Topics in Current Chemistry

109

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Wittig Chemistry

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Wittig Chemistry

Dedicated to Professor Dr. G. Wittig

With Contributions by
H. J. Bestmann, D. Hellwinkel, A. Krebs,
H. Pommer, U. Schöllkopf, P. C. Thieme,
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With 34 Figures and 22 Tables

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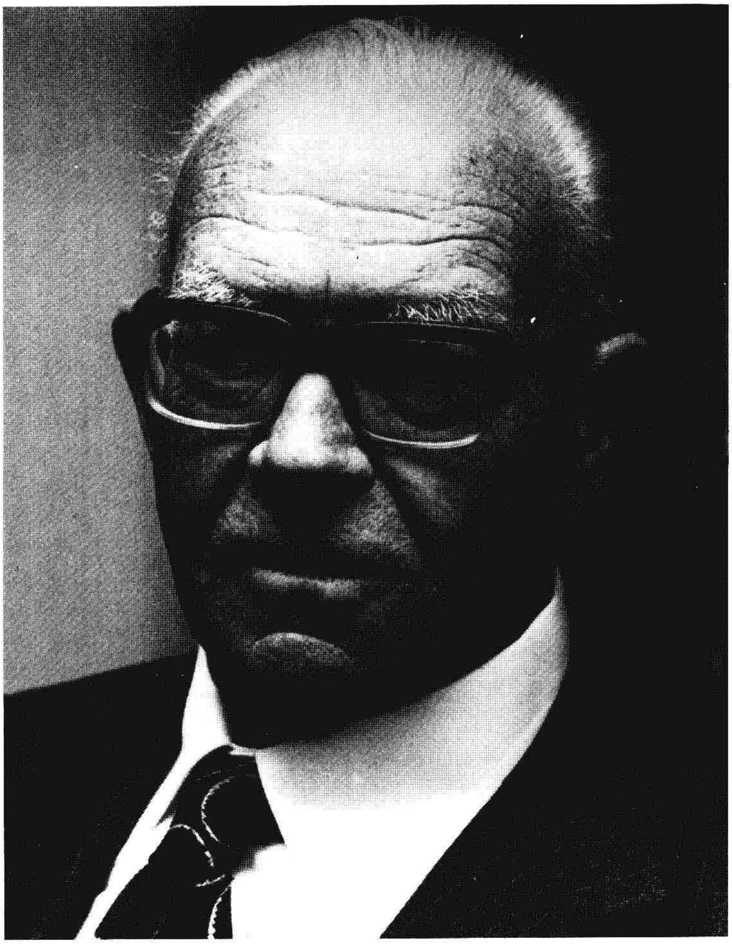

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Penta- and Hexaorganyl Derivatives of the Main Group Five Elements

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1 Introduction

The main goals of experimental chemistry have always been the generation of new compounds on the one hand and the development of new reactions on the other. But, as one can learn from more historically orientated studies, for many areas of chemistry these two objectives are most oftenly closely interrelated so that they stimulate and even necessitate each other in various, though sometimes quite incidental ways.

A demonstrative example for this may be seen in the "Wittig-Reaction" — the well-known carbonyl olefination by phosphorus ylides — whose origin can very precisely be traced back to a fortuitous outcome of a routine trapping experiment in the course of fundamental investigations in the field of phosphorus pentacoordination. In other words, the discovery of the Wittig reaction was not so much the result of a specifically designed search for new reactions, than a rather unexpected but of course highly welcomed offshoot from a totally different main stream of activities dedicated to the generation and study of pentacoordinated organic derivatives of the nitrogen/phosphorus group elements. Because of its high synthetic importance, the Wittig reaction quickly attracted the general attention of the chemical community, perhaps even at the expense of the interest in the underlying basic research program on new pentacoordinated molecules. But this did not really mean that the latter topic had now become less appealing and would therefore have been pursued with less endeavor. Quite the contrary: the continuation of work on pentaorganylphosphorus and homologous derivatives did in fact lead to a wealth of fascinating new compounds and concepts which were certainly as interesting, and perhaps even more interesting — at least from a more fundamental point of view — than the growing importance of the practical applications of the Wittig reaction to synthesis.

