

Ein gemischt methyl/phenyl-substituiertes Carbodiphosphan. Darstellung, Reaktionen und verwandte Verbindungen

A Mixed Methyl-/Phenyl-substituted Carbodiphosphorane. Synthesis, Reactions, and Related Compounds

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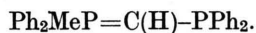
Bis-ylide, Carbodiphosphorane, Phosphino-ylide, ^{31}C NMR, ^1H NMR

From the reaction of bis-diphenylphosphino-methane and methyl bromide a di-quaternized onium salt is obtained, which is converted into the carbodiphosphorane $\text{MePh}_2\text{P}=\text{C}=\text{PPh}_2\text{Me}$ by sodium amide in THF. This bis-ylide was characterized by its reactions and its NMR spectra. With methyl chloride, the above diphosphine yielded the phosphino-phosphonium salt, which forms a phosphino-ylide upon dehydrohalogenation.

Introduction

Unlike the monofunctional phosphorus ylides, which have been studied quite extensively^{1,2}, the bis-ylides of the type $\text{R}_3\text{P}=\text{C}=\text{PR}_3$ have received little attention. Only two compounds of this series, with $\text{R}=\text{phenyl}$ and methyl , have so far been reported³⁻⁵. The chemical characteristics of these two species differ drastically due to the exchange of six methyl groups for six phenyl groups at the phosphorus atoms. We therefore have now synthesized bis-ylides having mixed aryl and alkyl groups on the phosphorus atoms, which should show intermediate properties between the two extreme cases.

This report is concerned with the synthesis and reactions of sym-dimethyltetraphenylcarbodiphosphorane, $\text{Ph}_2\text{MeP}=\text{C}=\text{PMePh}_2$, some precursors, and a related mono-ylide, diphenylmethyl(diphenylphosphinomethylene)phosphorane



Their properties and spectroscopic data are discussed.

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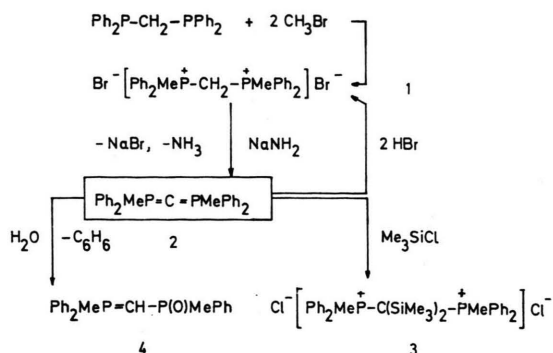
Results and Discussion

a) Synthesis and reactions of dimethyltetraphenylcarbodiphosphorane

The reaction of one mole of bis-diphenylphosphino-methane with more than two moles of methyl bromide at 80 °C in THF afforded the symmetrically substituted diquaternized dibromide (1). When an excess of sodium amide was added to the suspension of this bis-phosphonium salt in THF, ammonia gas was evolved. The dehydrobromination took place exclusively at the bridging methylene group, yielding almost quantitatively the yellow, low-melting sym-dimethyltetraphenylcarbodiphosphorane (2). Evidence for this structure is provided by the NMR spectra of the ylide and the nature of its derivatives. Ylide 2 represents a new member of the class of stable carbodiphosphoranes.

Reaction of 2 with ethereal HBr was found to lead back to the starting material. When 2 is added to Me_3SiCl , dissolved in benzene, the dichloride salt (3) was formed.

The bis-ylide 2 is extremely sensitive to moisture. When it was exposed to a stream of slightly moist nitrogen or to the atmosphere for a short period, a nearly complete conversion to an ylidic phosphine oxide (4) took place. The ylide 4 is an example of stable phosphinemethylenes, in which the carbanionic charge is stabilized by an adjacent phosphoryl



Scheme 1.

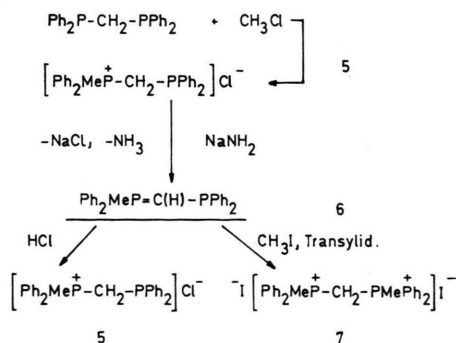
group. The reaction of **2** with moisture is similar to that of $\text{Ph}_3\text{P}=\text{C}=\text{PPh}_3$ ^{3,6}. The synthesis and the reactions of **2** are summarized in Scheme 1.

