diamine was added. After 24 hr, the red solution gradually turned pale yellow; the precipitated yellow crystalline product (XII) was separated, washed with water, dried (0.6 g), and recrystallized from dioxane, yield 0.33 g (9%), mp 210–213°.

Anal. Calcd for $C_{16}H_{24}N_2S_4$: C, 51.56; H, 6.49; N, 7.51; S, 34.42. Found: C, 51.24; H, 6.61; N, 7.84; S, 34.58.

Water (120 ml) was added to the filtrate; the precipitated yellow crystals (XI) were separated, washed with water, and dried. The crude product (XI, 3.1 g) was recrystallized from 3:2 water–methanol, yellow plates, yield 2.1 g (48.5%), mp 94–95°.

Anal. Calcd for $C_9H_{16}N_2S_2$: C, 49.95; H, 7.45; N, 12.95; S, 29.63. Found: C, 50.15; H, 7.72; N, 13.20; S, 29.57.

Preparation of XIII from XI.—XI (3.24 g, 0.015 mol) was dissolved in 35 ml of dioxane and 1.5 g (0.015 mol) of acetic anhydride was added below 30°. The precipitated yellow acetate of XI was separated, washed with methanol and dried, 1.3 g; after repeated recrystallization from 1:2 dioxane–methanol the melting point was 119–122°.

The filtrate was diluted with water and yellow crystals were separated. The product was recrystallized from methanol–water (1:2) and identified as the N-acetylated derivative of XI (XIII), yield 1.0 g (25%), mp 130–132°.

Anal. Calcd for $C_{11}H_{18}N_2OS_2$: C, 51.10; H, 7.00; N, 10.84; S, 24.82. Found: C, 50.80; H, 6.82; N, 10.97; S, 24.31.

Preparation of XIV from I.—I (1.6 g, 0.01 mol) was dissolved in a solution of 0.73 g (0.01 mol) of diethylamine in 20 ml of water; 0.75 g (0.01 mol) of 40% aqueous formaldehyde was added to the solution. After 1 hr, the precipitated yellow product was separated, washed with water, and dried, yield 1.7 g (70%), mp 97–99°.

Anal. Calcd for $C_{11}H_{20}N_2S_2$: C, 54.0; H, 8.24; N, 11.46; S, 26.24. Found: C, 53.76; H, 8.33; N, 11.02; S, 25.86.

Preparation of XV from II.—II (1.73 g, 0.01 mol) was dissolved in a solution of 0.73 g (0.01 mol) of diethylamine in 20 ml of water; 0.75 g (0.01 mol) of 40% aqueous formaldehyde was added. The yellow product, which separated out immediately, was separated, washed with water, dried, and recrystallized from 1:2 water–ethanol, yield 1.5 g (58%), mp 72°.

Anal. Calcd for $C_{12}H_{22}N_2S_2$: C, 55.80; H, 8.59; N, 10.84; S, 24.83. Found: C, 55.71; H, 8.66; N, 11.10; S, 25.04.

The nmr spectra were recorded in $CDCl_3$ solution on a Varian A-60D instrument at 60 MHz, using TMS as internal standard. One drop of TFA was used for acidifying the probes. Ir spectra were recorded on a Perkin-Elmer 457 spectrometer in KBr pellets and in $CDCl_3$ solution (0.1 mol/l.), respectively.

Registry No.—Ib, 20735-33-5; IIb, 34281-24-8; IIIb, 34281-25-9; IVb, 34281-26-0; Vb, 34281-27-1; VIb, 34281-28-2; VIIb, 34281-29-3; VIIIb, 34281-30-6; IXb, 34281-31-7; Xb, 37297-90-0; XIb, 34281-32-8; XIIb, 34281-33-9; XIIIb, 34281-34-0; XIVb, 34281-35-1; XVb, 34281-36-2.

Acknowledgment.—We are indebted to Miss M. Fodor for the microanalyses. Thanks are due to Mrs. C. Méhesfalvi, Miss A. Bede, Mr. I. Echter, and Mr. A. Fürjes for valuable technical assistance.

