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 $TiCl_3$–$LiAlH_4$. A slurry of 25 g of $TiCl_3$–$LiAlH_4$ (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 $C_{14}H_{22}O_2$: 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 **3**[13] (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 $C_{18}H_{26}O_4$: 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 $C_7H_{12}O$: 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 $C_{11}H_{18}O_2$: 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 $C_{14}H_{22}O_2$: 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.

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[19] D. C. Neckers and A. P. Schaap, *J. Org. Chem.*, **32**, 22 (1967).

Copper-Catalyzed Nonaqueous Ammonolysis of *p*-Chlorobenzotrifluoride. Effect of Potassium Fluoride[1]

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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 CaO/Cu_2Cl_2 combination catalyzes ammonolysis, but the product is hydrolyzed to aniline via reactions 1 and 2 (see Experimental Section and ref 4).

$$p\text{-}H_2NC_6H_4CF_3 + 2H_2O + 4NH_3 \rightarrow p\text{-}H_2NC_6H_4CO_2NH_4 + 3NH_4F \quad (1)$$

$$p\text{-}H_2NC_6H_4CO_2NH_4 \rightarrow C_6H_5NH_2 + CO_2 + NH_3 \quad (2)$$

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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[1] L. P. Seiwell, U.S. Patent 4096185 (1978).

[2] (a) A. J. Quick, *J. Am. Chem. Soc.*, **42**, 1033 (1920); (b) P. H. Groggins and W. V. Wirth in "Unit Processes in Organic Synthesis", 5th ed., P. H. Groggins, Ed., McGraw-Hill, New York, 1958, Chapter 8; (c) Kirk-Othmer "Encyclopedia of Chemical Technology", Vol. 2, 2nd ed., Wiley, New York, 1963, pp 332–373; (d) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951).

[3] (a) R. G. Jones, *J. Am. Chem. Soc.*, **69**, 2346 (1947); (b) W. R. Hasek, W. C. Smith, and V. A. Englehardt, *ibid.*, **82**, 543 (1960); (c) M. S. Raasch, *J. Org. Chem.*, **27**, 1406 (1962); (d) E. J. Forbes et al., *Tetrahedron*, **8**, 67 (1960); U.S. Patents 2087715 and 2093115.

Table I. Aqueous Ammonolysis of *p*-Chlorobenzotrifluoride[a]

catalyst	other (g)	% conversion	% yield[b]		
			p-$H_2NC_6H_4CF_3$	$C_6H_5CF_3$	$C_6H_5NH_2$
$CoCl_2 \cdot 6H_2O$		17	<1	85	14
$Ni(acac)_2$		11	<1	80	3
$CuCl_2$		13	0	83	15
Cu_2Cl_2		20	<1	86	13
Cu_2Cl_2	Cu^0 (0.3)	36	0.5	78	20
Cu_2Cl_2	CaO (1.5)	25	1.3	5.9	81
Cu_2Cl_2	Cu^0 (0.3) CaO (1.5)	31	0.9	6.9	79

[a] The reactions were run in 80-mL Hastelloy shaker tubes charged with 4 mL (29 mmol) of **1**, 28 mL of 28% aqueous ammonia, and 0.3 g of catalyst for 2 h at 240 °C. Analysis of product solutions was by GC. [b] Other products included phenol, bis(trifluoromethyl)biphenyls, and *m*-aminobenzotrifluoride (ammonolysis product of the *m*-chlorobenzotrifluoride impurity present in the starting material).

Table II. Nonaqueous Ammonolysis of *p*-Chlorobenzotrifluoride[a]

no.	wt, mg			solvent	% conversion	% yield[b]	
	Cu_2Cl_2	KF	NH_3			2	4
1[c]	27.1	0	786	C_2H_5OH	21.9	49.7	44.8
2[c]	25.7	244	769	C_2H_5OH	67.4	79.4	17.4
3	31.9	0	883	CH_3OH	15.6	60.3	39.7
4	29.6	208	829	CH_3OH	40.6	75.8	24.2
5[c]	0	268	891	C_2H_5OH	1.2	13.4	84.8
6	9.0	250	795	C_2H_5OH	11.0	85.2	3.5
7	17.0	250	795	C_2H_5OH	19.6	86.5	7.6
8	36.1	250	795	C_2H_5OH	43.2	85.6	12.0
9	49.7	250	795	C_2H_5OH	51.4	83.7	14.3
10	21.0	125	879	CH_3OH	32.8	79.7	20.3
11	20.5	285	887	CH_3OH	30.2	76.4	23.6
12	21.5	540	890	CH_3OH	29.0	67.1	32.8

[a] The reactions were run in sealed glass tubes containing 0.33 g of **1** and 1.3 g of solvent at 200 °C for 5 h unless noted otherwise. [b] *p*-Aminobenzamide accounts for the remainder of the yield. [c] Reaction time of 10 h.

