(15 mm); nmr, aromatic protons (δ 7.51, 5 H), aldimine protons (δ 6.54 and 6.59; 2 H, J_{AB} = 11.3 cps), and N-methyl protons (δ 3.01, 3 H).

Anal. Calcd for $C_8H_{10}N_2$: C, 71.60; H, 7.51; N, 20.93. Found: C, 71.60; H, 7.76; N, 20.73.

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Scope and Mechanism of the Reaction of Alkylidenephosphoranes with Nitriles

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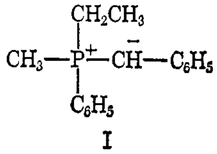
Abstract: The scope of the reaction of a phosphonium ylide with a nitrile, with subsequent acid-catalyzed hydrolysis of the adduct, has been explored. In reactions of both aliphatic and aromatic nitriles with ylides derived from ethyltriphenylphosphonium iodide, triphenylbenzylphosphonium iodide, tetra-*n*-butylphosphonium iodide, tri-*n*-butylbenzylphosphonium iodide, and methylethylphenylbenzylphosphonium iodide, very good yields of ketones were obtained. It was also found that the yield of the condensation product of nitrile and ylide was markedly dependent on the nature of the lithium salt (derived from the phosphonium halide and organolithium reagent in the generation of the ylide) present in the reaction mixture. Control experiments indicated that the effect was attributable to activation of the nitrile by Li^+. The lithium ion is functioning as an activating agent (Lewis acid) in the condensation step. The use of (+)-methylethylphenylbenzylphosphonium iodide in condensation reactions with benzonitrile, *p*-methylbenzonitrile, and *p*-chlorobenzonitrile also helped to clarify some of the details of the mechanism of the over-all reaction.

Some time ago, we reported[1] that the condensation of methylethylphenylbenzylidenephosphorane (I) with benzonitrile gave an adduct which, on base- or acid-catalyzed hydrolysis, afforded desoxybenzoin and methylethylphenylphosphine oxide in high yield. Some insight into the mechanism of the reaction was also gained by the use of optically active I in the same reaction sequence. We have now expanded the scope of this reaction by the use of a variety of phosphonium ylides and nitriles in the condensation reaction and we have looked further into the mechanism of the reaction by means of a study of the stereochemistry of the reaction of optically active I with some *para*-substituted benzonitriles and also by examination of certain metal cation effects.



$$CH_3-\overset{CH_2CH_3}{\underset{C_6H_5}{\overset{|}{\underset{|}{P^{+}}}}}-\overset{-}{C}H-C_6H_5$$

I

The results of the reactions of various nitriles with ylides derived from a number of fundamentally different types of phosphonium salts are given in Table I. In all cases reported in Table I, the initial adduct was subjected to acid-catalyzed hydrolysis.

As shown in Table I, ylides derived from phosphonium iodides react with nitriles to give, generally, quite high yields of ketones. However, under identical conditions, ylides derived from the corresponding phosphonium chlorides and phosphonium bromides are able to bring about little, if any, conversion of nitriles to ketones. It appears to be of fundamental importance that the phosphonium iodides react with the organolithium compounds to give, at the equivalence point, homogeneous solutions, whereas the corresponding chlorides and bromides give, at the equivalence point, heterogeneous mixtures. It was found, moreover, that a typical unreactive ylide mixture (generated by the action of methyllithium on triphenylbenzylphosphonium chloride) could be caused to react with *p*-chlorobenzonitrile, for example, by the addition of powdered, anhydrous lithium iodide to the reaction mixture. A yield of 81% of 4′-chlorodesoxybenzoin was thus obtained.

That the apparent "anion effect" is actually due to the presence of *dissolved* lithium ions rather than to iodide ions was demonstrated experimentally as follows. Addition of an equivalent quantity of tetraphenylphosphonium iodide to an unreactive ylide mixture (generated in benzene medium from triphenylbenzylphosphonium chloride) led to no increase in the yield of condensation product. However, treatment of an identical unreactive ylide mixture with an equivalent quantity of anhydrous lithium perchlorate brought about conversion of *p*-chlorobenzonitrile to 4′-chlorodesoxybenzoin in 68% yield. The fact that treatment of the unreactive ylide mixture with 0.2 equiv of lithium perchlorate led to the isolation of 4′-chlorodesoxybenzoin in but 19% yield indicates that the soluble lithium salts do not function as true catalysts, but are better described as activating reagents.

That lithium iodide remains dissolved in ether, dioxane, or benzene in the presence of the ylides, whereas lithium chloride and lithium bromide precipitate under identical circumstances, can be explained by the assumption that the ylides, being dipolar molecules, are able to interact with lithium iodide strongly enough

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[1] A. Blade-Font, W. E. McEwen, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **82**, 2646 (1960).

