[Contribution from the Department of Chemistry, University of New Hampshire]

Reactions of Diphenyltin[1]

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The reactions of diphenyltin with the following reagents have been examined: hydrogen peroxide, chlorine, bromine, iodine, sulfur, benzoquinone, benzoyl peroxide, dibenzyl disulfide, stannic chloride, mercuric chloride, diphenyltin dichloride. Diphenyltin forms a complex with boron trifluoride which disproportionates in boiling benzene to tetraphenyltin and metallic tin. Nitrobenzene and benzil catalyze the polymerization of diphenyltin.

The preparation of diphenyltin was first reported by Krause and Becker in 1920,[2] who described it as a yellow monomeric substance which deliquesces in benzene vapor. Chambers and Scherer[3] later prepared a highly insoluble modification, and Jensen and Clauson-Kaas[4] confirmed these reports. They also showed that diphenyltin is neither dipolar nor a free radical. The preparation of yellow modifications of intermediate solubility, and of two colorless modifications have been effected recently.[5] Beyond the fact that these substances react readily with oxygen and with bromine[2] very little regarding their reactions has been published.

Organic derivatives of divalent tin should be of particular value in the study of valence changes in the metal atom. In principle, at least, the presence of these groups makes possible rather wide, as well as subtle variations in the electron availability and steric hindrance at the tin atom. Furthermore, it would be of interest to examine potential applications of these compounds as reducing agents. This paper is a report of the reaction of diphenyltin with a number of reducible reagents.

In all of the reactions described below, except where specifically noted, the colorless modification of diphenyltin obtained by the decomposition of the hydride in methanol[5] was used.

Oxidation of solutions of all modifications of diphenyltin occurs readily in air. However, complete oxidation is not easily achieved. With 30% hydrogen peroxide, added to a benzene solution of the diphenyltin, oxidation to diphenyltin oxide occurred readily. The oxide has been prepared earlier by the hydrolysis of diphenyltin dichloride of diphenyltin oxychloride by potassium carbonate,[6] and by the hydrolysis of the dibromide by sodium hydroxide.[7]

The reaction of diphenyltin (from the reaction of phenylmagnesium bromide with stannous chloride) with bromine to form the dibromide has been reported earlier.[2] However, the dibromide was not isolated; it was converted to the difluoride (by reaction with sodium fluoride) which was isolated. We thought it desirable to examine the reaction of diphenyltin with chlorine, bromine and iodine in order to determine whether any side reactions occur. The reaction with chlorine yielded 98% of diphenyltin in carbon tetrachloride. Attempts to use chlorine generated *in situ* by the reaction of hydrogen chloride with *N*-chloroacetamide gave stannous chloride and, presumably, benzene as by-products. These are formed by the facile cleavage of diphenyltin by hydrogen chloride. Similar difficulty was encountered when methylene chloride was the solvent. In this case the hydrogen chloride is formed from the reaction of the solvent with chlorine. One earlier preparation of diphenyltin dichloride involved the reaction of tetraphenyltin with stannic chloride.[8] It has also been obtained by the reaction of diphenylmercury with stannous chloride.[9] Mercuric chloride and diphenyltin also react to produce diphenyltin dichloride and presumably mercurous chloride and metallic mercury. In a highly exothermic reaction diphenyltin and stannic chloride have been found to produce a 76% yield of diphenyltin dichloride and stannous chloride. This is in accord with the expected affinities of diphenyltin and stannous chloride for electrons. The former, with two aryl groups rather than two chlorines attached to the tin, should be better able to give up or share the electrons needed in going to the quadrivalent state.

Diphenyltin dibromide was isolated in 48% yield by the reaction of diphenyltin and bromine in benzene. The low yield obtained, in spite of the quantitative consumption of bromine, is a reflection of the difficulty of obtaining the product with a high melting point. It apparently has a large freezing point depression constant. Earlier preparations of the bromide involved the action of hydrogen bromide on diphenyltin oxide[4] and reaction of diphenylmercury with stannous bromide.[9]

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[1] (a) Support of this work by the Office of Ordnance Research, U. S. Army, is gratefully acknowledged. (b) Taken in part from the M. Sc. thesis of E. R. Jakusik, August, 1957.

[2] E. Krause and R. Becker, *Ber.*, **53**, 173 (1920).

[3] R. F. Chambers and P. C. Scherer, *J. Am. Chem. Soc.*, **48**, 1054 (1926).