In this article I shall present a coherent insight into that framework of research activities that led from very early ideas and experiments on nitrogen pentacoordination quite logically and, as I think, also stringently first to that important branching point where the Wittig reaction took its origin, and then via a plethora of interesting new compounds to the actual conceptions of the stereochemistry of pentacoordination. I will concentrate, however, on those compounds containing five or six carbon groups linked directly by covalent bonds to a nitrogen/phosphorus group elemental center, which mostly were investigated in the Heidelberg laboratories. Pertinent general results obtained with derivatives containing less than five element-carbon bonds will of course be included where necessary.

Before entering the material part proper of this review, a note on nomenclature has to be made. Although not really needed, the only partially IUPAC-approved terms "pentaorganylphosphorane, -arsorane, -stiborane and -bismuthorane" have asserted themselves widely in the literature instead of the less systematic but equally unambiguous names "pentaphenylphosphorus, -arsenic, -antimony and -bismuth". Chemical Abstracts, however, has only adopted the first two systematic terms, that is, "phosphorane" and "arsorane" as parent compound entries, whereas pentacoordinated antimony and bismuth derivatives have to be looked for under "antimony and bismuth, pentaorganyl" respectively. To stay consistent I shall use the systematic "-orane" set of names throughout. A similar naming dichotomy exists for the trivalent derivatives of these elements where the older and still IUPAC-approved and

CA-used terms "triorganylphosphine, -arsine, -stibine and -bismuthine" seem to become progressively replaced by the newer parent hydride-based names "triorganylphosphane, -arsane, -stibane and -bismuthane". Again I will exclusively use the first set of names which prevails by far in the works discussed in this paper. According to a recent IUPAC proposal which has already been adopted by some journals, parent hydrides with non-standard valence states can be designated by the λ^n symbol in front of the name of the standard hydride, where the bonding number n gives the total number of classical valence bonds originating from the central atom in question. Correspondingly, compound types PR_5, AsR_5, SbR_5, BiR_5 would be named as λ^5-phosphanes, λ^5-arsanes, λ^5-stibanes and λ^5-bismuthanes.

2 Early Developments

The history in this field goes very far back indeed. As early as 1862 Cahours had claimed [1] to have prepared pentamethylarsorane $(CH_3)_5As$ (*1*) by the reaction of tetramethylarsonium iodide with dimethylzinc. First attempts to synthesize pentaalkyl nitrogen compounds, e.g. pentaethylnitrogen (*2*) have been reported by Lachman in 1896 who, however, in reacting tetraethylammonium iodide and the triethylamine/bromine adduct with diethylzinc could only identify tetraethylammonium triiodide and the reduction product triethylamine respectively [2]. It may be noted that at this time the imagination of the experimentalist was not yet limited (or spoiled?) by too restrictive bonding theory considerations [3] as is clearly indicated in Lachman's own words: "*There is a priori no reason why nitrogen in its pentavalent state cannot combine with five like atoms or radicals . . .*" [2]

More conclusive results were obtained by Schlenk and Holz as much as twenty years later. In reactions of tetramethylammonium chloride with triphenylmethylsodium [4] and, later, benzylsodium [5], bright red compounds were formed which according to elemental analyses did contain five organic groups per nitrogen atom. Although the formulation of these compounds, e.g.

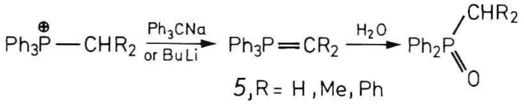
$$(C_6H_5)_3{\equiv}C-N{\equiv}(CH_3)_4$$

still reflected the "whishful thinking" of that time, their properties (intense color, electrical conductivity and high susceptibility to polar agents and oxygen) made it evident that they had to be considered as salt-like [6] ion pair structures such as

$$[C_6H_5CH_2]^{\ominus}\ [N(CH_3)_4]^{\oplus} \quad 4$$

At about the same time the famous octet principle based on the work of Kossel [7], Lewis [8] and Langmuir [9] was developed. It explained and, moreover, even postulated the nonexistence of five covalent bonds around a nitrogen center in a very stringent way. Notwithstanding these theoretically imposed restrictions, the conception of pentacoordinated nitrogen persisted in the minds of dedicated experimentalists. Thus, Staudinger and Meyer resumed the experiments for synthesizing pentamethylnitrogen and pentaethylphosphorane by the reaction of the corresponding onium salts with dimethyl- and diethylzinc, respectively, but again with negative results [10].