Methyl iodide or methyl bromide, when reacted with **2** under various conditions, yielded complex mixtures, due to transylidation reactions, and no clear-cut reaction products could be identified. Reaction of **2** with $\text{Me}_3\text{P}-\text{Au}-\text{CH}_3$ in benzene or ether did not produce mono- or di-substituted methyl-gold derivatives, contrary to the reaction of $\text{Me}_3\text{P}=\text{C}=\text{PMe}_3$, which is observed to form $(\text{Me}_3\text{P})_2\text{C}(\text{AuMe})_2$ ⁷.

b) Synthesis and reactions of diphenylmethyl-diphenylphosphinomethylene-phosphorane

In a sealed tube, one mole of bis-diphenylphosphinomethane in THF reacts with an excess of methyl chloride to form the monoquaternized diphosphine (**5**). When excess of NaNH_2 was added to the slurry of this salt, ammonia was evolved and exclusive dehydrohalogenation at the bridge methylene protons resulted in the low-melting mono-ylide **6**, previously reported by ISSLEIB *et al.*^{8,9}.

Reaction of the ylide **6** with ethereal HCl solution leads back to the starting material **5**. When ylide **6**

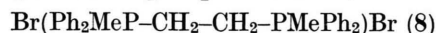


Scheme 2.

was reacted with slightly more than two moles of methyl iodide, the di-iodide salt (**7**) was formed. The synthesis and reactions of the ylide **6** are shown in Scheme 2. Again evidence for the structures are provided by elemental analyses and by the NMR spectra of the compounds.

c) Reaction of sodium amide with ethylene-1,2-bis-(methyl-diphenylphosphonium)dibromide

In connection with the work described above the diquaternized phosphonium salt,



was synthesised by a sealed tube reaction of methyl bromide and 1,2-diphenylphosphinoethane. Attempts for a dehydrohalogenation of **8** with sodium amide in THF were not successful. A 2:1 molar ratio of NaNH_2 and the salt, in THF under various reaction conditions, always resulted in the cleavage of the diphosphine. Diphenylmethylphosphine was identified as one of the reaction products by elemental analysis, by its derivatives and its NMR spectra. A similar cleavage reaction was observed¹⁰ when 1,2-ethylene-bis(triphenylphosphonium)dibromide was treated with phenyl lithium. In this case, triphenylphosphine was one of the reaction products. As a consequence of the P-C cleavage, vinyl phosphorus compounds are also obtained in these reactions¹⁰.

d) NMR spectral data

¹H NMR results

Proton NMR spectral data of the ylides and the related phosphonium salts are given in Table I.

The bridge protons of the phosphonium salts (**1**) and (**7**) (in CF_3COOH) appear as a 1:2:1 triplet at 5.23 to 5.50 ppm with $^2J(\text{HCP})$ coupling constants of about 16 Hz⁹. The spectrum of **5** in deuteriochloroform consists of a doublet ($^2J(\text{HCP})=15.8\text{ Hz}$) at 6.46 ppm for the methylene protons and a doublet at 4.30 ppm ($^2J(\text{HCP})=13.5\text{ Hz}$) for the methyl protons. The trivalent phosphorus methylene proton coupling was too small to be resolved. In trifluoroacetic acid, due to protonation of the trivalent phosphorus, a triplet for the methylene proton with a coupling of 15.8 Hz was observed. This triplet collapsed into a singlet in the $^1\text{H}-\{^{31}\text{P}\}$ spectrum. Removal of one of the acidic protons of the methylene bridge in **5** by base results in the ylide **6**, in which the remaining bridge proton appears as a doublet of doublets at 1.22 ppm, with

Table I. Proton NMR spectral data^a of the ylides and phosphonium salts.