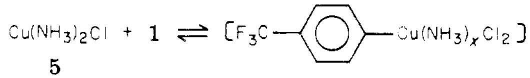
in ethanol gave strikingly improved results over conventional technology. The dramatic effect of this combination is illustrated by the results shown in Table II. The overall conversion to **2** is improved up to fivefold with the addition of KF (compare numbers 1 and 2, Table II). With optimum conditions, conversions greater than 40% and yields of 75–90% are consistently obtained (Table II, numbers 2 and 9). The success of this unusual combination seems to result from transitory formation of *p*-fluorobenzotrifluoride (**3**), which reacts with ethanolic NH_3 even in the absence of a catalyst.

The ammonolysis reaction is best run at 170–200 °C for 5 h. Increasing the concentration of KF has little effect on the reaction (Table II, numbers 10–12). A copper catalyst is essential (Table II, number 5), and the rate of ammonolysis is proportional to the concentration of Cu_2Cl_2 (Table II, numbers 6–9). Other copper catalysts, in approximate order of decreasing reactivity, are: $Cu_2Cl_2 \simeq Cu_2Br_2 \simeq$ the copper acetates $> Cu_2Cl_2 + CuCl_2 \simeq Cu_2I_2 \simeq CuCl_2(CH_3CN)_2 > CuSO_4 \simeq CuCl_2$. The copper oxides and cuprous cyanide are inactive as are iron, cobalt, and nickel compounds.

Suitable solvents for this reaction include: alcohols, C_6H_5CN, CH_3CN, and $HOCH_2CH_2OCH_3$. Reaction also occurs in the absence of a solvent, i.e., in **1**. Very low conversions are obtained in $HOCH_2CH_2OH$, $C_2H_5(OCH_2CH_2)_2OC_2H_5$, C_6H_6, $C_6H_5CH_3$, and *p*-dioxane.

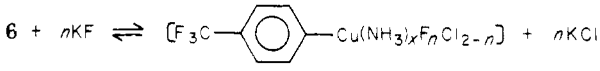
The major yield loss is conversion of **2** to *p*-cyanoaniline (**4**). Cuprous chloride catalyzes and KF promotes the conversion of **2** to **4**. Also, the rate of **4** formation is competitive with the rate of ammonolysis (see Experimental Section). Thus, a balance must be reached between high yields of **2** and low conversions of **1**.

The initial step in a possible mechanism for this reaction may be formation of a copper(I) amine chloride, $Cu(NH_3)_2Cl$ (**5**).[6] Subsequent oxidative addition of **1** to **5** (eq 3) would generate the Cu(III) species **6**, which is similar



(3)

5 **6**



(4)

7

$n = 1$ or 2

to intermediates proposed by Cohen.[8] Fluoride ion exchange for Cl^- in **6** (eq 4) followed by reductive elimination would give either **2** directly or **3**, which reacts readily with ethanolic NH_3.[7] KF has no effect on the ammonolysis of **3**. Electron donation by NH_3 would stabilize Cu(III) in **6** analogous to the role postulated by Cohen for NH_3 in Ullman-type couplings.[8]

In addition to promoting the formation of **3**, KF may also increase the nucleophilicity of NH_3 by hydrogen

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(4) D. N. Kozachuk, Yu. A. Fialkov, and L. M. Yagupol'skii, *Zh. Org. Khim.*, 7, 1906 (1971); *J. Org. Chem. USSR*, (*Engl. Transl.*), 7, 1976 (1971); (b) R. Grinter et al., *Tetrahedron Lett.*, 3845 (1968); (c) C. G. Moreland and C. L. Bumgardner, *J. Magn. Reson.*, 4, 20 (1971), and ref 2a.

