

AN INVESTIGATION OF THE CHEMISTRY OF
LITHIOTRIPHENYLPHOSPHINEACETYLMETHYLENE,

by

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TO MY HUSBAND

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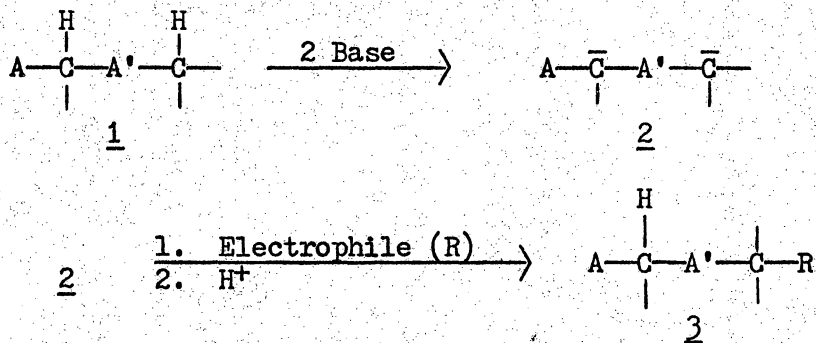
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I. INTRODUCTION AND LITERATURE SURVEY

The utility of carbanions in synthetic organic chemistry has been recognized for many years.^{1,2} One of the major areas to which considerable time and effort has been directed is the use of multiple carbanion intermediates in the synthesis of new compounds.

Among the most interesting and useful multiple anions which have been studied are resonance stabilized 1,3-dianions, represented by structural formula 2.



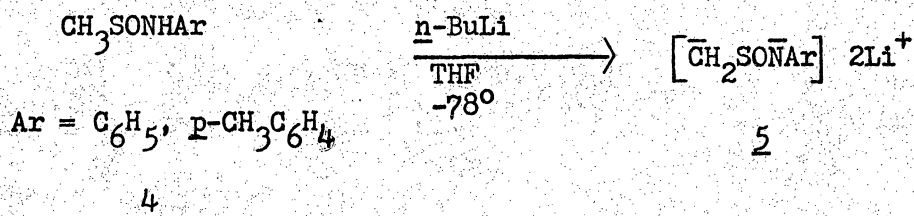
When compounds such as 1, containing appropriate anion stabilizing groups A and A' are treated with two molecular equivalents of base, dianions of type 2 are generated. Reactions of 2 with electrophilic reagents result in new compounds, 3, where the R group, corresponding to the electrophile used, is introduced at the carbanion site stabilized by A'. The major advantage of these intermediates is that they undergo regiospecific reactions with electrophilic reagents at the more nucleophilic carbanion site.

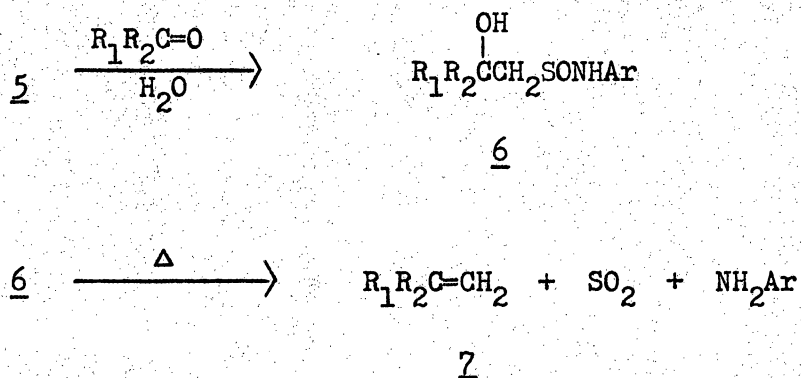
Among the types of active hydrogen compounds, 1, from which dianions of type 2 have been generated are those in which activating groups A and A' are carbonyl functions.³ These include β -diketones,⁴⁻⁶

β -keto aldehydes⁷⁻⁹ and β -keto esters.¹⁰⁻¹⁵ Such dianion intermediates have been used mainly to elaborate the parent structure, e.g., the synthesis of new β -diketones from various β -diketone dianions.

It seemed possible that the synthetic utility of dianions of type 2 might be expanded in an interesting new direction if activating group A could be removed in an efficient way after regiospecific introduction of group R. Group A would be used to direct the electrophile to the more basic carbanion site, that is, it would be acting as a control element¹⁶ after which it could be removed to give compounds differing significantly from the starting material. In this way a variety of compounds could be prepared from a single dianion precursor. The purpose of the present study was to investigate the formation and reactions of the dianion, lithiotriphenylphosphineacetylmethylene, where the control element (A) was the $(C_6H_5)_3P^+$ grouping.

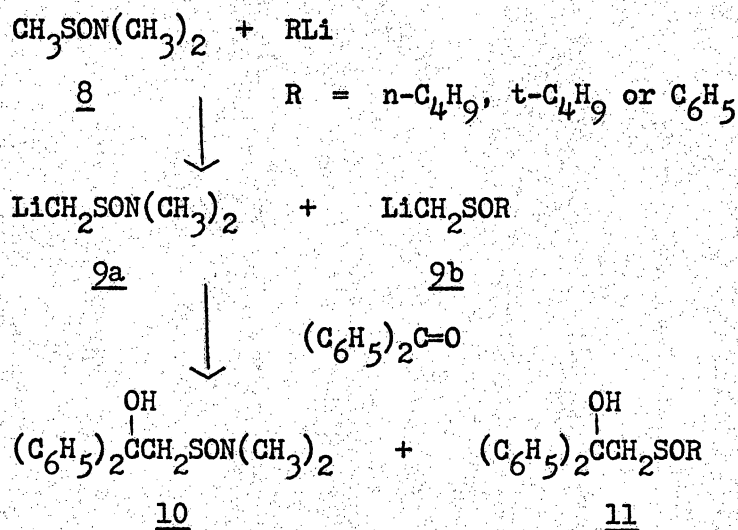
The first report of such a dianion in which one of the activating groups functioned as a control element was that of Corey and Durst¹⁷⁻¹⁸ who made use of the 1,3-dianions of sulfinamides to synthesize olefins and ketones. They converted N-monosubstituted methanesulfinamides of type 4 to the dilithio derivatives, 5, by treating them with two molecular equivalents of *n*-butyllithium in tetrahydrofuran (THF) at -78° .



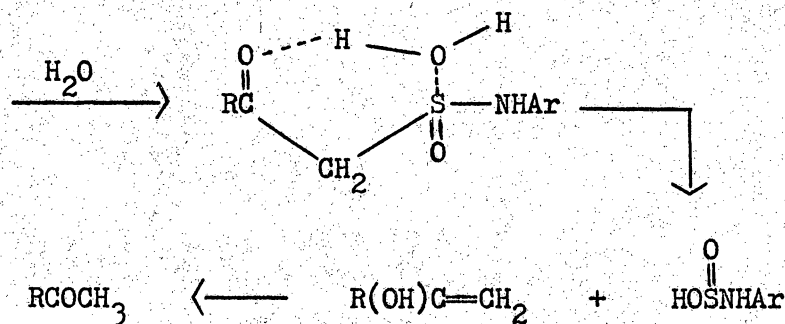
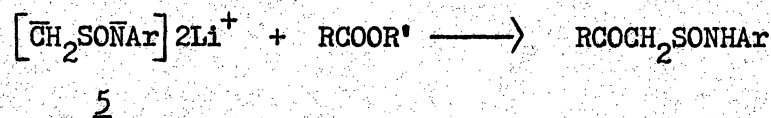


Reaction of 5 with aldehydes and ketones afforded β -hydroxy sulfina-
mides (6) in good yields. Adducts 6 decomposed when heated alone at
the melting point, or when refluxed in dry benzene or toluene, to
give the corresponding olefins, 7, aryl amines, and sulfur dioxide.
The decomposition was shown to occur by a cis elimination pathway.¹⁹
The elimination rates of β -hydroxysulfina-
mides (6) obtained from 5
and aldehydes were slower than those for ketone adducts, and higher
boiling solvents such as toluene were usually used.

The metalation of N,N-disubstituted methanesulfina-
mides (8) with
alkyl lithium reagents did not give the lithio derivative 9a cleanly
because upon reaction with benzophenone, the unexpected product, 11,
was obtained along with the product 10. Sulfoxide 11 was derived
from the reaction of benzophenone with the sulfoxide anion (9b)
obtained by displacement of dimethylamine by the alkyl group of the
organolithium reagent.

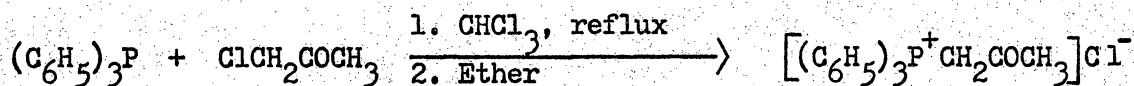
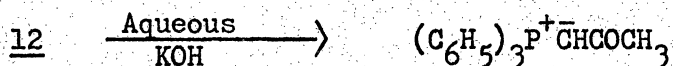


These same workers also studied¹⁸⁻¹⁹ the reaction of dilithio derivatives 5 with esters and obtained methyl ketones in good yields.

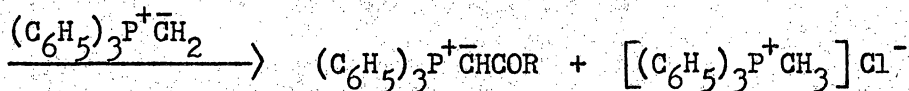
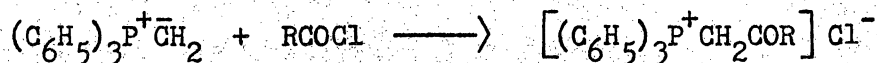


Later, a new type of 1,3-dianion was obtained from acetyl-triphenylphosphonium chloride (12) by Wolfe and Taylor.²⁰⁻²² Although β -ketophosphonium salts containing α -hydrogens were known²³⁻²⁵ to react with basic reagents to form stable β -ketophosphonium ylides, this was the first report of dual ionization of such compounds to give an ylide anion such as 14.

Acetonyltriphenylphosphonium chloride (12) was obtained by alkylating triphenylphosphine with chloroacetone according to the procedure of Ramirez and Dershowitz.²⁴

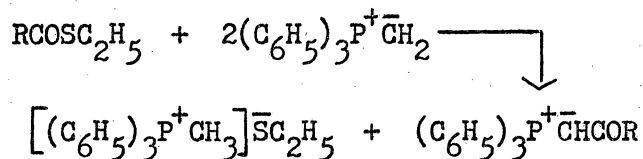
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In order to prevent attack of strongly basic reagents at the electrophilic phosphorus or carbonyl functions, 12 was first converted to triphenylphosphineacetylmethylene* (13) by means of aqueous potassium hydroxide. Ylides such as 13 have also been obtained by two other methods developed by Bestmann and Arnason.²⁵ Thus, triphenylphosphine-methylene was acylated with acyl halides or thioesters to give a series of β -ketophosphonium ylides as shown below.

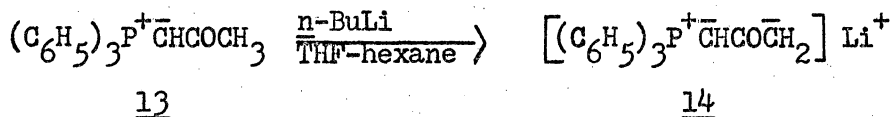


* Throughout this thesis, naming of ylides will be based on phosphinemethylene^{24,26}, $\text{H}_3\text{P}=\text{CH}_2$. Thus, $(\text{C}_6\text{H}_5)_3\text{P}=\text{CH}_2$ would be triphenylphosphinemethylene and $(\text{C}_6\text{H}_5)_3\text{P}=\text{CHCOCH}_3$ would be triphenylphosphineacetylmethylene. Such compounds can also be named as phosphorane derivatives.^{24,27} Thus, $(\text{C}_6\text{H}_5)_3\text{P}=\text{CHCOCH}_3$ would be acetylmethylenetriphenylphosphorane.

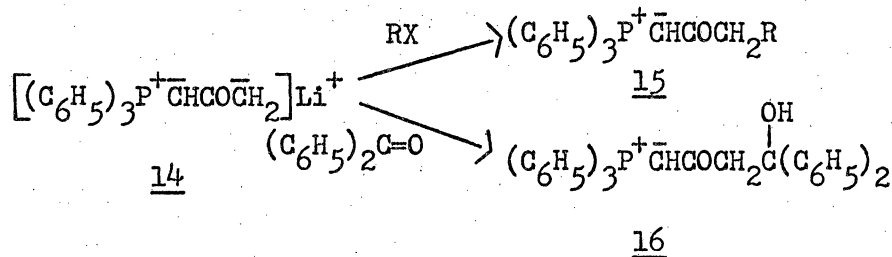
or



Ylide 13 was then treated with a series of strongly basic reagents in aprotic media in order to effect removal of a methyl hydrogen. It was found that ylide anion formation was best accomplished by addition of *n*-butyllithium in hexane to a solution of ylide 13 in THF at -78° under a nitrogen atmosphere.²⁰⁻²² Quenching

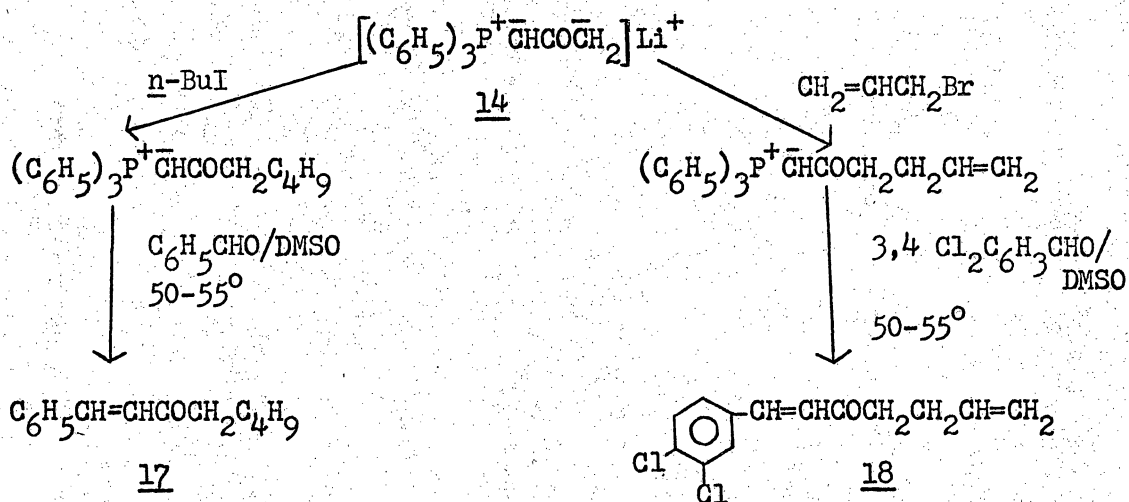


the reaction mixture with deuterium oxide regenerated ylide 13 containing 0.9 deuterium at the methyl carbon as shown by proton magnetic resonance (pmr); recovery of 13 was 60%. Ylide anion 14 was then treated with several electrophiles. Reaction with alkyl halides resulted in terminal alkylations to give compounds of type 15. Condensation of 14 with benzophenone resulted in formation of alcohol 16.