Compound	No.	δCH_3 [ppm]	$^2J(\text{HCP})$ [Hz]	δCH [ppm]	$^2J(\text{HCP})$ [Hz]	$\delta\text{C}_6\text{H}_5$ [ppm]	$o\text{-C}_6\text{H}_5$ [ppm]	$m\text{-}, p\text{-C}_6\text{H}_5$ [ppm]	Solvent	Ref.
$\text{Me}_3\text{P}=\text{C}=\text{PMe}_3$	—	1.21 d ^b	11.1	—	—	—	—	—	C_6D_6	5
$\text{Br}[\text{Ph}_2\text{MeP}^+-\text{CH}_2-\text{P}^+\text{MePh}_2]\text{Br}^-$	1	2.50 d	13.5	5.50 t	16.5	7.92 m	—	—	CF_3COOH	9
$\text{Ph}_2\text{MeP}=\text{C}=\text{PMePh}_2$	2	1.43 d ^b	12.3	—	—	—	7.68 m	6.93 m	C_6D_6	—
$\text{Ph}_2\text{MeP}=\text{C}(\text{H})\text{P}(\text{O})\text{MePh}^c$	4	1.76 d	13.8	0.96 m	—	—	7.75 m	7.00 m	C_6D_6	—
$[\text{Ph}_2\text{MeP}^+-\text{CH}_2-\text{P}^+\text{Ph}_2]\text{Cl}^-$	5	4.30 d 2.75 d	13.5 13.5	6.46 d ^d 5.23 t	15.8 15.8	10.80 m 7.83 m	— —	— —	CDCl_3 CF_3COOH	— —
$\text{Ph}_2\text{MeP}=\text{C}(\text{H})-\text{PPh}_2$	6	1.56 d.d	12.8 0.7	1.22 d.d	12.1 2.5	—	7.70 m	7.00 m	C_6D_6	—
$\text{I}[\text{Ph}_2\text{MeP}^+-\text{CH}_2-\text{P}^+\text{MePh}_2]\text{I}^-$	7	2.53 d	13.5	5.53 t	16.5	7.88 m	—	—	CF_3COOH	9

^a Relative to ext. TMS = 0 ppm. ^b Filled-in doublets. ^c For $\text{P}(\text{O})\text{CH}_3$ -protons $\delta\text{CH}_3 = 1.41$ ppm, d.d, with splittings of 13.5 and 2.3 Hz. ^d Really a doublet of doublets with trivalent phosphorus-methylene proton coupling being too small to be resolved.

splittings of 12.1 and 2.5 Hz. A similar doublet of doublets was observed¹¹ for the corresponding bridge proton in the ylide $\text{Me}_3\text{P}=\text{C}(\text{H})-\text{PMe}_2$ with coupling constants of 13.5 and 2.6 Hz. This upfield shift of about 4 ppm in the ylide compared to the monoquaternized salt (5) is evidence for the generation of a carbanionic charge upon deprotonation.

The methyl protons of the bis-ylide (2) appear as a triplet, made up of a sharp doublet ($N = 12.3$ Hz) enclosing a broad symmetrically spaced peak (Fig. 1). The overall triplet nature of the signal arises from the strong coupling between the two ^{31}P nuclei and is typical for $\text{X}_n\text{AA}'\text{X}_n'$ systems as described in general by HARRIS¹². The virtual coupling nature of the triplet was confirmed by recording the ^{31}P -decoupled proton NMR spectrum, in which the resonance appeared as a sharp singlet at 1.43 ppm. The spectrum of $\text{Ph}_2\text{MeP}=\text{C}(\text{H})-\text{P}(\text{O})\text{MePh}$ (4) shows

the methyl protons attached to the ylidic phosphorus as a simple doublet at 1.76 ppm with a splitting of 13.8 Hz. The methyl protons attached to the phosphoryl phosphorus appeared as a doublet of doublets at 1.41 ppm with splittings of 13.5 and 2.3 Hz. The phosphorus-31 decoupled proton spectrum of 4 clearly showed three sharp singlets in the aliphatic region, corresponding to the two types of methyl protons and the bridge methylene proton.

The methyl protons in the phosphonium salts 1, 5 and 7 show different patterns. The virtual coupling effects are much weaker and the methyl protons in these salts appear as simple doublets at 2.50 to 2.75 ppm with splittings of 13 Hz. Removal of one of the acidic protons in 5 (\rightarrow 6) leads from a simple doublet to a doublet of doublets in 6. Again P-P and long range P-H couplings are clearly increased upon ylide formation.

The *phenyl protons* in the ylidic species 2, 4 and 6 produce two complex multiplets centered at about 7.00 and 7.70 ppm in a 3:2 area ratio (*m*-, *p*- versus *o*-protons).

^{31}P - and ^{13}C -NMR results

Phosphorus-31 spectral data of all the compounds and a carbon-13 spectrum of the bis-ylide 2 are given in Table II. Values for some related compounds are also included for comparison. The ^{31}P NMR of the ylide 2 showed a single peak at -6.70 ppm for the two identical phosphorus nuclei. In the ylidic phosphine oxide (4) two peaks were observed for the two different phosphorus nuclei, with $^2J(\text{PCP}) = 9.1$ Hz.