Table I. Yields of Ketones from Reactions of Phosphonium Ylides with Nitriles

Phosphonium salt	Nitrile	Solvent	Ketone	Yield, %
$Ph_3\overset{+}{P}CH_2CH_3\ \overset{-}{I}$	p-ClC_6H_4CN	Ether	p-$ClC_6H_4COCH_2CH_3$	91
$Ph_3\overset{+}{P}CH_2CH_3\ \overset{-}{I}$	C_6H_5CN	Ether	$PhCOCH_2CH_3$	85
$Ph_3\overset{+}{P}CH_2CH_3\overset{-}{I}$	p-$CH_3C_6H_4CN$	Ether	p-$CH_3C_6H_4COCH_2CH_3$	76
$Ph_3\overset{+}{P}CH_2CH_3\ \overset{-}{I}$	$CH_3(CH_2)_3CN$	Ether	$CH_3(CH_2)_3COCH_2CH_3$	64
$Ph_3\overset{+}{P}CH_2Ph\ \overset{-}{Cl}$	p-ClC_6H_4CN	Ether[a]	. . .	0
$Ph_3\overset{+}{P}CH_2Ph\ \overset{-}{Cl}$	p-ClC_6H_4CN	Benzene[a]	. . .	0
$Ph_3\overset{+}{P}CH_2Ph\ \overset{-}{Cl}$	p-ClC_6H_4CN	Benzene[b]	. . .	0
$Ph_3\overset{+}{P}CH_2Ph\ \overset{-}{Cl}$	p-ClC_6H_4CN	p-Dioxane[b]	p-$ClC_6H_4COCH_2Ph$	4
$Ph_3\overset{+}{P}CH_2Ph\ \overset{-}{I}$	p-ClC_6H_4CN	Benzene	p-$ClC_6H_4COCH_2Ph$	90
$Ph_3\overset{+}{P}CH_2Ph\ \overset{-}{I}$	C_6H_5CN	Benzene	$PhCOCH_2Ph$	87
$Ph_3\overset{+}{P}CH_2Ph\ \overset{-}{I}$	p-$CH_3C_6H_4CN$	Benzene	p-$CH_3C_6H_4COCH_2Ph$	89
$Ph_3\overset{+}{P}CH_2Ph\ \overset{-}{I}$	$CH_3(CH_2)_3CN$	Benzene	$CH_3(CH_2)_3COCH_2Ph$	50
$Ph_3\overset{+}{P}CH_2Ph\overset{-}{I}$	p-ClC_6H_4CN	p-Dioxane	p-$ClC_6H_4COCH_2Ph$	80
$Ph_3\overset{+}{P}CH_2Ph\ \overset{-}{Br}$	p-ClC_6H_4CN	Benzene	p-$ClC_6H_4COCH_2Ph$	4
n-$Bu_4\overset{+}{P}\ \overset{-}{I}$	p-ClC_6H_4CN	Ether	p-$ClC_6H_4CO(CH_2)_3CH_3$	98
n-$Bu_4\overset{+}{P}\ \overset{-}{I}$	C_6H_5CN	Ether	$PhCO(CH_2)_3CH_3$	75
n-$Bu_4\overset{+}{P}\ \overset{-}{I}$	p-$CH_3C_6H_4CN$	Ether	p-$CH_3C_6H_4CO(CH_2)_3CH_3$	95
n-$Bu_4\overset{+}{P}\ \overset{-}{I}$	$CH_3(CH_2)_3CN$	Ether	$CH_3(CH_2)_3CO(CH_2)_3CH_3$	84
n-$Bu_3\overset{+}{P}CH_2Ph\ \overset{-}{I}$	p-ClC_6H_4CN	Benzene	p-$ClC_6H_4COCH_2Ph$	97
n-$Bu_3\overset{+}{P}CH_2Ph\ \overset{-}{I}$	p-ClC_6H_4CN	Ether	p-$ClC_6H_4COCH_2Ph$	99
n-$Bu_3\overset{+}{P}CH_2Ph\ \overset{-}{I}$	C_6H_5CN	Ether	$PhCOCH_2Ph$	82
n-$Bu_3\overset{+}{P}CH_2Ph\ \overset{-}{I}$	p-$CH_3C_6H_4CN$	Ether	p-$CH_3C_6H_4COCH_2Ph$	90
n-$Bu_3\overset{+}{P}CH_2Ph\ \overset{-}{I}$	$CH_3(CH_2)_3CN$	Ether	$CH_3(CH_2)_3COCH_2Ph$	73
n-$Bu_3\overset{+}{P}CH_2Ph\ \overset{-}{Cl}$	p-ClC_6H_4CN	Ether	p-$ClC_6H_4COCH_2Ph$	35
n-$Bu_3\overset{+}{P}CH_2Ph\ \overset{-}{Cl}$	p-ClC_6H_4CN	Benzene	p-$ClC_6H_4COCH_2Ph$	6

[a] Reaction mixture refluxed for 6 hr. [b] Reaction mixture refluxed for 48 hr.

