

Conversion of Cyclohexyl Cyanide to Cyclohexylcarboxamide. A three-neck flask fitted with two addition tubes,¹⁷ a two-way stopcock, and a magnetic stirrer was employed. The system was swept with dry air while being assembled, and a positive pressure of dry air was maintained throughout the reaction. One addition tube contained 1.78 g (ca. 32 mmol) of 90+% sodium superoxide (Alfa Inorganics), which had been powdered in a mortar and pestle under dry nitrogen in a glove bag and then transferred to the tared tube in the glove bag. The other addition tube held 1.0 g (9.2 mmol) of cyclohexyl cyanide. Finally, 15 mL of Me₂SO¹⁸ (dried by standing over type 4A molecular sieves) was placed in the flask. Stirring was instituted, the nitrile was added to the Me₂SO without opening the flask,¹⁷ and after it had dissolved the NaO₂ was introduced. The resulting mixture was stirred for 7 h at room temperature, after which it was poured into ice-water and extracted with ethyl acetate. The ethyl acetate solution was washed with water and dried (anhydrous Na₂SO₄), and the solvent was removed by vacuum evaporation at room temperature; this gave 0.980 g of white crystals, mp 178–182 °C. Recrystallization from water gave 0.93 g (85% yield) of pure cyclohexylcarboxamide: mp 186–187 °C (lit.¹⁹ mp 185–186 °C); IR (KBr) 3340, 3180, 1630 cm⁻¹.

Conversion of Mesitronitrile to Mesitamide. This was carried out as in the cyclohexyl cyanide case using 10 mL of Me₂SO, 1.0 g (7 mmol) of mesitronitrile, and 1.3 g (ca. 23 mmol) of the 90+% NaO₂. The resulting mixture was stirred for 7 h and then poured into ice-water. Dry ice was added to reduce the alkalinity, and when the solid CO₂ was gone the mixture was extracted with chloroform. The chloroform extracts were washed with water and dried, and the solvent was removed by vacuum evaporation. The resulting pale yellow solid (1.0 g) melted from 100 to 177 °C. It was dissolved in acetone and treated with Norite at the boiling point for several minutes, the mixture was filtered, and the solvent was evaporated. The resulting white solid (mp 103–180 °C; 0.95 g) was leached several times with cold water, and the aqueous extracts were vacuum evaporated at ca. 35 °C. This gave 0.1 g of white crystalline dimethyl sulfone, mp 105–108 °C (lit.²⁰ mp 107–108 °C). This material exhibits IR and NMR spectra identical with those reported for dimethyl sulfone.²¹ This was the only case in which chloroform was used for extraction and the only time that Me₂SO₂ was isolated.

The water-insoluble material was dried and recrystallized from benzene and 0.3 g (73% yield) of mesitamide (mp 186–188 °C) was obtained: lit.²² mp 187–188 °C; IR (KBr) 3400, 3260, 3180, 1640 cm⁻¹.

Conversion of *p*-Cyano- α -nitrocumene to *p*-Carboxamido- α -nitrocumene. The procedure was that of the cyclohexyl cyanide case except that this was one of the first systems studied, thus dry oxygen was employed instead of dry air and the reaction vessel was exposed to two 20-W fluorescent lights. Ten milliliters of Me₂SO, 0.5 g (2 mmol) of the nitrile, and 0.65 g (ca. 11 mmol) of NaO₂ were allowed to react at room temperature for 5 h. Workup gave 0.4 g of a white solid, mp 150–155 °C, which was recrystallized from benzene: 0.37 g (68% yield); mp 155–156 °C; NMR (Me₂SO-*d*₆) δ 1.95 (s, 6 H), 3.3 (s, 2 H), 7.35–7.95 (m, 4 H); IR (KBr) 3300, 3200, 1660, 1610, 1520, 1340, 850, 790 cm⁻¹.

Anal. Calcd for C₁₀H₁₂N₂O₃: C, 57.68; H, 5.80; N, 13.45. Found: C, 57.65; H, 5.56; N, 13.30.