In the twenties, another series of experiments aimed at the synthesis of pentacoordinated nitrogen compounds became known through Hager and Marvel. They dealt with the reactions of the much more reactive lithium alkyls with tetraalkylammonium salts. But again nitrogen proved its inability or at least great reluctance to take on a fifth ligand, in that no pentaalkyl nitrogen derivatives, but only mixtures of amines and hydrocarbons, could be isolated [11]. In another series of experiments with the same aim, tetraethylphosphonium iodide was used together with triphenylmethylsodium as nucleophile, but again no pentacoordinated structure was produced [12]. When, however, triphenylalkylphosphonium salts were treated with tritylsodium or butyllithium in diethyl ether, orange solutions were obtained which were shown to contain triphenylphosphinemethylenes *5*, a compound class, in principle already known through the work of Staudinger and Meyer [13]. Besides hydrolysis no further chemistry was done with these compounds at that time [12].



5, R = H, Me, Ph

At the end of the paper dealing with this work a casual but highly interesting remark is made (l.c. [12] p 3498). It states, that by studying compounds not having "*one group which carries a hydrogen atom on the carbon attached to the phosphorus atom . . . pentaalkyl phosphorus compounds may (thus) be obtained*". In a way this remark anticipates the further development in this field by more than two decades. Analogous experiments were then performed with tetraalkylarsonium salts where again no pentaalkyl derivatives of arsenic could be isolated [14].

The investigations reported so far consisted of more or less limited sets of experiments which evidently did not lead to any more systematic studies. Probably, the octet rule stifled any initiative to do so. Looking back it appears now that only a more general and more broadly designed research program could instigate such coherent systematic investigations as would be necessary to bring about real progress in the field.

Such a comprehensive and fundamental program was started in the laboratories of G. Wittig when, in the early thirties, he systematically began to explore the synthetic potential of organyllithium compounds [15], particularly of phenyllithium [16]. In the course of these investigations many interesting new research areas were disclosed and a first climax was reached with the formulation of the dehydrobenzene concept at the beginning of the forties [17]. The encouraging and highly stimulating experiences thus made with the now readily accessible phenyllithium led naturally back to the question of pentacoordinate nitrogen, since it could be hoped that this strongly nucleophilic reagent would eventually be able to overcome the inherent resistence of nitrogen in ammonium salts to accepting a fifth covalently bonded ligand.

In this respect the experiments were again a total failure since no pentacoordinated nitrogen compound could be identified. But in contrast to all previous researchers, Wittig did not acknowledge this failure as such, instead, he considered it merely as an unexpected result which nevertheless had to be explored thoroughly. In doing so, he laid the foundations for the ultimate success of his early and original ideas on

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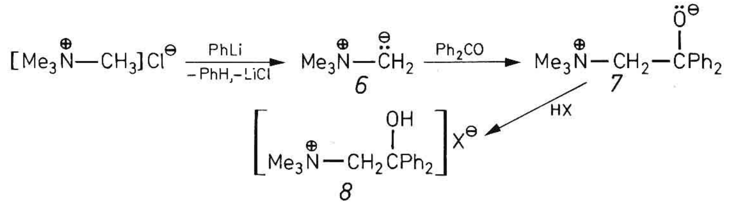
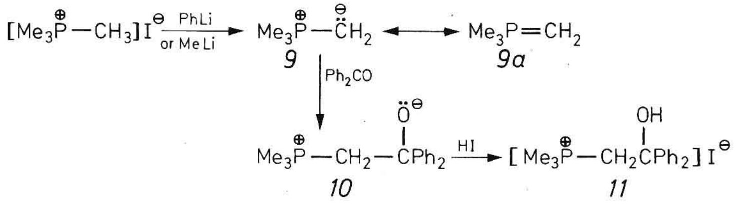
pentacoordination if not of nitrogen, but of the higher elements of main group five. At the same time, this perseverance opened up the way to a quite different line of research which very soon would prove even further reaching. And this all came about as follows.