Synthesis and Some Reactions of 3,3-Dimethoxycyclopropene[1,2]

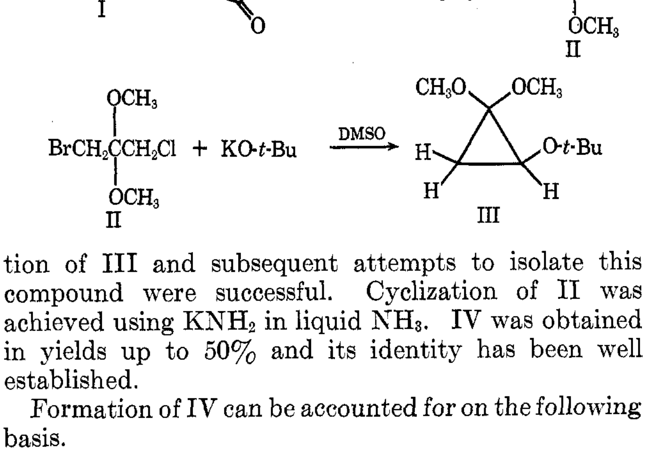
KEITH B. BAUCOM AND GEORGE B. BUTLER*[3]

Department of Chemistry, University of Florida, Gainesville, Florida 32601

Received October 5, 1971

During the course of attempts to synthesize compounds potentially capable of intramolecular charge-transfer interaction, an easy and relatively simple procedure for the preparation of 3,3-dimethoxycyclopropene (IV) was developed. The starting material for this synthesis is the commercially available 2,3-dichloropropene (I). Reaction of I with methanol and *N*-bromosuccinimide, using an acid catalyst, yields 1-bromo-3-chloro-2,2-dimethoxypropane (II) in 33–40% yield. Reaction of II with potassium *tert*-butoxide (KO-*t*-Bu) in dimethyl sulfoxide (DMSO) led to 1,1-dimethoxy-2-*tert*-butoxycyclopropane (III) which has been identified and characterized by nmr, ir, mass spectroscopy, and elemental analysis. IV was considered to be an intermediate and subsequent attempts to isolate this compound were successful. Cyclization of II was achieved using KNH_2 in liquid NH_3. IV was obtained in yields up to 50% and its identity has been well established. When IV was hydrolyzed, cyclopropenone was obtained. Reaction of IV with 1,3-diphenylisobenzofuran gave the adduct V which was converted to 1,4-diphenyl-2-carbomethoxynaphthalene (VI) using trifluoroacetic acid. VI was identified by conversion to its known hydrazide derivative. IV dimerizes at room temperature to 3,3,6,6-tetramethoxytricyclo[3.1.0.0^{2,4}]cyclohexane (VII) which was characterized by its spectral properties and elemental analysis. Reaction of IV with anhydrous dimethylamine led to 1,1-dimethoxy-2-(dimethylamino)cyclopropane (VIII).

An easy and relatively simple procedure for the preparation of 3,3-dimethoxycyclopropene (IV) was developed during the course of attempts to synthesize compounds potentially capable of intramolecular charge-transfer interaction. The starting material for this synthesis is the commercially available 2,3-dichloropropene (I). Reaction of I with methanol and *N*-bromosuccinimide, using an acid catalyst, yields 1-bromo-3-chloro-2,2-dimethoxypropane (II) in 33–40% yield. Reaction of compound II with KO-*t*-Bu in DMSO led to 1,1-dimethoxy-2-*tert*-butoxycyclopropene (III), which has been identified and characterized by nmr, ir, mass spectroscopy, and elemental analysis. IV was postulated to be an intermediate in the formation of III and subsequent attempts to isolate this compound were successful. Cyclization of II was achieved using KNH_2 in liquid NH_3. IV was obtained in yields up to 50% and its identity has been well established.



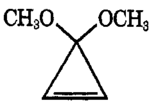
Formation of IV can be accounted for on the following basis.

---

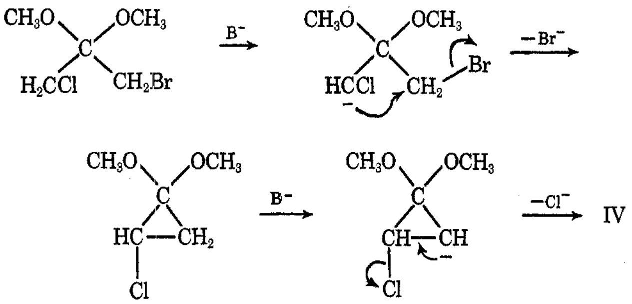
[1] We acknowledge the support of this work by the National Institutes of Health under Grant No. CA-06838.