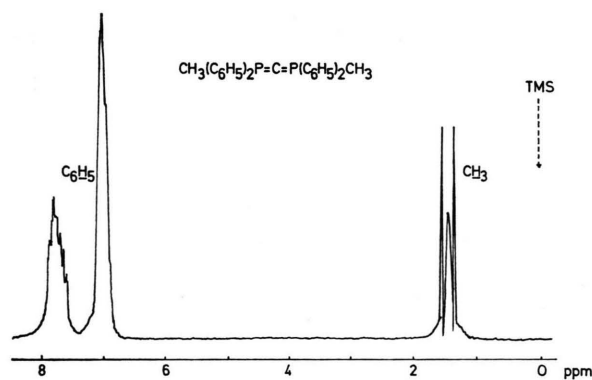


Fig. 1. Proton NMR spectrum of tetraphenyldimethylcarbodiphosphorane (2).

Table II. $^{13}\text{C}\{^1\text{H}\}^{\text{a}}$ and $^{31}\text{P}\{^1\text{H}\}^{\text{b}}$ spectral data for the ylides and phosphonium salts.

$^{13}\text{C}\{^1\text{H}\}$	No.	$\delta\text{P-C-P}$ [ppm]	$^1J(\text{P}=\text{C})$ [Hz]	$\delta\text{CH}_3\text{-P}$ [ppm]	$^1J(\text{P-CH}_3)$ [Hz]	Ref.
$\text{Me}_3\text{P}=\text{C}=\text{PMe}_3$	—	10.8 t	78.1	23.9 m	34.2	5
$\text{Ph}_2\text{MeP}=\text{C}=\text{PMePh}_2$	2	12.6 t	92.8	20.5 m	31.74	e

$^{31}\text{P}\{^1\text{H}\}$	No.	δP_a [ppm]	δP_b [ppm]	$J(\text{P}_a\text{-P}_b)$ [Hz]	Solvent	Ref.
$\text{Ph}_3\text{P}_a=\text{C}=\text{P}_b\text{Ph}_3$	—	+ 3.5	—	—	CH_2Cl_2	3
$\text{Me}_3\text{P}_a=\text{C}=\text{P}_b\text{Me}_3$	—	—29.6	—	—	C_6D_6	5
$\text{Ph}_2\text{MeP}_a=\text{C}=\text{P}_b\text{MePh}_2$	2	— 6.70	—	—	C_6D_6	—
$\text{Ph}_2\text{MeP}_a=\text{C}(\text{H})\text{P}_b\text{Ph}_2$	6	15.04 d	—19.70 d	153.6	C_6D_6	—
$\text{Br}[\text{Ph}_2\text{Me}\overset{+}{\text{P}}_a\text{-CH}_2\text{-}\overset{+}{\text{P}}_b\text{MePh}_2]\bar{\text{Br}}$	1	19.06	—	—	CF_3COOH	—
$\text{I}^- \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{I}^-$	7	19.20	—	—	CF_3COOH	—
$\text{Ph}_2\text{MeP}_a=\text{C}(\text{H})\text{-P}_b(\text{O})\text{MePh}$	4	15.25 d	6.62	9.1	C_6D_6	—
$[\text{Ph}_2\text{Me}\overset{+}{\text{P}}_a\text{-CH}_2\text{-P}_b\text{Ph}_2]\bar{\text{Cl}}$	5	20.20 d	— 3.66 d	8.0	CF_3COOH	—
	5	23.70 d	—24.43 d	59.2	CDCl_3	—

^a Relative to ext. TMS. ^b Relative to external 85% H₃PO₄. ^c A multiplet at 140.4 ppm was observed for C-1 of the phenyl-groups.

An AB spectrum was also observed for the two inequivalent phosphorus atoms in the ylide **6**, with $^2J(\text{PCP}) = 153.6$ Hz. The ^{31}P chemical shifts and $^2J(\text{PCP})$ could also be determined for $\text{Ph}_2\text{MeP}=\text{C}(\text{H})-\text{PPh}_2$. The value of 153.6 Hz for $^2J(\text{PCP})$ is of the order of the coupling constant observed¹³ in some bicyclic phosphorus compounds. The ^{31}P NMR spectra of the phosphonium salts **1** and **5** were as expected.