Contrary to the resonance stabilized triphenylmethyl-[4], benzyl-[5] and fluorenyl-anions[8], phenyllithium did not leave the tetramethylammonium ion unaffected. Instead, it removed a proton to form trimethylammonium-methylide (*6*)[19], the prototype of that interesting class of zwitter-ionic compounds for which Wittig coined the name "ylides"[20].



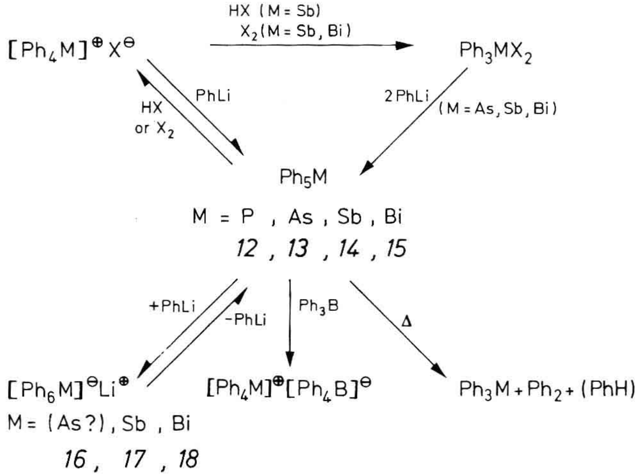
The constitution of *6* was proved primarily by trapping it with benzophenone to give another zwitter-ion *7* which easily yielded the adducts *8* with various acids. Since it was now perfectly clear that even the most nucleophilic agents would attack only the periphery, not the nitrogen center of tetraalkylammonium salts, extension of the investigations to the next heavier element of the group, phosphorus, was only logical. This was especially so, since it was known, in principal at least, that this element could combine covalently with five like ligands, as in phosphorus-pentachloride and -pentafluoride[21].

In a similar sequence of experiments as in the case of the ammonium analogue, tetramethylphosphonium iodide reacted with phenyl- or methyllithium first to give trimethylphosphoniummethylide (Wittig also used the name trimethylphosphine-methylene to account for the doubly-bound resonance form *9a*), which again was trapped with benzophenone to yield *10* and its hydroiodic acid adduct *11* respectively[22].



Thus, in alkylphosphonium salts too the C—H functions adjacent to the positively charged key atom were too acidic to let the attacking nucleophile proceed on its way towards the phosphorus center. A way out of this dilemma should consist in the application of a phosphonium salt with less acidic neighboring C—H functions. Such a salt was tetraphenylphosphonium iodide which in the reaction with phenyllithium did indeed lead to the first compound containing five covalent carbon-element bonds, pentaphenylphosphorane, $(C_6H_5)_5P$ (*12*)[23]. Its covalent nature was clearly demonstrated by its stability towards water, its relatively low melting point (124 °C under decomposition), its solubility in cyclohexane and its thermal decomposition into triphenylphosphine and biphenyl in a radical reaction. Polar reagents such as hydrohalogenic acids led to regeneration of the tetraphenylphosphonium cation. Later it was shown by Russian workers that many of the thermal reactions of pentaphenylphosphorane in the absence or presence of other reaction partners can be explained on the basis of initial phenyl radical formation [24].

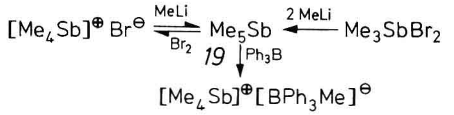
After this decisive breakthrough, the preparation of the higher homologues of pentaphenylphosphorane was only a question of time. Thus, by similar methods of synthesis pentaphenylarsorane (*13*) [25], pentaphenylstiborane (*14*) [25] and pentaphenylbismuthorane (*15*) [26] were obtained in rapid succession. The reactions of all these new compounds are in principle very similar, as can be seen from the following scheme:



Several points, though, need special consideration. Whereas pentaphenylphosphorane, -arsorane and -stiborane are colorless to slightly yellowish, pentaphenylbismuthorane forms violet crystals. On the basis of the decomposition points of substituted derivatives it was argued that the increasing stability in going from the severly congested pentaarylphosphorus to the much more relaxed pentaarylantimony compounds is primarily due to the increase of the central atom radius. Along this line pentaphenylbismuthorane should be even more stable than the quite resistent pentaphenylstiborane. In fact it is much less stable than even pentaphenylphosphorane [27,28]. In anticipation of later research it might be mentioned here that under mass spectroscopical conditions all the pentaphenyl derivatives showed very poor stability. The molecular ions are either very weak ($(C_6H_5)_5P$, As, Sb) or not observable at all ($(C_6H_5)_5Bi$), and the most intense fragments nearly all belong to a mass level below $M - 2\,C_6H_5$ which corresponds to the triphenyl derivatives [29].