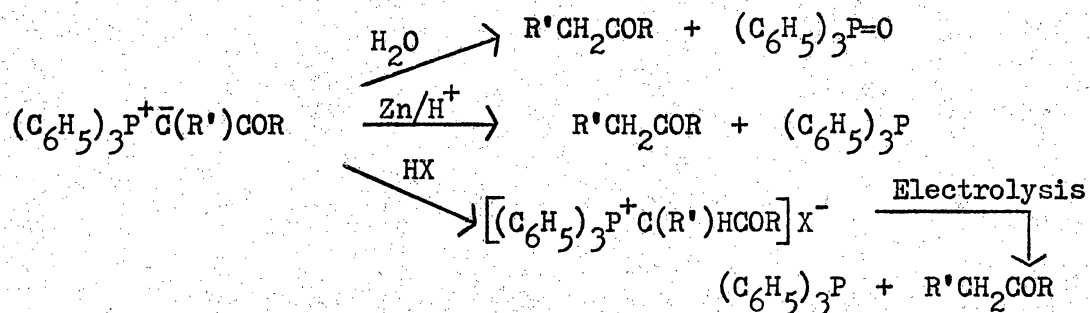


Reactions at low temperatures resulted in higher yields than reactions at 0° . This was attributed^{21,22} to the presence of 14 as solvent separated ion pairs at -78° , so that the carbanion can easily attack the electrophile to afford higher yields, whereas at 0° 14 may exist as an intimate ion pair and the carbanion is less reactive toward the electrophile. Also, the fact that only 60% of the ylide was recovered in the deuteration experiments pointed out that some decomposition of the ylide anion occurred in the reaction mixture. The lower temperatures would be expected to reduce the extent of decomposition and thus increase the yield of products.

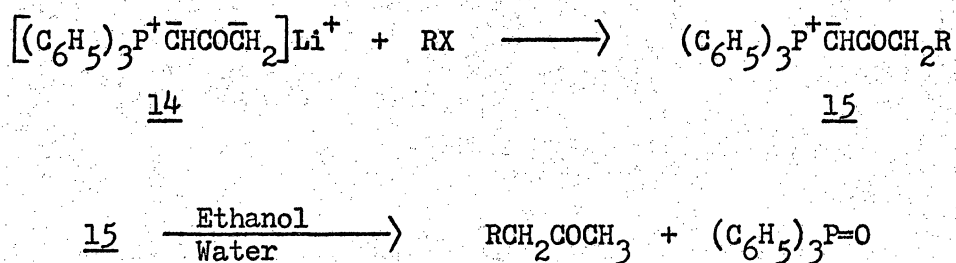
Some sequential reactions performed with ylide anion 14 were also reported.²⁰⁻²² Thus, 14 was first alkylated with *n*-butyl iodide or allyl bromide and then Wittig type reactions of these terminally substituted ylides were carried out using benzaldehyde and 3,4-dichlorobenzaldehyde in dimethyl sulfoxide (DMSO) at $50-55^{\circ}$ to afford trans-1-phenyl-1-octen-3-one (17) and trans-1-(3,4-dichlorophenyl)-1,6-heptadien-3-one (18), respectively.



Bestmann and Arnason²⁵ have demonstrated that β -ketophosphonium ylides can be converted into ketones by either hydrolytic or reductive cleavage of the $(\text{C}_6\text{H}_5)_3\text{P}^+$ moiety.



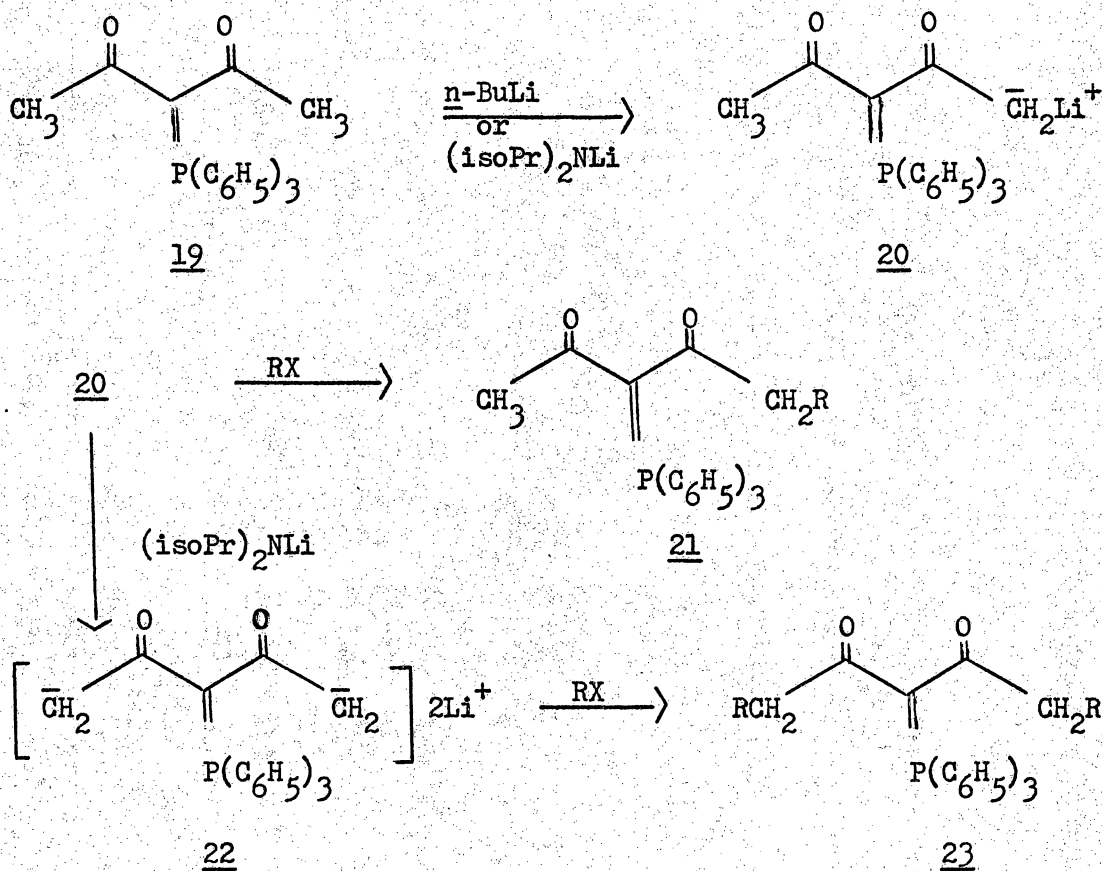
Recently, Cooke²⁸ used lithiotriphenylphosphineacetylmethylene (14) for the introduction of the acetyl group by nucleophilic displacements on alkyl halides. Treatment of ylide anion 14 with a series of primary halides at 0° afforded alkylated ylides, 15, which were hydrolyzed by heating in aqueous ethanol under neutral or slightly basic conditions to give methyl ketones.



Cooke and Goswami²⁹ generated both the mono and dianion of diacetylmethylenetriphenylphosphorane (19). Treatment of 19 with 1.2 molecular equivalent of either *n*-butyllithium or lithium diisopropylamide in THF at -78° afforded the mono anion 20, which

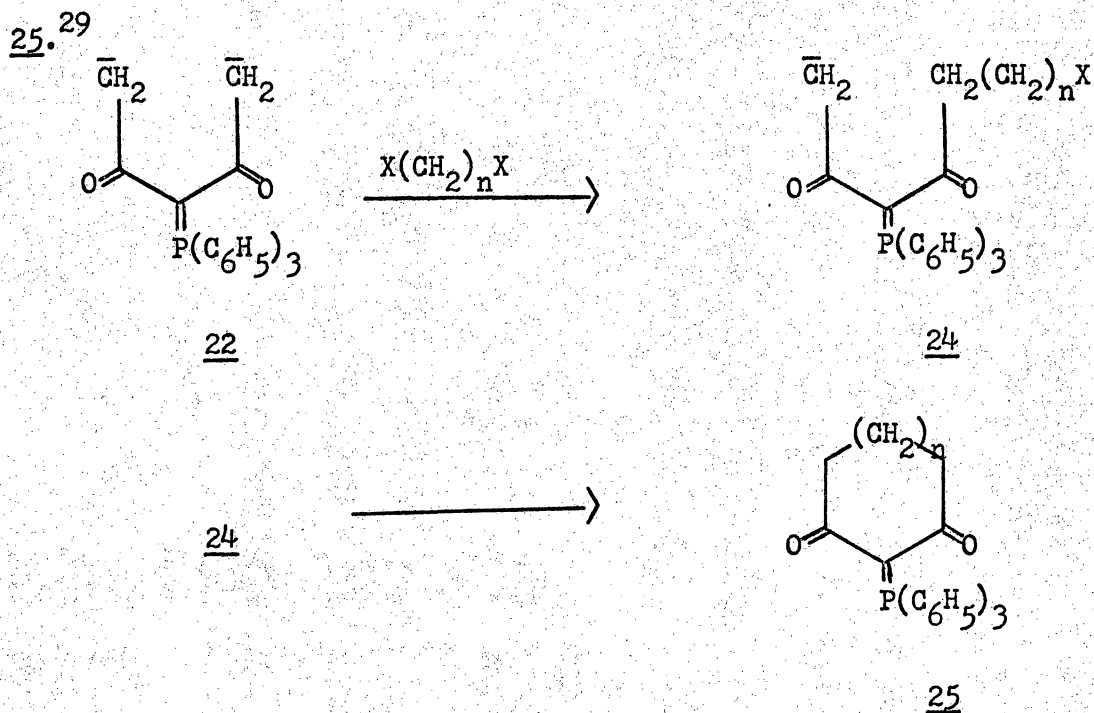
reacted with alkyl halides to form the substituted ylides 21.

Addition of 1.1 molecular equivalent of lithium diisopropylamide to the red monoanion 20 gave the black dianion 22, which also reacted with alkyl halides to give dialkylated ylides 23 along with some monoalkylated product.

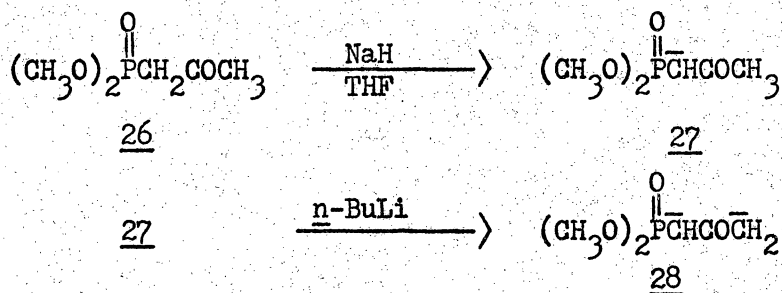


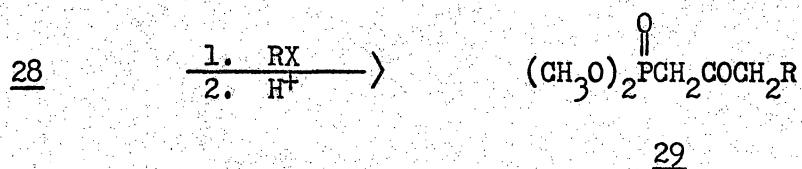
Pmr studies done^{30,31} on acetylmethylenetriphenylphosphoranes have shown that the carbonyl group in these compounds adopts a cis orientation with respect to the phosphonium group. Also the fact that the pmr spectrum of 19 has a single methyl resonance suggested that this compound may exist in a "U" conformation where the oxygen atoms of both ketone groups are cis to the phosphonium group. If

this were the case, the ring presumably could be closed by reacting 22 with dihaloalkanes. Although methylene iodide and 1,2-dibromoethane were ineffective, 1,3-diiodopropane afforded the cyclic ylide, 25.²⁹

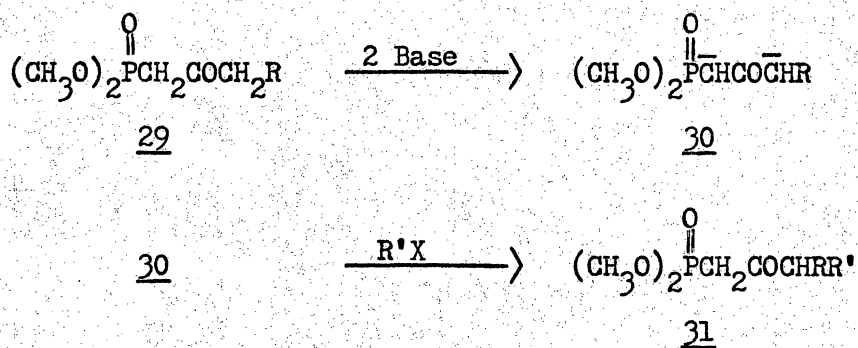


Recently Grieco and Pogonowski^{32,33} used 1,3-dianions derived from β -keto phosphonates in the synthesis of various other β -keto phosphonates³² and cyclohexenones³³. Upon treatment of dimethyl (2-oxopropyl)phosphonate (26) with sodium hydride in THF, monoanion 27 was produced. Then metalation of 27 with *n*-butyllithium gave dianion 28.

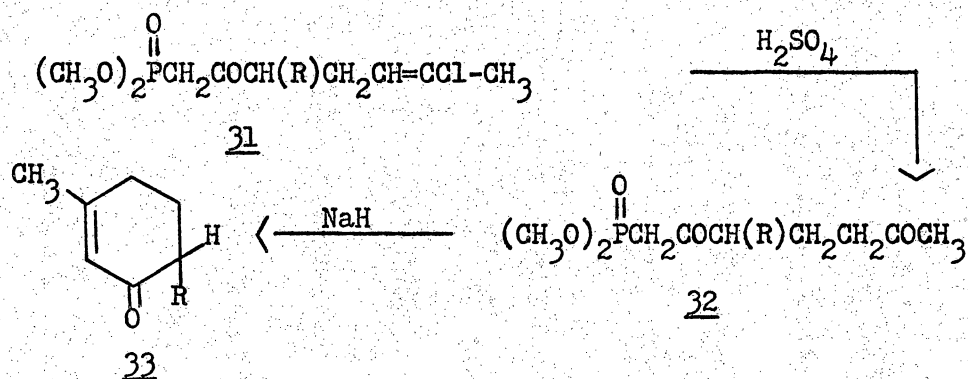




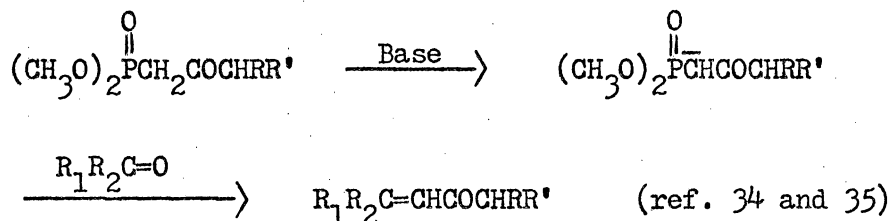
Reaction of dianion 28 with various alkylating agents afforded γ -substituted β -keto phosphonates 29. Dianions, 30, of these alkylated products, 29, could also be generated and alkylated with a second alkylating agent to yield disubstituted phosphonates 31.



