Dearylation of Tetraphenyltin with N-Bromosuccinimide

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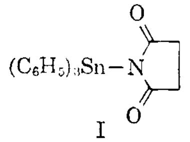
It has been found that N-bromosuccinimide can cleave phenyl groups from tin. The reaction of tetraphenyltin with N-bromosuccinimide (1:1 molar ratio) in refluxing carbon tetrachloride gave succinimide, bis(triphenyltin) oxide, bromobenzene, tetraphenyltin, and diphenyltin oxide. Some evidence for the intervention in this reaction of an intermediate having a hydrolytically unstable tin–nitrogen bond is presented. The reaction of tetraphenyltin with N-bromosuccinimide (1:2 molar ratio) gave succinimide and diphenyltin oxide. The reaction between triphenyltin hydride and N-bromosuccinimide in refluxing benzene gave triphenyltin bromide and succinimide.

Cleavage of the tin–carbon bond in tetraaryltin compounds has been effected by a large variety of reagents. These cleavage reactions have been reviewed.[1] More recently, dearylation of tetraphenyltin by iodine trichloride has been reported.[2]

It has now been found that the tin–carbon bond in tetraphenyltin can be cleaved with N-bromosuccinimide. From the reaction of tetraphenyltin with N-bromosuccinimide (1:1 molar ratio) there was isolated succinimide (94.8%), bis(triphenyltin) oxide (51.4%), tetraphenyltin, and diphenyltin oxide. In another run bromobenzene was isolated in 67.0% yield.

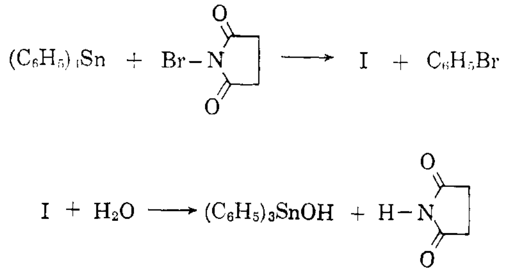
To account for the necessary oxygen and hydrogen present in the above products, water must somehow be involved in the reaction. It is known that when N-bromosuccinimide is used as a brominating agent, the succinimide which is formed rises to the surface of the carbon tetrachloride.[3] In the present case, however, a clear solution remained after reaction. This observation meant that the succinimide recovered in the present reaction probably resulted from the hydrolysis of an intermediate which was soluble in carbon tetrachloride. The succinimide was isolated by allowing the carbon tetrachloride to evaporate in air and then extracting the residue with water. Evaporation of the water yielded the succinimide. It was possible that the intermediate reacted with the added water to give the succinimide and bis(triphenyltin) oxide. The added water, however, was not responsible for the observed products. This fact was determined by examining the infrared spectrum of the material remaining after removal of the carbon tetrachloride. The infrared spectrum had a strong absorption band at 12.9 μ. This band is very strong in the spectrum of bis(triphenyltin) oxide. An absorption band at 3.1 μ was also present. This band is present in the spectrum of succinimide and is probably due to the N—H linkage. Thus, the bis(triphenyltin) oxide and succinimide were present before addition of the water. This meant that the intermediate must have reacted with the moisture in the air to give the observed products. Thus, the intermediate must have contained a bond which is very hydrolytically unstable.

One possible compound which seemed a likely intermediate in the present reaction was succinimidyltriphenyltin (I).



I

The following equations involving I can be written to explain the observed products



$$2(C_6H_5)_3SnOH \longrightarrow (C_6H_5)_3Sn{-}O{-}Sn(C_6H_5)_3 + H_2O$$

$$(C_6H_5)_3Sn{-}O{-}Sn(C_6H_5)_3 \xrightarrow[\Delta]{} (C_6H_5)_4Sn + (C_6H_5)_2SnO$$

The last equation represents a possible source of the diphenyltin oxide. Bis(triphenyltin) oxide is reported to disproportionate at 130–140° into tetraphenyltin and diphenyltin oxide.[4] In separate experiments it was found that disproportionation to tetraphenyltin and diphenyltin oxide occurred on refluxing an ethanol or acetonitrile solution of bis(triphenyltin) oxide.