The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of the new bis-ylide **2** gave detectable signals for all carbon atoms only after addition of a trace amount of chromium acetylacetonate as a paramagnetic relaxation promoter to the samples. Under these conditions the bridging carbon atom appears as a first order 1:2:1 triplet signal, with $^1J(\text{PC}) = 92.8$ Hz. This value is much larger than in the permethylated analog, for which $^1J(\text{PC})$ is 78.1 Hz, indicating a significant influence of the methyl/phenyl substitution. The methyl carbons give rise to an AXX' -multiplet and the same is true for the ^{13}C -carbon atoms of the phenyl rings (Fig. 2). According to theoretical predictions, a strong P-C-P coupling should produce a symmetrical five-line pattern with three very intense central lines^{14,15}. This pattern is indeed observed, though the two outer lines are only detectable at high gain. The remaining ring carbon atoms show the usual shift and coupling characteristics.

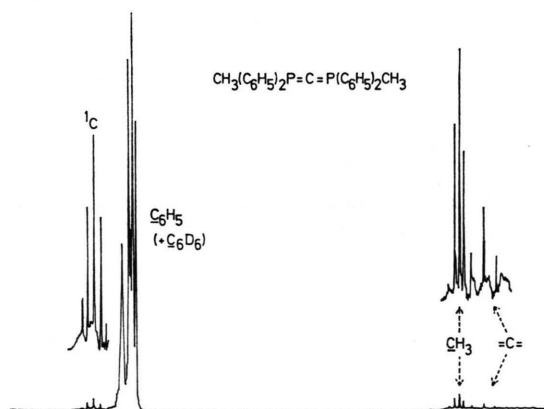


Fig. 2. ^{13}C $\{^1\text{H}\}$ spectrum of $\text{Ph}_2\text{MeP}=\text{C}=\text{PMePh}_2$ (**2**).

Experimental

Diphosphines were obtained from Strem Chemicals Inc., Danvers, Mass., USA, and were used without further purification. Solvents were dried by usual methods and were distilled before using. All experiments were performed under an oxygen-free dry nitrogen atmosphere. Proton NMR spectra were recorded with JEOL C-60 HL (60 MHz) and Varian Model EM-360 (60 MHz) spectrometers. External TMS was used as a reference in all measurements. Phosphorus-31 NMR spectra were obtained either on JEOL C-60 HL or on Bruker XL-90, using 85% phosphoric acid as an external standard. The carbon-13 NMR spectrum of the bisylide was recorded on the Bruker XL-90 (22.63 MHz).

Infrared spectra were obtained with a Perkin Elmer Model 577 Grating Spectrophotometer. Melting points are reported uncorrected. Microanalyses were performed by Mr. M. BARTH and Mr. K. WAGNER at the Institute of Inorganic Chemistry, TU München.

Methylene-bis(methyldiphenylphosphonium)-dibromide (1)

Bis-diphenylphosphino-methane, 8.22 g (21.40 mMoles), was dissolved in 40 ml of dry THF, in a 50 cm long (35 mm) tube. An excess of methyl bromide was condensed on the diposphine solution at liquid nitrogen temperature. The tube was sealed and slowly brought to room temperature. It was finally heated for two days at 85 °C in a protecting metallic tube. Some white solid was formed. The tube was unsealed after cooling and unreacted methyl bromide slowly removed under reduced pressure. The solid was filtered and washed several times with THF. Yield: 12.3 g (95%). The diiodide analog is known⁹.

$C_{27}H_{28}P_2Br_2$ (574.29), m. p. = 320–322 °C.

Calcd C 56.47 H 4.91,

Found C 55.70 H 5.08.

Sym-dimethyltetraphenylcarbodiphosphorane (2)

To a suspension of 6.0 g (10.45 mMoles) of the dibromide salt 1 in 50 ml THF was added 1.29 g (33 mMoles) of sodium amide portionwise over a period of 20 minutes under nitrogen atmosphere with constant stirring. Ammonia was evolved and the slurry became light yellow. The suspension was stirred for 24 hours at room temperature and finally refluxed at 65 °C till ammonia ceased to evolve. The final solution was dark yellow after filtration from sodium bromide. This solution was cooled to –18 °C for 12 hours to separate any dissolved, unreacted sodium amide or sodium bromide. THF was removed from the clear solution in a vacuum to obtain an orange-yellow low-melting product, which precipitated from diethylether upon cooling in the form of yellow crystals.