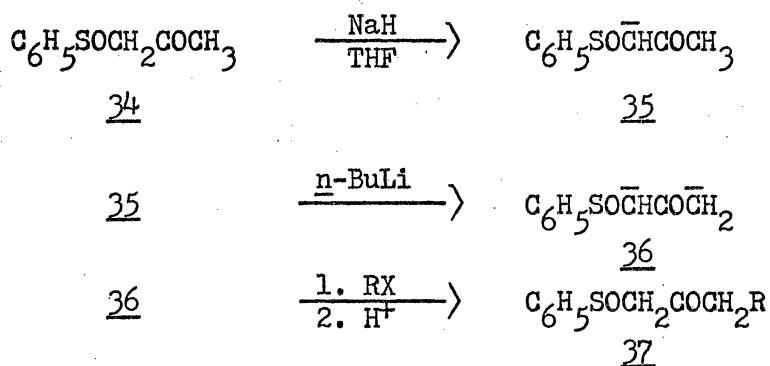
Dianion 30 was also alkylated with 1,3-dichloro-2-butene, which represents a masked 3-keto butyl group, to yield 31 ($\text{R}' = -\text{CH}_2\text{CH}=\text{CCl}-\text{CH}_3$). The enol chloride was then hydrolyzed with sulfuric acid to give diketone 32, which was cyclized by treatment with sodium hydride in anhydrous 1,2-dimethoxyethane.



This sequence of reactions constitutes a method for the preparation of the alkylated cyclohexenones of type 33 in good yields. Also, the various β -keto phosphonates obtainable by the above method could presumably be used in the Horner-Emmons modification of the Wittig olefin synthesis as shown below.



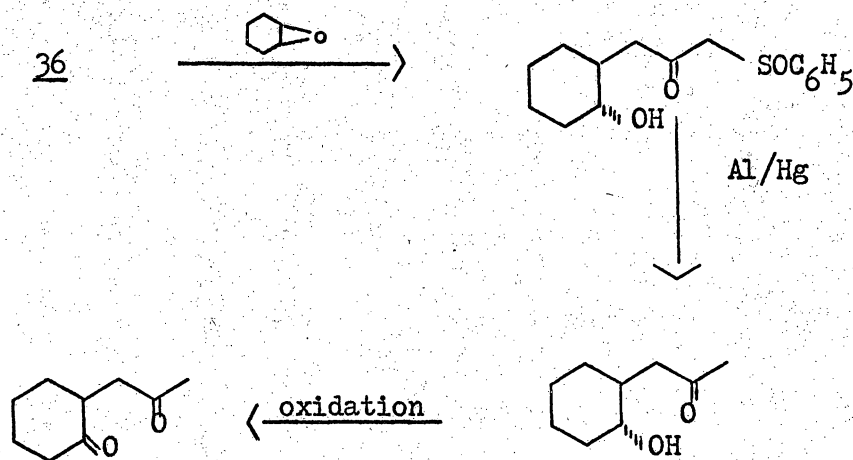
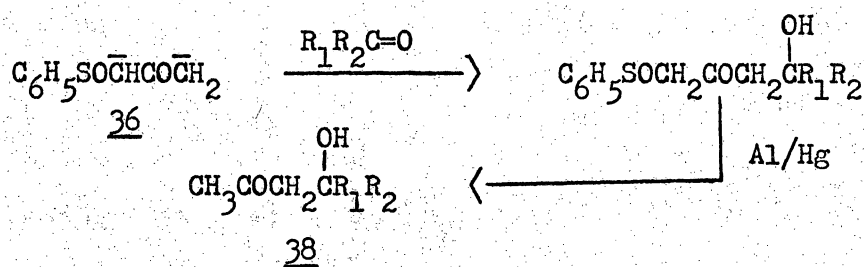
Grieco and Pogonowski³⁶ also worked on dianions from β -keto sulfoxides (34) and reported the synthesis of ketones, 1,4-diketones and aldols from them. Dianions of the β -keto sulfoxides were also prepared by first using sodium hydride in anhydrous THF to obtain the soluble monoanion 35, and then metalation was carried out using *n*-butyllithium to generate dianion 36.



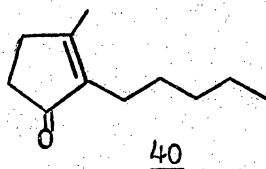
The dianion of phenyl (2-oxopropyl)sulfoxide (36) was then treated with a variety of alkyl halides to afford monoalkylated products 37 in good yields. These γ -substituted β -keto sulfoxides

were also alkylated successfully. The carbon-sulfur bond in these types of compounds can be reductively cleaved³⁷ using aluminum amalgam to yield various methyl ketones. Cleavage was achieved in 10% aqueous THF at 80° in about one hour.

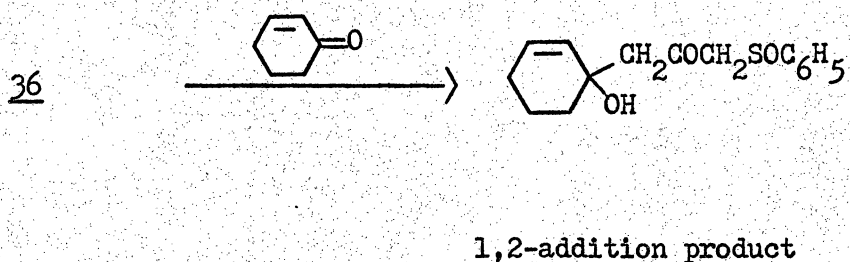
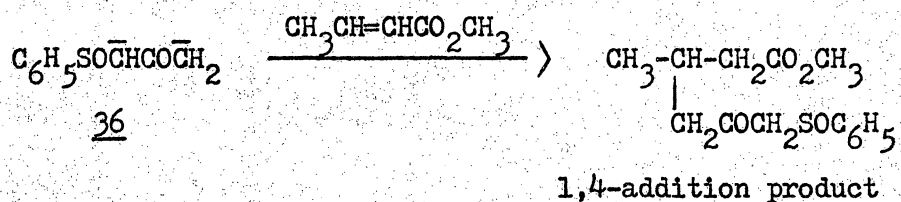
Dianions of β -keto sulfoxides also reacted with aldehydes and ketones to give aldol condensation products 38, and with epoxides to yield 1,4-diketones 39.



Dihydrojasmane (40) was also obtained by the same sequence of reactions starting with the epoxide derived from 1-octene.



Kuwajima and Iwasawa³⁸ also investigated the chemistry of the dianion of phenyl (2-oxopropyl)sulfoxide (36). Besides the reactions of 36 with alkyl halides and condensations with aldehydes and ketones, they also examined the reactions of dianion 36 with α - β -unsaturated carbonyl compounds and found that 1,4-addition took place exclusively when they used an α - β -unsaturated ester such as methyl crotonate, but they isolated the 1,2-addition product in the case of an α - β -unsaturated ketone, 2-cyclohexen-1-one.

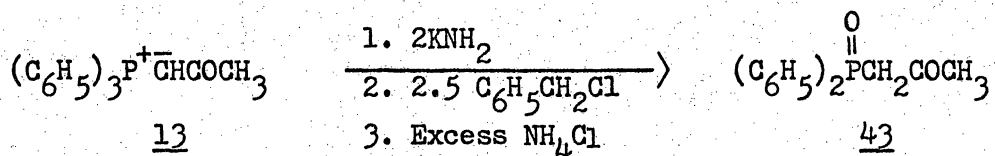


II. DISCUSSION OF RESULTS

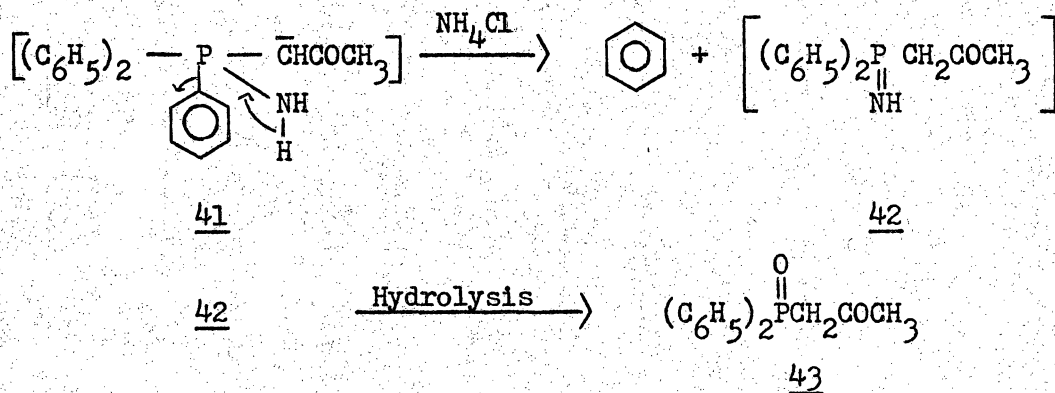
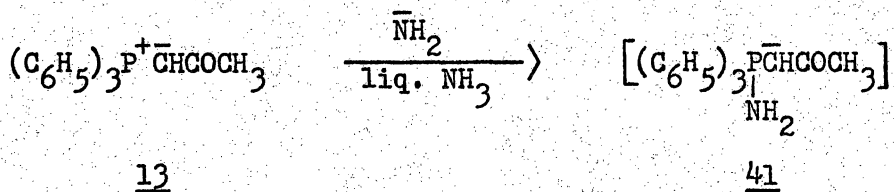
Because of the promising preliminary results obtained with ylide anion 14, in which condensations with several alkyl halides and benzophenone exhibited a high degree of regiospecificity for the terminal carbanion site, the present study was undertaken to determine the scope and limitations of reactions of 14 with a variety of electrophiles.

A. Attempted Generation of Potassiotriphenylphosphineacetylmethylene

Previously, an attempt²¹ to form the ylide anion 14, as the potassio salt, from triphenylphosphineacetylmethylene (13) using potassium amide in liquid ammonia resulted in formation of acetyldiphenylphosphine oxide (43). Thus, when 13 was treated with 2 molecular equivalents of potassium amide in liquid ammonia, followed by 2.5 molecular equivalents of benzyl chloride, neutralization of the reaction mixture with excess solid ammonium chloride resulted in 80% recovery of benzyl chloride and a 57% yield of acetyldiphenylphosphine oxide (43).

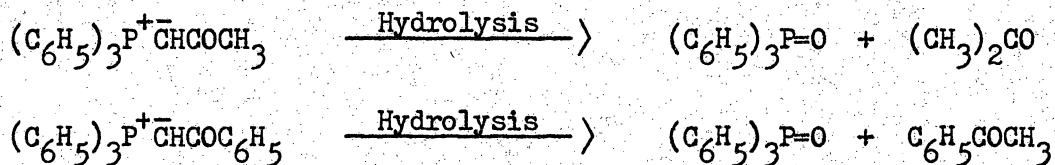


Structural assignment 43 was based on elemental analysis, ir and pmr spectra, and also on agreement of its melting point with the literature value.³⁹ The mechanism shown below was proposed²¹ for the formation of 43.



Since none of the expected benzylated product was obtained from the above reaction, evidently potassium amide is not effective in abstracting the methyl proton of 13 to give ylide anion 14. Instead it was proposed²¹ that the amide ion attacks the electrophilic phosphorus to form intermediate 41. This intermediate then eliminates phenyl anion which presumably leads to formation of benzene. However, no attempt was made to detect benzene in these earlier experiments. Elimination of benzene gives the iminophosphorane type intermediate, 42, which then undergoes hydrolysis upon work up to give phosphine oxide 43.

Ramirez and Dershowitz²⁴ have reported that hydrolysis of triphenylphosphineacetylmethylene (13) and triphenylphosphinebenzoylmethylene gave triphenylphosphine oxide and acetone and acetophenone, respectively. In such hydrolytic cleavages the β -keto carbanions



which are eliminated would be more stable than the phenyl anion. In the case of intermediate 41, ejection of the acetyl group should be less likely than expulsion of phenyl anion because the former already carries a negative charge.

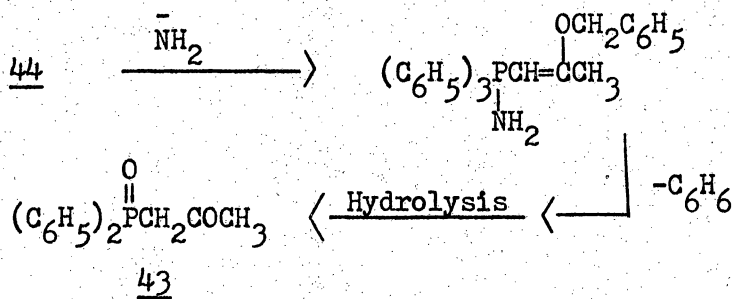
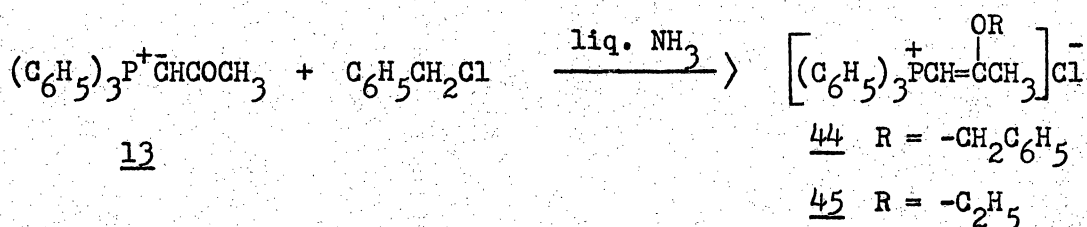
Because of the questions about the mechanism of formation of acetyldiphenylphosphine oxide (43), this reaction was studied in some detail and isolation of the proposed intermediate 42 was attempted.