to overcome its lattice energy but not strongly enough to overcome the higher lattice energy of lithium chloride or lithium bromide.[2]

The presence of an insoluble substance (presumably lithium chloride) in the reaction mixtures in which lithium perchlorate was used as an additive made it impossible to determine visually whether or not the added lithium perchlorate was soluble in the presence of the ylide before addition of the nitrile. The fact that the lithium perchlorate–ylide–lithium chloride mixture darkened markedly upon addition of *p*-chlorobenzonitrile, however, while no color change was observed when *p*-chlorobenzonitrile was added to the lithium iodide–ylide mixture may be explained by the assumption that lithium perchlorate remains insoluble in the presence of the ylide, but dissolves in the presence of *p*-chlorobenzonitrile to give a dark lithium perchlorate–nitrile complex.[3]

In view of all of the facts cited above, there can be little doubt that lithium ion complexes with the nitrile and thereby increases the electrophilic reactivity of the carbon atom of the cyano group in the condensation reactions under consideration. The probable mecha-

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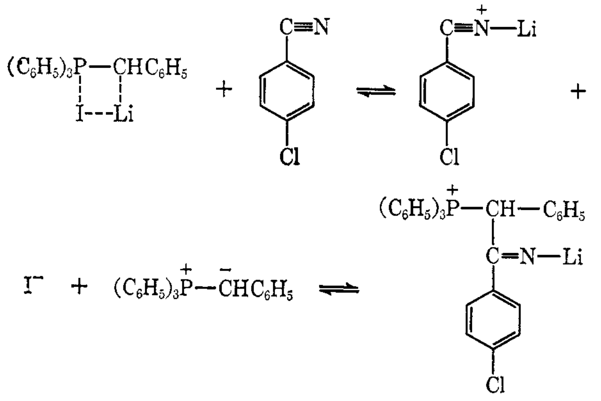
(2) J. Kleinberg, W. J. Argersinger, Jr., and E. Griswold, "Inorganic Chemistry," D. C. Heath and Co., Boston, Mass., 1960, p 156.

(3) M. M. Markowitz, W. N. Hawley, D. A. Boryta, and R. F. Harris [*J. Chem. Eng. Data*, 6, 325 (1961)] have made a quantitative study of the solubility of anhydrous lithium perchlorate in a wide variety of organic solvents ranging from nonpolar substances, such as hydrocarbons, to highly polar substances, such as alcohols, carbonyl compounds, and, notably, acetonitrile and benzonitrile. These workers found that, at 25°, anhydrous lithium perchlorate is soluble in acetonitrile to the extent of 16.3 ± 0.1 g/100 g of acetonitrile (mole fraction of lithium perchlorate = 0.059). Even more striking is the fact that the solubility of anhydrous lithium perchlorate in benzonitrile was found to be 21.9 g/100 g of benzonitrile (mole fraction of $LiClO_4$ = 0.175). Also, we have measured the solubility of anhydrous lithium perchlorate in anhydrous benzene and have found it to be only 0.0013 g per 17.0905 g of benzene at 80°.

nism of the condensation step in the reaction of the ylide derived from triphenylbenzylphosphonium iodide and methyllithium with *p*-chlorobenzonitrile is shown in Scheme I.

Scheme I



It is of interest to note that the reactions of nitriles with ylides derived from quaternary salts of tri-*n*-butylphosphine proceed faster, and generally give higher yields of ketones, than do reactions carried out with ylides derived from the corresponding quaternary salts of triphenylphosphine. These observations are in keeping with the fact that ylides derived from quaternary salts of trialkylphosphines exhibit greater nucleophilicity than do ylides derived from the corresponding quaternary salts of triphenylphosphine.[4-6]

Since the condensation of phosphonium ylides with nitriles and subsequent hydrolysis of the adducts represents a new method of synthesis of ketones, it is of interest to compare this method with other known procedures[7-22] for converting nitriles into ketones, most of which consist of the condensation of a nitrile with an organometallic reagent. The most important conclusion which emerges from such a comparison is that the phosphonium ylide method seems to be superior to the Grignard method when an alkyl cyanide having α-hydrogen atoms is used as the substrate. To cite a specific comparison, the reaction of *n*-valeronitrile with *n*-butylmagnesium bromide has been reported[13] to give di-*n*-butyl ketone in only 20% yield, whereas we have found that reaction of the nitrile with the ylide derived from tetra-*n*-butylphosphonium iodide gives the ketone in 84% yield. However, there is very little difference in yield between the Grignard and phosphonium ylide methods when aromatic nitriles are used.[7,11,12,19] Also, the use of organolithium reagents gives comparable results with the use of phosphonium ylides in the condensation with nitriles.[14,17,18,20-22]