Evidence for the intervention of intermediate I was obtained by allowing sodium succinimide to react with triphenyltin chloride. This reaction, which would be expected to give I, yielded sodium chloride, succinimide, and bis(triphenyltin) oxide. Further evidence for the intervention of an intermediate having a hydrolytically unstable Sn—N

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(1) R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 511 (1960).

(2) Z. M. Manulkin, *Uzbeksk. Khim. Zh., No.* **2**, 66 (1960).

(3) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed., Longmans, Green and Co., Inc., New York, 1956, p. 926.

(4) O. Schmitz-Dumont, *Z. anorg. allgem. Chem.*, **248**, 289 (1941).

bond was obtained by allowing triphenyltin bromide to react with ammonia. The products of this reaction were bis(triphenyltin) oxide (93.2%) and ammonium bromide (93.6%). These products are explained by the following equations

$$(C_6H_5)_3SnBr + 2NH_3 \longrightarrow (C_6H_5)_3SnNH_2 + NH_4Br$$

$$(C_6H_5)_3SnNH_2 + H_2O \longrightarrow (C_6H_5)_3SnOH + NH_3$$

$$2(C_6H_5)_3SnOH \longrightarrow (C_6H_5)_3Sn{-}O{-}Sn(C_6H_5)_3 + H_2O$$

It was thought that intermediate I might be formed by the reaction of triphenyltin hydride with N-bromosuccinimide. This reaction gave triphenyltin bromide (86.4%) and succinimide (94.7%). The same results were obtained when this reaction was carried out in the presence of pyridine. This reaction is being further investigated.

Another attempt was made to prepare intermediate I by allowing triphenyltin hydride to react with succinimide in refluxing benzene. The products isolated were succinimide (96.3%) and triphenyltin chloride (91.1%). The triphenyltin chloride must have arisen from the reaction of unchanged triphenyltin hydride with carbon tetrachloride, which was used in the processing of the reaction mixture. This reaction has been observed by others.[5]

There is some evidence from the literature which supports the possible existence and hydrolytic instability of an intermediate such as I. The hydrolytic instability of the Sn—N bond has been reported by Thomas,[6] who synthesized a compound having this bond as follows

$$SnCl_4 + 4LiNEt_2 \longrightarrow \underset{\text{II}}{Sn(NEt_2)_4} + 4LiCl$$

The Sn—N bond in II was found to be extremely sensitive to moisture, and special precautions were required to prevent hydrolysis. Alleston and Davies[7] have found that dialkyl or diaryltin halides react with tertiary amines to produce compounds of the general formula III.

$$2R_2SnX_2 + 2R_3'N + H_2O \longrightarrow 2R_3'NHX + \underset{\text{III}}{R_4Sn_2X_2O}$$

It is possible that this reaction proceeds *via* some Sn—N intermediate, with subsequent hydrolysis to produce III. These workers postulate that the water necessary for the reaction is adventitious water present in the solvent.

Reaction of tetraphenyltin with N-bromosuccinimide (1:2 molar ratio) gave succinimide (77.8%) and diphenyltin oxide (62.5%). No attempt was made to isolate any bromobenzene from this reaction.

Experimental

Melting points were determined with a Mel-temp capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, New York. The N-bromosuccinimide was obtained from Distillation Products Industries and was used without further purification.

Reaction of Tetraphenyltin with N-Bromosuccinimide (1:1 Molar Ratio). Run No. 1.—Tetraphenyltin (10.00 g., 0.0234 mole), N-bromosuccinimide (4.16 g., 0.0234 mole), m.p. 180–182°, and carbon tetrachloride (200 ml.) were placed in a 500-ml. flask fitted with a truebore-stirrer and condenser equipped with a calcium chloride drying tube. The mixture was heated on a steam bath with good stirring for 16 hr. At the end of this time, a clear solution remained, and a test for positive bromine with starch–iodide paper was negative. The carbon tetrachloride was allowed to evaporate in air on a steam bath until a mushy solid having the odor of bromobenzene remained. The mushy solid was stirred with a small quantity of petroleum ether (b.p. 37.4–51.5°) and filtered affording 10.44 g. of white solid. The infrared spectrum showed a strong band at 12.9 μ and another band at 3.1 μ. Stirring the solid with 50 ml. of hot water, filtering, and evaporation of the water from the filtrate on a steam bath gave 2.20 g. (94.8%) of succinimide, m.p. 122.5–124.5°, whose melting point did not depress that of an authentic sample and whose infrared spectrum was superimposable upon that of an authentic sample. The infrared spectrum had an absorption band at 3.1 μ which is probably due to the N—H linkage.