[2] Presented before the Organic Division, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, No. 139.

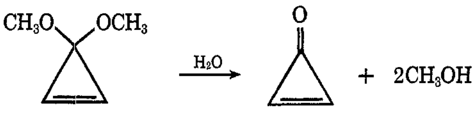
[3] To whom all correspondence should be addressed.



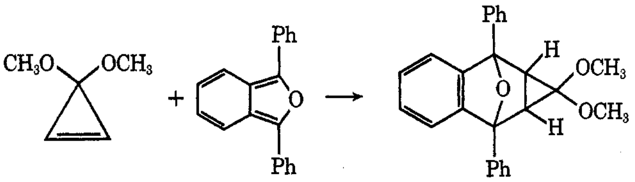
IV



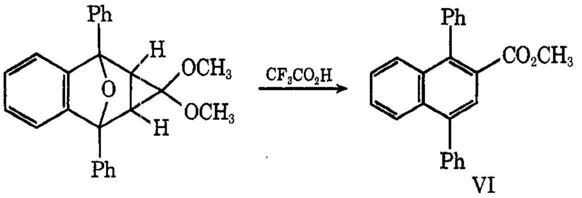
When a pure sample of IV was hydrolyzed, cyclopropenone was obtained.



Reaction of IV with 1,3-diphenylisobenzofuran yielded the adduct V, which was then converted to the unexpected and previously unreported 1,4-diphenyl-2-carbomethoxynaphthalene (VI) by treatment with trifluoroacetic acid. The latter compound was identified by conversion to its known hydrazide derivative.

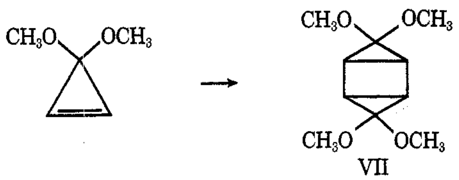


V

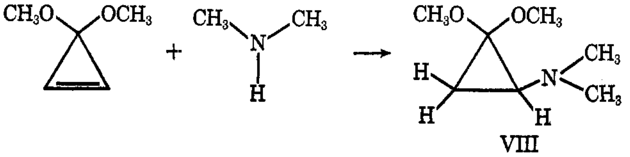


VI

When pure IV is allowed to stand at room temperature it is readily converted to the dimer VII, which was characterized by its spectral properties and elemental analysis. Reaction of IV with anhydrous dimethylamine led to 1,1-dimethoxy-2-(dimethylamino)cyclopropane (VIII).



VII



VIII

Experimental Section

Preparation of 1-Bromo-3-chloro-2,2-dimethoxypropane (II).—This reaction should be carried out in a hood. To a three-necked, 1-l., round-bottom flask equipped with magnetic stirrer and condenser was added 300 ml of anhydrous methanol, 92 ml (1.0 mol) of 2,3-dichloropropene (I), and 2 drops of concentrated sulfuric acid. To this was added in small portions through the condenser 178 g (1.0 mol) of *N*-bromosuccinimide. After the final addition of *N*-bromosuccinimide, the reaction solution was stirred for 1 hr. Then 5 g of sodium carbonate was added to neutralize the acid catalyst. The reaction was stirred for 15 min longer.

The alcoholic solution was poured into an equal volume of water. The organic layer was removed, and the aqueous layer was extracted twice with pentane. The pentane extracts were combined with the original organic layer and were washed twice with an equal volume of water. The pentane solution was then dried over anhydrous magnesium sulfate, filtered, and placed in a 500-ml Erlenmeyer flask equipped with a rubber stopper. The flask was then cooled in a Dry Ice–isopropyl alcohol bath for 45 min. The pentane was then decanted from the white crystalline product. The product was redissolved in pentane and again frozen. Yields varied from 72 to 88 g (33–40%). II, mp 69.5–70.5°, gave a 2,4-dinitrophenylhydrazone, mp 118–119°, compared to mp 116–119° for the literature value for the 2,4-dinitrophenylhydrazone of 1-bromo-3-chloropropanone-2:[4] ir (CCl_4) 2960 (s), 2850 (s), 1445 and 1425 (s), 1295 and 1280 (s), 1205 and 1180 (s), and 1075 cm^{-1} (broad); nmr (CCl_4) τ 6.40 (s, 1), 6.54 (s, 1), an 6.75 (s, 3). The mass spectrum showed no parent peak but gave $P - 31$, $P - 35$, and $P - 79$ fragments with correct isotope effects.