As reported previously,[1] when optically active I, prepared by the action of phenyllithium on levorotatory methylethylphenylbenzylphosphonium iodide,[23-25] was caused to react with benzonitrile, and the resulting adduct was treated with aqueous, methanolic potassium hydroxide solution, the methylethylphenylphosphine oxide (II) obtained was optically active, $[\alpha]^{25}\text{D}$ $+8.3°$ (*c* 3.856, water). Inasmuch as optically pure II has a specific rotation of 22.8°,[25-27] and since it has been demonstrated[24,25] that levorotatory methylethylphenylbenzylphosphonium iodide belongs to the same configurational family as levorotatory II, it follows that the reaction of I with benzonitrile and the subsequent treatment with alkali gave II with 68% inversion of the configuration of the phosphorus atom. It was suggested[1] that there were two competing steps in the hydrolysis of the ylide–nitrile adduct, one involving attack of hydroxide ion on phosphorus with inversion of configuration of the phosphorus atom and the other involving attack of the hydroxide ion on the imino carbon atom of the adduct, the hydrated intermediate then undergoing an intramolecular Wittig-type attack of oxygen on phosphorus to give products with retention of the configuration of the phosphorus atom. In the present work, the hydrolysis of the ylide–nitrile adducts were carried out in an acid medium and therefore the mechanisms are modified as in Scheme II.

It was reasoned that the rate of path a would be affected only very slightly by the nature of a substituent *para* to the original cyano group but that the rate of path b would be strongly affected by a change in the nature of the *para* substituent. It was also felt that hydration of the imino group to give III would be fast relative to either of the steps that entail the breaking of the P–C bond. Thus, it was reasoned that the presence of an electron-withdrawing group *para* to the original cyano group would inhibit path b owing to the decreased nucleophilicity of the hydroxyl group of III and thus lead to an increase in the per cent of inversion of the configuration of the phosphorus atom as against the unsubstituted case since the rate of path a would be relatively unaffected by the presence of the substituent. This proved to be true, as shown in Table II.

Table II. Stereochemical Results of Condensation of Ylide Derived from (+)-Methylethylphenylbenzylphosphonium Iodide with Nitriles

Nitrile	$[\alpha]^{25}\text{D}$ MeEtPhPO, deg	Inversion of phosphorus, %
p-ClC_6H_4CN	-16	83
C_6H_5CN	-9.7	70
p-$CH_3C_6H_4CN$	-9.5	70

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(4) A. W. Johnson and R. B. LaCount, *Tetrahedron*, **9**, 130 (1960).

(5) D. B. Denney and M. J. Boskin, *J. Am. Chem. Soc.*, **81**, 6330 (1959).

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(13) A. Bourgom *ibid.*, **33**, 101 (1924).

(14) H. Gilman and R. H. Kirby, *J. Am. Chem. Soc.*, **55**, 1265 (1933).

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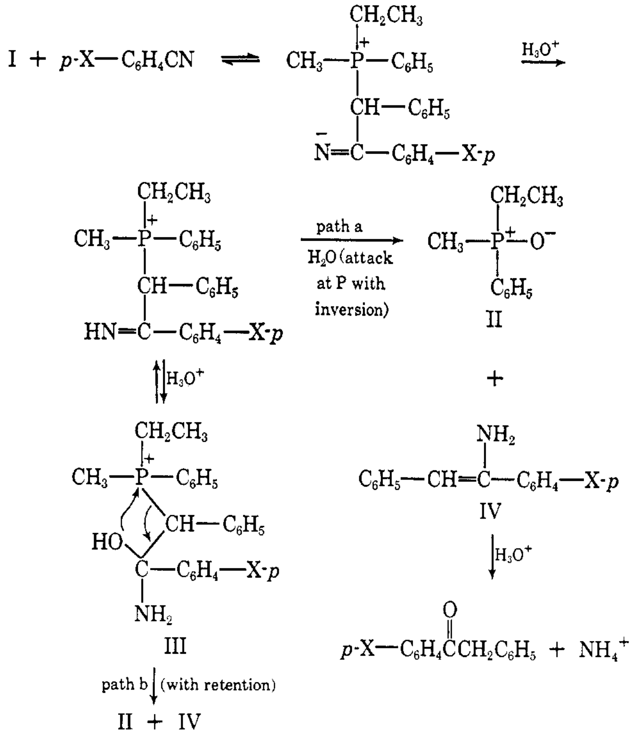
(24) A. Blade-Font, C. A. VanderWerf, and W. E. McEwen, *ibid.*, **82**, 2396 (1960).

(25) W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. VanderWerf, *ibid.*, **86**, 2378 (1964).

(26) K. F. Kumli, W. E. McEwen, and C. A. VanderWerf, *ibid.*, **81**, 3805 (1959).

(27) (a) J. Meisenheimer and L. Lichtenstadt, *Ber.*, **44**, 356 (1911); (b) J. Meisenheimer, J. Casper, M. Horing, W. Lauter, L. Lichtenstadt, and W. Samuel, *Ann.*, **449**, 213 (1926).