(5) Solvents used included CH_3OH, C_2H_5OH, CH_3CN, C_6H_6, glycols, dioxane, DMF, and acetone. Various reaction conditions (200–300 °C for 2–10 h), copper catalysts (Cu_2Cl_2, $CuCl_2$, Cu^0), NH_3 pressures, and promoters (CaO, PPh_3, $P[OPh]_3$) were also examined. Conversions to **2** were less than 10%.

(6) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Wiley, New York 1972.

(7) Ammonolysis of **3** with ethanolic NH_3 at 200 °C in the absence of a catalyst gives 30–40% conversions and >90% yield of **2**.

(8) T. Cohen and J. G. Tirpak, *Tetrahedron Lett.*, 143 (1975); T. Cohen, J. Wood, and A. G. Dietz, Jr., *ibid.*, 3555 (1974).

bonding.[9] Potassium acetate, which provides a strong hydrogen-bonding anion, also shows some promoting effect in this reaction. The absence of **3** in product solutions suggests its formation is rate limiting. However, the use of KBr in place of KF gives both p-$BrC_6H_4CF_3$ and **2**.

The conversion of **2** to **4** likely occurs by a mechanism involving ammonolysis of the CF_3 substituent to give p-$H_2NC_6H_4CF_2NH_2$. Subsequent elimination of HF would generate **4**.[10]

Experimental Section

Materials. All reagents were commercially available and used without further purification. Anhydrous KF was handled under N_2 to prevent deliquescence. Precautions were taken to prevent oxidation of cuprous chloride.

Ammonolysis of *p*-Chlorobenzotrifluoride. Two procedures were used for the ammonolysis reactions. For the first procedure, an 80-mL Hastelloy shaker tube was charged with reactants, catalysts, and promoters. The tube was chilled to −80 °C, evacuated, and, if desired, additional gas added prior to heating for a specified time. After reaction, the tube contents were removed and analyzed by GC or GC/mass spectrometry. The second, and most frequently used, procedure is similar to that described by Cramer.[11] The reaction components were charged by weight to matched glass tubes (internal volume of 4.8–6.0 mL). Ammonia was condensed into the chilled, evacuated tubes, using standard vacuum line techniques, and the tubes were sealed. A 400-mL autoclave was charged with the tubes (usually five) with ethanol (as the heat transfer fluid) and N_2 (for external pressure) and heated with agitation for the specified time.

After reaction, the glass tubes were chilled, opened, and stoppered with a rubber septum containing a hollow needle through which the ammonia distilled as the tubes warmed to room temperature. The tube contents were then quantitatively transferred to 25-mL volumetric flasks with carrier solution (79.7% cyclopentane, 20% chloroform, and 0.3% morpholine) for analysis by high-pressure liquid chromatography, high-pressure LC. Alternatively, the reactions were run with 1% *n*-undecane as internal standard for GC analysis. Experimental results are summarized in Table II.[12]

Hydrolysis of *p*-Aminobenzotrifluoride (2). A mixture of 4.0 mL of **2**, 0.3 g each of copper powder and Cu_2Cl_2, 1.5 g of CaO, and 28 mL of 28% aqueous ammonia was heated for 2 h at 240 °C. Analysis by GC of the resulting solution showed that **2** had been completely consumed. No fluorine-containing components were detected by ^{19}F NMR. GC/mass spectrometry and ^1H NMR confirmed that aniline was the only aromatic product. Under these same reaction conditions, *p*-aminobenzoic acid, which is postulated as the initial hydrolysis product in the conversion of **2** to aniline (eq 1), was also converted quantitatively to aniline. The hydrolysis of **2** does not occur in ethanolic ammonia in the presence of Cu_2Cl_2, Cu^0, and CaO.

Conversion of *p*-Aminobenzotrifluoride (2) to *p*-Cyanoaniline (4). A solution of 0.318 g of **2** in 1.27 g of C_2H_5OH with 855 mg of NH_3 was heated for 5 h at 200 °C in a sealed glass tube. Only 1.5% of **2** is converted to **4**. Addition of 19.1 mg of Cu_2Cl_2 raises this conversion to 5.9%. With 20.4 mg of Cu_2Cl_2 and 191 mg of KF, the conversion is 15%. The rate at which **2** is converted to **4** is competitive with the rate of ammonolysis. A sealed glass tube was charged as follows: 0.532 mmol of **2**; 17.8 mg of Cu_2Cl_2; 1.158 mmol of **1**; 255 mg of KF; 1.17 g of CH_3OH; 793 mg of NH_3; 27.9 mg of NH_4Cl (equivalent to the amount generated during formation of **2**). The tube was heated for 5 h at 200 °C. Analysis of the resulting solution by high-pressure LC showed 0.768 mmol of **1**, 0.310 mmol of **2**, and 0.630 mmol of **4**. Assuming $1 \rightarrow 2 \rightarrow 4$, this product distribution corresponds to 34% conversion of **1** to **2** and 66% conversion of **2** to **4**. Formation of **4** is somewhat slower in C_2H_5OH but still competitive.