The reaction described by Taylor²¹ was repeated using 1.0 molecular equivalent of triphenylphosphineacetylmethylene (13), 2 molecular equivalents of potassium amide and 2.5 molecular equivalents of benzyl chloride, the only difference being that starting ylide 13 was added as a solution in THF, since it is not very soluble in liquid ammonia. The work up procedure described by Taylor²¹ was followed and at the end, a solid melting at 182-191^o was obtained. The pmr spectrum of this material showed some aromatic protons and a broad singlet at 6.88 ppm with a ratio of approximately 4.3:1. Elemental analysis of this compound showed the presence of no nitrogen. No further attempts were made to establish the structure of this material. From this reaction some stilbene was isolated also, but thin layer chromatography (tlc) analysis showed only trace amounts of acetyldiphenylphosphine oxide (43).

The above reaction was carried out again, without using THF. Acetonyldiphenylphosphine oxide (43) was obtained in 30% yield from this reaction along with some of the high melting, unidentified compound and some stilbene.

In trying to establish what was responsible for the formation of phosphine oxide 43, the reaction was repeated as before without using any potassium amide. That is, a solution of 13 in THF was treated with benzyl chloride in liquid ammonia followed by addition of ammonium chloride. This resulted in quantitative recovery of 13.

It was thought that perhaps O-benylation of 13 might occur in liquid ammonia and that amide might then attack the positive phosphorus of the resulting vinyl ether, 44, rather than the phosphorus atom of ylide 13 (see page 16). So, starting ylide, 13, in liquid ammonia



was treated with benzyl chloride but acid hydrolysis of the reaction mixture was omitted. From this reaction, triphenylphosphineacetyl-

methylene (13) was obtained in quantitative yield. These results indicate that O-benylation of 13 does not occur under the reaction conditions, and that amide does indeed attack 13. Also, it was found that the known O-ethyl derivative, 45, was not converted to phosphine oxide 43 by means of potassium amide.

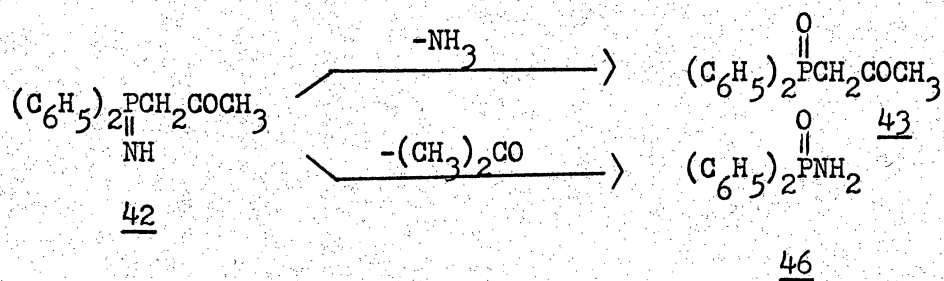
The reaction of 13 with 1.15 molecular equivalents of potassium amide in liquid ammonia, without addition of any benzyl chloride also resulted in formation of phosphine oxide 43 in 42% yield, establishing positively that benzyl chloride does not play any role, but that amide alone is responsible for formation of 43.

Next, experiments designed to detect the presence of benzene and iminophosphorane 42 in the potassium amide reactions were carried out. Ylide 13 was treated with 1.15 equivalents of potassium amide in liquid ammonia, but the reaction mixture was not hydrolyzed. Instead, after replacing the liquid ammonia with ether, the resulting suspension was filtered and the filtrate was analyzed by gas chromatography (G.C.) for the presence of benzene. Benzene was detected as evidenced by its retention time. Also addition of some benzene to the ethereal solution resulted in enlargement of the G.C. peak which corresponds to benzene.

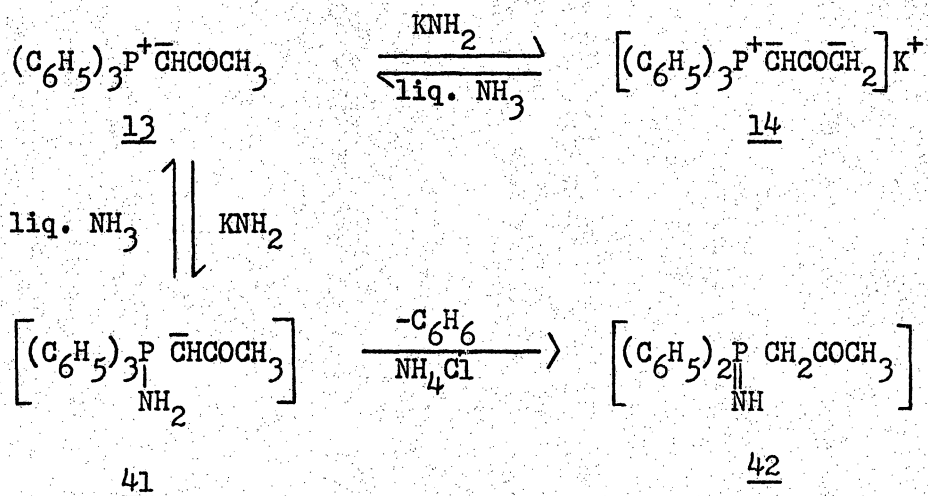
After detection of benzene, isolation of the proposed iminophosphorane type intermediate, 42, was attempted. In an identical experiment, the ethereal solution obtained from the reaction was evaporated. The resulting beige solid was recrystallized from 95% ethanol-heptane. The pmr spectrum of this recrystallized material showed a singlet at 3.84 and multiplet at 7.76 ppm, with a ratio of 1:5. The mass spec-

trum had a molecular ion at m/e 217. Elemental analysis and the ir spectrum of this compound was also obtained, and all of above information supported the fact that the compound isolated was diphenylphosphinic amide (46). Its melting point also was in agreement with literature values.⁴⁰⁻⁴⁴ Thinking that even if iminophosphorane intermediate, 42, had been formed, it may have undergone hydrolysis upon recrystallization, the above reaction was repeated and the pmr spectrum of the crude product was taken. It showed the presence of diphenylphosphinic amide as evidenced by its pmr absorption and subsequent isolation of this material. The crude product also contained some acetyldiphenylphosphine oxide (43) as indicated by the doublet at 3.62 ppm characteristic of the methylene protons of 43.

Although we were unable to isolate the proposed intermediate 42, it still may be formed, because it is known⁴⁵ that iminophosphoranes are not very stable and undergo hydrolysis easily. So, 42 may be produced during the reaction but undergoes hydrolysis upon exposure to atmospheric moisture to give acetyldiphenylphosphine oxide (43), when the =NH grouping is cleaved, or to give diphenylphosphinic amide (46) when the acetyl group is ejected.

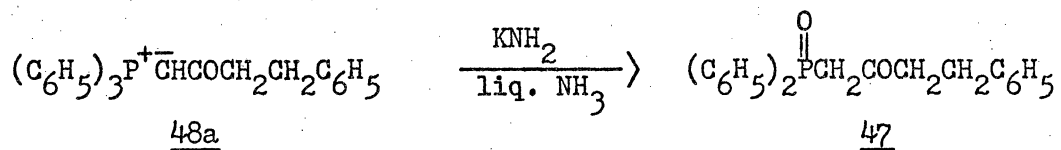


In all of the above reactions, triphenylphosphineacetylmethylene (13) was added to a potassium amide suspension and was stirred for about one hour before addition of benzyl chloride or ammonium chloride. It was observed that when 13 first entered the ammonia solution, the color turned brown, and after about ten minutes, it became grayish, like the original amide color. It was thought that perhaps ylide anion 14 forms first, in a reversible kinetic process which may then be followed by an attack at phosphorus. So attempts were made to trap



ylide anion 14 by addition of benzyl chloride and benzophenone a few minutes after appearance of the brown color. Some starting ylide 13 was recovered at the end of these two reactions, along with some of phosphine oxide 43 in the first case, and phosphinic amide 46 in the second instance. The absence of appreciable amounts of phosphine oxide may indicate that amide attacks the added electrophile in preference to phosphorus. This was supported by the detection of stilbene in the experiment with benzyl chloride.

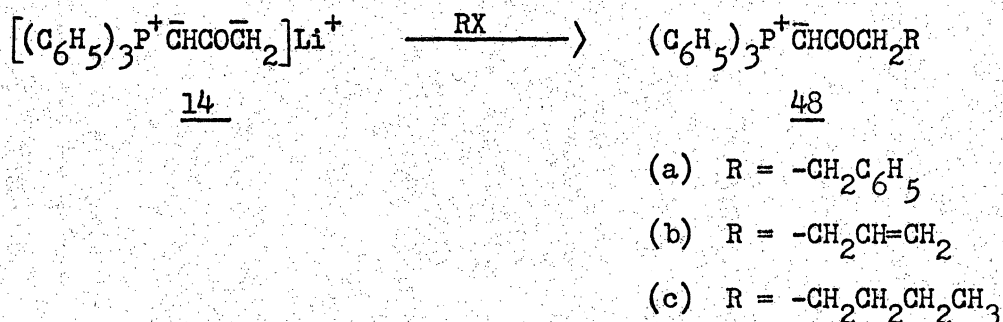
To test the possible generality of the reaction in which acetyldiphenylphosphine oxide (43) was formed, triphenylphosphine-(3-phenylpropionyl)methylene (48a) was treated with potassium amide in liquid ammonia in expectation of obtaining (2-oxo-4-phenylbutyl)-diphenylphosphine oxide (47); however, starting material (48a) was largely recovered.



Since potassium amide in liquid ammonia failed to effect the ionization of triphenylphosphineacetylmethylene (13), other basic reagents were investigated. *n*-Butyllithium did ionize a methyl hydrogen of 13 as found previously²⁰⁻²², so in all of the reactions reported herein, 1.2 molecular equivalents of *n*-butyllithium in THF-hexane was used to generate ylide anion 14.

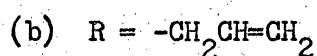
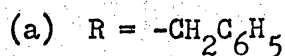
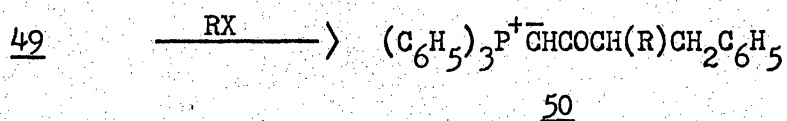
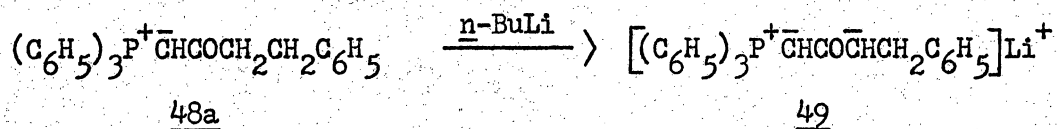
B. Alkylations of Lithiotriphenylphosphineacetylmethylene (14)

Previously, ylide anion 14 was successfully alkylated²⁰⁻²² with benzyl chloride, benzyl bromide, allyl chloride and butyl iodide to give products 48a-c.



More recently, Cooke²⁸ extended these reactions to include six other primary alkyl halides but found that secondary alkyl halides were less satisfactory because of their susceptibility to E2 elimination. In view of the generality of alkylations of 14 demonstrated by Cooke it did not appear necessary to further extend this line of investigation to include other simple halides. However, we were interested in determining if substituted ylides of type 48 could be ionized to form ylide anions, and if such species would also undergo alkylation. Thus ylide 48a was treated with *n*-butyllithium at -78° to form anion 49. To the resulting dark red solution of ylide anion, 49, was added benzyl chloride and disubstituted ylide 50a was obtained in 37% yield.* Similarly, 49 was alkylated with allyl bromide to give

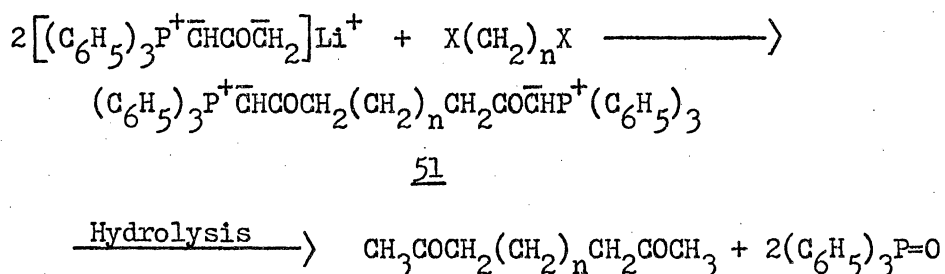
*Thanks are due to Dr. J. V. Hay for preparing this compound.



50b. The structure of 50a was established by its pmr spectrum and elemental analysis. 50b could not be recrystallized to give the pure product, but its pmr spectrum was in accordance with the proposed structure. The spectrum of 50a had a multiplet for twenty five aromatic protons at 7.32 ppm. The ylide proton was at 3.36 ppm as a broad singlet, and four methylene and one methine protons appeared as a complex multiplet centered at 2.88 ppm.

The pmr spectrum of 50b showed multiplet absorption due to twenty aromatic protons at 7.56 ppm. The signal due to one vinylic proton at the substituted carbon was at 6.00 ppm as a multiplet and the absorption for the other two vinyl protons was at 5.08 ppm as a triplet containing additional splitting. The ylide proton was present as a broad singlet at 3.4 ppm, and absorption of four methylene and one methine protons appeared as a multiplet at 2.6 ppm. The pmr spectrum showed the presence of approximately 20% starting ylide 48a.

It was also thought that alkylations involving two molecular equivalents of 14 and one molecular equivalent of a polymethylene dihalide could lead to bis ylides such as 51, and that subsequent hydrolytic cleavage of $(C_6H_5)_3P^+$ moieties could give diketones as shown below.

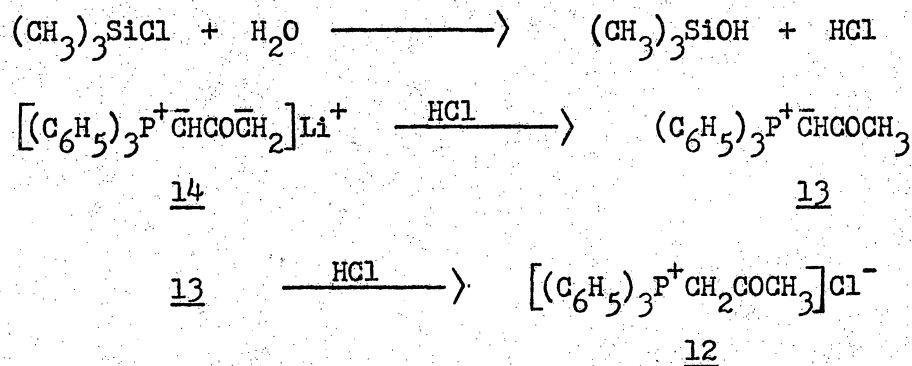


A series of alkylation reactions were carried out with several dihalides. The dihalides used were: 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,10-dibromodecane, α - α' -dibromo-o-xylene, α - α' -dibromo-m-xylene, and α - α' -dibromo-p-xylene. When 1,2-dibromoethane and the α - α' -dibromoxylenes were used as alkylating agents, they reacted quickly at Dry Ice temperature as evidenced by a color change from dark red-brown to orange-yellow. Other dihalides did not react at -78° but reacted when the Dry Ice-acetone bath was removed and replaced with an ice-water bath.