[4] K. A. Jensen and N. Clauson-Kaas, *Z. anorg. u. allgem. Chem.*, **250**, 277 (1943).

[5] H. G. Kuivila, A. K. Sawyer, and A. C. Armour, *J. Org. Chem.*, **26**, 1426 (1961).

[6] B. Aronheim, *Ann.*, **194**, 145 (1878).

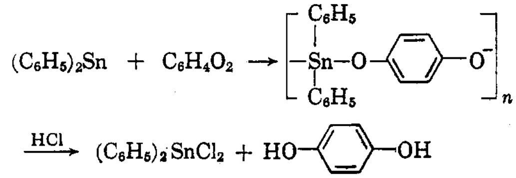
[7] C. Quintin, *Ing. Chem.*, **14**, 205 (1930); *Chem. Abstr.*, **26**, 2183 (1932).

[8] H. Zimmer and H. W. Sparmann, *Chem. Ber.*, **87**, 645 (1954); K. A. Kocheshkov, *Ber.*, **62**, 996 (1929).

Diphenyltin reacted readily with iodine in methanol to provide an 86% yield of the diiodide, which had been prepared earlier by the cleavage of tetraphenyltin with iodine.[10a]

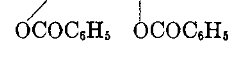
Diphenyltin sulfide can be prepared readily by the reaction of elemental sulfur with diphenyltin, either by refluxing a solution of the reactants in toluene for an hour, or by allowing the solution to stand for a few days at room temperature. We have found this method, which yields 85% of the product, to be more convenient and effective than the preparation from the reaction of hydrogen sulfide and diphenyltin dichloride reported by Eskin, Nesmeyanov, and Kocheshkov,[10b] although their method involves only a single step from diphenyltin dichloride.

When a benzene solution of equimolar amounts of diphenyltin and benzoquinone is allowed to stand for twenty-four hours, a 93% yield of an insoluble, pale buff-colored material is formed. Its analysis corresponds to a 1:1 adduct of the reactants. When treated with dry hydrogen chloride in methylene chloride a 68% yield of diphenyltin dichloride and a 33% yield of hydroquinone have been isolated from separate experiments. The reaction sequence involved is probably



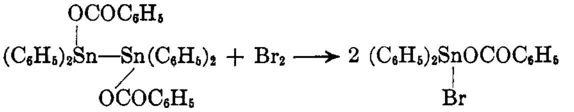
The highly polymeric nature of the first product is indicated by its insolubility in organic solvents; the phenoxide structure is consistent with the ready cleavage with hydrogen chloride.

The reaction of diphenyltin with benzoyl peroxide was investigated in order to determine whether it would function as a free radical "trap." A slightly exothermic reaction occurred between the compounds at room temperature, whereas benzoyl peroxide solutions are stable up to about 80°. Thus a direct reacion occurs; its course is as follows:



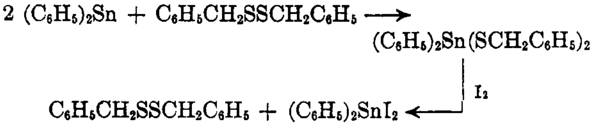
$$2\ (C_6H_5)_2Sn + (C_6H_5)_2COO)_2 \longrightarrow \underset{OCOC_6H_5}{(C_6H_5)_2Sn}-\underset{OCOC_6H_5}{Sn(C_6H_5)_2}$$

The structure of the product was established by the following observations: (1) an 81% yield of 1,1,2,2-tetraphenyl-1,2-dibenzoyloxyditin was obtained when the reactants were used in the stoichiometry indicated; (2) the elemental analysis was in accord with that expected; (3) it reacted with one mole of bromine as required by the following equation; (4) its melting point was undepressed when mixed with a sample prepared by the reaction of benzoic acid with diphenyltin dihydride.[11] This reaction constitutes a new method for the synthesis of compounds containing the tin-tin bond. It is known that triphenylphosphine reacts with acyl peroxides with the removal of one oxygen atom leading to the formation of triphenylphosphine oxide and benzoic anhydride.[12]



$$(C_6H_5)_2\overset{OCOC_6H_5}{Sn}-\underset{OCOC_6H_5}{Sn}(C_6H_5)_2 + Br_2 \longrightarrow 2\ (C_6H_5)_2\underset{Br}{Sn}OCOC_6H_5$$

