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.

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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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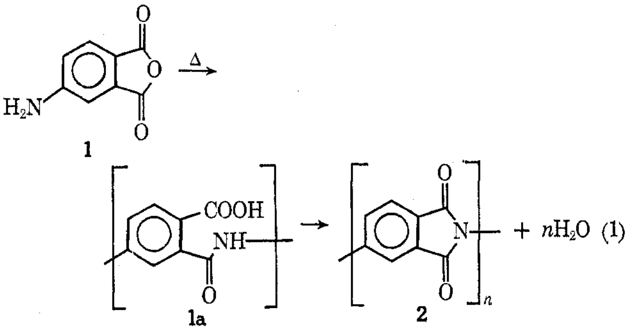
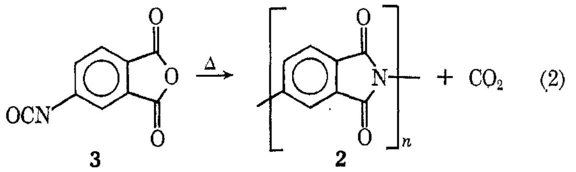
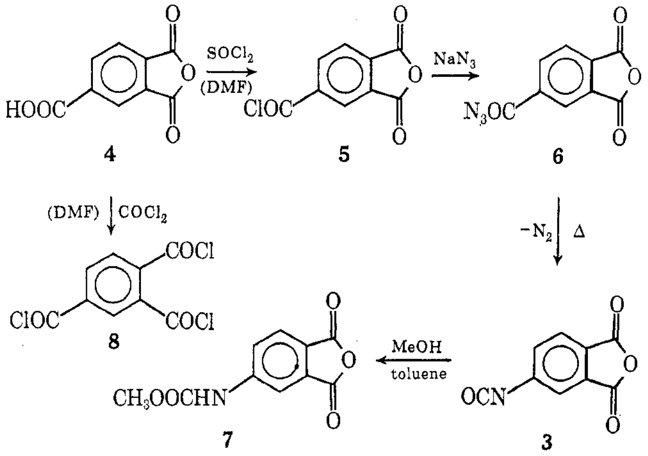
The incorporation of two different polymerizable groups into one molecule capable of undergoing a polycondensation reaction is an interesting concept because only one monomer is required to construct the macromolecule. Stoichiometric problems are eliminated and the purity of the monomers and possible 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) 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



Scheme I



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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).

amounts of *N,N*-dimethylformamide gave high yields of **5**. This compound was converted to the azide **6** by treatment with NaN_3 in acetone or acetonitrile, and on thermolysis (or photolysis) the isocyanatophthalic anhydride **3**, mp 80–82°, was obtained in high yield.

If carbonyl chloride was used instead of thionyl chloride in the conversion **4** to **5**, the trichloride **8** was formed in high yield. This method of synthesis of **8** is superior to the one described previously.[4]

The anhydride isocyanate **3** reacted selectively on the isocyanate group when treated with 1 equiv of methanol in toluene, giving the carbamate **7** in high yield. Studies to evaluate **3** or the more stable **7** as useful precursors of condensation polymers are underway.

Experimental Section

4-Chloroformylphthalic Anhydride (5).[4]—A suspension of 100 g (0.52 mol) of trimellitic anhydride in 100 g (0.85 mol) of thionyl chloride and 100 mg of *N,N*-dimethylformamide was stirred under reflux (bath temperature 115°) until the gas evolution ceased and a clear yellow solution was formed (2.0–2.5 hr). The excess thionyl chloride was removed under reduced pressure and vacuum distillation of the residue gave 105 g (96%) of **5**, bp 120–124° (0.1 mm), mp 69°.