Scheme II



The per cent of inversion was distinctly greater when *p*-chlorobenzonitrile was used in place of benzonitrile. The fact that the presence of a *p*-methyl group exerted but little effect as against the unsubstituted case is not of any great significance, inasmuch as a *p*-methyl group would exert only a very weak inductive electron-releasing effect.

Experimental Section

Reaction of Ylide (from a Phosphonium Iodide) with Nitrile. All of the reactions were carried out in essentially the same manner and the following is a generalized description of the procedure. A 0.02-mole sample of pulverized quaternary phosphonium iodide was covered with 100 ml of anhydrous ether. To the stirred suspension was added over a period of 1 hr a solution of 0.02 mole of *n*-butyllithium (or methyllithium) in ether, the mixture being maintained in a nitrogen atmosphere. A red-orange color quickly developed in the suspension. The mixture was refluxed for 1 hr and a clear, red-orange solution was formed.[28] A small additional amount of the quaternary phosphonium iodide was added and the mixture was refluxed for 1 additional hr. At the end of this period, a small amount of undissolved salt could be seen at the bottom of the flask; thus, all of the *n*-butyllithium (or methyllithium) had been consumed.

A solution of 0.02 mole of purified nitrile in 50 ml of ether was added dropwise to the vigorously stirred ylide solution over a period of 1 hr. The color of the solution gradually faded, a pale yellow solution and a finely divided white precipitate being formed. After the mixture had been refluxed until most of the color had faded (2–48 hr), solvent was removed by evaporation. Hydrolysis of the residue was accomplished by addition of 20 ml each of methanol, water, and concentrated hydrochloric acid and by refluxing the mixture for 2 hr. The mixture was than steam distilled until no more ketone could be detected in the distillate.

The method of collection and purification of the ketone depended on its physical properties. Solids were collected by filtration and recrystallized from a suitable solvent, usually methanol–water. Liquid ketones were extracted into ether and purified by distillation, *in vacuo* if necessary. In all cases, the ketone was characterized by means of its infrared spectrum and by the preparation of two solid derivatives.

The aqueous residue from the steam distillation contained the phosphine oxide. If this was triphenylphosphine oxide, it remained as a solid precipitate and was collected by filtration and purified by crystallization from water. If the phosphine oxide was tri-*n*-butylphosphine oxide, it remained as a brown oil. This was taken into ether solution, dried over anhydrous potassium carbonate, and distilled. Tri-*n*-butylphosphine oxide, when distilled *in vacuo*, solidified in the condenser and was then purified further by sublimation. In all cases, the yield of phosphine oxide corresponded closely to the yield of ketone.

Attempted Reaction of Triphenylbenzylidenephosphorane (from Triphenylbenzylphosphonium Chloride) with *p*-Chlorobenzonitrile. Triphenylbenzylphosphonium chloride (7.78 g, 0.02 mole) was covered with 100 ml of ether and to this stirred suspension 1.25 equiv of ethereal methyllithium (Foote Mineral Co.) was added, dropwise, over a period of 1 hr. The suspension underwent the usual white to yellow to red-orange color change, but a finely divided white solid remained in suspension at the end of the addition of the methyllithium. Refluxing for 2 hr did not change the appearance of the mixture.

p-Chlorobenzonitrile (2.75 g, 0.02 mole) dissolved in 50 ml of ether was added dropwise to the heterogeneous ylide mixture over a period of 1 hr. The mixture was refluxed for 6 hr and stirred at room temperature for an additional 12 hr. The orange color of the still heterogeneous mixture had not faded noticeably at the end of this period.

The solvent was evaporated as before and a 2-hr reflux period with the usual hydrolysis mixture resulted in the formation of yellow oil drops suspended in the aqueous phase. Steam distillation resulted in the rapid accumulation of long, white, aromatic needles in the condenser. When no more organic product was noted in the distillate, the cooled distillate was filtered, giving 2.40 g of material, mp 87–91°. Recrystallization from ethanol raised this melting point to 92–93°. A mixture with authentic *p*-chlorobenzonitrile gave no depression of melting point. Further, the infrared spectrum of the recovered substance was identical with that of an authentic sample of *p*-chlorobenzonitrile.

Crude triphenylphosphine oxide (5.45 g) was collected by filtration of the cooled residue from the steam distillation.

An identical experiment (except that benzene was used as solvent) to that described above was carried out. The same color changes and solubility characteristics were noted as before. Steam distillation resulted in the recovery of 2.28 g of *p*-chlorobenzonitrile.

A third attempt to cause the ylide generated from triphenylbenzylphosphonium chloride to react with *p*-chlorobenzonitrile was carried out by refluxing a mixture of 0.027 mole of the ylide (prepared as before in benzene solution) with 0.02 mole of the nitrile for 48 hr. This time, 2.05 g of *p*-chlorobenzonitrile was recovered unchanged.

Prolonged steam distillation resulted in the isolation of 0.17 g of a new, yellow solid from the distillate. Two recrystallizations from aqueous alcohol gave white plates, mp 115–122°. Occasionally, in other similar experiments, small amounts of this material were isolated. This substance was shown by infrared and nmr analysis to be *trans*-stilbene.