Recrystallization of the water-insoluble solid from ethanol-water afforded 3.20 g. of white crystals, m.p. 120–122° (opaque melt), and a second crop weighing 1.33 g., m.p. 121–122.5° (clear melt). Recrystallization of the first crop afforded 2.98 g. of white crystals, m.p. 122–123° (clear melt), which did not depress the melting point of authentic bis(triphenyltin) oxide and whose infrared spectrum was superimposable upon that of authentic bis(triphenyltin) oxide (strong band at 12.9 μ).

Anal. Calcd. for $C_{36}H_{30}Sn_2O$: C, 60.39; H, 4.22; Sn, 33.16. Found: C, 60.42; H, 4.21; Sn, 33.34.

The ethanol-insoluble solid (1.63 g.) began to melt at 228°, but most of it remained unmelted at 300°. This material was refluxed with 50 ml. of benzene, and the mixture was filtered. Evaporation of the benzene from the filtrate gave 0.62 g. of white solid, m.p. 225–229°. Recrystallization from benzene gave 0.5 g. of white crystals, m.p. 228.5–231°, melting point undepressed on admixture with an authentic sample of tetraphenyltin, infrared spectrum superimposable upon that of an authentic sample of tetraphenyltin.

The benzene-insoluble solid (0.27 g.) did not melt or decompose up to 300°. The infrared spectrum was superimposable upon that of an authentic sample of diphenyltin oxide.[8] An oxime derivative was prepared as follows: 0.2 g. of the benzene-insoluble material was added to a solution of 0.2 g. of 8-hydroxyquinoline and 1.0 g. of sodium acetate in 150 ml. of ethanol. The mixture was refluxed for 3.5 hr. and then was filtered to give yellow crystals, m.p. 254–256°, after a single recrystallization from ethanol, melting point undepressed on admixture with the oxine derivative of authentic diphenyltin oxide, infrared spectrum superimposable upon that of the oxine derivative of authentic diphenyltin oxide. The reported[9,10] m.p. is 231–233°.

Anal. Calcd. for $C_{30}H_{22}N_2SnO_2$: C, 64.20; H, 3.95; N, 4.99; Sn, 21.15. Found: C, 64.17; H, 4.07; N, 5.20; Sn, 20.94.

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(5) D .H. Lorenz and E. I. Becker, *J. Org. Chem.*, in **27**, 3370 (1962).

(6) I. M. Thomas, *Can. J. Chem.*, **39**, 1386 (1961).

(7) D. L. Alleston and A. G. Davies, *Chem. Ind.* (London), 949 (1961).

(8) Purchased from Metal and Thermite Corporation, Rahway, New Jersey.

(9) G. E. Coates, "Organo-Metallic Compounds," 2nd ed., John Wiley & Sons, New York, 1960, p. 190.

(10) D. Blake, G. E. Coates, and J. M. Tate, *J. Chem. Soc.*, 756 (1961).

Run No. 2.—A mixture of tetraphenyltin (70.00 g., 0.1638 mole), N-bromosuccinimide (29.12 g., 0.1638 mole), and carbon tetrachloride (500 ml.) was heated on a steam bath with good stirring for 8 hr. At the end of this time, a test for positive bromine with starch–iodide paper was negative. Distillation of the mixture afforded 11.5 ml. (67.0%) of bromobenzene, b.p. 157°, $n^{20}D$ 1.5596 (lit.[11] b.p. 155–156°, $n^{20}D$ 1.55977). The infrared spectrum was superimposable upon that of an authentic sample of bromobenzene.

Disproportionation of Bis(triphenyltin) Oxide. (A). In Ethanol.—A solution of 2.92 g. of bis(triphenyltin) oxide in 50 ml. of ethanol was refluxed on a steam bath for 18.5 hr. White solid was present at the end of this time. The mixture was allowed to cool and 50 ml. of ethanol were added. Filtration of the mixture gave 0.35 g. of a white solid, which was continuously extracted with 60 ml. of benzene for 2.5 hr. Evaporation of the benzene gave 0.14 g. of tetraphenyltin, m.p. 225–229°, after a single recrystallization from benzene, melting point undepressed on admixture with an authentic sample of tetraphenyltin.