Triphenylphosphine reacts readily with acyl disulfides to form triphenylphosphine sulfide, but dibenzyldisulfide is unreactive.[13] Diphenyltin, on the other hand, reacts readily with this disulfide in refluxing benzene yielding 93% of an oil whose molecular weight and elemental analysis correspond to diphenyltin dithiobenzylate. It reacted with one mole of iodine to produce dibenzyl disulfide in 84% yield. The disulfide and the diiodide were separated by addition of pyridine which formed a complex with the latter. This complex, however, was sufficiently unstable so that drying *in vacuo* removed all of the pyridine and left pure diphenyltin diiodide.



$$2\ (C_6H_5)_2Sn + C_6H_5CH_2SSCH_2C_6H_5 \longrightarrow (C_6H_5)_2Sn(SCH_2C_6H_5)_2 \xrightarrow{I_2} C_6H_5CH_2SSCH_2C_6H_5 + (C_6H_5)_2SnI_2$$

As diphenyltin reacted readily with benzoquinone, its reactions with other reducible functions containing oxygen were examined. Nitrobenzene and benzil were chosen as substrates. In benzene solution at room temperature each led to the polymerization of the diphenyltin to a less soluble yellow modification. The polymerization induced by the nitrobenzene occurred much faster, but more polymer was obtained from the benzil reaction. Whether this was due to a higher yield of polymer or a lower solubility of the polymer was not ascertained. This appears to be the first instance in which a rapid polymerization of diphenyltin has been effected.

When diphenyltin is heated to about 250°, it disproportionates into tetraphenyltin and metallic tin. Below 200° it is quite stable thermally.

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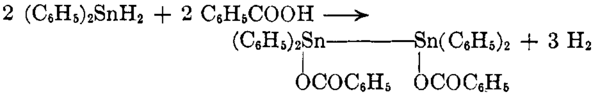
(9) A. N. Nesmeyanov and K. A. Kocheshkov, *Ber.*, **63**, 2496 (1930).

(10)(a) R. H. Bullard and W. B. Robinson, *J. Am. Chem. Soc.*, **49**, 1369 (1927). (b) I. T. Eskin, A. N. Nesmeyanov, and K. A. Kocheshkov, *J. Gen. Chem., U.S.S.R.*, **8**, 35 (1938); *Chem. Abstr.*, **32**, 5386 (1938).

(11) The reaction, discovered in these laboratories, is



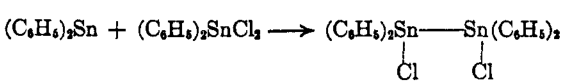
$$2\ (C_6H_5)_2SnH_2 + 2\ C_6H_5COOH \longrightarrow \underset{OCOC_6H_5}{(C_6H_5)_2Sn}-\underset{OCOC_6H_5}{Sn(C_6H_5)_2} + 3\ H_2$$

(12) See for example D. B. Denney and M. A. Greenbaum, *J. Am. Chem. Soc.*, **79**, 979 (1957) for a discussion of the mechanism.

(13) A. Schonberg, *Ber.*, **68**, 163 (1935).

Disproportionation can be induced at a much lower temperature with the aid of boron trifluoride. If the gas is passed into a benzene solution of diphenyltin a nearly colorless precipitate appears and the light yellow color originally present in the solution disappears. When this reaction product mixture is heated, the precipitate turns black. Upon work-up, tetraphenyltin can be isolated in 67% yield and the black precipitate, after extraction in a Soxlet extractor with benzene, contains 93.5% tin.

The compound 1,1,2,2-tetraphenyl-1,2-dichloroditin has been reported by Johnson and colleagues[14] to be the product formed upon addition of diphenyltin dichloride to an ethanol solution of hydrazine. The possibility that such a product might result from the reaction of diphenyltin with diphenyltin dichloride was considered. When the reactants



$$(C_6H_5)_2Sn + (C_6H_5)_2SnCl_2 \longrightarrow (C_6H_5)_2\underset{Cl}{Sn}\text{——}\underset{Cl}{Sn}(C_6H_5)_2$$

(using diphenyltin from the reaction of phenyllithium with stannous chloride) were heated at 130° for three hours a reaction occurred according to the following equation:

$$(C_6H_5)_2Sn + 2\ (C_6H_5)_2SnCl_2 \longrightarrow 2\ (C_6H_5)_3SnCl + SnCl_2.$$

EXPERIMENTAL

All melting points are uncorrected.