Conversion of Methyl Laurate to Lauric Acid. Here again, an oxygen atmosphere and two 20-W fluorescent lights were employed; it is highly probable that they are not needed. Otherwise the procedure was the same as that used for cyclohexyl cyanide. A mixture consisting of 2 g (9 mmol) of methyl laurate, 1.4 g (ca. 27 mmol) of NaO₂, and 30 mL of Me₂SO was stirred at room temperature for 3 h. The product was poured into ice-water and then sodium laurate was isolated by filtration. It

was suspended in water, and the mixture was acidified with 25% hydrochloric acid; the lauric acid was isolated by filtration, washed with water, and dried: 1.65 g (91% yield), mp and mmp 44–45 °C (lit.²³ mp 44 °C).

The Influence of Nitrobenzene. The reaction of *p*-methoxycyanobenzene in the presence of 50 mol % of nitrobenzene is typical of the experiments summarized in Table II. The procedure used for cyclohexyl cyanide was followed except that 0.54 mL (50 mol %) of nitrobenzene was introduced after the NaO₂. The initially yellow suspension gradually became brown. After 2 h at room temperature, the reaction mixture was worked up in the usual way. The pale yellow solid (1.67 g) so obtained melts from 48–152 °C. It was washed with pentane and recrystallized from benzene. This gave 0.5 g of pale yellow crystals, mp 165–167 °C, which after being dissolved in acetone and treated with Norite gave white crystals of *p*-methoxybenzamide (0.49 g; 32% yield), mp 167–168 °C. The benzene mother liquor on evaporation yielded 0.79 g of material which was dissolved in acetone and treated with Norite. The 0.63 g of yellow solid so obtained had mp 55–59 °C. It was dissolved in benzene and chromatographed on silica gel. In this way 0.59 g (42% recovery) of white, crystalline *p*-methoxybenzamide, mp 57–59 °C, was obtained.

Acknowledgment. We thank the National Science Foundation for generous support.

Registry No. *n*-Undecyl cyanide, 2244-07-7; cyclohexyl cyanide, 766-05-2; benzonitrile, 100-47-0; isophthalonitrile, 626-17-5; *o*-chlorobenzonitrile, 873-32-5; *m*-methoxybenzonitrile, 1527-89-5; *p*-methoxybenzonitrile, 874-90-8; *p*-cyano- α -nitrocumene, 58324-82-6; 2,6-dichlorobenzonitrile, 1194-65-6; mesitronitrile, 2571-52-0; ethyl *p*-cyanobenzoate, 7153-22-2; *n*-undecylamide, 2244-06-6; cyclohexylcarboxamide, 1122-56-1; benzamide, 55-21-0; isophthalamide, 1740-57-4; *o*-chlorobenzamide, 609-66-5; *m*-methoxybenzamide, 5813-86-5; *p*-methoxybenzamide, 3424-93-9; *p*-carboxamido- α -nitrocumene, 71648-09-4; 2,6-dichlorobenzamide, 2008-58-4; mesitamide, 4380-68-1; *p*-carboxamidobenzoic acid, 6051-43-0; terephthalic acid, 100-21-0; dimethyl terephthalate, 120-61-6; methyl laurate, 111-82-0; lauric acid, 143-07-7; methyl myristate, 124-10-7; myristic acid, 544-63-8; dimethyl sulfone, 67-71-0; sodium superoxide, 12034-12-7.

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Tetracyclopropylethylene Glycol

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Received June 11, 1979

As part of our interest in cyclopropyl chemistry, we have prepared tetracyclopropylethylene glycol.¹⁻³ While the diol has been reported,⁴ no synthetic procedure is available, although it was probably prepared from tetracyclopropylethylene. The latter has been reported from at least three routes, each of which is either long and tedious^{5,6} (six steps from dicyclopropyl ketone), produces a mixture of products⁷ (the pyrolysis of the tosylhydrazone salt of dicyclopropyl ketone gives five products), or gives low yields (6% overall,^{5,6} 11%,^{7,8} 7%⁹).