The benzene-insoluble material (0.16 g.) did not melt up to 350°. An oxine derivative was prepared as described previously except that no sodium acetate was used. Recrystallization from ethanol afforded yellow crystals, m.p. 253–256°, melting point undepressed on admixture with the oxine derivative of authentic diphenyltin oxide.

Evaporation of the ethanol from the initial filtration gave 2.40 g. (82.2%) of the starting bis(triphenyltin) oxide, m.p. 122–124°, melting point undepressed on admixture with an authentic sample of bis(triphenyltin) oxide.

(B). In Acetonitrile.—A solution of 2.00 g. of bis(triphenyltin) oxide in 50 ml. of acetonitrile was refluxed on a steam bath for 8 hr. At the end of this time white solid was present. The mixture was allowed to cool and then was filtered to give solid material which did not melt up to 350°. The infrared spectrum was superimposable upon that of an authentic sample of diphenyltin oxide.

Evaporation of the acetonitrile from the filtrate gave a yellow solid, m.p. 108–120°, with unmelted material remaining up to 150°. A few milliliters of acetonitrile were added, and the mixture was warmed and filtered affording 0.11 g. of tetraphenyltin, identified by mixed melting point determination and infrared comparison with an authentic sample.

Reaction of Triphenyltin Chloride with Sodium Succinimide.—The sodium succinimide was prepared as follows: A mixture of sodium (2.3 g., 0.10 g.-atom) and 400 ml. of toluene was refluxed and stirred under nitrogen until a fine dispersion of sodium had been produced. Succinimide (9.91 g., 0.10 mole) dissolved in 200 ml. of dioxane was then slowly added over a period of 3 hr., the reaction mixture gradually becoming a creamy white. When the addition was completed, the refluxing was continued for 3 hr. Then the reaction mixture was cooled to 0° and filtered. The white solid obtained was washed with 100 ml. of dioxane to remove any unchanged succinimide. There was obtained 9.17 g. (75.8%) of sodium succinimide, m.p. 190–200°.

Triphenyltin chloride (9.01 g., 0.0234 mole), sodium succinimide (2.83 g., 0.0234 mole), and 500 ml. of xylene were refluxed under nitrogen with stirring for 21 hr. Evaporation of the solvent left 11.88 g. of solid material. An infrared spectrum of this material had a strong band at 12.9 μ. Stirring the solid with 200 ml. of water followed by filtration and then evaporation of the water from the filtrate on a steam bath afforded 2.60 g. of solid. This solid was continuously extracted with ethanol for 2 hr. Evaporation of the ethanol gave 1.98 g. (85.3%) of succinimide, m.p. 123–124°, melting point undepressed on admixture with an authentic sample of succinimide, infrared spectrum superimposable upon that of an authentic sample of succinimide.

The ethanol-insoluble material weighed 0.59 g. This was dissolved in water and precipitated with silver nitrate solution to give 1.38 g. (41.0%) of silver chloride.

The water-insoluble material from the initial filtration weighed 8.78 g. The presence of bis(triphenyltin) oxide in this material was indicated by a strong band at 12.9 μ in the infrared spectrum. This strong band is a characteristic feature of bis(triphenyltin) oxide.

Reaction of Triphenyltin Bromide with Ammonia.—Anhydrous ammonia was passed for 2.5 hr. into a solution of 3.00 g. (0.00697 mole) of triphenyltin bromide[12] in 600 ml. of ether. The precipitate which formed was filtered to give 0.64 g. (93.6%) of ammonium bromide, infrared spectrum superimposable upon that of an authentic sample of ammonium bromide.

The ether was evaporated from the filtrate to give 2.51 g. of a white solid, m.p. 116–121°. Recrystallization from acetonitrile gave 2.33 g. (93.2%) of bis(triphenyltin) oxide, m.p. 117–120°, melting point undepressed upon admixture with an authentic sample, infrared spectrum superimposable upon that of an authentic sample of bis(triphenyltin) oxide.