In each case tlc analysis of the reaction mixtures showed the presence of four or five products with a major component appearing as a spot at the base line. In one case, the reaction of 14 with 1,3-dibromopropane, this least mobile product was isolated in 36% yield and identified as 51 ($n=3$). The pmr spectrum of this compound showed absorption due to thirty aromatic protons at 7.92 ppm as a

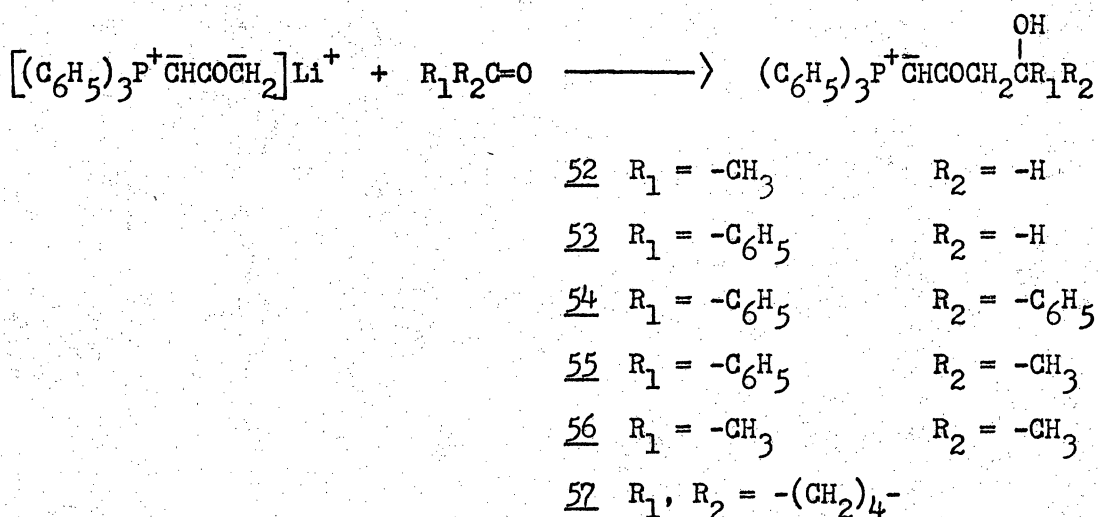
Next, the alkylation of 14 with trimethylchlorosilane was tried. The reaction was carried out using one molecular equivalent of halide. The anion color did not disappear even after stirring the reaction mixture for 5 hours at room temperature. Following work up, starting material was recovered. The reaction was repeated with two molecular equivalents of trimethylchlorosilane. Again the anion color did not disappear after stirring at room temperature. When the reaction mixture was quenched and processed, a beige solid melting at 234-237° was obtained. This material was identified as acetyltriphenylphosphonium chloride (12). The pmr spectrum exhibited absorption due to fifteen aromatic protons at 7.6 ppm. The P⁺-CH₂ protons appeared as a doublet at 6.21 and the methyl protons as a singlet at 2.46 ppm.

Presumably trimethylchlorosilane is not effective as an alkylating agent, so when the reaction was quenched with water, the silyl halide was hydrolyzed to form hydrochloric acid, which protonated ylide anion 14 to give starting material 13. When two molecular equivalents of trimethylchlorosilane was used, the first equivalent of liberated hydrochloric acid protonated the terminal site of ylide anion 14 and the second equivalent protonated the ylide carbanion of 13 to give the chloride salt 12.



C. Condensations of Lithiotriphenylphosphine-acetylmethylene (14) with Aldehydes and Ketones

Since in the original report on the chemistry of ylide anion 14, only one carbonyl compound, benzophenone, had been employed as an electrophile, a series of reactions were carried out on 14 using various aldehydes and ketones.



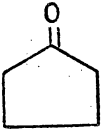

The reaction conditions for aldol condensations were essentially the same as for alkylations. The reactions were carried out under nitrogen at -78° . They were very rapid, the anion color disappearing and an orange-yellow color replacing it as soon as the carbonyl compound had been added to the ylide anion solution. The acetaldehyde employed for the reaction was generated by heating paraldehyde with a catalytic amount of p-toluenesulfonic acid. Acetaldehyde was distilled directly into the reaction flask containing the ylide anion solution and addition was continued until the dianion color was discharged.

The yields from the reactions carried out with acetaldehyde and benzaldehyde were lower than those from the ketone condensations. The yield of triphenylphosphine-(3-hydroxybutanoyl)methylene (52) was a little lower than triphenylphosphine-(3-hydroxy-3-phenylpropionyl)methylene (53), presumably because of the susceptibility of methyl protons of acetaldehyde to ionization by the ylide anion.

The aldol condensation reactions were carried out on small scales, using 3-7 millimols of triphenylphosphineacetylmethylene (13). In the case of ketone condensations the yields were around 63%. The reaction with benzophenone was repeated on a large scale using 119 millimols of ylide anion 14. The yield of crude product obtained from this reaction was 100% and the purified yield of 54 was 81%. This supports the fact that although great care was taken in every one of above runs to exclude all moisture from the reaction medium, the small amount of moisture that may be present makes a lot of difference, as far as the yields go, when reactions were done on small scales. When reaction mixtures were checked with tlc, there was always some unreacted starting material whereas in the large scale benzophenone reaction, tlc showed the presence of only one spot, the product. So the yield of this large scale reaction may be more representative of all aldol condensations. The aldol products obtained and their yields are given on page 30, Table I. In all cases, the structures of the products were assigned on the basis of their elemental analysis, and pmr and ir spectra. Pmr spectra were taken in CDCl_3 and were consistent with the fact that reactions occurred at the terminal carbanion site of the ylide anion 14. The original

TABLE I

Reactions of Lithiotriphenylphosphineacetylmethylene (14)with Aldehydes and Ketones

<u>Aldehyde or Ketone</u>	<u>Product (No.)</u>	<u>% Yield</u>
CH_3CHO	$(\text{C}_6\text{H}_5)_3\text{P}^+\text{CHCOCH}_2\overset{\text{OH}}{\underset{ }{\text{C}}}\text{HCH}_3$ (52)	43
$\text{C}_6\text{H}_5\text{CHO}$	$(\text{C}_6\text{H}_5)_3\text{P}^+\text{CHCOCH}_2\overset{\text{OH}}{\underset{ }{\text{C}}}\text{HC}_6\text{H}_5$ (53)	50
$(\text{C}_6\text{H}_5)_2\text{CO}$	$(\text{C}_6\text{H}_5)_3\text{P}^+\text{CHCOCH}_2\overset{\text{OH}}{\underset{ }{\text{C}}}(\text{C}_6\text{H}_5)_2$ (54)	81
$\text{C}_6\text{H}_5\text{COCH}_3$	$(\text{C}_6\text{H}_5)_3\text{P}^+\text{CHCOCH}_2\overset{\text{OH}}{\underset{ }{\text{C}}}(\text{CH}_3)\text{C}_6\text{H}_5$ (55)	66
$(\text{CH}_3)_2\text{CO}$	$(\text{C}_6\text{H}_5)_3\text{P}^+\text{CHCOCH}_2\overset{\text{OH}}{\underset{ }{\text{C}}}(\text{CH}_3)_2$ (56)	63
	$(\text{C}_6\text{H}_5)_3\text{P}^+\text{CHCOCH}_2\overset{\text{OH}}{\underset{ }{\text{C}}}$  (57)	59

methyl signal which appears at 2.06 ppm in the spectrum of the ylide 13 was replaced by resonance arising from methylene hydrogens, also resonance due to the original ylide proton was still present, indicating that substitution did not occur at the ylide carbanion. All peaks in the pmr spectra could be accounted for, except that the hydroxyl proton was missing in every case. In each instance, the integration of the aromatic region was larger than it should have been, so it was concluded that the hydroxyl proton appears in the aromatic region. The pmr spectra of aldol products are given on page 32, Table II. In the ir spectra of these compounds, a broad band due to O-H stretching appeared in the 3100-3500 cm^{-1} region. In the pmr spectra, the methylene protons appeared as singlets except in cases where the products had a chiral center, (compounds 52, 53 and 55). In triphenylphosphine-(3-hydroxy-3-phenylbutanoyl)methylene (55) the methylene protons were diastereotopic and split each other to give an AB type pattern with $J_{AB} = 14$ Hz. The chemical shifts of the protons A and B were calculated to be 2.99 and 2.71 ppm respectively. Compounds 52 and 53 showed an ABX type spectrum. The non-equivalent methylene protons (A and B) split each other; they were also split by the methine proton (X) on the neighboring carbon atom. Also X, in turn, was split by the A and B protons. The chemical shift and coupling constant values were calculated for these compounds. (See Experimental Section)

After the aldol condensations had been carried out at the terminal site of ylide anion 14, an attempt was made to remove the $(\text{C}_6\text{H}_5)_3\text{P}^+$

TABLE II

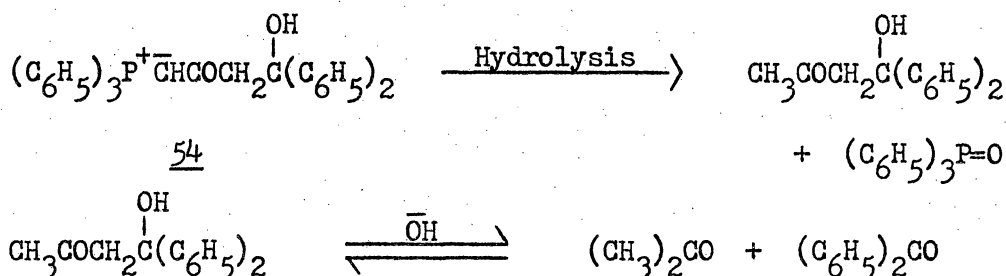
Pmr Absorptions of Aldol Products

<u>Product No.</u>	<u>Aromatic and hydroxyl</u>	<u>+ -PCH-</u>	<u>-CH₂-</u>	<u>-CH₃</u>
<u>52*</u>	7.7 (m)	3.8 (s, broad)	2.59 (m) 2.32 (m)	1.2 (d)
<u>53*</u>	7.56 (m)	3.68 (d, broad)	2.79 (m) 2.65 (m)	-
<u>54</u>	7.52 (m)	3.72 (d, broad)	3.28 (s)	-
<u>55</u>	7.44 (m)	3.6 (s, broad)	2.99 (d) 2.71 (d)	1.48 (s)
<u>56</u>	7.52 (m)	3.78 (d, broad)	2.46 (s)	1.24 (s)
<u>57**</u>	7.56 (m)	3.8 (s, broad)	2.6 (s)	-

* The methine proton of 52 appeared at 4.2 ppm and that of 53 at 5.10 ppm as multiplets.

**The methylene protons of the cyclopentanol group had multiplet absorption at 1.74 ppm.

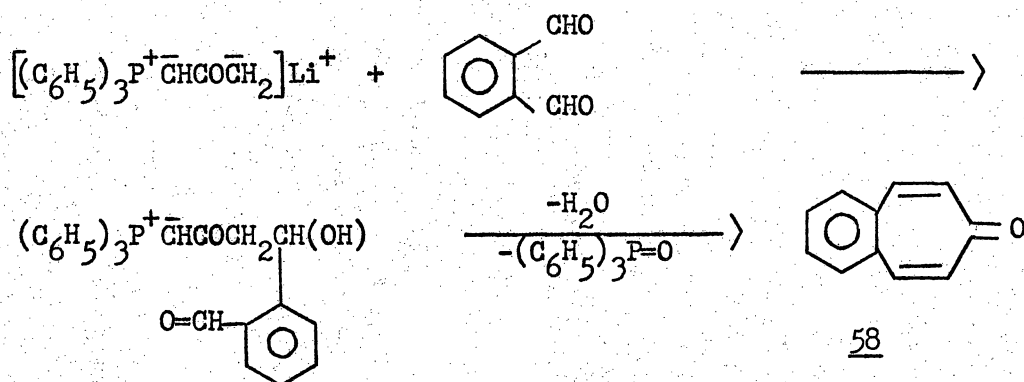
control element. Hydrolytic cleavage of the triphenylphosphine group from aldol condensation product 54 with aqueous ethanol at steam bath temperature for 2.5 days resulted in formation of triphenylphosphine oxide, indicating that cleavage took place. Distillation of the oil obtained after separation of the triphenylphosphine oxide afforded only benzophenone. These results indicate that a retro aldol reaction had taken place either during hydrolysis or upon distillation.



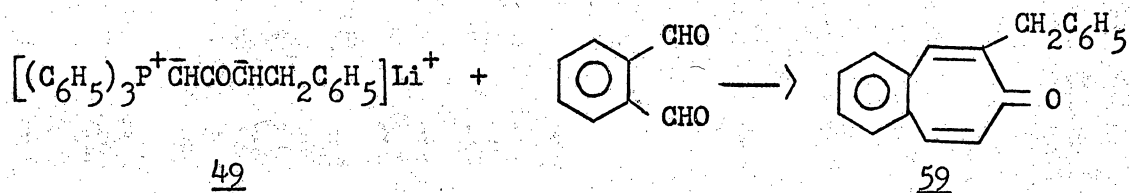
Since aldol condensations produced carbinols 52 - 57 in reasonably good yields, it seemed possible that this could be combined with an intramolecular Wittig type reaction if a suitable carbonyl compound were used. So, the reaction of lithiotriphenylphosphineacetylmethylene (14) with o-phthalaldehyde was attempted. The reaction conditions were the same as for aldol condensations. Reaction was rapid, o-phthalaldehyde reacting at Dry Ice temperature. Tlc analysis of the crude reaction mixture showed the presence of four products. Triphenylphosphine oxide, o-phthalaldehyde, and phthalic acid were detected by comparison of the R_f values with authentic samples. The mixture was chromatographed using silica gel and a small amount of pure 4,5-benzotropone was obtained. The structural assignment of this compound was supported by elemental analysis, pmr spectrum⁴⁶ and melting point.⁴⁷ Triphenylphosphine oxide formed as a by product during the Wittig

reaction was difficult to separate from benzotropone. Upon chromatography, most of the benzotropone was eluted from the column as a mixture with triphenylphosphine oxide. Crystallization efforts of the reaction mixture were unsuccessful. An identical experiment was carried out and the yield of 4,5-benzotropone was estimated to be 49% by gas chromatography using benzalacetophenone as the internal standard.

The present procedure constitutes a new, one-step method for synthesizing 4,5-benzotropone (58).

