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Volume V

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Newer Methods of Preparative Organic Chemistry

Volume V

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Foreword

The same general remarks apply to the present volume as to volume IV: the contributions have been expanded and up-dated since their appearance in "Angewandte Chemie".

The subject matter covers a wide diversity of topics. The editor considers it better to provide this kind of report on advances made in preparative organic chemistry than to plan separate volumes or series of articles treating closely related subjects. Our system has the advantage that it ensures rapid publication of the most recent information available in each of the specialist fields while freeing us from the encumbrance of subject continuity.

The reviews on preparative organic chemistry in "Angewandte Chemie" and this series of volumes will be continued along the same lines under the future co-editorship of H. Grünewald.

The technical editing of this volume, and of volume IV, was in the capable hands of Gerlinde Kruse.

Heidelberg, June 1968 W. FOERST

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New Reactions of Alkylidenephosphoranes and Their Preparative Uses*

Part I: The Acid-Base Character of Phosphonium Salts and Alkylidenephosphoranes

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Phosphonium salts may be regarded as Brønsted acids, and alkylidenephosphoranes as the conjugate bases. Compounds of the two classes exist in equilibrium with each other. Phosphonium salts and alkylidenephosphoranes can be obtained by this "transylidation". Other methods are also given for the preparation of members of both classes.

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* This article was originally published in three parts. References, formulae, and tables are numerated separately in each part.

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1. Introduction

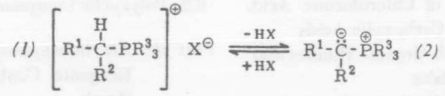
The discovery by WITTIG and co-workers [1] that alkylidenetriphenylphosphoranes react with aldehydes and ketones to form olefins and triphenylphosphine oxide has supplied the incentive to a large number of investigations. The Wittig reaction has already been discussed by SCHÖLLKOPF [2] and by TRIPPETT [3], as well as by BERGELSON and SCHEMJAKIN [4].

The aim of the present series of articles is to show that the recently discovered reactions of alkylidenephosphoranes with polar compounds are also of interest in preparative chemistry.

2. Phosphonium Salts and Alkylidenephosphoranes as Conjugate Acid-Base Pairs

Strong bases eliminate HX from phosphonium salts *(1)* to form alkylidenephosphoranes *(2)*. STAUDINGER [5] found that the latter in turn can add HX, with re-formation of the phosphonium salts *(1)*.

Thus phosphonium salts can be regarded as Brønsted acids, and alkylidenephosphoranes as the conjugate bases.



(1) *(2)*

The basicity of the ylides *(2)* is also apparent in their reaction with water [1b, 1c, 2, 6, 7], in which addition of a proton to the free electron pair of the open C—P double bond leads to formation of the phosphonium hydroxide *(3)*.

The hydroxides *(3)* decompose *via* the compounds *(4)* of pentavalent phosphorus into a hydrocarbon *(5)* and a phosphine oxide *(6)* [8, 9]. The ligand

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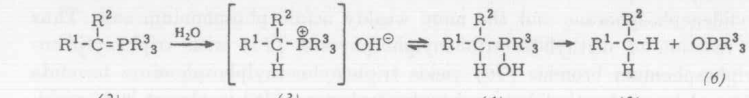
eliminated from the phosphorus of *(3)* as a hydrocarbon is always the most strongly electronegative or the most highly resonance stabilized of the four [9, 10].



(2) *(3)* *(4)* *(5)* *(6)*

The acid-base strength of the phosphonium salts *(1)* and the alkylidenephosphoranes *(2)* depends mainly on R^1 and R^2. Electron-attracting groups increase the acidity of the phosphonium salt *(1)* and lower the basicity of the corresponding ylide *(2)*. Thus dilute sodium carbonate solution is sufficient to precipitate the ylide *(8)* from an aqueous solution of triphenylmethoxycarbonylmethylphosphonium bromide *(7)*, which is a very strong acid owing to the presence of the ester group [11, 12]. Compound *(8)* is

(7), (9) *(8), (10)*

(7), (8): $R^3 = C_6H_5$; *(9), (10)*: R^3 = cyclohexyl

stable towards cold water, since the ester group lowers the basicity and so hinders the attack of a proton on the lone electron pair of the open C—P double bond. The alkylidenephosphorane *(8)* decomposes with water into methyl acetate and triphenylphosphine oxide only on boiling.

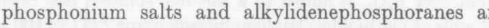
The acid and base strengths of *(1)* and *(2)* are also determined by R^3. The electron-attracting inductive effect of the three phenyl groups in *(7)* loosens the H atoms of the CH_2 group. If the triphenylphosphine residue in *(7)* is replaced by a tricyclohexylphosphine residue, the (—I) effect of the three cyclohexyl groups in the phosphonium bromide *(9)* strengthens the CH bonds of the methylene group. The deprotonation of *(9)* can no longer be effected with sodium carbonate solution, but requires the use of dilute sodium hydroxide solution [12].