Also, the inability of pentaphenylphosphorane to form a hexaphenylphosphate complex with phenyllithium can be explained solely by steric overcrowding. In the light of this, the hexaphenylbismuthate ion *18* should be more stable than the hexaphenylantimonate complex *17*, but again this is not the case. As could be shown many years later, pentaphenylbismuthorane (*15*) reacts with excess phenyllithium only at —70 °C to give the yellow lithium hexaphenylbismuthate (*Li-18*) which readily regenerates the violet starting material *15* on warming to room temperature.[30] Pentaphenylarsorane also forms an unstable yellowish precipitate with phenyllithium in tetrahydrofurane at —70 °C but it is not clear whether this really does consist of lithium hexaphenyl arsenate (*Li-16*) or of a rather labile adduct, $(C_6H_5)_5As \cdot C_6H_5Li$ [30].

With this wealth of experimental experience gained in the study of the above pentaphenyl derivatives as background, renewed efforts to obtain similar pentaalkyl derivatives were made. When dibromotrimethylstiborane or tetramethylstibonium bromide were treated with methyllithium, pentamethylstiborane (*19*) was obtained as a distillable, water-sensitive liquid [31] whose reactions obeyed the same principles as established for pentaphenylstiborane.



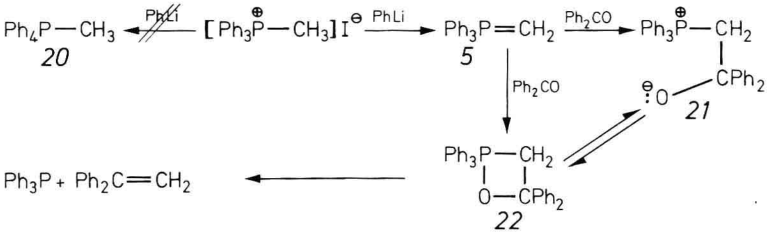
Similar experiments with analogous arsenic precursors did not allow the isolation of pentamethylarsorane (*1*), whose existence, however, could be made probable by some trapping reactions [31].

With these experiments, a somewhat clearer picture relating to main group five element pentacoordination began to emerge. Thus, in the form of the pentaaryl derivatives, more or less stable model compounds for all the elements except nitrogen had become accessible, which were to particularly facilitate the study of the stereochemical questions pertinent to this field. For the pentaalkyl derivatives, however, the situation was much less satisfying and pentamethylstiborane remained the sole clearly characterized representative at that time. A compromise was therefore sought, which would also make the preparation of alkyl derivatives of pentacoordinate phosphorus possible. Such a compromise could, for example, consist in the generation of mixed aryl-alkylphosphoranes [32], an idea, which turned out to be very successful, but in a totally unexpected and yet most significant way.

3 The Discovery of the Wittig Reaction

That the "carbonyl olefination by phosphorus ylides" was in fact discovered rather incidentally in the course of experiments aimed at the study of pentaphenylphosphorane and the syntheses of new derivatives thereof is clearly demonstrated in the title of the original publication by Wittig and Geissler: "Zur Reaktionsweise des Pentaphenylphosphors und einiger Derivate" [33].

When, with the objective of synthesizing methyltetraphenylphosphorane (*20*), methyltriphenylphosphonium iodide was reacted with phenyllithium, the nucleophile was once again caught by the acidified hydrogens of the methyl group and thus prevented from reaching the phosphorus center. Instead, the known triphenylphosphinemethylene *5* (R = H) [12] was formed. So far, everything was quite normal and could have been predicted from earlier investigations [12]. The crucial point, however, was reached when the routine trapping experiment with benzophenone was performed. In this case the reaction went straight beyond the potential initial zwitterionic addition product *21* to the cyclic phosphorane *22* which then collapsed to 1,1-diphenylethylene and triphenylphosphine oxide [33]. It must be noted here that a precursor to that type of reaction had already been described as early as 1919 by Staudinger and Meyer [13b] but was not explored any further. A proper evaluation of this and other relevant earlier work has been given by Wittig in a special review dealing with the more historical aspects of the phosphororganic carbonyl olefination reaction [34].