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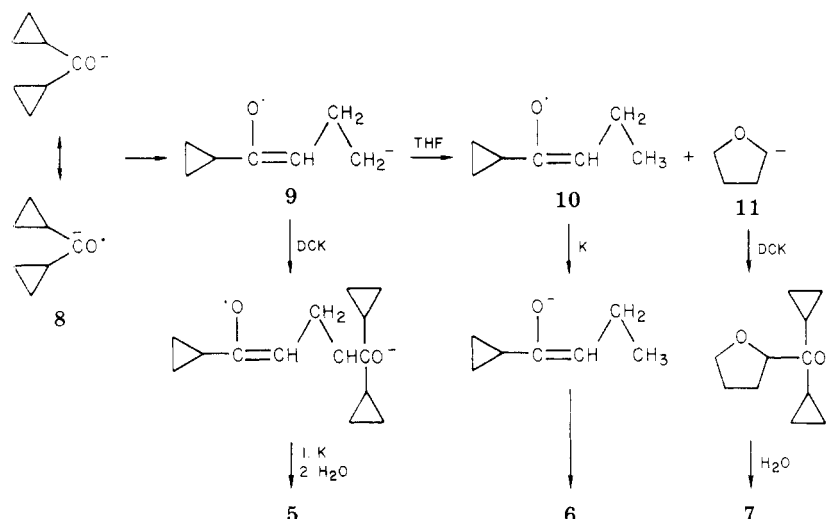
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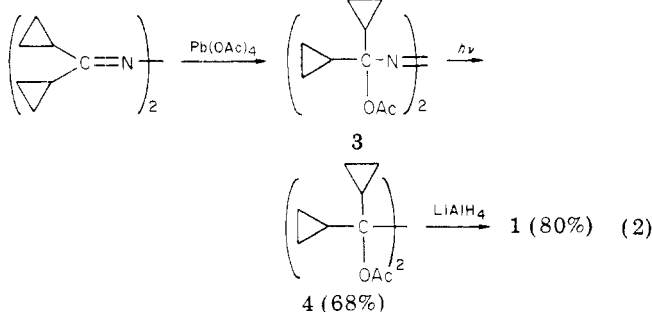
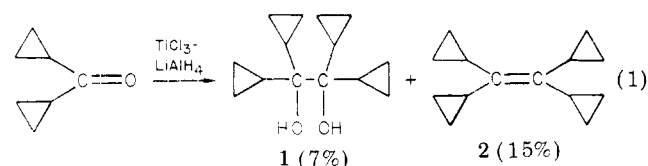
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Scheme I



The two successful methods¹⁰ for preparation of tetracyclopropylethylene glycol are shown in eq 1 and 2. The



coupling of dicyclopropyl ketone (DCK) with McMurry reagent¹¹ gives glycol 1 and olefin 2, which are easily separated by chromatography in 7 and 15% yields. The ethylene is readily converted into the glycol. The alternative method involves conversion of DCK to azine¹² and the latter in turn to azo diacetate¹³ 3. The deazotization of 3 was accomplished by solid state irradiation of 3 (Pyrex, 450 W Hanovia) at 25 °C. Irradiation of 3 in benzene under identical conditions gives no nitrogen evolution either by direct irradiation or by sensitization. We have not further investigated the inertness of 3 in solution but note that under these conditions light is undoubtedly being absorbed (3, λ_{max} 360 nm) and that normally diazenes of this type are photochemically quite labile.¹⁴⁻¹⁶ The re-

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Table I. Rate of Decomposition of Bis(1,1-dicyclopropyl-1-acetoxymethyl)diazene in Diphenyl Ether by Nitrogen Evolution¹⁷

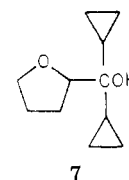
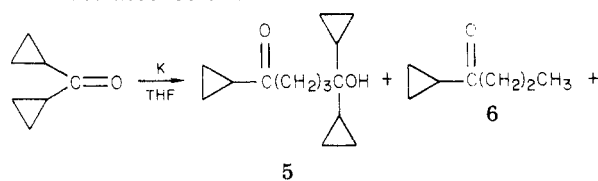
temp, °C	$k \times 10^4$, s ⁻¹	temp, °C	$k \times 10^4$, s ⁻¹
143.7	1.23	163.7	7.13
155.0	3.32	171.0	16.2
160.0	6.50	174.5	21.0

$$\Delta H^\ddagger = 33.9 \pm 1.3 \text{ kcal/mol}; \Delta S^\ddagger = 4.1 \pm 3.2 \text{ eu}$$

duction of the coupled diacetate proceeds smoothly and in good yield to tetracyclopropylethylene glycol (1).