Methoxycarbonylmethylidenetricyclohexylphosphorane *(10)* is more strongly basic than the triphenyl compound *(8)*. In contrast to *(8)*, *(10)* decomposes simply on standing for a short time in cold water.

3. Transylidation

Since phosphonium salts and alkylidenephosphoranes are related as an acid-base pair, and since the strength of these acids and bases is governed by R^1 and R^2, an acid-base equilibrium is set up between alkylidenetriphenylphosphoranes *(11)* and triphenylphosphonium salts *(12)* [13].

(11) *(12)*



(13) *(14)*

The position of the equilibrium is governed by the residues R^1 and R^2. If the basicities of *(11)* and *(14)* or the acid strengths of *(12)* and *(13)* are very different, the equilibrium always favors the formation of the more weakly basic alkylidenephosphorane and the more weakly acidic phosphonium salt. Thus the reaction of methylidenetriphenylphosphorane *(15)* with triphenylphenacylphosphonium bromide *(16)* yields triphenylmethylphosphonium bromide *(17)* and benzoylmethylidenetriphenylphosphorane *(18)* in almost 90% yield. This is an example of a reaction which we shall refer to as transylidation.

$$\underset{(15)}{H_2C{=}P(C_6H_5)_3} + \underset{(16)}{[H_5C_6\text{-}CO\text{-}CH_2\text{-}\overset{\oplus}{P}(C_6H_5)_3]\,Br^{\ominus}} \rightleftarrows \underset{(17)}{[H_3C\text{-}\overset{\oplus}{P}(C_6H_5)_3]\,Br^{\ominus}} + \underset{(18)}{H_5C_6\text{-}CO\text{-}CH{=}P(C_6H_5)_3}$$

Transylidation provides a method of comparing the strengths of the mesomeric or inductive effects of the substituents on the acidity of the methylene group α to the P atom in the phosphonium salt or on the basicity of the alkylidenephosphorane. Such a comparison gives the sequence:

$$C_6H_5{-}CO > CO_2CH_3 > C_6H_5 > \text{alkyl}$$

The reaction of phosphonium salts

$$[R^1{-}CH_2{-}P^{\oplus}(C_6H_5)_3]X^{\ominus}$$

with alkylidenephosphoranes $R^2{-}CH{=}P(C_6H_5)_3$ in which R^2 lies to the right of R^1 in the above series leads to transylidation.

Experiments with phosphonium salts labelled with tritium have shown that transylidation also takes place if R^1 and R^2 in *(11)* and *(12)* are identical, or if the inductive or mesomeric effects of R^1 and R^2 differ only slightly [13].

Procedure:

Preparation of Benzoylmethylidenetriphenylphosphorane by Transylidation [13]

Finely powdered triphenylphenacylphosphonium bromide *(16)* (9.24 g), which has been dried in vacuum over P_2O_5, is added to a salt-free solution (see Section 4.2 for preparation) of 0.02 mole of methylidenetriphenylphosphorane *(15)* in 100 ml of anhydrous toluene [14], and the mixture is refluxed for 24 h in the absence of moisture and oxygen. The benzoylmethylidenetriphenylphosphorane *(18)* is filtered off, the precipitate is washed with toluene, and the solution is evaporated in vacuum. The crystalline residue is mixed with 15 to 20 ml of ethyl acetate and filtered. A small second fraction is obtained by slow evaporation of the filtrate. Total yield 6.65 g (87.5%); m.p. and mixed m.p. with benzoylmethylidenetriphenylphosphorane 180 °C.

The salt filtered off from the solution in ethyl acetate weighs 7.8 g. It is dissolved in 60 ml of water by warming, and the pH of the solution is adjusted to 13–14 with dilute sodium hydroxide solution, whereupon 0.65 g of *(18)*, formed from unchanged triphenylphenacylphosphonium bromide *(16)*, precipitates. This is filtered off, and the aque-

ous solution is acidified with acetic acid, heated to boiling, and a solution of 3 g of NaI in 10 ml of water is added. Triphenylmethylphosphonium iodide crystallizes on cooling; yield 4.9 g (60.8%), m.p. and mixed m.p. 182 °C (from isopropanol).