Reaction of Triphenyltin Hydride with N-Bromosuccinimide.[13]—Triphenyltin hydride[14] (4.10 g., 0.0117 mole), N-bromosuccinimide (2.08 g., 0.0117 mole), and 100 ml. of benzene was refluxed on a steam bath in a nitrogen atmosphere for 8 hr. The benzene was removed *in vacuo*, and the residue was refluxed with 100 ml. of carbon tetrachloride for 0.25 hr. The mixture was filtered to give 1.30 g. solid material which was recrystallized from ethanol to give 1.1 g. (94.7%) of succinimide, m.p. 123–125°, melting point undepressed on admixture with an authentic sample of succinimide. There was also obtained 0.075 g. of ethanol-insoluble material which gave no melting up to 360°. This material was not identified.

Evaporation of the carbon tetrachloride and recrystallization of the residue from *n*-propyl alcohol yielded 4.35 g. (86.4%) of triphenyltin bromide, m.p. 118–120°, melting point undepressed on admixture with an authentic sample of triphenyltin bromide.

The same results as above were obtained when the reaction was run in the presence of pyridine (0.92 g., 0.0117 mole).

Attempted Reaction of Triphenyltin Hydride with Succinimide.[13]—Triphenyltin hydride[14] (4.10 g., 0.0117 mole), succinimide (1.35 g., 0.0117 mole), and 100 ml. of benzene were refluxed on a steam bath under nitrogen for 8 hr. The benzene was distilled *in vacuo* and the residue was refluxed with carbon tetrachloride for 0.25 hr. Filtration of the mixture gave 1.30 g. (96.3%) of succinimide, m.p. 123–125°, melting point undepressed on admixture with an authentic sample of succinimide.

The carbon tetrachloride was allowed to evaporate from the filtrate and the residue was recrystallized from acetonitrile to give 4.1 g. (91.1%) of triphenyltin chloride, m.p. 104–106°, melting point undepressed on admixture with an authentic sample of triphenyltin chloride.

Reaction of Tetraphenyltin with N-Bromosuccinimide (1:2 Molar Ratio).—Tetraphenyltin (10.00 g., 0.0234 mole), N-bromosuccinimide (8.32 g., 0.0468 mole), and 250 ml. of carbon tetrachloride were refluxed on a steam bath with good stirring for 18 hr. At the end of this time, a test for positive bromine with starch–iodide paper was negative. The carbon tetrachloride was allowed to evaporate on a steam bath, and the residue was allowed to dry in air. Stirring of the

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[11] "Handbook of Chemistry and Physics," 40th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1959, p. 831.

[12] D. Blake, G. E. Coates, and J. M. Tate, *J. Chem. Soc.*, 618 (1960).

[13] The authors wish to thank Mr. Robert J. Kiesel for carrying out this reaction.

[14] G. J. M. van der Kirk, J. C. Noltes, and J. G. A. Luijten, *J. Appl. Chem.* (London), **7**, 366 (1957).

crude product (11.22 g.) with 250 ml. of hot water followed by filtration and then evaporation of the water from the filtrate on a steam bath gave 3.6 g. (77.8%) of succinimide, m.p. 118–122°, melting point undepressed on admixture with an authentic sample of succinimide, infrared spectrum superimposable upon that of an authentic sample of succinimide.

The water-insoluble solid was continuously extracted with benzene for 2 hr. There remained 4.24 g. (62.5%) of benzene-insoluble material which did not melt up to 400°. Its infrared spectrum was superimposable upon that of an authentic sample of diphenyltin oxide. An oxine derivative, prepared as described above, was identical to the oxine derivative of authentic diphenyltin oxide.