4-Azidoformylphthalic Anhydride[5] **(6).**—To a solution of 10.2 g (0.048 mol) of freshly distilled 4-chloroformylphthalic anhydride in 60 ml of acetone, 3.25 g (0.05 mol) of sodium azide and 2 drops of triethylamine were added. The suspension was stirred rapidly at room temperature and the progress of the initially exothermic reaction was followed by ir (maximum absorption of the azide band at 2150 cm^{-1} with shoulder at 2200 cm^{-1} which occurred after approximately 2 hr). The precipitated sodium chloride was removed by filtration and the solvent was evaporated under vacuum, care being taken not to exceed a bath temperature of 50–55°.[6] Thus, 10.60 g (97%) of colorless needles of **6** were obtained, mp 100–103°.

Anal. Calcd for $C_9H_3N_3O_4$: C, 49.79; H, 1.39; N, 19.35. Found: C, 49.57; H, 1.32; N, 19.40.

4-Isocyanatophthalic Anhydride[5] **(3).**—To a solution of 31.5 g (0.15 mol) of 4-chloroformylphthalic anhydride in 100 ml of acetone, 11.3 g (0.175 mol) of sodium azide was added. After stirring for 2 hr at room temperature, 100 ml of toluene was added to the suspension, and the reaction flask was immersed in an oil bath and slowly heated to a bath temperature of 115°. During the heating period (1–2 hr) acetone was removed by distillation. Overheating and splashing of concentrated liquid onto hot surfaces of the apparatus has to be avoided because of the danger of explosion. After the evolution of nitrogen ceased the precipitated sodium chloride was removed by filtration, and the filtrate was evaporated under reduced pressure (bath temperature 60°). The crude product, 28.4 g (quantitative), mp 70–75°, can be purified by sublimation to give colorless crystals, mp 80–82°, ir (KBr) 2260 cm^{-1} (NCO).

Anal. Calcd for $C_9H_3NO_4$: C, 57.16: H, 1.60; N, 7.40. Found: C, 57.16; H, 1.49; N, 7.28.

4-Methylcarbamatophthalic Anhydride (7).—A solution of 4.8 g (0.15 mol) of methanol in 30 ml of toluene was added dropwise with stirring to a solution of 28.4 g (0.15 mol) of 4-isocyanatophthalic anhydride in 100 ml of toluene over a period of 15–20 min. The slightly exothermic reaction was controlled at 40–50°, and the reaction product precipitated as a yellow amorphous solid. Filtration and washing with diethyl ether gave 27.5 g (83%) of **7**, mp 150–154° dec.

Anal. Calcd for $C_{10}H_7NO_5$: C, 54.30; H, 3.19; N, 6.33. Found: C, 53.97; H, 3.07; N, 6.03.

1,2,4-Benzenetricarboxylic Acid Trichloride (8).—A suspension of 50 g (0.26 mol) of trimellitic anhydride in 250 ml of benzene containing 100–200 mg of *N,N*-dimethylformamide was heated to 65° and carbonyl chloride was added until a clear yellow solution was obtained (approximately 90 min). Excess carbonyl chloride was removed with nitrogen and vacuum distillation yielded 60.4 g (87%) of **8**, bp 124° (0.1 mm) [lit.[4] bp 143–148° (3 mm)].

Anal. Calcd for $C_9H_3Cl_3O_3$: C, 40.72; H, 1.14; Cl, 40.06. Found: C, 40.51; H, 1.06; Cl, 39.2.

Registry No.—**3**, 40139-36-4; **4**, 552-30-7; **5**, 1204-28-0; **6**, 40139-39-7; **7**, 40139-40-0; **8**, 3867-55-8; sodium azide, 12136-89-9; thionyl chloride, 7719-09-7; carbonyl chloride, 75-44-5.

[4] G. Drechsler and S. Heidenreich, *J. Prakt. Chem.*, **27**, 152 (1965).

[5] *Caution!* All reactions involving azides should be carried out behind safety shields.

[6] Impure samples of azide, obtained by using undistilled acid chloride in the reaction, decomposed sometimes spontaneously during the drying process.