Registry No. **1**, 98-56-6; **2**, 455-14-1; **3**, 402-44-8; **4**, 873-74-5; $C_6H_5CF_3$, 98-08-8; $C_6H_5NH_2$, 62-53-3; KF, 7789-23-3.

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[9] J. H. Clark and J. Emsley, *J. Chem. Soc., Dalton Trans.*, 2129 (1975).

[10] Y. Kobayashi and I. Kumadaki, *Acc. Chem. Res.*, 11, 197 (1978).

[11] R. Cramer and D. R. Coulson, *J. Org. Chem.*, 40, 2267 (1975).

[12] High-pressure LC analyses were run using a 25 cm × 4.6 mm column of PSM-149-3 or PSM-149-2 (porous silicone microspheres-50, 6 μm particle size, 50 Å pore size, 300 m^2/g surface area) at ambient temperature. A carrier solution flow rate from 2.86 to 1.11 mL/min at 1000 to 725 psig was maintained. Components as they eluted were detected by ultraviolet absorption at 254 nm. GC analyses were run using an 8 ft × $^1/_8$ in. column of Tenax GC 60/80 and a temperature programmed from 175 to 300 °C at 16 °C/min; % conversion = (total mol of product/mol of reactant) × 10^2; % yield of X = (mol of X/total mol of product) × 10^2; % conversion to X = (mol of X/mol of reactant) × 10^2.

N-Bromosuccinimide–Dimethylformamide: A Mild, Selective Nuclear Monobromination Reagent for Reactive Aromatic Compounds

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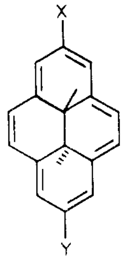
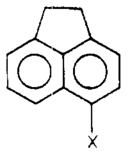
Although electrophilic substitution of aromatic hydrocarbons by bromine is a well-known organic reaction,[1] no reliable[2] and mild method exists for the selective monobromination of reactive aromatic hydrocarbons. This point was reinforced for us when we required a sample of 2-bromo-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**2**).



1, X = Y = H
2, X = Br; Y = H
3, X = Y = Br



4, X = H
5, X = Br

Boekelheide[3] had reported that treatment of the parent, **1**, with bromine produced a mixture of polysubstituted[4] bromo compounds, whereas *N*-bromosuccinimide (NBS) in CCl_4, under free-radical conditions, gave ~19% of the 2,7-dibromide **3**. The electrophilic substitution of an aromatic ring by NBS in nonpolar solvents such as CCl_4 is in fact well documented,[5] although the results are highly variable in terms of both products and yields. The use of NBS in polar solvents, however, is less well-known.[5] Ross et al.[6] have studied the reaction of toluene, fluorene, and acenaphthene (**4**) in propylene carbonate, where predominantly nuclear bromination takes place. In the case of

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[1] For reviews see: R. C. Fuson, "Reactions of Organic Compounds", Wiley, New York, 1962, pp 58–65, 98–102; R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds", Elsevier, New York, 1965, pp 130–2; H. P. Braendin and E. T. McBee, "Friedel-Crafts and Related Reactions", Vol. III, G. A. Olah, Ed., Wiley, New York, 1964, Chapter 46.

[2] Perusal of "Organic Syntheses" shows examples where monobromination can be achieved often in excellent yields, but each example has its own specific set of conditions.

[3] J. B. Phillips, R. J. Molyneux, E. Sturm, and V. Boekelheide, *J. Am. Chem. Soc.*, 89, 1704 (1967).

[4] We have found that even at −78 °C a complex mixture of bromides results.

[5] C. Djerassi, *Chem. Rev.*, 48, 271 (1948); L. Horner and E. H. Winkelmann, "Newer Methods of Preparative Organic Chemistry", Vol. III, W. Foerst, Ed., Academic Press, New York, 1964, p 151.

[6] S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, 80, 4327 (1958).