Orthoamides and Formamidinium Salts

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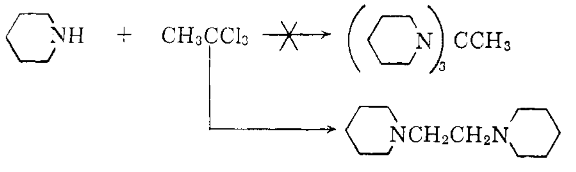
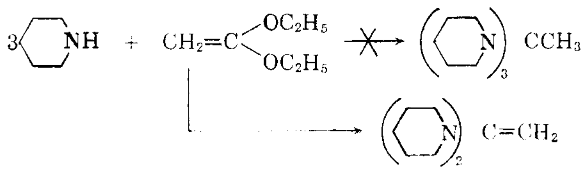
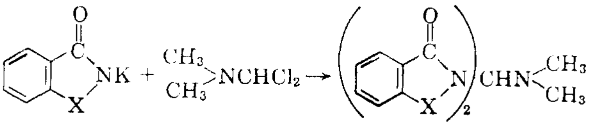
Several orthoformamides were prepared by the reaction of sodium salts of *N*-alkylanilines with chlorodifluoromethane. The orthoformamides, on treatment with mineral acids, alkyl or acyl halides give formamidinium salts in excellent yield. The formamidinium salts react with sodium hydride to yield methylenedianilines, with alkoxide ion to yield alkoxydiaminomethanes, and with phenyllithium to yield benzaldianilines. With primary amines they yield substituted formamidines and with sodium trichloroacetate they form trichloromethyldiaminomethanes. The formamidinium salts may also be nitrated in good yield.

The chemistry of 1,1,1-triaminoalkanes or orthoamides is not well known. In 1887 Kekule[1] reported that the reaction of piperidine with 1,1,1-trichloroethane produced 1,1,1-tripiperidinoethane. McElvain[2] also reported the synthesis of this compound by the reaction of ketenediethylacetal with piperidine.



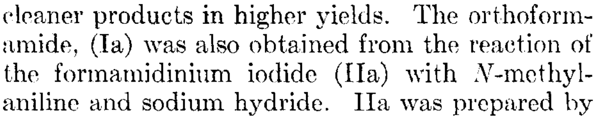


Bohme and Soldan[3] have recently re-examined the work of both of these authors and identified the compound reported by Kekule as 1,2-dipiperidinoethane and that reported by McElvain as 1,1-dipiperidinoethylene. They also prepared derivatives of orthoformamide by reaction of *N*,*N*-dimethyldichloroformamide with the potassium salts of phthalimide and saccharine.



Bredereck, *et al.*,[4] have also recently reported the synthesis of a series of triacyl orthoformamides.

By a variety of methods we have synthesized several triaryltrialkyl orthoformamides which were found to be readily convertible to a series of formamidinium salts.[5] The preferred method for preparing orthoformamides is the reaction of the sodium salt of an *N*-alkylaniline with chlorodifluoromethane. The reaction was found to be quite general and was applied to *N*-methylaniline, *N*-ethylaniline, and *p*-nitro-*N*-methylaniline to produce the series of orthoformamides, Ia–c.



Ia. $X = —H$ $R = —CH_3$
Ib. $X = —H$ $R = —C_2H_5$
Ic. $X = p\text{-}NO_2$ $R = —CH_3$

Chlorodifluoromethane was found superior to both dichlorofluoromethane and chloroform, producing cleaner products in higher yields. The orthoformamide, (Ia) was also obtained from the reaction of the formamidinium iodide (IIa) with *N*-methylaniline and sodium hydride. IIa was prepared by methylation of diphenylformamidine with methyl iodide and sodium hydride to give *N*,*N'*-diphenyl-*N*-methylformamidine followed by quaternization with methyl iodide in acetonitrile. This synthesis serves as compelling evidence for the assigned structures of both the formamidinium iodide (IIa) and the triaminomethane (Ia). It was found that

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(1) A. Kekule, *Ber.*, **20**, 3247 (1887).

(2) H. M. Barnes, D. Kundiger, and S. M. McElvain, *J. Am. Chem. Soc.*, **62**, 1281 (1940); **67**, 202 (1945).

(3) H. Bohme and F. Soldan, *Ber.*, **94**, 3109 (1961).

(4) H. Bredereck, R. Gompper, H. Rempfer, H. Keck, and K. Klemm, *Angew. Chem.*, **70**, 269 (1958); H. Bredereck, R. Gompper, H. Rempfer, K. Klemm, and H. Keck, *Ber.*, **92**, 329 (1959); H. Bredereck, R. Gompper, F. Effenberger, H. Keck, and H. Heise, *ibid.*, **93**, 1398 (1960).

(5) For a brief preliminary account of the work see D. H. Clemens and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 2588 (1961).