Preparation of 3,3-Dimethoxycyclopropene (IV).—A dry 500-ml, three-necked, round-bottom flask equipped with a stirring bar, Dry Ice condenser, ammonia inlet, and nitrogen inlet was purged with dry nitrogen for about 5 min. The Dry Ice condenser was then filled with Dry Ice–isopropyl alcohol. A Dry Ice–isopropyl alcohol bath was placed under the flask. The nitrogen flow was reduced to a slow rate, and the condensation of ammonia was begun. After about 450 ml of ammonia had condensed, a small piece (0.5 g) of clean potassium metal was added to the ammonia. The Dry Ice–isopropyl alcohol bath was removed. A catalytic amount of ferric chloride was added to the ammonia solution. When the ammonia reached reflux temperature, the blue color of the dissolved potassium had been replaced by a gray color. The remainder of 11.7 g (0.30 mol) of clean potassium was added in about 0.5-g pieces at such a rate that the reflux rate was controllable. After the final addition of potassium, the color of the solution was gray.

At this point, 21.7 g (0.10 mol) of finely ground II was added very slowly. Care was taken to prevent the finely ground ketal from being blown out of the powder funnel by the rapid vaporization of ammonia. After the addition was completed, the entire reaction assembly was placed in a subzero reaction box thermostatically controlled at −50°. A nitrogen inlet reaching to the bottom of the reaction vessel was used for stirring. A gas outlet from the reaction extended to the hood. The reaction was maintained under these conditions overnight.

The next morning, the reaction vessel was removed from the cold box, and 10.8 g (0.20 mol) of ammonium chloride was added. As the ammonia evaporated, anhydrous ethyl ether was added to replace it. This evaporation process was accelerated by placing the reaction vessel in a heated methanol bath (*ca.* −10°). After most of the ammonia had evaporated, the solution was filtered to remove inorganic salts (if extensive decomposition has not occurred, the salts will be light in color). The ethereal solution was then subjected to *ca.* 50–80 mm with the vacuum being pulled through a reflux condenser maintained at *ca.* −20° and then through a Dry Ice trap. This process was hastened by warming the pot in a methyl alcohol bath. When the quantity of residue seemed to remain constant, the receiver was changed, and the coolant in the reflux condenser was removed. The pressure was then lowered to *ca.* 1–2 mm. Nmr was used to show the absence of ether in the distillate. Yields of IV varied from 4 to 5 g (40–50%). The product should be stored below 0°. The boiling range of the product was *ca.* 25–30° (25 mm); ir (CCl_4) 3000 (w), 2960 (m), 2940 (w), 2905 (w), 2830 (s), 1600 (m), 1450 (w), 1275 (s), 1200 (w), 1075 cm^{-1} (s); nmr (CCl_4) τ 6.77 (s, 6) and 2.23 (s, 2).

---

[4] A. Roedig, H. G. Kleppe, and G. Markl, *Chem. Ber.*, **95**, 1245 (1962).

Preparation of Cyclopropenone.—When a pure sample of IV was added to D_2O, it was immediately hydrolyzed to cyclopropenone and methyl alcohol, nmr (D_2O) τ 1.0 (s). The water solution of cyclopropenone was saturated with sodium chloride and extracted with methylene chloride. This was dried over magnesium sulfate: nmr (CH_2Cl_2) τ 1.0–1.1 (s); ir (CH_2Cl_2) 1870, 1835, and 1730 cm^{-1}. All of these spectral data agree with those reported by Breslow and Ryan.[5]