4. Preparation of Phosphonium Salts and Alkylidenephosphoranes

4.1. Phosphonium Salts

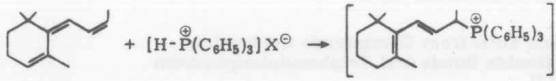
Phosphonium salts *(21)* are generally prepared from alkyl halides *(19)* and triphenylphosphine *(20)* [2].

$$\underset{(19)}{R\text{-}X} + \underset{(20)}{P(C_6H_5)_3} \longrightarrow \underset{(21)}{[R\text{-}\overset{\oplus}{P}(C_6H_5)_3]X^{\ominus}}$$

The following method is of great preparative interest [15, 16]:

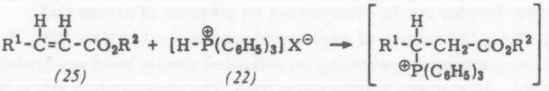
$$R\text{-}OH + \underset{(22)}{[H\text{-}\overset{\oplus}{P}(C_6H_5)_3]X^{\ominus}} \longrightarrow \underset{(21)}{[R\text{-}\overset{\oplus}{P}(C_6H_5)_3]X^{\ominus}} + H_2O$$

A phosphonium salt *(21)* is obtained from an alcohol by reaction with triphenylphosphonium halides *(22)* (preferably the bromide). Triphenylphosphonium bromide *(22)*, X = Br, adds onto the ends of many polyene chains by ω,ω′-addition. Thus 1,6-addition of the bromide *(22)*, X = Br, to the triene *(23)* leads to the phosphonium salt *(24)* [16].



(23) *(22)* *(24)*

Phosphonium salts can also be obtained from compounds containing polarzed C—C double bonds (*e.g.* α,β-unsaturated nitriles, esters of carboxylic acids *(25)*, and nitro compounds) by reaction with the bromide *(22)*, X = Br [17].

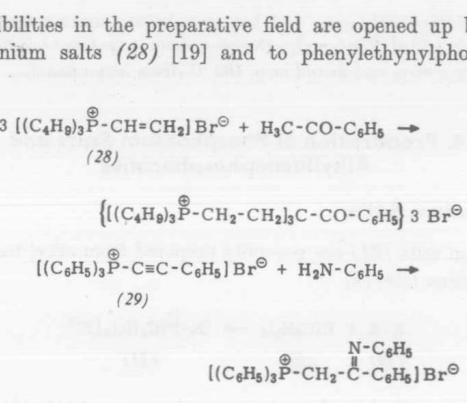


(25) *(22)*

The reaction of quaternary ammonium salts of Mannich bases *(26)* with triphenylphosphine also allows the preparation of phosphonium salts *(27)* which are difficult or impossible to obtain by other methods [18].

$$\underset{(26)}{[R\text{-}CH_2\text{-}\overset{\oplus}{N}(CH_3)_3]X^{\ominus}} + P(C_6H_5)_3 \longrightarrow \underset{(27)}{[R\text{-}CH_2\text{-}\overset{\oplus}{P}(C_6H_5)_3]X^{\ominus}} + N(CH_3)_3$$

New possibilities in the preparative field are opened up by additions to vinylphosphonium salts *(28)* [19] and to phenylethynylphosphonium salts *(29)* [20].



The possibility of synthesizing phosphonium salts from alkylidenephosphoranes and halogen compounds is discussed in Part II.

Procedures:

β-Methoxyethyltriphenylphosphonium Bromide [15]

A mixture of 34 g of triphenylphosphonium bromide *(22)*, X = Br, and 8 g of glycol monomethyl ether is refluxed for 7 h with 50 g of anhydrous tetrahydrofuran. When the reaction mixture is cooled, 17 g of β-methoxyethyltriphenylphosphonium bromide *(21)*, R = $H_3C-O-CH_2CH_2$, m.p. 216 °C, separates out. A further 7 g is obtained by concentration of the mother liquor.

Phosphonium Salts from Compounds Containing Activated Double Bonds and Triphenylphosphonium Bromide [17]

Method a: 2.62 g (10 mmole) of triphenylphosphine *(20)* and 10 mmole of the component containing an activated double bond are heated with stirring at 100 °C with 5 ml of 48% aqueous HBr for 5–15 min. The mixture is then diluted with about 10 ml of water, extracted with ether to remove any unchanged starting material, and the phosphonium salt is allowed to crystallize or is extracted with chloroform, depending on its solubility. Iodides can be precipitated by addition of excess NaI.

Method b: 3.4 g (10 mmole) of triphenylphosphonium bromide *(22)*, X = Br, and 10 mmole of the component containing an activated double bond are heated in 5 ml of acetonitrile for 5–15 min on a boiling water bath. The phosphonium salt is then precipitated with ethyl acetate or ether, and purified as described under a.

Skatyltriphenylphosphonium Methylsulfate [18]

Three grams of gramine methylsulfate is boiled with 15 mmole of triphenylphosphine *(20)* in 30 ml of methanol for 90 min under nitrogen (trimethylamine is liberated). The precipitate formed on cooling is washed with methanol, and can be recrystallized from water to give a pale pink salt, m.p. = 185–186 °C.