Efforts to distill the ylide resulted in decomposition of the product. Except under strictly anhydrous conditions, samples of the ylide become very rapidly contaminated with $Ph_2MeP=C(H)-P(O)MePh$. The ylide can be stored at –18 °C in a THF solution under nitrogen atmosphere with a few mg of sodium amide.

$C_{27}H_{26}P_2$ (412.45), m. p. = 86–88 °C, dec.

Calcd C 78.63 H 6.35,

Found C 78.25 H 6.50.

Reaction of 2 with HBr

An excess (over 2:1 of HBr:ylide) of anhydrous ethereal solution of HBr was added slowly with constant stirring to a THF solution of the ylide. A white crystalline dibromide salt precipitated almost

immediately, was washed with THF and dried under vacuum. The yield was quantitative. Proton NMR and infrared spectra of the product were identical with those of the starting dibromide salt 1.

$C_{27}H_{28}P_2Br_2$ (574.29), m. p. = 322–323 °C.

Calcd C 56.47 H 4.91,

Found C 55.96 H 4.84.

Reaction with Me_3SiCl (3)

A solution of 1.03 g (2.5 mMole) of the ylide in benzene was added with stirring to 0.64 g (6.00 mMole) of Me_3SiCl , also dissolved in about 5 ml of benzene. A white salt precipitated within a few minutes. The suspension was stirred further for another two hours and the solid was filtered and washed with benzene and dried under vacuum. The solid was soluble in chloroform and methylene chloride, but decomposed within a few minutes, preventing further purification.

$C_{33}H_{44}P_2Si_2Cl_2$ (629.73), m. p. = 192–195 °C.

Calcd C 62.94 H 7.04,

Found C 62.22 H 6.69.

Reaction with moisture (4)

With moisture the ylide 2 becomes contaminated with the ylidic phosphine oxide (4). The reaction with moisture was studied by the disappearance of the filled-in doublet and appearance of the complex spectrum of 4 with time in the NMR spectra on prolonged exposure to slightly contaminated nitrogen or momentary exposure to the atmosphere. Under all of these conditions, nearly complete conversion of 4 takes place. The product is a light yellow powder below –5 °C, and is a sticky solid at room temperature. It has a strong broad IR-doublet at 1190 and 1155 cm^{-1} and a shoulder at 1240 cm^{-1} , which are characteristic infrared absorption bands for the $-P=O$ group.

Diphenyl-diphenylphosphinomethyl-methylphosphoniumchloride (5)

A slight excess over the 1:1 mole ratio of methyl chloride was condensed at liquid nitrogen temperature into a solution of 9.02 g (23.49 mMole) of $Ph_2PCH_2PPh_2$ in 35 ml THF in a long glass tube. The tube was sealed and warmed for two days at 65 °C to obtain a white crystalline solid, which was filtered and washed with THF and dried under vacuum. The yield was 95%. (The iodide analog is known⁸.)

$C_{26}H_{25}P_2Cl$ (434.88), m. p. = 179–181 °C.

Calcd C 71.82 H 5.79,

Found C 71.65 H 6.50.

Diphenylmethyl-(diphenylphosphino)methylene-phosphorane (6)

To a slurry of 6.39 g (14.69 mMoles) of 5 in 50 ml THF, was added 1.18 g (30.26 mMoles) of sodium

amide slowly with stirring. The light yellow solution was stirred further for 4 days at room temperature till ammonia gas ceased to evolve. The solid was filtered and THF was removed under vacuum to obtain a low melting light solid, which became a dark yellow viscous oil on slight warming or prolonged storage at room temperature. The oil was partially soluble in ether and could be recrystallized by adding an excess of ether to the THF solution of the ylide and cooling to -78°C .

The ylide is extremely sensitive to air and stable only under a strictly anhydrous nitrogen atmosphere. The properties are as reported earlier⁸.

Reaction with HCl: The monochloride salt (5) was obtained by treating 5 mmoles of the ylide in THF with about 8 mmoles of HCl in anhydrous ether at room temperature under nitrogen. The yield was quantitative and the NMR and infrared spectra of

the product were identical with the starting material 5.

Reaction with CH_3I : An excess over the 2:1 mole ratio of methyl iodide was added to 5 mmoles of the ylide in 15 ml THF. The white solid, which appeared instantly, was washed with THF and dried under vacuum.

$\text{C}_{27}\text{H}_{28}\text{P}_2\text{I}_2$ (668.26), m. p. 203–207 $^{\circ}\text{C}$ (decomposed).

Calcd C 48.52 H 4.22,

Found C 48.43 H 4.45.

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