Diphenyltin was prepared according to methods described previously.[5] It was stored in evacuated ampoules. A nitrogen atmosphere was always used to protect solutions of the diphenyltin.

Tin analyses were carried out by the method of Gilman and Rosenberg.[15] Other analyses were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Reactions of diphenyltin. With hydrogen peroxide. Diphenyltin, 5.44 g. (0.020 mole) was dissolved in 15 ml. of benzene. Then 2.5 g. (0.022 mole) of 30% hydrogen peroxide was added with swirling over 15 min. Some warming occurred during this time and continued for some time afterward. After 1.25 hr. the white precipitate which had formed was filtered and washed with benzene and dried overnight *in vacuo.* The yield of diphenyltin oxide was 5.60 g. (97%).

Anal. Calcd. for $C_{12}H_{10}SnO$: Sn, 41.10. Found: Sn, 41.10, 41.03.

With sulfur. A solution of 0.80 g. (0.025 mole) of sulfur in 10 ml. of toluene was added to 5.45 g. (0.020 mole) of diphenyltin dissolved in 15 ml. of toluene. The resulting solution was refluxed for 3.5 hr., cooled to room temperature, and filtered. The solid (0.025 g.) was discarded. Concentration of the filtrate to about 15 ml. produced 4.37 g. of white diphenyltin sulfide, m.p. 179–180.5°. Further concentration to about 3 ml. yielded another 0.81 g. of product, m.p. 177–178.5°; total yield, 85%.

If equimolar amounts of reactants were used, the reaction product contained a brown precipitate; if a larger excess of sulfur was used, separation of the diphenyltin sulfide from the sulfur became a problem.

With chlorine. A solution of 2.72 g. (0.010 mole) of diphenyltin in 20 ml. of carbon tetrachloride was prepared. Considerable heat was evolved as the solid dissolved. Chlorine was generated in another flask by the reaction of potassium permanganate and hydrogen chloride and passed into the diphenyltin solution. (A quantitative yield of chlorine would be 0.015 mole.) The carbon tetrachloride was concentrated to half its volume and the small amount of white precipitate present filtered off and discarded. The filtrate was then evaporated to dryness leaving a 98% yield of diphenyltin dichloride; m.p. 40–41°.

With bromine. To a solution of 1.36 g. (0.0050 mole) of diphenyltin in 10 ml. of benzene was added liquid bromine dropwise until the color of the bromine persisted. The solution was evaporated under reduced pressure until an oil remained. It was placed in the refrigerator for 2 days after which the material became a crystalline mass. This was placed on a filter paper and allowed to stand in the air for several hours. The yield of product, m.p. 36–38.5°, was 1.03 g. (48%). It appears to be characteristic of the dibromide that it is much more difficult to crystallize than the other halides.

With iodine. To a slurry of 2.72 g. (0.010 mole) of diphenyltin in 10 ml. of methanol was added 2.80 g. (0.011 mole) of iodine over 15 min. with vigorous stirring. The mixture was heated at 50–55° for an hour, cooled to room temperature, filtered, and concentrated to about 10 ml. at room temperature. The amber crystals which appeared were filtered, and the filtrate concentrated to 3 ml. whereupon more crystals were obtained. The combined crops became colorless upon drying in air; 4.52 g. (86%), m.p. 71.5–72.5°. Diphenyltin diiodide decomposes to some extent, as indicated by iodine formation, in hot methanol, and to a greater extent in hot ligroin.

With stannic chloride. To a solution of 1.67 g. (0.00612 mole) of diphenyltin in 10 ml. of benzene and 5 ml. of petroleum ether (b.p. 60–90°), cooled in an ice bath, was added a solution of 1.16 g. (0.00612 mole) of stannic chloride in 17 ml. of benzene over a period of 15 min. The ice bath was removed and the reaction mixture heated to reflux for a half hour, cooled, and filtered. The crystals (1.14 g.) were washed with benzene and dried for an hour at 110°. These crystals were no doubt stannous chloride (theoretical yield, 1.16 g.). The filtrate was concentrated to an oil and taken up in 7 ml. of petroleum ether (b.p. 40–60°), filtered, concentrated to about 3 ml., and cooled, yielding 1.29 g. (76%) of crystals, m.p. 39.5–41.0°, undepressed upon admixture with authentic diphenyltin dichloride.