The thermal behavior of bis(1-acetoxy-1,1-dicyclopropylmethyl)diazene (3) is as expected, and it extrudes nitrogen. However, the products, as analyzed by NMR, show considerable ring opening. The first order rates of decomposition are listed in Table I,¹⁷ and the results are in accord with earlier studies on rate enhancements in formation of cyclopropylcarbinyl radicals.^{2,18} The rate acceleration of 3 over the corresponding tetramethyl derivative at 150 °C is a factor of 180.² This compares favorably with the relative rate difference of 240 for the corresponding azo dinitrile series $[(\text{C}_3\text{H}_5)_2\text{C}(\text{CN})\text{N}=\text{N}]_2$ vs. $[(\text{CH}_3)_2\text{C}(\text{CN})\text{N}=\text{N}]_2$ reported some years ago¹⁸ and supports the belief that cyclopropyl groups stabilize radicals.

While an attempt to prepare tetracyclopropylethylene glycol by reaction of DCK with potassium metal was not synthetically useful, it is interesting in its own right and is illustrated below.



Even though no evidence has been obtained for any of the

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intermediates illustrated in the speculative sequence shown below (Scheme I), they account for the products as illustrated. Compounds 5 and 7 are suggestive of carbanion attack (9 and 11) on DCK, and as such we prefer to represent the ring opened radical anion 9 with negative charge on carbon rather than oxygen. Furthermore, the lack of coupling of DCK ketyl (8) or ring opened ketyl (9) is also indicative, since the radical formed from hydrogen abstraction from dicyclopropylcarbinol has been reported to ring open and dimerize to give 1,8-dicyclopropyl-1,8-octanedione.¹⁹

Experimental Section

Reaction of Dicyclopropyl Ketone with $\text{TiCl}_3\text{-LiAlH}_4$. A slurry of 25 g of $\text{TiCl}_3\text{-LiAlH}_4$ (McMurry reagent Alfa) in 150 mL of dry THF under nitrogen was stirred from 1.5 h at 0 °C, during which a black suspension formed. Dicyclopropyl ketone, 10 g (91 mmol) in 25 mL of THF, was added dropwise over 2 h, and stirring was continued for 2 days at 45 °C. The excess TiCl_3 reagent was destroyed by careful addition of 200 mL of 0.1% NaOH solution followed by extraction with ether, drying (MgSO_4), and concentration. Chromatography on silica gel gave 2.5 g (15%) of tetracyclopropylethylene (2) [NMR (CDCl_3) δ 0.10–0.80 (m, 16 H) and 1.10–1.70 (m, 4 H)] and 1.5 g (7%) of tetracyclopropylethylene glycol (1) [mp (hexane) 44–45 °C; NMR (CDCl_3) δ 0.10–0.60 (m, 16 H), 0.80–1.20 (m, 4 H), and 1.69 (s, 2 H); IR 3580 and 3250–3550 cm^{-1}].

Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_2$: C, 75.63; H, 9.97. Found: C, 75.41; H, 9.92.

Solid State Photolysis of Bis(1,1-dicyclopropyl-1-acetoxymethyl)diazine (3). Finely ground azoacetate 3¹³ (200 mg) was spread out on the surface of a glass plate, covered with a watch glass, and irradiated for 14 h at room temperature through a Pyrex cooling jacket with a 450W Hanovia lamp located 5 cm from the sample. Recrystallization from hexane gave 125 mg (68%) of diacetate 4: mp 159–161 °C; NMR (CDCl_3) δ 0.30–0.70 (m, 16 H), 1.10–1.68 (m, 4 H), and 1.81 (s, 6 H); IR 1740 cm^{-1} .

Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{O}_4$: C, 70.54; H, 8.57. Found: C, 70.36; H, 8.55.

Tetracyclopropylethylene Glycol. To 0.1 g of LiAlH_4 dissolved in 10 mL of ether at 0 °C was added dropwise 50 mg (16 mmol) of diacetate 4 in 5 mL of ether. The mixture was refluxed for 6 h. Excess LiAlH_4 was destroyed by the addition of 0.1% NaOH solution. Extraction, drying (MgSO_4), concentration, and recrystallization from hexane gave 29 mg (80%) of tetracyclopropylethylene glycol identical with that obtained as above.

Reaction of Dicyclopropyl Ketone with Potassium. To 50 mL of dry THF cooled at 0 °C was added 12.0 g (0.3 g-atom) of freshly cut potassium. Dicyclopropyl ketone, 8.0 g (73 mmol) in 25 mL of THF, was added dropwise. Stirring was continued for 12 h at room temperature, after which the unreacted potassium was removed and the mixture poured onto crushed ice and extracted with ether. The ether extracts were washed with water, dried (MgSO_4), and concentrated in vacuo. Distillation of the residue gave three fractions identified as: *n*-propyl cyclopropyl ketone (6), 1.1 g (14%), bp 32–34 °C (3 mm), NMR (CDCl_3) δ 0.75–1.15 (m, 7 H), 1.35–2.13 (m, 3 H), and 2.40–2.65 (t, 2 H); IR 1690 cm^{-1} ; semicarbazone mp 117.5–118.5 °C.