Anhydrous dioxane, stored over sodium wire, was used as solvent in a fourth attempt to cause the ylide derived from triphenylbenzylphosphonium chloride to react with *p*-chlorobenzonitrile. Conversion of 24 mmoles of the salt (suspended in 100 ml of dioxane) to the ylide, with ethereal methyllithium, gave the usual red solution over a finely divided white solid. Addition of 0.02 mole (2.75 g) of *p*-chlorobenzonitrile, dissolved in 50 ml of dioxane, and a subsequent 48-hr reflux period caused no visible change in the mixture. Solvent evaporation, hydrolysis, and steam distillation, as before, gave 1.83 g of *p*-chlorobenzonitrile.

Prolonged steam distillation gave 0.19 g of a nonaromatic white substance, mp 100–105°. Two recrystallizations from aqueous alcohol gave white plates, mp 106–107°, undepressed when mixed with authentic 4′-chlorodesoxybenzoin. The infrared spectrum of the pure material, taken in chloroform solution, was identical with that of authentic 4′-chlorodesoxybenzoin.

Reaction of Triphenylbenzylidenephosphorane (from Triphenylbenzylphosphonium Chloride) with *p*-Chlorobenzonitrile in the Presence of Lithium Iodide. Triphenylbenzylphosphonium chloride (9.34 g, 24 mmoles) was suspended in 100 ml of benzene, and this salt was converted to the ylide as in prior reactions. After a reflux period of 1 hr, a finely divided white solid was noted to be

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[28] The solution remained colorless when tetra-*n*-butylphosphonium iodide was converted into the ylide and it turned only pale yellow when tri-*n*-butylbenzylphosphonium iodide was used as starting material. However, a clear solution resulted in each case. After addition of an aromatic nitrile, the solution was refluxed for 4 hr. An 8-hr period of refluxing was required when valeronitrile was used.

Table III

		Ketones isolated		
Nitrile	Ketone	Mp of crude ketone, °C	Mp of pure ketone, °C	Yield of crude ketone, %
p-$CH_3C_6H_4CN$	p-$CH_3C_6H_4COCH_2C_6H_5$	101–108	108.5–110	85
C_6H_5CN	$C_6H_5COCH_2C_6H_5$	54–56	55–56.5	62
p-ClC_6H_4CN	p-$ClC_6H_4COCH_2C_6H_5$	101–105	105–107	82

	Methylethylphenylphosphine oxide isolated		
Nitrile	Yield of crude MeEtPhPO, %	Mp of distilled MeEtPhPO, °C	$[\alpha]^{25}D$, deg, distilled MeEtPhPO
p-$CH_3C_6H_4CN$	76	49–54	−9.5 (*c* 0.997, CH_3OH)
C_6H_5CN	83	42–51	−9.7 (*c* 1.945, CH_3OH)
p-ClC_6H_4CN	71	43–50	−16 (*c* 2.350, CH_3OH)

suspended in the red solution. Powdered anhydrous lithium iodide (4.14 g, 31 mmoles) (K & K Laboratories, Inc.) was added, and the apparently unchanged mixture was refluxed for 1 hr. The usual 20 mmoles of *p*-chlorobenzonitrile, dissolved in benzene, was added to the ylide mixture. The complete reaction mixture was refluxed for 48 hr. At the end of the reflux period, the mixture was still red and contained a white precipitate. The usual work-up, including steam distillation, gave 0.24 g of crude *p*-chlorobenzonitrile.

Prolonged steam distillation gave 3.74 g (81%) of 4′-chlorodesoxybenzoin, mp 103–106°. Two recrystallizations from aqueous alcohol raised the melting point to 106–107°, undepressed when mixed with authentic 4′-chlorodesoxybenzoin.

Attempted Reaction of Triphenylbenzylidenephosphorane (from Triphenylbenzylphosphonium Chloride) with *p*-Chlorobenzonitrile in the Presence of Tetraphenylphosphonium Iodide. Triphenylbenzylphosphonium chloride (4.67 g, 12 mmoles), suspended in benzene, was converted to the ylide as before. To the heterogeneous mixture was added 12 mmoles (5.58 g) of powdered tetraphenylphosphonium iodide.[29] The mixture underwent no change in appearance after a 2-hr reflux period; it remained a white solid suspended in a red liquid phase. Addition of 12 mmoles (1.38 g) of *p*-chlorobenzonitrile, dissolved in benzene, followed by a 52-hr reflux period, did not change the appearance of the mixture. The solvent was evaporated as before and the residue was hydrolyzed by refluxing for 2 hr with a proportional quantity of the usual hydrolysis mixture. Steam distillation resulted in the recovery of 1.27 g (92%) of *p*-chlorobenzonitrile.