With diphenyltin dichloride. Diphenyltin (from the phenyllithium-stannous chloride reaction, not pure) (1.72 g., 0.00632 mole), and diphenyltin dichloride (4.34 g., 0.01246 mole), were ground together in a mortar and then placed in a 50 ml. Erlenmeyer flask. The flask was heated on the steam bath until a homogeneous solution resulted (10 min.). It was then transferred to an oil bath and heated at 130–140° for 5 hr. No further change in the reaction mixture appeared to take place after the first 3 hr. After cooling, 25 ml. of ligroin (b.p. 60–90°) was added, the mixture heated to a boil, filtered and cooled, yielding 3.53 g. (77%) of triphenyltin chloride, m.p. 103–105°.

With mercuric chloride. The mercuric chloride, 1.98 g., (0.00729 mole) was dissolved in 70 ml. of ether, and 2.00 g. (0.00733 mole) of diphenyltin was added. Immediate reaction occurred as revealed by the formation of a gray precipitate which contained droplets of mercury. The filtrate was concentrated to about 3 ml., filtered and cooled in the refrigerator, yielding 1.24 g. (58%) of diphenyltin dichloride, m.p. 35–38°. Recrystallization from a minimum amount of petroleum ether (b.p. 30–60°) provided 0.81 g. m.p. 41–42°, undepressed upon admixture with an authentic sample.

With boron trifluoride. A solution of 2.73 g. (0.010 mole) of diphenyltin in 20 ml. of benzene was prepared. Boron trifluoride was passed in for 20 min., whereupon a gelatinous

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[14] O. H. Johnson, H. E. Fritz, D. O. Halvorson, and R. L. Evans, *J. Am. Chem. Soc.*, **77**, 5857 (1955).

[15] H. Gilman and S. D. Rosenberg, *J. Am. Chem. Soc.*, **75**, 3592 (1953).

precipitate appeared and the originally light yellow supernatant became essentially colorless. After standing for a day the precipitate was filtered off, dried *in vacuo* (2.11 g.), placed in the cup of a Soxlet extractor and extracted for 4 hr. with methylene chloride. The residue in the cup (1.09 g.) was digested with hot water, filtered, washed, and dried yielding 0.50 g. of black material which gave no green boron flame and contained 93.5% tin.

The benzene and methylene chloride solutions were combined and evaporated to dryness, yielding 1.46 g. (68%) of quite impure tetraphenyltin, m.p. 178–210°. Recrystallization from toluene left 0.72 g. (34%) of tetraphenyltin, m.p. 222–225°, undepressed upon admixture with an authentic sample.

With benzoquinone. A solution of 2.71 g. (0.00993 mole) of diphenyltin in 10 ml. of benzene was added to 10 ml. of benzene containing 1.07 g. (0.00993 mole) of benzoquinone. Within 2 min. the solution turned a dark green; a dark green precipitate appeared and the supernatant became greenish yellow within 5 min. After 0.5 hr. a white precipitate began to appear. After 8 hr. the product was heated on the steam bath for 15 min. and filtered. The precipitate was washed with benzene and dried; 3.24 g. (86%).

Anal. Calcd. for $C_{16}H_{14}SnO_2$: C, 56.75; H, 3.70; Sn, 31.16. Found: C, 56.35; H, 3.96; Sn, 31.32, 31.45.

Hydrogen chloride was passed through a suspension of 1.50 g. of the product in methylene chloride until the originally dense precipitate became flocculent. The product mixture was filtered and the filtrate evaporated near dryness, digested with 3 ml. of petroleum ether (b.p. 40–60°), filtered, and cooled. Crystals of diphenyltin dichloride which formed were filtered off and dried in air; 0.92 g. (67.5%), m.p. 40–43° undepressed upon admixture with an authentic sample.

With benzoyl peroxide. To a solution of 0.77 g. (3.13 mmoles) of benzoyl peroxide in 10 ml. of benzene was added 1.70 g. (6.25 mmoles) of diphenyltin. A slightly exothermic reaction occurred. Crystals began to appear after 15 min. After standing overnight 2.0 g. (81%) of 1,1,2,2-tetraphenyl-1,2-dibenzoxyditin, m.p. 172–177° was obtained. Recrystallization from benzene provided an analytical sample, 1.41 g., m.p. 184–185°, undepressed when mixed with a sample prepared from the reaction of diphenyltin dihydride with benzoic acid.[11]

Anal. Calcd. for $C_{38}H_{30}O_4Sn_2$: C, 57.92; H, 3.84; Sn, 30.12. Found: C, 57.82; H, 3.79; Sn, 30.25, 30.28.