Preparation of 1,1-Dimethoxy-2-*tert*-butoxycyclopropane (III).—To 30 ml of dry dimethyl sulfoxide in a 50-ml round-bottom flask was added 2.17 g (0.01 mol) of II and 3.36 g (0.03 mol) of KO-*t*-Bu. The solution turned black quickly. It was stirred at room temperature under a drying tube overnight, after which it was poured into water and extracted several times with ether. (Trouble with emulsion formation was experienced). The ethereal solution was dried over anhydrous magnesium sulfate and filtered. The ether was removed by distillation at atmospheric pressure and the residue was distilled bulb-to-bulb at atmospheric pressure. The product was then chromatographed over silica gel using petroleum ether (bp 20–40°) as eluent. III was shown to be pure by vpc. The yield of clear, colorless product was *ca.* 0.8 g (50%): ir (neat) 3110 (w), 2990 (s), 2850 (s), 1450 (s), 1390 (m), 1365 (s), 1295 (s), 1220 (m), 1195 (w), 1150 (s), 1050 (s), 980 (m), and 880 cm^{-1} (m); nmr (CCl_4) τ 8.83–9 (m, 2), 8.74 (s, 9), 6.69 (s, 3), 6.55 (s, 3), and 6.69–6.78 (m, partially hidden, 1). The hidden proton at τ 6.69–6.78 was shown to exist by double resonance at this region while observing the other cyclopropyl protons at τ 8.83–9.30. The double resonance caused the high-field multiplet to collapse to an AB quartet. The mass spectrum did not give a parent peak but did give P − 57 for loss of *tert*-butyl radical. *Anal.* Calcd for $C_9H_{18}O_3$: C, 62.04; H, 10.41. Found: C, 62.20; H, 10.47.

Preparation of an Adduct between 1,3-Diphenylisobenzofuran and IV.—To a CCl_4 solution of IV (prepared from 0.01 mol of II) was added 2.7 g (0.01 mol) of 1,3-diphenylisobenzofuran. The reaction was allowed to continue for 1 week at room temperature. At the end of this time, the solvent was removed under vacuum. The residue was dissolved in hot methanol and allowed to cool. The solution was filtered, and the methanol was allowed to evaporate slowly at room temperature in a crystallization dish. The product (V) was isolated as clear hexagonal crystals: mp 140–141.5°; yield 1.1 g (30%); ir (KBr) 3070 (w), 3040 (w), 2940 (m), 2840 (w), 1600 (w), 1500 (w), 1450 (s), 1375 (s), 1340 (s), 1325 (w), 1305 (s), 1240 (s), 1190 (m), 1120 (s), 1090 (w), 1055 (s), 1015 (m), 995 (m), 975 (w), 900 (w), 860 (m), 800 (m), 760 (s), 700 cm^{-1} (s); nmr (CCl_4) τ 7.90 (s, 2), 7.02 (s, 3), 6.68 (s, 3), and 2.16–3.08 (m, 14). The mass spectrum gave a parent peak at *m/e* 370. *Anal.* Calcd for $C_{25}H_{22}O_3$: C, 81.06; H, 5.99. Found: C, 80.92; H, 6.00.

V was warmed with trifluoroacetic acid, which converted it to 1,4-diphenyl-2-methylnaphthoate. The ester was recrystallized from methanol to give a white crystalline solid: mp 162–162.5°; ir (CCl_4) 3080 (m), 3050 (w), 3005 (w), 2970 (m), 1730 (vs), 1600 (w), 1500 (w), 1440 (m), 1390 (m), 1350 (w), 1255 (s), 1230 (s), 1165 (m), 1130 (m), and 1120 cm^{-1} (m); nmr (CCl_4) τ 6.50 (s, 3), 2.84–2.33 (m, 14), and 2.26 (s, 1). The mass spectrum gave a parent peak at *m/e* 338 (also the base peak) and an intense peak at *m/e* 307 indicative of loss of $CH_3O\cdot$ *Anal.* Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.26; H, 5.42. The hydrazide was prepared from the ester using hydrazine hydrate. The hydrazide had mp 174–176°, compared to the literature value of 179° for the hydrazide of VI.[6]

Dimerization of 3,3-Dimethoxycyclopropene.—A sample of 3,3-dimethoxycyclopropene was placed in a sublimator and left at room temperature for 6 days. During this time white crystals of a new product formed on the condenser and walls of the sublimator. The product was removed from the sublimator and then sublimed twice at 60° (1 mm): ir (CCl_4) 3060 (m), 3005 (m), 2970 and 2950 (s), 2910 (w), 2850 (m), 1440 (m), 1380 (s), 1220 (s), 1180 (m), 1110 (s), 1040 (s), 1010 cm^{-1} (m); nmr (CCl_4) τ 8.27 (s, 2), 6.72 (s, 3), and 6.65 (s, 3). The mass spectrum gave fragments at *m/e* 169, 154, and 126. The parent peak was not observed. These results show the product VII to be 3,3,6,6-tetramethoxytricyclo[3.1.0.$0^{2,4}$]cyclohexane. *Anal.* Calcd for $C_{10}H_{16}O_4$: C, 59.99; H, 8.06. Found: C, 59.62; H, 7.81.

