponding anhydride acid chloride **5**, both readily available raw materials. However, since the commerical **5** required purification, we preferred to prepare the material prior to use and found that treating **4** with thionyl chloride in the presence of catalytic

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[1] J. D. Seddon (ICI), British Patent 1,192,001 (1970); it was already observed by M. T. Bogert and R. R. Renshaw, *J. Amer. Chem. Soc.*, **30**, 1135 (1908), that heating of 4-aminophthalic anhydride resulted in loss of water.

[2] W. J. Farrissey, Jr., J. S. Rose, and P. S. Carleton, *J. Appl. Polym. Sci.*, **14**, 1093 (1970).

[3] C. K. Sauers, C. L. Gould, and E. S. Ioannou, *J. Amer. Chem. Soc.*, **94**, 8156 (1972).