Reaction of Triphenylbenzylidenephosphorane (from Triphenylbenzylphosphonium Chloride) with *p*-Chlorobenzonitrile in the Presence of Lithium Perchlorate. Triphenylbenzylphosphonium chloride (0.01575 mole, 6.10 g), suspended in benzene, was converted to the ylide by the use of methyllithium. An equivalent quantity, 1.68 g, of anhydrous lithium perchlorate (K & K Laboratories, Inc.) was added to the ylide mixture and the apparently unchanged mixture was refluxed for 1 hr. *p*-Chlorobenzonitrile (1.65 g, 12 mmoles), dissolved in 50 ml of benzene, was slowly added to the mixture, causing the red color of the ylide mixture to become a very deep red, approaching black. During a 48-hr reflux period, the color of the mixture gradually lightened to a red-orange and a precipitate formed around the edge of the flask.

Following the usual work-up, steam distillation gave 1.87 g of a white solid, mp 102–105°, which distilled very slowly. No indication of unchanged nitrile in the distillate was observed. Two recrystallizations of the crude steam volatile product raised the melting point to 106–107°, undepressed when mixed with authentic 4′-chlorodesoxybenzoin (yield of crude 4′-chlorodesoxybenzoin, 68%).

The experiment described above was repeated in every detail except that only 0.2 mole equiv of lithium perchlorate (0.34 g) was used. Addition of the nitrile caused only a slight darkening of the mixture. After it had been refluxed for 48 hr, the mixture presented an appearance similar to that before addition of the nitrile. Steam distillation gave (rapidly) 1.05 g (64%) of cryde recovered *p*-chlorobenzonitrile. Prolonged steam distillation gave 0.47 g (19%) of 4′-chlorodesoxybenzoin.

Quaternary Phosphonium Halides. Ethyltriphenylphosphonium iodide was prepared by reaction of triphenylphosphine with an excess of ethyl iodide and was recrystallized from ethyl acetate–ethanol, mp 167.0–168.5° (lit.[30] mp 164–165°). Triphenylbenzylphosphonium chloride, prepared by reaction of triphenylphosphine with an excess of benzyl chloride, was recrystallized from 95% ethanol, mp 317–318° (lit.[31] mp 317–318°). Triphenylbenzylphosphonium iodide, prepared from triphenylphosphine and benzyl iodide in benzene solution, was recrystallized from ethyl acetate–ethanol, mp 250–256° dec (lit.[30] mp 253°). Tetraphenylphosphonium iodide, prepared by the method of Chatt and Mann,[29] was recrystallized from ethyl acetate–ethanol, mp 336–343° dec (lit.[29] mp 333–343°). Triphenylbenzylphosphonium bromide, prepared from triphenylphosphine and benzyl bromide in benzene solution, was recrystallized from ethyl acetate–ethanol, mp 290–295° dec (lit.[32] mp 288°). Tetra-*n*-butylphosphonium iodide was prepared by treatment of tri-*n*-butylphosphine with *n*-butyl iodide in a nitrogen atmosphere. The crude salt was first recrystallized from benzene–petroleum ether (bp 60–69°) and then washed for 3 days with ethyl ether in a Soxhlet extractor, mp 102–104° (lit.[33] mp 98°). Tri-*n*-butylbenzylphosphonium iodide, prepared from tri-*n*-butylphosphine and benzyl iodide by refluxing in methanol solution for 12 hr, was recrystallized from ethyl acetate–ethanol, mp 139.0–140.5°.

Anal. Calcd for $C_{19}H_{34}PI$: C, 54.3; H, 8.15; I, 30.2; P, 7.37. Found: C, 54.3; H, 8.41; I, 30.5; P, 7.40.

Tri-*n*-butylbenzylphosphonium chloride was prepared from tri-*n*-butylphosphine and benzyl chloride in refluxing methanol and was washed with ether in a Soxhlet extractor for 24 hr, mp 163–164° (lit.[34] mp 164.3–164.5°). Racemic and (+)-methylethylphenylbenzylphosphonium iodide were prepared as described previously.[25]

Reaction of Racemic Methylethylphenylbenzylidenephosphorane with *p*-Methylbenzonitrile. Finely ground, vacuum-dried racemic methylethylphenylbenzylphosphonium iodide (6.67 mmoles, 2.47 g), mp 167–168°, was suspended in 100 ml of ether and converted to the ylide by the action of *ca.* 1.3 equiv of *n*-butyllithium in hexane (Foote Mineral Co.). Care was taken to add just enough organolithium compound to cause all of the phosphonium salt to dissolve. As with other phosphonium iodides, the mixture became homogeneous (medium orange) at the equivalence point of the "titration."

To the stirred ylide solution was added a solution of 0.88 ml (7.34 mmoles, 0.86 g) of *p*-methylbenzonitrile, dissolved in 50 ml of ether, over a period of 0.5 hr. The mixture was refluxed for 24 hr. At the end of the reflux period, the orange color had faded to yellow and a finely divided white precipitate could be seen around the edges of the stirred mixture.