Preparation of 1,1-Dimethoxy-2-dimethylaminocyclopropane (VIII).—To a small pressure bottle was added 1.0 g (0.01 mol) of IV, and 5 ml of dry dimethylamine was condensed into the bottle. The bottle was sealed and heated at 50° for 3 hr. The next day the dimethylamine was distilled from the product. The residue was then distilled at atmospheric pressure: bp 120–140°; yield 0.9 g (60%); ir (neat) 3100 (w), 3000 (w), 2950 (s), 2920 (w), 2840 (m, doublet), 2780 (m), 1660 (m), 1460 (s), 1280 (s), 1220 (s), 1160 (s), 1090 (s), 1060 and 1040 (s), 995 (m), 925 (m), and 880 cm^{-1} (m); nmr (CCl_4) τ 9.17 (m, 2), 8.28 (m, 1), 7.75 (s, 6), 6.77 (s, 3), and 6.63 (s, 3). The mass spectrum gave fragments at P − 1, *m/e* 144, and a base peak at P − 15, *m/e* 130. The hydrochloride had mp 157–159°; ir (KBr) 2760–2300 (ammonium salt), 3100 cm^{-1} (cyclopropyl). *Anal.* Calcd for $C_7H_{16}NO_2Cl$: C, 46.37; H, 8.71; N, 7.71; Cl, 19.52. Found: C, 46.28; H, 8.88; N, 7.71; Cl, 19.64.

Registry No.—II, 22089-54-9; II 2,4-DNP, 34219-71-1; III, 34219-72-2; IV, 23529-83-1; V, 34219-74-4; VI, 34219-75-5; VII, 34219-76-6; VIII, 34219-77-7; VIII HCl, 34219-78-8.

Acknowledgment.—The authors are grateful to Professor M. A. Battiste and Dr. C. A. Sprouse for many helpful discussions during the course of this work.

---

[5] R. D. Breslow and G. Ryan, *J. Amer. Chem. Soc.*, **89**, 3073 (1967).

[6] A. Etienne and M. Delepine, *C. R. Acad. Sci.*, **219**, 397 (1944).

The Reaction of Organozinc Compounds with Carbon Monoxide[1]

MICHAEL W. RATHKE* AND HELEN YU

Department of Chemistry, Michigan State University, East Lansing, Michigan 48823

Received July 30, 1971

Di-*n*-butylzinc and diisopropylzinc react with carbon monoxide at atmospheric pressure in the presence of potassium *tert*-butoxide to furnish, after hydrolysis, the corresponding acyloins. In the absence of the base, the two organozinc compounds are inert to carbon monoxide. Diphenylzinc absorbs only small amounts of carbon monoxide in the presence of potassium *tert*-butoxide and the only identified product is biphenyl. A possible mechanism for the base-promoted carbonylation of dialkylzinc compounds is presented.

The absorption of carbon monoxide by Grignard reagents was first observed by Vinay in 1908.[2] Since that date, the reaction has been studied in detail by a large number of workers using a variety of reaction conditions and catalysts. A host of products has been reported including trialkylcarbinols, ketones, olefins, and acyloins.[3] In contrast, the action of carbon monox-

---

[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[2] E. Farrario and H. Vinay, *Arch. Sci. Phys. Nat.*, **25**, 513 (1908).

[3] (a) V. Egorova, *J. Russ. Phys. Chem. Soc.*, **46**, 1319 (1914); (b) F. Gottwalt Fischer and O. Stoffers, *Justus Liebigs Ann. Chem.*, **500**, 253 (1933); (c) W. L. Gilliland and A. A. Blanchard, *J. Amer. Chem. Soc.*, **48**, 410 (1926); (d) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, New York, N. Y., 1954, pp 910–1913.