Anal. Calcd for $\text{C}_7\text{H}_{12}\text{O}$: C, 74.95; H, 10.52. Found: C, 74.75; H, 10.57.

α,α -Dicyclopropyltetrahydrofurfuryl alcohol (7): 0.5 g (6%); bp 79–81 °C (3 mm); NMR (CDCl_3) δ 0.20–0.64 (m, 8 H), 0.70–1.10 (m, 2 H), 1.70–2.15 (m, 5 H), and 2.72–4.00 (m, 3 H); IR 3350–3700 cm^{-1} ; mass spectra, *m/e* 182.

Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}_2$: C, 72.49; H, 9.95. Found: C, 72.32; H, 9.95.

1-Hydroxy-1,1,5-tricyclopropyl-5-pentanone (5) (4.2 g, 53%): bp 129–130 °C (3 mm); NMR (CCl_4) δ 0.13–0.51 (m, 8 H), 0.53–1.05 (m, 6 H), 1.24–2.10 (m, 6 H), and 2.37–2.67 (t, 2 H); IR 3300–3650 and 1670 cm^{-1} ; mass spectra, *m/e* 222.

Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_2$: C, 75.63; H, 9.97. Found: C, 75.37; H, 9.87.

Acknowledgment. The authors wish to acknowledge Professor J. C. Martin under whose direction a portion of this work originated and who either graciously or wisely rejects coauthorship.

Registry No. 1, 37614-40-7; 2, 23534-93-2; 3, 15813-21-5; 4, 71838-23-8; 5, 71838-24-9; 6, 6705-46-0; 7, 71838-25-0; dicyclopropyl ketone, 1121-37-5.

Copper-Catalyzed Nonaqueous Ammonolysis of *p*-Chlorobenzotrifluoride. Effect of Potassium Fluoride¹

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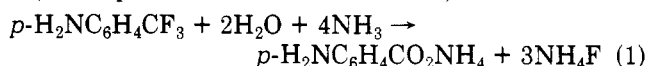
Received February 27, 1979

The reaction of aromatic halides with ammonia to give the corresponding anilines is usually run in aqueous ammonia at elevated temperatures and pressures and, frequently, in the presence of a copper catalyst.² Organic solvents are generally not used for this reaction because of lower ammonia solubility and possible solvent reactivity.^{2b} Consequently, ammonolyses involving hydrolytically unstable aromatics can be difficult. This paper describes the ammonolysis of *p*-chlorobenzotrifluoride (1) to the hydrolytically unstable *p*-aminobenzotrifluoride (2).

The literature discloses four routes for the synthesis of *p*-aminobenzotrifluoride (2). The bromination of *p*-nitrotoluene to *p*-nitrobenzotribromide followed by reaction with SbF_3 and subsequent reduction is reported to give 2 in about 50% yield.^{3a} The reaction of SF_4 with either *p*-nitrobenzoic acid^{3b} or *p*-aminobenzoic acid^{3c} provides a route to 2. *N*-(*p*-Tolyl)phthalimide gives 10–40% yield of 2 upon chlorination, fluorination, and hydrolysis with hydrazine.^{3d} A potentially more direct route to 2 is the ammonolysis of commercially available *p*-chlorobenzotrifluoride (1).

Results and Discussion

Conventional ammonolysis catalysts and conditions gave very low yields and conversions to 2. In aqueous NH_3 with cobalt, nickel, or copper catalysts, the reduction of 1 to benzotrifluoride is the predominate reaction (Table I). The $\text{CaO/Cu}_2\text{Cl}_2$ combination catalyzes ammonolysis, but the product is hydrolyzed to aniline via reactions 1 and 2 (see Experimental Section and ref 4).



Hydrolysis of 2 does not occur in nonaqueous solvents (see Experimental Section), but attempts to ammonolyze 1 using existing technology gave disappointingly low conversions and yields.⁵ A combination of Cu_2Cl_2 and KF

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