In the first report on this famous reaction, Wittig expressed a clear preference for the cyclic phosphorane intermediate *22* such as had already been formulated by Staudinger and Meyer in their earlier work. This view became generally accepted only many years later [35]. In this respect, the Wittig reaction did indeed still reflect some prominent features of the underlying research program on pentacoordinated molecules, from which it now evolved rapidly to a very active life of its own [36].

In conclusion of this line of experiments, the first mixed arylalkylphosphorane *23* could finally be synthesized by the reaction of triphenyl(triphenylmethyl)phosphonium chloride with phenyllithium.

$$[(C_6H_5)_3P^{\oplus}-C(C_6H_5)_3]\,Cl^{\ominus} + C_6H_5Li \rightarrow (C_6H_5)_4P-C(C_6H_5)_3 \qquad 23$$

Unlike the formally analogous, but in reality ionic, tetramethyl(triphenylmethyl)-nitrogen compound *3* of Schlenk and Holtz [4], tetraphenyl(triphenylmethyl)phosphorane (*23*) was unambiguously proven to be a covalent compound [33]. Alkinyltetraphenylphosphoranes *24* were prepared only many years later [37] and shown to be stable only below —20 °C.

$$[Ph_4P]^{\oplus}Cl^{\ominus} + KC{\equiv}CR \xrightarrow[-\,KCl]{(NH_3)_{liquid}} Ph_4P{-}C{\equiv}CR \xrightarrow{H^{\oplus}} Ph_4P^{\oplus} + HC{\equiv}CR$$

24

R = Me, OMe, p(MeO)C_6H_4

$$[Ph_4P]^{\oplus}Br^{\ominus} + LiCH{=}CH_2 \xrightarrow{Et_2O} Ph_4P{-}CH{=}CH_2 \rightarrow Ph_3P + PhHC{=}CH_2$$

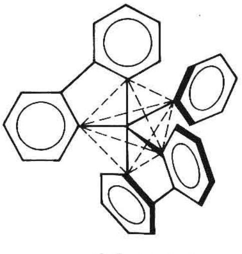
24a

Similarly, a detailed study of the reaction of tetraphenylphosphonium bromide with vinyl- and isopropenyllithium gave evidence of the intermediacy of tetraphenylvinylphosphorane derivatives *24a* [38].

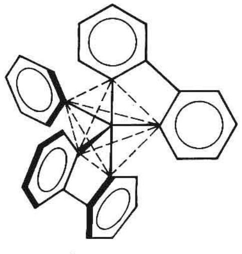
4 Further Investigations in the Field of Penta- and Hexaaryl Phosphorus Compounds

With the accessibility of the fairly stable pentaphenylphosphorane (*12*) and its even more stable homologues, there arose the intriguing question of the stereochemistry of such species. The first speculations were of course based on a trigonal bipyramidal model, since this structure type had already been proved for phosphorus pentahalides [21]. It was not possible, however, to differentiate in chemical reactions between the unlike ligands in compounds such as tetraphenyl(triphenylmethyl)-phosphorane (*23*) and tetraphenyl-p-tolylphosphorane [33] or in pentaphenylphosphorane derivatives appropriately labeled with deuterium or ^{14}C [39].

To my knowledge, the first detailed discussion dealing with the stereochemical implications of five unlike ligands around a pentacoordinated phosphorus center was presented in 1959 in the doctoral thesis of Kochendoerfer [40]. The later general development of these questions, especially under consideration of skeletal nonrigidity, can be followed in a more recent review by Gielen [41]. At the beginning, in the late fifties, however, the conception of a potential inner flexibility of a pentacoordinate molecular framework did not yet play a major role in stereochemical discussions. Thus, for a rigid trigonal bipyramidal phosphorane with five different ligands, 20 stereoisomers, that is, 10 diastereomeric pairs of enantiomers could be predicted, a number much too high to allow reasonable experimental studies. The utmost reduction of stereochemical possibilities for such compounds which still left a system from which relevant stereochemical information could potentially be expected consisted in the introduction of two bidentate ligands. Thus, the spirocyclic bis-2,2′-biphenylylenephenylphosphorane (*25*) was designed, for which, on the basis of a trigonal-bipyramidal structure with axial-equatorial linking of the chelate groups to the central atom, only one pair of enantiomeres was possible [40,42]. At the same time, such spirophosphoranes were expected to be more stable than pentaphenylphosphorane itself because of significantly reduced steric overcrowding.