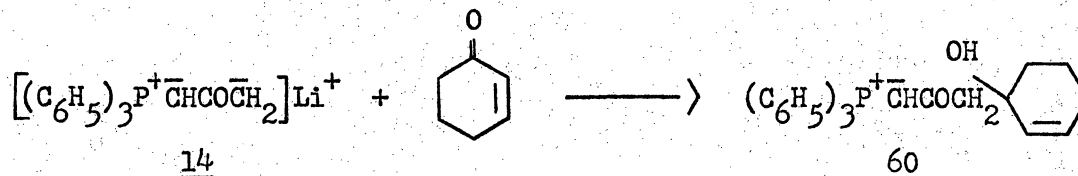


A similar reaction was repeated using triphenylphosphine-(3-phenylpropionyl)methylene (48a) as a possible route to 2-benzyl-4,5-benzotropone (59).



The desired reaction apparently did take place but separation of pure 59 from the crude reaction mixture could not be accomplished.

Reactions of ylide anion 14 with two α,β -unsaturated carbonyl compounds (cinnamaldehyde and 2-cyclohexen-1-one) were also tried to see if they would give 1,2- or 1,4-addition products. With cinnamaldehyde tlc analysis showed that reaction took place, but upon chromatography, the product decomposed. In the case of 2-cyclohexen-1-one, crystallization efforts on the mixture obtained were unsuccessful but the pmr spectrum of the crude product showed that it was mainly the 1,2-addition product (60).

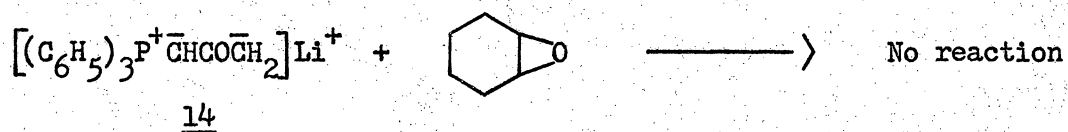


In the pmr spectrum of crude 60 a multiplet due to fifteen aromatic protons and one hydroxyl proton was centered at 7.76 ppm. The ylide proton was at 3.88 ppm as a broad doublet and the methylene protons gave rise to a complex multiplet at 1.94 ppm. Two vinyl protons appeared at 5.88 ppm as a singlet although they would be expected to split each other, and also further splitting by neighboring methylene protons would be expected. By comparison it may be noted that in the spectrum of cyclohexene⁴⁸, the vinyl proton multiplet is very narrow.

Reactions of lithiotriphenylphosphineacetylmethylene (14) with isophthalaldehyde, terephthalaldehyde and meta- and para- diacetylbenzenes were also tried. The condensations were very rapid, as evidenced by disappearance of the anion color, as soon as the carbonyl compounds had been added to the solution of 14. But in all

of these cases the product mixtures were so complex that a single pure component could not be isolated from any of the reactions.

Lithiotriphenylphosphineacetylmethylene (14) did not react with cyclohexene oxide. Even after the reaction mixture was allowed to stir overnight at room temperature, the anion color did not disappear. After quenching and processing the reaction mixture, starting material 13 was recovered.



III. EXPERIMENTAL

A. General

Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Temperatures were recorded in centigrade degrees.

Elemental analyses were performed in this department, mostly by Mr. Tom E. Glass, using a Perkin-Elmer 240 Elemental Analyzer.

Infrared (ir) spectra were taken on a Beckman IR 20A-X infrared spectrophotometer using 10% chloroform solutions. Band positions were recorded in reciprocal centimeters (cm^{-1}).

Proton magnetic resonance (pmr) spectra were recorded on a JEOL JNM-PS-100 spectrometer, using deuteriochloroform (CDCl_3) or deuterio-dimethyl sulfoxide (DMSO-d_6) as solvents. Tetramethylsilane (TMS) was used as internal standard. Chemical shifts were measured to the center of a singlet or multiplet and are given in δ units, parts per million (ppm). In all pmr descriptions, s=singlet, d=doublet, t=triplet, and m=multiplet.

Mass spectra were taken by Mr. Fred Battrel using a Hitachi-Perkin-Elmer RMU-7 spectrometer.

Thin layer chromatography (tlc) was carried out using Eastman Chromatogram Sheets (Silica Gel) type 6060 with fluorescent indicator. Acetone-benzene (1:1) was generally used as the developing solvent. Spots were visualized with ultraviolet light.

The yield of 4,5-benzotropone (58) was obtained on a Varian Aerograph Model 90-P gas chromatograph, equipped with a 6 ft. column,

packed with 6.3% carbowax 20M, on gas chrom Z 30/60, at a column temperature of 200°.

n-Butyllithium, as a 2.04 M solution in hexane, was purchased from Ventron Co., Alfa Products, Beverly, Massachusetts. Liquid ammonia was obtained from The Matheson Co., E. Rutherford, New Jersey and was dried prior to use with potassium metal. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride immediately prior to use. Unless otherwise specified, chemicals were commercial reagent grade and were used without further purification.

B. Preparation of Triphenylphosphineacetylmethylene (13)

The procedure of Ramirez and Dershowitz²⁴ was followed. A solution of 52.4 g (0.20 mol) of triphenylphosphine and 22.2 g (0.24 mol) of chloroacetone in 150 ml of chloroform was refluxed for 2 hr. After cooling, the solution was poured into 900 ml of ether to precipitate acetyltriphenylphosphonium chloride (12). This solid was then extracted into water and the pH of the solution was adjusted to 11 with 5% aqueous potassium hydroxide to precipitate the crude product. The product was then extracted into chloroform with three 200 ml portions. The combined chloroform extracts were washed with 200 ml of water, dried (MgSO_4) and concentrated to give 60 g (94%) of crude 13. This material was recrystallized from ethyl acetate to yield 40.68 g (64%) of triphenylphosphineacetylmethylene (13), mp 205-206.5° (lit.²⁴ 205-206°); pmr (CDCl_3) δ 7.6 (m, 15, phenyl), 3.62 (broad d, 1, P=CH) and 2.06 (d, 3, CH_3); ir (CHCl_3) 2950 (C-H), and 1530 cm^{-1} (C=O).

Anal. Calcd. for $\text{C}_{21}\text{H}_{19}\text{OP}$: C, 79.23; H, 6.02. Found: C, 78.97; H, 5.96.

C. Attempted Generation of Potassiotriphenylphosphineacetyl-
methylene

Attempted Formation and Benzylation of Potassiotriphenylphosphine-
acetylmethylene Using THF.- In a 500 ml three-necked round-bottomed flask equipped with a mechanical stirrer and a Dry Ice condenser, 0.0162 mol of potassium amide was formed in 250 ml of anhydrous liquid ammonia. To this amide suspension was added 2.5 g (0.008 mol) of triphenylphosphineacetylmethylene (13) as a solution in 100 ml of anhydrous THF. As this solution entered the ammonia, the reaction mixture became brownish first, then it was allowed to stir for 1 hr. During this time the color turned to greenish black. To this solution, 2.565 g (0.020 mol) of benzyl chloride in 15 ml of anhydrous ether was added. The purple color characteristic of stilbene formation⁴⁹ was observed indicating the presence of excess amide. The reaction mixture was stirred for 1 hr before neutralization with excess solid ammonium chloride. Then the liquid ammonia was evaporated and replaced with 250 ml of anhydrous ether. The resulting suspension was poured over a slurry of 7.5 ml of 12 N HCl and 75 g of ice and stirred until dissolution was complete. The ethereal layer was separated and the acidic aqueous phase was extracted with two 100 ml portions of ether. The combined ethereal extracts were dried ($MgSO_4$) and concentrated in vacuo to give an oil which solidified quickly and smelled strongly like benzyl chloride.

The acidic aqueous solution was made basic with 10% aqueous potassium hydroxide (pH=11) and then extracted with two 100 ml portions

of chloroform. The combined chloroform extracts were dried (MgSO_4) and concentrated to give a trace amount of solid. Thin layer chromatography [acetone-benzene (1:1)] showed the presence of benzyl chloride and stilbene in the ethereal extract and the presence of the same two spots in both the ether and chloroform extracts.

Thinking that perhaps the solution was not acidic enough and that if the benzylation occurred, the salt of the benzylated ylide did not form and separate from benzyl chloride, the solid obtained from the ethereal extract was treated with aqueous HCl, but most of the solid did not dissolve, so the crystals were filtered. The aqueous HCl solution was extracted twice with 50 ml aliquots of ether, the combined ethereal extracts were dried (MgSO_4) and concentrated to give some solid which smelled like benzyl chloride. This solid was recrystallized from 95% ethanol to yield 0.218 g (12%) of stilbene, as evidenced by pmr and tlc analysis, mp $117-122^\circ$ (lit.⁵⁰ 124°).

The acid insoluble solid was recrystallized from 95% ethanol-heptane, and 0.74 g of white crystals were obtained, mp $182-191^\circ$; pmr (DMSO-d_6) δ 7.6 (m), and 6.88 (broad s) ratio 4.3:1.

Anal. Found: C, 65.48; H, 5.08.

This material was not characterized further.

Attempted Formation and Benzylation of Potassiotriphenylphosphine-acetylmethylene without THF. - The same procedure and molar amounts of reagents as described above were used, but triphenylphosphineacetylmethylene (13) was added to the potassium amide suspension as a solid. Observations were the same, including the purple stilbene formation.

After evaporating and replacing the liquid ammonia with ether, this ethereal suspension was poured over a slurry of 75 g of ice and 7.5 ml of 12 N HCl and stirred. The ethereal layer was separated and the acidic aqueous phase was extracted with two 100 ml portions of ether. The combined ethereal extracts were dried (MgSO_4) and concentrated to give 0.61 g of a beige solid. Thin layer chromatography [acetone - benzene (1:1)] of the ethereal extracts showed stilbene, an unidentified compound which appeared, by comparison of R_f values, to be the same as that obtained in the reaction using THF. Acetyldiphenylphosphine oxide (43) was also present.

After making the acidic solution basic (pH=11) with 10% aqueous potassium hydroxide and extracting it with two 100 ml portions of chloroform, some solid was obtained upon evaporation of the chloroform. Tlc analysis of this material revealed the presence of only 43.

The solid from the chloroform extract was recrystallized from benzene-heptane and identified as acetyldiphenylphosphine oxide (43) by its pmr spectrum. However, its melting point ($117 - 119^\circ$) was lower than the reported value³⁹, so it was sublimed at $120 - 135^\circ/5-6$ mm Hg to give 0.6 g (30%) of 43, mp $127-128^\circ$ (lit³⁹, $127-129^\circ$); pmr (CDCl_3) δ 7.76 (m, 10, phenyl), 3.64 (d, 2, CH_2), and 2.32 (s, 3, CH_3).

Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{O}_2\text{P}$: C, 69.76; H, 5.86. Found: C, 70.00; H, 5.58.

The solid obtained from the ethereal extracts, the tlc of which showed the presence of stilbene, phosphine oxide 43 and the unidentified compound, was washed with ether to remove the stilbene. It was

then washed with chloroform to remove the small amount of acetyl-diphenylphosphine oxide (43) leaving 0.281 g of the unidentified compound, mp 182-191°. The total amount of stilbene obtained from this reaction was 0.48 g (27%).

Treatment of Triphenylphosphineacetylmethylene (13) with Benzyl Chloride and Ammonium Chloride in Liquid Ammonia. - To 200 ml of liquid ammonia was added 2.579 g (0.0081 mol) of triphenylphosphineacetylmethylene (13) as a solution in 125 ml of THF. It was allowed to stir for 30 min, then 1.127 g (0.0081 mol) of benzyl chloride was added and the reaction mixture was stirred for 1 hr before addition of solid ammonium chloride. The liquid ammonia was evaporated and replaced with 200 ml of ether. This ethereal suspension was then poured over 75 g ice and 6 ml of 12 N HCl and stirred until everything had dissolved. The ethereal layer was separated, the acidic aqueous solution was extracted with three 100 ml portions of ether, all the ethereal extracts were combined, dried (MgSO_4) and concentrated to give 100% of recovered benzyl chloride.

The acidic aqueous layer was then adjusted to pH=11 with 10% aqueous potassium hydroxide. Some white precipitate appeared and it was extracted into three 100 ml portions of chloroform. The combined chloroform extracts were washed with 10% aqueous sodium chloride, dried (MgSO_4) and concentrated to give 100% of recovered triphenylphosphineacetylmethylene (13).

Treatment of Triphenylphosphineacetylmethylene (13) with Benzyl Chloride in Liquid Ammonia. - A 2.0 g (0.0063 mol) sample of triphenyl-

phosphineacetylmethylene (13) was added to 200 ml of liquid ammonia and stirred for 1 hr. Then 0.795 g (0.0063 mol) of benzyl chloride was added and the reaction mixture was allowed to stir for 2.5 hr. Evaporation of the liquid ammonia resulted in quantitative recovery of triphenylphosphineacetylmethylene (13).

Treatment of Triphenylphosphineacetylmethylene (13) with Potassium Amide in Liquid Ammonia. - To 0.0092 mol of potassium amide suspension in 250 ml of anhydrous liquid ammonia was added 2.549 g (0.008 mol) of triphenylphosphineacetylmethylene (13). The reaction mixture was allowed to stir for 75 min and then neutralized with excess solid ammonium chloride. After the usual acid-base work up, tlc analysis of both ether and chloroform extracts showed the presence of mostly acetyldiphenylphosphine oxide (43) along with some of the unidentified compound. Recrystallization from benzene-heptane afforded 0.87 g (42%) of acetyldiphenylphosphine oxide (43).

Detection of Benzene and Attempted Isolation of the Iminophosphorane Intermediate (42). - The reaction was carried out again using the same amounts of reagents as described above. At the end of the reaction the liquid ammonia was evaporated and replaced with ether. The resulting suspension was filtered and the filtrate was checked for the presence of benzene by gas chromatography, using a 6 ft column, packed with 6.3% carbowax 20M, on gas chrom Z 30/60 at a column temperature of 50°. Benzene was identified by its retention time, also addition of some benzene to the ethereal solution resulted in enlargement of the appropriate peak.

An identical experiment was run again, but the filtrate obtained as described above was concentrated and the resulting solid was recrystallized from 95% ethanol-heptane, to give 0.19 g of diphenylphosphinic amide (46), mp 163.5-164.5° (lit⁴⁰⁻⁴⁴, values vary between 160° and 168°); pmr (CDCl₃) δ 7.76 (m, 10, phenyl) and 3.84 (s, 2, NH₂); ir (CHCl₃) 3420, 3340, 2960, 1550, 1440, 1175, 1125 and 880 cm⁻¹.

Anal. Calcd. for C₁₂H₁₂NOP: C, 66.36; H, 5.57; N, 6.45.

Found: C, 66.41; H, 5.66; N, 6.56.