With dibenzyldisulfide. To 20 ml. of a benzene solution containing 5.46 g. (20.0 mmoles) of diphenyltin was added 4.93 g. (20.0 mmoles) of dibenzyldisulfide. The resulting mixture was heated under reflux for 7.5 hr., cooled, and filtered. The solvent was removed at reduced pressure, leaving 9.6 g. (92%) of light yellow diphenyltin dithiobenzylate, n_D^{26} 1.6610.

Anal. Calcd. for $C_{26}H_{24}S_2Sn$: C, 60.13; H, 4.66; S, 12.35; Sn, 22.86; mol. wt., 519.3. Found: C, 60.02; H, 4.70; S, 12.57; Sn, 22.58; mol. wt. 497.4 (cryoscopic in benzene).

Reaction of diphenyltin dithiobenzylate with iodine. To a suspension of 3.12 g. (6.00 mmoles) of diphenyltin dithiobenzylate in 5 ml. of methanol was added a solution of 1.52 g. (6.00 mmoles) of iodine in 10 ml. of methanol. All of the iodine was consumed. The solution was evaporated to dryness leaving the theoretical weight of a mixture of diphenyltin diiodide and dibenzyl disulfide. This was dissolved in 20 ml. of ether, cooled in an ice bath, and 2.37 g. (30.0 mmoles) of pyridine was added. The precipitate which appeared was filtered and washed with warm ether. It was dried in the air for 0.5 hr., m.p. 138–142°. Upon further drying in a vacuum desiccator for 3 days, there remained 2.7 g., m.p. 70–72°, undepressed upon admixture with authentic diphenyltin diiodide.

Anal. Calcd. for $C_{12}H_{10}I_2Sn$: Sn, 22.54. Found: Sn, 22.74, 22.62.

The ether filtrate was warmed to remove the ether and the resulting solid, 1.25 g. (84%), m.p. 67–70°, was recrystallized from ethanol, yielding 0.94 g., m.p. 69–71°, undepressed upon admixture with authentic dibenzyl disulfide.

Polymerization initiated by nitrobenzene. To a solution of 2.21 g. (0.00810 mole) of diphenyltin in 10 ml. of benzene was added 0.85 ml. (0.0114 mole) of nitrobenzene. The mixture was allowed to stand overnight, filtered, and dried. The bright yellow precipitate weighed 2.10 g. and contained 40.8% tin. This may be low because of adsorbed nitrobenzene, whose odor was very apparent. Another similar experiment provided a product containing 41.9% tin.

Polymerization initiated by benzil. A solution of 2.10 g. (10.0 mmoles) of benzil and 2.73 g. (10.0 mmoles) of diphenyltin was allowed to stand at room temperature for a week. The yellow solid was filtered off, washed with ether, and dried; 2.12 g., 78%; tin, 43.07%.

Acknowledgment. We thank K. V. Nahabedian and J. H. Polevy for technical assistance.

DURHAM, N. H.

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Cleavage Reactions of Phosphinemethylenes

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As part of a program of research in organophosphorus chemistry, an attempt was made to prepare bisphosphinemethylenes which would be stable under ambient conditions. Attempts to effect mutual resonance stabilization of two phosphinemethylene groups in the same molecule either by conjugation through an ethylenic double bond or by cross-conjugation through a carbonyl group were unsuccessful. However, a bisphosphinemethylene with no conjugation between the two ylide linkages was prepared in which the two phosphorus-carbon semipolar bonds were stabilized by α-ester carbonyl groups.

Attempts to alkylate the ylide-like compounds resulting from reaction of tertiary phosphines with benzalmalononitrile resulted in cleavage of these complexes into the original benzalmalononitrile and the methiodide of the tertiary phosphine.

Phosphinemethylenes (ylides) may be prepared by treating phosphonium compounds, in which at least one hydrogen is present on a carbon bound to phosphorus, with a base.[1] Ordinary phosphinemethylenes (in which R′ is alkyl or hydrogen) are unstable to air and moisture, which tend to cleave them into tertiary phosphine oxides (and

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(1) G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 28.