The ether was removed under a stream of dry nitrogen gas and the yellow, gummy residue was refluxed for 2 hr with a mixture of 20 ml of methanol, 20 ml of distilled water, and 10 ml of concentrated hydrochloric acid. The mixture was subjected to steam distillation until no more organic product was seen in the condenser. The distillate was cooled to 0° and the white solid therein was collected by filtration. When dry, this white solid weighed 1.11 g, mp 100–109° (yield of crude ketone = 85%). One recrystallization from 90% alcohol gave 0.97 g of material of mp 108.5–110°, undepressed when mixed with authentic 4′-methyldesoxybenzoin.

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The residue from the steam distillation was allowed to cool to room temperature and was filtered to remove a small amount of a yellow substance. The clear filtrate was extracted with a 100-ml portion of ether. Evaporation of the ether left no residue.

The aqueous phase from the ether extraction was made strongly basic with potassium hydroxide pellets until a yellow oil separated on the surface of the aqueous phase. The mixture was extracted with three 40-ml portions of benzene. The combined benzene extract was dried by stirring for 2 hr over potassium hydroxide pellets. The benzene phase was decanted into a 250-ml beaker and was evaporated on a hot plate under a stream of anhydrous nitrogen until approximately 1 ml of a viscous yellow oil remained. The beaker was placed in a vacuum desiccator and the residue was evacuated under full pump vacuum overnight.

The yellow oil was transferred into a 3-ml distilling flask which had been previously tared. The yield of crude methylethylphenylphosphine oxide was 0.91 g (80%). Distillation *in vacuo* gave a colorless oil which solidified in an ice bath, mp 52–54° (lit.[25] mp 52–56°).

Reaction of (+)-Methylethylphenylbenzylidenephosphorane with *p*-Methylbenzonitrile, Benzonitrile, and *p*-Chlorobenzonitrile. Experiments identical in every respect with those described under the previous heading were carried out, proportional quantities of the three nitriles specified in the heading being used. The results are tabulated in Table III.

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N,N′-Diboryloxamidines[1]

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Abstract: A new class of bicyclic, boron-bridged compounds has been prepared from *sym*-tetrasubstituted oxamidines and diverse boranes. Their synthesis and properties are discussed.

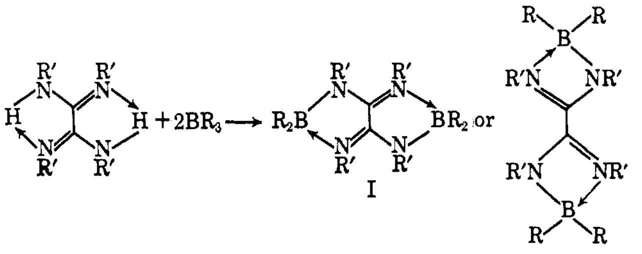
Numerous examples are known of a BR$_2$ group replacing the hydrogen bridge in chelating agents. In most of these cases only one such bridge was involved; the few examples containing two BR$_2$ bridges are pyrazaboles,[2] some transition metal dipyrazolylborates,[3] and the BR$_2$-bridged Ni(II)[4] and Co(II)[5] dimethylglyoximates.

We now report the synthesis and properties of a new class of metal-free compounds containing two intramolecular BR$_2$ bridges. These compounds, of general structure I, were prepared by the reaction of diverse boranes with *sym*-tetraalkyl- and *sym*-tetraaryloxamidines.

Results and Discussion

When a 2:1 mixture of triethylborane and *sym*-tetraethyloxamidine was refluxed in toluene, 2 equiv of ethane were rapidly evolved and compound I (R = R′ = Et), mp 165°, was obtained in 96% yield. The structure assignment was consistent with the following data.

Elemental analysis, molecular weight determination, and the stoichiometry of hydrogen evolution indicated replacement of both active hydrogens by diethylboryl groups. The infrared spectrum lacked the NH band of the starting material and contained a very strong and broad band at 1675 cm^{-1} (C–N multiple bonding). The nmr spectrum indicated two types of ethyl groups present in equal numbers: one, displaying a normal quadruplet and triplet pattern at τ 6.71 and 8.76 (J = 7 cps), respectively, assigned to the N-ethyl groups, the other, a narrow (~10 cps) "triplet" at τ 9.5, assigned to the B-ethyl groups. Such shift of the methylene hydrogens to overlap with those of the methyl group has been noted in bridging BEt$_2$ groups before.[6] The B^{11} nmr peak fell likewise into the range of "chelated" BEt$_2$ groups.[6]



I

II

Of the two possible structures (I and II) satisfying these data, structure I appears more plausible for steric reasons.

The fact that only two types of ethyl groups are discernible in the nmr implies either an interconversion of the two tautomers of I at a rate faster than the nmr time scale or a resonance hybrid of charge-separated structures such as III. The molecule is given the representation IV, which shows the D$_{2h}$ symmetry apparently present.

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