Thinking that even if iminophosphorane intermediate 42 was formed, it may have undergone hydrolysis upon recrystallization, the reaction was repeated, using the same procedure and molar equivalents of reagents. The liquid ammonia was evaporated and replaced with ether. This ethereal suspension was filtered, and the ether evaporated. The pmr spectrum of the crude material showed the presence of some diphenylphosphinic amide (46) and some acetyldiphenylphosphine oxide (43). Crystallization of this solid afforded 0.31 g of amide 46.

To the solid remaining after filtering the ethereal suspension was added some chloroform and most of the material dissolved, the chloroform suspension was filtered and the residue was shown to be water soluble, inorganic material. The chloroform extract was concentrated and the resulting crude solid was recrystallized from benzene to give 0.47 g of diphenylphosphinic amide (46), thus bringing the yield of 46 to 0.78 g (44%).

Attempts to Trap Potassiotriphenylphosphineacetylmethylene with Benzyl Chloride and Benzophenone. - The reaction was carried out using

the same molar amounts of reagents. After the addition of triphenylphosphineacetylmethylene (13) to the potassium amide suspension, it was stirred for 4 min and then benzyl chloride was added before the disappearance of the brown color. The reaction mixture was stirred for 75 min and neutralized. After the acid-base work up as described before, from the ethereal extract 0.3 g of stilbene, 0.1 g of acetyl-diphenylphosphine oxide (43) and 0.26 g of the unidentified compound (mp 183-192°) were isolated. From the chloroform extract 0.9 g of starting ylide 13 was recovered.

Trapping was also tried with benzophenone. When benzophenone was added, the reaction mixture went through a spectrum of colors very quickly, changing from a dark color to blue, purple, pink, dark beige and finally grayish beige. At the end of the reaction, the liquid ammonia was replaced with ether, the ethereal suspension was filtered, and from the evaporation of the filtrate 0.85 g of diphenylphosphinic amide (46) was obtained. To the ether insoluble solid some water was added and shaken vigorously, some of the solid dissolved. The 0.25 g of undissolved material was shown to be the starting ylide 13. The aqueous solution was extracted with some ether first to give a trace amount of solid, tlc of which showed the presence of benzophenone and phosphinic amide 46. The aqueous phase was then extracted with chloroform to give a trace amount of solid which appeared to be the phosphinic amide 46 by tlc and mp.

Attempted Reaction of Triphenylphosphine-(3-phenylpropionyl)methylene (48a) with Potassium Amide in Liquid Ammonia. - To a suspen-

sion of 0.0044 mol of potassium amide in 200 ml of anhydrous liquid ammonia, 1.559 g (0.0038 mol) of solid triphenylphosphine-(3-phenylpropionyl)methylene (48a) was added. The ylide did not dissolve. The resulting light gray suspension was stirred for 1 hr and neutralized with excess solid ammonium chloride. The liquid ammonia was then evaporated and replaced with 200 ml of ether. The ethereal suspension was poured over a slurry of 50 g of ice and 5 ml of 12 N HCl and stirred until everything had dissolved. The ethereal layer was separated, the acidic aqueous phase was extracted twice with 75 ml portions of ether. All of the ethereal extracts were combined and concentrated, but no residual material was obtained.

The acidic solution was adjusted to pH=11 with 10% aqueous potassium hydroxide, some white precipitate appeared. This precipitate was extracted into three 75 ml portions of chloroform. The combined chloroform extracts were dried and concentrated to give 1.176 g (75%) of recovered triphenylphosphine-(3-phenylpropionyl)methylene (48a), mp 145-148°.

D. Alkylations of Lithiotriphenylphosphineacetylmethylene (14)

With Benzyl Chloride. - A 5.00 g (0.0157 mol) sample of triphenylphosphineacetylmethylene (13) was dissolved in 300 ml of anhydrous THF under a nitrogen atmosphere. The solution was cooled by means of a Dry Ice-acetone bath and then 9.23 ml (0.0188 mol) of n-butyllithium in hexane was added. The red-brown ylide anion solution was stirred for 20 min before the addition of 2.385 g (0.0188 mol) of benzyl chloride in 30 ml of anhydrous THF. The reaction mixture was stirred for 1 hr and then allowed to warm to room temperature. During this time the dark ylide anion color was discharged. The orange solution was poured into 300 ml of water-ether (2:1) and stirred for 5 min. The ethereal layer was separated, the basic aqueous solution was extracted three times with 150 ml portions of chloroform. All the organic layers were combined, washed with 10% aqueous sodium chloride, dried (MgSO_4) and concentrated to give an oil which solidified upon standing to yield 5.9 g of beige solid. Thin layer chromatography [acetone-benzene (1:1)] of the reaction mixture indicated the presence of mainly one product, along with some benzyl chloride and starting ylide 13. The crude product was recrystallized from ethyl acetate to give 3.02 g (47%) of triphenylphosphine-(3-phenylpropionyl)methylene (48a). An analytical sample had mp 147.5-149 (lit.²⁵ 148-150°); pmr (CDCl_3) δ 7.56 (m, 20, phenyl), 3.56 (broad s, 1, P=CH), and 2.86 (m, 4, $-\text{CH}_2-\text{CH}_2-$).

Anal. Calcd. for $\text{C}_{28}\text{H}_{25}\text{OP}$: C, 82.33; H, 6.17. Found: C, 82.05; H, 6.39.

With 1,3-Dibromopropane. - To a solution of 1.908 g (0.006 mol) of triphenylphosphineacetylmethylene (13) in 70 ml of anhydrous THF, under a nitrogen atmosphere, cooled in a Dry Ice-acetone bath, was added 3.53 ml (0.0072 mol) of *n*-butyllithium in hexane. The red-brown solution was stirred for 15 min, afterwards 0.727 g (0.0036 mol) of freshly distilled 1,3-dibromopropane was added. Stirring the reaction mixture at -78° for 1 hr was followed by allowing it warm to room temperature. During this period, an orange color replaced the dark ylide anion color. The orange solution was processed as described above and an oil was obtained, which solidified when triturated with ether-hexane. Thin layer chromatography [acetone-benzene (1:1)] showed the presence of four spots. The crude product was recrystallized from ethyl acetate to yield 1.22 g (36%) of bis ylide 51 ($n=3$). A sample prepared for analysis had mp $200-207^{\circ}$, mmp with starting ylide 13 $182-197^{\circ}$; pmr (CDCl_3) δ 7.92 (m, 30, phenyl), 4.2 (broad s, 2, P=CH), 2.34 (m, 4, $-\text{COCH}_2-$), and 1.64 (m, 6, $-(\text{CH}_2)_3-$).

Anal. Calcd. for $\text{C}_{45}\text{H}_{42}\text{O}_2\text{P}_2$: C, 79.85; H, 6.27. Found: C, 80.19; H, 6.25.

When similar experiments were carried out using 1,2-dibromoethane, 1,4-dibromobutane, 1,10-dibromodecane, α,α' -dibromo-*p*-xylene, α,α' -dibromo-*o*-xylene, and α,α' -dibromo-*m*-xylene as alkylating agents, complex mixtures of products were obtained which could not be purified.

Attempted Alkylation of 14 With 1 Molecular Equivalent of Trimethylchlorosilane. - The same procedure and molar quantities of reagents as described above were used until the addition of 0.781 g

(0.0072 mol) of trimethylchlorosilane in 5 ml of anhydrous THF. The reaction mixture was stirred in Dry Ice-acetone bath for 1 hr and then allowed to warm to room temperature. Even after stirring for 5 hr at 25°, the dark ylide anion color did not disappear. This solution was poured into 150 ml of water-ether (2:1) and stirred for 5 min. The organic layer was separated and the basic aqueous solution was extracted with two 75 ml portions of chloroform. All the organic extracts were combined, washed with 10% aqueous sodium chloride, dried (MgSO₄) and concentrated to give a beige solid. Thin layer chromatography [acetone-benzene (1:1)] indicated that it was starting material. Recrystallization from ethyl acetate gave 1.214 g (64%) of starting ylide 13, mp 202-202.5° (lit.²⁴ 205-206°).

Attempted Alkylation of 14 With 2 Molecular Equivalents of Trimethylchlorosilane. - The same procedure and molar quantities of reagents were used as described before until 1.499 g (0.0138 mol) of trimethylchlorosilane in about 10 ml of anhydrous THF was added. The red-brown ylide anion color did not disappear after stirring the reaction mixture at room temperature for about 2 hr. It was processed as before to give an oil, most of which solidified upon standing. After removal of residual solvent under vacuum, a beige solid melting at 240° was obtained. This was recrystallized from chloroform-benzene-petroleum ether to yield 1.019 g (48%) of acetonyltriphenylphosphonium chloride (12), mp 234-237° (lit.²⁴ 237-238°); pmr (CDCl₃) δ 7.6 (m, 15, phenyl), 6.21 (d, 2, CH₂), and 2.46 (s, 3, CH₃).

Alkylation of Triphenylphosphine-(3-phenylpropionyl)methylene

(48a) With Allyl Bromide. - A 0.817 g (0.002 mol) sample of triphenylphosphine-(3-phenylpropionyl)methylene (48a) was dissolved in 45 ml of anhydrous THF under a nitrogen atmosphere and cooled by means of a Dry Ice-acetone bath. Then 1.18 ml (0.0024 mol) of *n*-butyllithium in hexane was injected. The formation of dark red-brown lithiotriphenylphosphine-(3-phenylpropionyl)methylene (49) was instantaneous. The ylide anion was stirred for 15 min, before the addition of 0.290 g (0.0024 mol) of allyl bromide in 10 ml of anhydrous THF. The reaction mixture was then stirred for 1 hr, during this time the color changed from red-brown to light orange. Then the Dry Ice bath was removed and the contents of the reaction flask was allowed to warm to room temperature; the color became yellow. The reaction mixture was poured into 150 ml of water-ether (2:1) and stirred for 5 min. The organic layer was separated and the aqueous solution was extracted with three 50 ml portions of chloroform. The combined organic extracts were dried ($MgSO_4$) and concentrated to give a dark yellow oil. After trituration with ether, 0.91 g of semi solid was obtained. Thin layer chromatography [acetone-benzene (1:1)] indicated the presence of mainly one product along with some starting ylide (48a), but recrystallization efforts were unsuccessful. The pmr spectrum ($CDCl_3$) of the crude product (50b) had peaks at δ 7.56 (m, 20, phenyl), 6.0 (m, 1, $-CH=C-$), 5.08 (t, 2, $-C=CH_2$), 3.4 (broad s, 1.25, $P=CH$) and 2.6 (m, 7, $-CH(CH_2)_2-$). The pmr spectrum indicated the presence of approximately 20% of starting ylide 48a.

E. Condensations of Lithiotriphenylphosphineacetylmethylene (14)With Aldehydes and Ketones

With Acetaldehyde. - To a 100 ml, three-necked, round-bottomed flask, equipped with a magnetic stirring bar and a nitrogen inlet was added 1.908 g (0.006 mol) of triphenylphosphineacetylmethylene (13). Then anhydrous THF was injected (75 ml) until the ylide dissolved. The solution was cooled to -78° by means of a Dry Ice-acetone bath which was followed by addition of 3.53 ml (0.0072 mol) of *n*-butyllithium in hexane. The ylide anion was then stirred for 15 min. The acetaldehyde needed was generated by heating paraldehyde with a catalytic amount of *p*-toluenesulfonic acid. The aldehyde was distilled directly into the reaction flask already containing the ylide anion solution and was added until the anion color disappeared. (From the amount of paraldehyde used, it was calculated that about 0.029 mol of acetaldehyde had been added.) The Dry Ice bath was removed and the reaction mixture was allowed to warm to room temperature. The orange solution was then poured into 150 ml water-ether (2:1) and stirred for 5 min. The organic phase was separated and the aqueous solution was extracted three times with 75 ml aliquots of chloroform. The combined organic extracts were washed with 10% aqueous sodium chloride, dried (MgSO_4) and concentrated in vacuo to give a yellowish solid. Thin layer chromatography [acetone-benzene (1:1)] showed the presence of mainly one product and some starting ylide. The crude product was recrystallized from ethyl acetate to give 0.934 g (43%) of triphenylphosphine(3-hydroxybutanoyl)methylene (52), mp $160-161^{\circ}$,

pmr (CDCl_3) δ 7.7 (m, 16, phenyl and hydroxyl), 4.2 (m, 1, CH_x), 3.8 (broad s, 1, $\text{P}=\text{CH}$), 2.32 and 2.59 (m, 2, CH_AH_B), and 1.2 (d, 3, CH_3); $J_{AB} = 15$ Hz, $J_{AX} = 9.43$ Hz and $J_{BX} = 2.57$ Hz. Ir (CHCl_3) 3500-3160 (O-H), 3000 (C-H), and 1530 cm^{-1} (C=O).

Anal. Calcd. for $\text{C}_{23}\text{H}_{23}\text{O}_2\text{P}$: C, 76.23; H, 6.40. Found: C, 75.94; H, 6.65.

With Benzaldehyde. - To a solution of 0.954 g (0.003 mol) of triphenylphosphineacetylmethylene (13) in 40 ml of anhydrous THF maintained at -78° (Dry Ice-acetone bath) under a nitrogen atmosphere was added 1.8 ml (0.0036 mol) of *n*-butyllithium in hexane. The anion formation was instantaneous. The red-brown solution was stirred for 15 min before the addition of 0.382 g (0.0036 mol) of benzaldehyde in 10 ml anhydrous THF. The reaction was rapid, the ylide anion color disappearing and an orange color replacing it as soon as the benzaldehyde had been added. The reaction mixture was allowed to stir for 50 min at Dry Ice temperature and then to warm to room temperature. The reaction mixture was processed as before. After evaporation of the solvent in vacuo an oil was obtained which solidified upon standing overnight. Thin layer chromatography [acetone-benzene (1:1)] of the oil obtained indicated the presence of one product along with some starting ylide. The crude product was recrystallized from ethyl acetate to yield 0.639 g (50%) of triphenylphosphine-(3-hydroxy-3-phenylpropionyl)methylene (53). A sample prepared for analysis had mp 163° ; pmr (CDCl_3) δ 7.56 (m, 21, phenyl and hydroxyl), 5.10 (m, 1, CH_x), 3.68 (broad d, 1, $\text{P}=\text{CH}$) and 2.65 and 2.79 (m, 2, CH_AH_B); $J_{AB} = 15$ Hz, $J_{AX} = 11.57$ Hz and $J_{BX} = 3.43$ Hz. Ir (CHCl_3) 3480-3120 (O-H),

2290 (C-H), and 1520 cm^{-1} (C=O).

Anal. Calcd. for $\text{C}_{28}\text{H}_{25}\text{O}_2\text{P}$: C, 79.23; H, 5.94. Found: C, 78.98; H, 5.79.