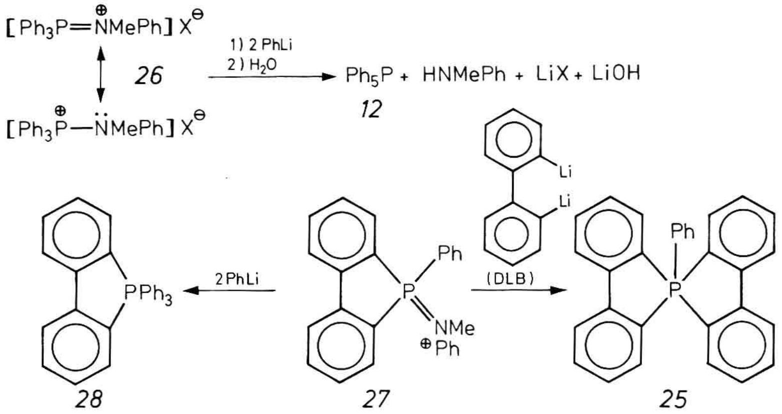
25 M(R)



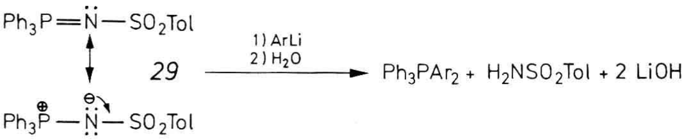
25 P(S)

Here again a note on nomenclature is needed. If compounds of type *25* are considered as substituted phosphoranes, names such as the one given above are appropriate. If, on the other hand, their heterocyclic nature stays in the foreground, the correct names (as used by Chemical Abstracts) are such as: 5-phenyl-5,5′-spirobi[5H-dibenzophosphole]. Both naming procedures are consistent with IUPAC rules and are applicable to similar arsenic, antimony- and bismuth-heterocycles as well (see later chapters).

Since the earlier methods could not be used for preparing *25* and similar compounds, a more general and also more convenient synthesis for pentaarylphosphoranes was developed. This consisted in the reaction of quaternized triarylphosphine imines with two equivalents of aryllithium [40,42].

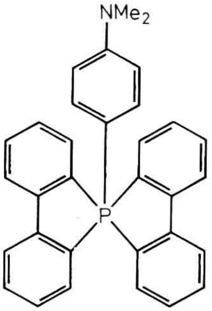


Obviously, in the precursor immonium compounds *26*, *27* the phosphorus bears enough partial positive charge to allow easy attack by aryl anions. Along similar lines of argument an even simpler synthetic procedure could be found in using analoguous p-toluenesulfonylimine (tosylimine) derivatives *29* [43], which had the appropriate polarization of the P=N double bond already built in [44].



$$Ph_3P{=}\ddot{N}{-}SO_2Tol \longleftrightarrow Ph_3\overset{\oplus}{P}{-}\overset{\ominus}{\ddot{N}}{-}SO_2Tol \xrightarrow[2)\ H_2O]{1)\ ArLi} Ph_3PAr_2 + H_2NSO_2Tol + 2\ LiOH$$

With these methods a number of substituted spirophosphoranes, e.g. *30–32*, was easily obtainable [42,45].



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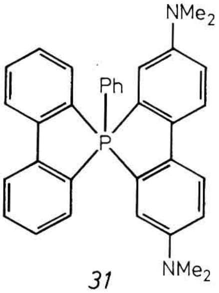

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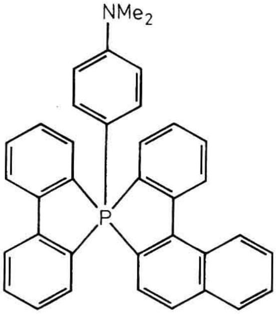

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