Photochemical Deconjugation as a Synthetic Route to 1,2,3,6-Tetrahydropyridine-4-acetic Acid Esters from $\Delta^{4,\alpha}$-Piperidine-4-acetic Acid Esters[1]

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The Wittig reaction employing carbalkoxymethylphosphonates makes esters of $\Delta^{4,\alpha}$-piperidine-4-acetic acids readily available from the corresponding substituted 4-piperidones.[2] These α,β-unsaturated esters can subsequently be converted to the endocyclic isomers by acid- or base-catalyzed equilibration.[2a–f] We report here that photochemical deconjugation[3] constitutes an alternative method for effecting this transformation and that the photochemical method often has the advantage of effecting complete conversion in contrast to the catalytic equilibration procedures.

Ethyl 1-methyl-$\Delta^{4,\alpha}$-piperidine-4-acetate (**1a**) can be prepared in good yield from 1-methyl-4-piperidone.[2b] The compound is isomerized by base or heat to a mixture of **1a** and **2a**. A 4:7 mixture was obtained on isomerization with sodium ethoxide[2f] while a 25:75 mixture was obtained by the thermal method.[2b] The conversion to pure **2a** is 36% in the base-catalyzed method. Irradiation of **1a** in methanol or ethanol effected complete conversion to **2a**, identified by spectral data. The most informative spectral change which accompanies the isomerization is a shift in the carbonyl frequency from 1715 cm^{-1} for **1a** to 1740 cm^{-1} for **2a**. In the nmr spectrum, the singlet at δ 5.62 due to the exocyclic vinyl hydrogen is replaced by a broad unresolved multiplet at δ 5.5. The *N*-benzyl analog **1b** was isomerized to **2b** under similar conditions

[1] Supported by NSF Grant GP-19374 and NCI Grant 12940.

[2] (a) R. J. Sundberg, W. V. Ligon, Jr., and L.-S. Lin, *J. Org. Chem.*, **36**, 2471 (1971); (b) L. D. Quin, J. W. Russell, Jr., R. D. Prince, and H. E. Shook, Jr., *ibid.*, **36**, 1495 (1971); (c) R. J. Sundberg and F. O. Holcombe, Jr., *ibid.*, **34**, 3273 (1969); (d) N. Whittaker, *J. Chem. Soc. C*, 94 (1969); (e) H. T. Openshaw and N. Whittaker, *J. Chem. Soc.*, 1461 (1963); (f) R. F. Borne and H. Y. Aboul-Enein, *J. Heterocycl. Chem.*, **9**, 869 (1972); (g) C. Szantay, L. Töke, and P, Kolonits, *J. Org. Chem.*, **31**, 1447 (1966); (h) S. Sugasawa and H. Matsuo, *Chem. Pharm. Bull.*, **8**, 819 (1960); (i) F. O. Holcombe, Ph.D. Thesis, University of Virginia, 1971.

[3] For studies of the synthetic utility of photochemical deconjugation in aliphatic systems see (a) R. R. Rando and W. v. E. Doering, *J. Org. Chem.*, **33**, 1671 (1968). For mechanistic studies see (b) J. R. Scheffer and B. A. Boire, *J. Amer. Chem. Soc.*, **93**, 5490 (1971); (c) M. J. Jorgenson, *ibid.*, **91**, 198 (1969); (d) J. A. Barltrop and J. Wills, *Tetrahedron Lett.*, 4987 (1968); (e) M. J. Jorgenson and L. Gundel, *ibid.*, 4991 (1968); (f) R. Noyori, H. Inoue, and M. Kato, *J. Amer. Chem. Soc.*, **92**, 6699 (1970); (g) J. K. Crandall and C. F. Mayer, *J. Org. Chem.*, **35**, 3049 (1970); P. J. Kropp and H. J. Krauss, *ibid.*, **32**, 3222 (1967).