With Benzophenone. - This large scale reaction was carried out in a 2 l. three-necked, round-bottomed flask, under a nitrogen atmosphere. 38g (0.119 mol) of triphenylphosphineacetylmethylene (13) was dissolved in 1000 ml of anhydrous THF. But when the solution was cooled to -78° , ylide 13 precipitated, so an additional 400 ml of anhydrous THF was added, but dissolution was still incomplete. Then 70.1 ml (0.143 mol) of *n*-butyllithium in hexane was added. The reaction color was very dark red-brown. The ylide anion solution was allowed to stir for 20 min and 26.06 g (0.143 mol) of benzophenone in 200 ml of anhydrous THF was added. The reaction mixture was stirred for 75 min in the Dry Ice-acetone bath and then allowed to warm to room temperature. The color was very dark but when most of it was poured into 1200 ml water-ether (2:1) and only a few hundred ml of solution was left in the flask, it was red. After the usual work-up, 59.4 g (100%) of a beige solid was obtained. Thin layer chromatography [acetone-benzene (1:1)] showed the presence of only one spot. The crude product was recrystallized from acetone to yield 48.25 g (81%) of triphenylphosphine-(3-hydroxy-3,3-diphenylpropionyl)-methylene (54), mp $180-182^\circ$ (lit.²¹⁻²² $175-177^\circ$); pmr (CDCl_3) δ 7.52 (m, 26, phenyl and hydroxyl), 3.72 (broad d, 1, P=CH), and 3.28 (s, 2, CH_2); ir (CHCl_3) $3400-3150$ (O-H), 3000 (C-H), and 1535 cm^{-1} (C=O).

Anal. Calcd. for $\text{C}_{34}\text{H}_{29}\text{O}_2\text{P}$: C, 81.58; H, 5.84. Found: C, 81.32; H, 5.53.

With Acetophenone. - To a solution of 1.272 g (0.004 mol) of triphenylphosphineacetylmethylene (13) in 50 ml of anhydrous THF maintained at -78° (Dry Ice-acetone bath) under a nitrogen atmosphere was added 2.4 ml (0.0048 mol) of *n*-butyllithium in hexane. The resulting red-brown ylide anion solution was stirred for 15 min and then 0.577 g (0.0048 mol) of freshly distilled acetophenone in 10 ml of anhydrous THF was added. The color of the reaction mixture changed to orange immediately. The resulting solution was stirred in Dry Ice bath for 50 min and then was allowed to warm to room temperature. After processing the reaction mixture as described before, a yellow oil was obtained which solidified upon standing. Thin layer chromatography [acetone-benzene (1:1)] of the reaction mixture showed that mainly one product was present along with some starting ylide. Recrystallization from ethyl acetate gave 1.152 g (66%) of triphenylphosphine-(3-hydroxy-3-phenylbutanoyl)methylene (55), mp $187-187.5^{\circ}$; pmr (CDCl_3) δ 7.44 (m, 21, phenyl and hydroxyl), 3.6 (broad s, 1, P=CH), and 2.99 and 2.71 (q, 2, CH_AH_B), $J_{AB} = 14$ Hz, 1.48 (s, 1, CH_3); ir (CHCl_3) 3460-3140 (O-H), 3010 (C-H), and 1530 cm^{-1} (C=O).

Anal. Calcd. for $\text{C}_{29}\text{H}_{27}\text{O}_2\text{P}$: C, 79.43; H, 6.21. Found: C, 79.58; H, 6.12.

With Acetone. - In a 100 ml three-necked, round-bottomed flask, 1.908 g (0.006 mol) of triphenylphosphineacetylmethylene (13) was dissolved in 70 ml of anhydrous THF, under a nitrogen atmosphere. The solution was cooled by using a Dry Ice-acetone bath and then 3.53 ml (0.0072 mol) of *n*-butyllithium in hexane was injected. The resulting red-brown solution was stirred for 15 min before the addition

of 0.418 g (0.0072 mol) of acetone. The color of the reaction mixture changed to orange as soon as acetone entered the ylide anion solution. It was allowed to stir in Dry Ice bath for 50 min and then warm to room temperature. The resulting yellow solution was quenched with 150 ml water-ether (2:1). The organic phase was separated, the aqueous solution was extracted three times with 75 ml portions of chloroform. The combined organic extracts were washed with 10% aqueous sodium chloride, dried (MgSO_4) and concentrated to give an oil which solidified upon standing. The crude product was recrystallized from ethyl acetate and 1.413 g (63%) of triphenylphosphine-(3-hydroxy-3-methylbutanoyl)methylene (56) was obtained. The analytical sample had mp 185-187°; pmr (CDCl_3) δ 7.52 (m, 16, phenyl and hydroxyl), 3.78 (broad d, 1, P=CH), 2.46 (s, 2, CH_2) and 1.24 (s, 6, CH_3); ir (CHCl_3) 3500-3120 (O-H), 2990 (C-H), and 1530 cm^{-1} (C=O).

Anal. Calcd. for $\text{C}_{24}\text{H}_{25}\text{O}_2\text{P}$: C, 76.58; H, 6.69. Found: C, 76.32; H, 6.73.

With Cyclopentanone. - To a solution of 2.226 g (0.007 mol) of triphenylphosphineacetylmethylene (13) in 75 ml of anhydrous THF maintained at -78° (Dry Ice-acetone bath) under a nitrogen atmosphere was added 4.12 ml (0.0084 mol) of n-butyllithium. The resulting ylide anion solution was stirred for 15 min and then 0.707 g (0.0084 mol) of freshly distilled cyclopentanone was added in 10 ml of anhydrous THF. The red-brown anion color changed to orange immediately. The reaction mixture was stirred for 50 min in the Dry Ice bath and then was allowed to warm to room temperature. It was worked up as described before to

yield a yellow oil which solidified upon standing overnight. The product was recrystallized from ethyl acetate to give 1.392 g (50%) of triphenylphosphine- [(1-hydroxycyclopentyl)acetyl]methylene (57). An additional 0.257 g was isolated from mother liquor, bringing the total yield of 57 to 59%. The analytical sample had mp 154-155°; pmr (CDCl₃) δ 7.56 (m, 16, phenyl and hydroxyl), 3.8 (broad s, 1, P=CH), 2.6 (s, 2, CH₂), and 1.74 (m, 8, cyclopentane); ir (CHCl₃) 3480-3140 (O-H), 2980 (C-H), and 1540 cm⁻¹ (C=O).

Anal. Calcd. for C₂₆H₂₇O₂P: C, 77.59; H, 6.76. Found: C, 77.33; H, 6.97.

Attempted Reaction of Lithiotriphenylphosphineacetylmethylene (14)

With Cyclohexene Oxide. - A 1.590 g (0.005 mol) sample of triphenylphosphineacetylmethylene (13) was dissolved in 60 ml of anhydrous THF under a nitrogen atmosphere and cooled by means of a Dry Ice-acetone bath. n-Butyllithium (2.94 ml, 0.006 mol) in hexane was injected and the ylide anion solution was stirred for 15 min, then 0.564 g (0.0058 mol) of cyclohexene oxide in 10 ml of anhydrous THF was added. The dark red-brown ylide anion color did not disappear even after stirring the reaction mixture at room temperature. So it was allowed to stir overnight but the anion color still did not disappear. Thin layer chromatography [acetone-benzene (1:1)] showed that reaction did not take place. After processing the reaction mixture as described before, starting ylide 13 was recovered.

With *o*-Phthalaldehyde. - A 2.544 g (0.008 mol) sample of triphenylphosphineacetylmethylene (13) was dissolved in 100 ml anhydrous THF

under a nitrogen atmosphere and cooled by means of a Dry Ice-acetone bath. Then 4.51 ml (0.0092 mol) of *n*-butyllithium in hexane was injected and the ylide anion solution was stirred for 15 min before the addition of 1.23 g (0.0092 mol) of *o*-phthalaldehyde. The reaction mixture was stirred for 1 hr, then allowed to warm to room temperature. The resulting dark orange solution was poured over 150 ml of water-ether (2:1) and stirred. The organic phase was separated and the aqueous solution was extracted twice with 75 ml portions of chloroform. All the organic extracts were combined, washed with 10% aqueous sodium chloride, dried (MgSO_4) and concentrated to give a dark yellow oil. Tlc analysis [acetone-benzene (1:1)] of the reaction mixture indicated the presence of four products. The presence of triphenylphosphine oxide, *o*-phthalaldehyde, and phthalic acid were detected by comparison of their R_f values with authentic samples. The reaction mixture was chromatographed using silica gel to afford 0.12 g of pure 4,5-benzotropone, mp 66-67° (lit.⁴⁷ 65-66°); pmr (CDCl_3) δ 7.66 (m, 4, phenyl), 7.44 (d, 2, $-\text{C}=\text{C}_{2,7}\text{H}$), and 6.7 (d, 2, $\text{HC}_{3,6}=\text{C}-$)

Anal. Calcd. for $\text{C}_{11}\text{H}_8\text{O}$: C, 84.59; H, 5.16. Found: C, 84.63; H, 5.15.

The same reaction as above was repeated, the dark orange reaction mixture was poured over a slurry of 60 g of ice and 5 ml of 12 N HCl and stirred in order to separate unreacted starting material 13. The aqueous solution was then extracted with ether, benzene, and chloroform. Thin layer chromatography [acetone-benzene (1:1)] of each of these organic extracts showed the presence of the same components, so all the organic extracts were combined, washed with 5% aqueous sodium

bicarbonate, dried (MgSO_4) and concentrated to give a dark yellow oil. The yield of 4,5-benzotropone in this mixture was calculated to be 49% using a Varian Aerograph Model 90-P gas chromatograph equipped with a 6 feet column which was packed with 6.3% carbowax 20M, on gas chrom Z 30/60, at a column temperature of 200° . Benzalacetophenone was employed as the internal standard.

With 2-Cyclohexen-1-one. - To a solution of 6.367 g (0.02 mol) of triphenylphosphineacetylmethylene (13) dissolved in 400 ml of anhydrous THF, maintained at -78° under a nitrogen atmosphere was added 11.76 ml (0.024 mol) of *n*-butyllithium in hexane. The resulting ylide anion solution was stirred for 15 min and then 2.307 g (0.024 mol) of 2-cyclohexen-1-one was added. Reaction occurred immediately. The reaction mixture was stirred at -78° , then warmed to room temperature and processed in the usual manner to give an oil which solidified when triturated with cold petroleum ether. Thin layer chromatography [acetone-benzene (1:1)] of the reaction mixture showed the presence of mainly one product, along with some starting ylide and three other small spots. The product could not be purified by crystallization. The pmr spectrum of the crude product indicated that the 1,2-addition product (60) was obtained. Pmr (CDCl_3) δ 7.76 (m, 16, phenyl and hydroxyl), 5.88 (s, 2, $-\text{CH}=\text{CH}-$), 3.88 (broad d, 1, $\text{P}=\text{CH}$), 2.6 (s, 2, CH_2) and 1.94 (m, 16, CH_2 's of cyclohexene and solvent).

IV. SUMMARY

Treatment of triphenylphosphineacetylmethylene (13) with 1.2 molecular equivalents of *n*-butyllithium in THF-hexane under a nitrogen atmosphere, at -78° gave lithiotriphenylphosphineacetylmethylene (14). The ylide anion 14 reacted selectively at the terminal carbanion site with alkyl halides to form substituted β -keto ylides. Triphenylphosphine-(3-phenylpropionyl)methylene (48a) also underwent ionization with *n*-butyllithium at -78° and alkylation with benzyl chloride and allyl bromide afforded triphenylphosphine-(2-benzyl-3-phenylpropionyl)-methylene (50a) and triphenylphosphine-(2-benzyl-4-pentenoyl)methylene (50b), respectively. Complex mixtures were obtained from the reaction of 2 molecular equivalents of ylide anion 14 and 1.0 molecular equivalent of polymethylene dihalides. Only when 1,3-dibromopropane was used as the alkylating agent, the desired bis ylide 51 ($n=3$) was isolated. It was found that trimethylchlorosilane was not reactive toward ylide anion 14.

Condensations of 14 with various aldehydes and ketones gave aldol products resulting from selective attack of the carbonyl compound at the terminal anion center. The yields from aldehyde condensations were slightly lower than those involving ketones. An attempt was made to hydrolyze the alcohol obtained from the benzophenone condensation. Triphenylphosphine oxide was isolated indicating that hydrolysis took place but the product underwent a retro aldol reaction either during the hydrolysis or during distillation of the oil obtained from the reaction. Reaction of ylide anion 14 with *o*-phthalaldehyde

resulted in terminal aldol condensation accompanied by intramolecular Wittig reaction to give 4,5-benzotropone. This constitutes a new, one step synthesis of 4,5-benzotropone.

Condensation of 14 with 2-cyclohexen-1-one gave the 1,2-addition product as evidenced by the pmr spectrum, but the product could not be purified by crystallization. It was found that cyclohexene oxide was not reactive toward lithiotriphenylphosphineacetylmethylene (14).

Attempts to form potassiotriphenylphosphineacetylmethylene using potassium amide in liquid ammonia gave the unexpected product acetyl-diphenylphosphine oxide (43). Efforts were made to verify an earlier proposed mechanism for the formation of 43. The presence of benzene, was detected by gas chromatography. The postulated iminophosphorane intermediate, 42, could not be isolated, presumably because of hydrolysis upon exposure to atmospheric moisture to give diphenylphosphinic amide (46) and acetyldiphenylphosphine oxide (43). An unidentified compound was also isolated from these potassium amide reactions.

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AN INVESTIGATION OF THE CHEMISTRY OF LITHIOTRI-
PHENYLPHOSPHINEACETYL METHYLENE

by

Emre Ayse Sancaktar

(ABSTRACT)

The ylide anion, lithiotriphenylphosphineacetylmethylene was obtained by treatment of triphenylphosphineacetylmethylene with 1.2 molecular equivalents of n-butyllithium in tetrahydrofuran-hexane under a nitrogen atmosphere at -78° . This ylide anion reacted selectively with alkyl halides to form γ -substituted β -keto phosphonium ylides. Subsequent ionization of triphenylphosphine-(3-phenylpropionyl)methylene with n-butyllithium at -78° followed by alkylation produced γ,γ -disubstituted ylides. Condensation of the ylide anion with various aldehydes and ketones afforded δ -hydroxy- β -keto ylides in reasonable yields, uncontaminated by normal Wittig products. Reaction of the ylide anion with o-phthalaldehyde resulted in terminal aldol condensation accompanied by an intramolecular Wittig reaction to give 4,5-benzotropone. The condensation of lithiotriphenylphosphineacetylmethylene with 2-cyclohexene-1-one gave the 1,2-addition product, although it could not be completely purified. Attempts to form potassiotriphenylphosphineacetylmethylene by means of potassium amide in liquid ammonia gave the unexpected product, acetyldiphenylphosphine oxide. An earlier proposed mechanism for this reaction was partially verified by detection of benzene as a by product. An unidentified compound was isolated from these potassium amide reactions.