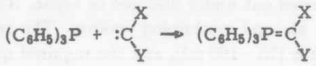
4.2. Alkylidenephosphoranes

The best method of preparing alkylidenephosphoranes is the action of bases on phosphonium salts [*(1)→(2)*] (see Section 2). The strength of the base necessary for deprotonation depends on the acidity of the phosphonium salt. A base recently found to be particularly useful is the methylsulfinyl carbanion obtained from dimethyl sulfoxide and sodium hydride and used in dimethyl sulfoxide as solvent [21a].

In many of the reactions described below, it is important that the ylide solutions used should be free from lithium salts, since these react with the ylide to form complexes which strongly interfere with the reaction. The most suitable method for the preparation of such solutions is the sodamide method [21b] described below.

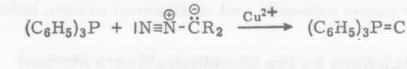
SCHÖLLKOPF [2] has made reference to elimination reactions which can hinder ylide formation. The action of bases on phosphonium salts containing activated hydrogen β to the phosphorus atom can lead to decomposition of the initially formed ylide into an olefin and triphenylphosphine by intermolecular proton migration [22] (cf. also Part II, Section 3.1. on the Hofmann degradation of quaternary phosphonium salts). In such cases, sodium alkoxides should not be used as bases, since these compounds strongly favor the Hofmann degradation [22].

Ylides are also formed from triphenylphosphine and carbenes *(30)*. Alkylidenephosphoranes with halogen atoms on the C-Atom α to the C—P double bond have become available by this method [23, 24].



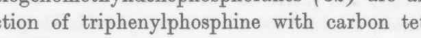
(30)

Aliphatic diazo compounds can also be used as sources of carbenes for the preparation of ylides. However, they must be decomposed in the presence of copper salts [25], since the reaction of diazo compounds with triphenylphosphine generally leads to phosphazines *(31)* [26].



(31)

The dihalogenomethylidenephosphoranes *(32)* are also readily obtainable by the reaction of triphenylphosphine with carbon tetrachloride or carbon tetrabromide [27].



X = Cl, Br *(32)*

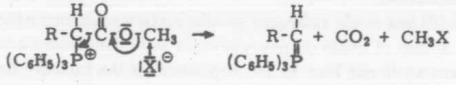
The reaction of acrylic acid derivatives *(33)* with triphenylphosphine leads to ylides *(34)* which can be intercepted with carbonyl compounds by a Wittig reaction [28, 28a]*, and which are difficult to obtain by other methods owing to the ease with which the Hofmann degradation takes place.

$$(C_6H_5)_3P + H_2C{=}CHR \longrightarrow (C_6H_5)_3P{=}CH\text{-}CH_2R$$

(33) *(34)*

$R = -CO_2R^1;\ -CONH_2;\ -C{\equiv}N,$

Alkylidenephosphoranes are also formed on thermal decomposition of triphenyl-α-methoxycarbonylalkyl-phosphonium salts *(35)* [29].



(35)

The ylides formed can be isolated if they are stable. They can also be intercepted by various reagents, or undergo intramolecular reactions.

Procedures:

Salt-free Alkylidenephosphorane Solutions

All operations are carried out under nitrogen or argon. Ammonia is condensed in a trap cooled with liquid air and containing sodium. The resulting dry ammonia is distilled into a second tube (75—100 ml), and the required quantity of finely chopped sodium (up to 25% excess) and a few grains of ferric nitrate are added. When the blue sodium solution has turned grey, the absolutely dry and finely powdered phosphonium salt is added, stirred for a short time with a glass rod, and the ammonia is then evaporated off through a mercury valve. The evaporation is accelerated by heating the tube with hot air. To the residue is added 100 ml of an inert, anhydrous solvent, *e.g.* benzene, toluene, ether, or tetrahydrofuran, and the solution is boiled for about 10 min to remove residual gas, the reflux condenser being sealed with mercury. The solid residue is then filtered off using a G-3 frit. The filtration can be dispensed with if the subsequent reactions are not affected by excess sodamide and undissolved sodium halide.

Preparation of Ylide Solutions by the Dimethylsulfinate Method

The preparation must be carried out under nitrogen and in the strict absence of moisture. The stoichiometric quantity of sodium hydride (as a 50% suspension in mineral oil) is freed from mineral oil by repeated washing on a sintered glass filter with anhydrous petroleum ether, and placed in the reaction vessel. Dimethyl sulfoxide (dried over calcium hydride) is added (50 ml of dimethyl sulfoxide per 100 mmole of NaH), a reflux condenser with a mercury valve is fitted to the vessel, and the mixture

* Cf. also the analogous formation of ylide from triphenylphosphine and maleic anhydride: [28a].

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