Classic Paper Presentation

"FROM DIYLS TO YLIDES TO MY IDYLL"

- ***Prof Georg Wittig***

Nobel Prize in Chemistry ,1979

Presented by

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FROM DIYLS TO YLIDES TO MY IDYLL

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by
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Translation from the German text

Chemical research and mountaineering have much in common. If the goal or the summit is to be reached, both initiative and determination as well as perseverance are required. But after the hard work it is a great joy to be at the goal or the peak with its splendid panorama. However, especially in chemical research - as far as new territory is concerned - the results may sometimes be quite different: they may be disappointing or delightful. Looking back at my work in scientific research, I will confine this talk to the positive results (1).

The process of proton-metal cation exchange appeared to us to be of fundamental importance, since the electron density at the carbon atom is enhanced after metalation. Thus the question arose of how carbanions, with their negative charge, would behave compared to carbonium ions, with their positively charged carbon atoms.

At the time we were not sure whether hydrogen bound to carbon would be proton-labile in quaternary ammonium salts. We came to this conclusion with an absurd experiment to prepare pentamethylnitrogen from tetramethylammonium salts by using the reaction of tetramethylammonium halide with methyllithium (13).

It was confirmed experimentally that the octet principle is strictly valid for the elements of the first eight-element period. The object of synthesizing compounds with a pentacoordinate central atom was reached only when we studied the higher elements of the fifth main group - that is, phosphorus, arsenic, antimony, and bismuth. It was easy to synthesize their pentaphenyl derivatives (14) and, in the case of antimony, also pentamethylantimony, which (as a nonpolar compound) is a liquid with a boiling point of 126°C (15).

Tetramethylammonium chloride reacting with methyl- or phenyllithium loses one proton and forms a product that we called trimethylammonium methylide (II) (Fig. 10). We gave the name *N*-ylides to this new class of substances since the bonding of the carbon to the neighboring nitrogen is homopolar (yl) and ionic (ide) at the same time. Trimethylammonium fluorenylide (12) could be isolated salt-free, thus its ylide structure is unambiguous (16). Subsequently, ylides as well as cryptoylides were studied more thoroughly (17).

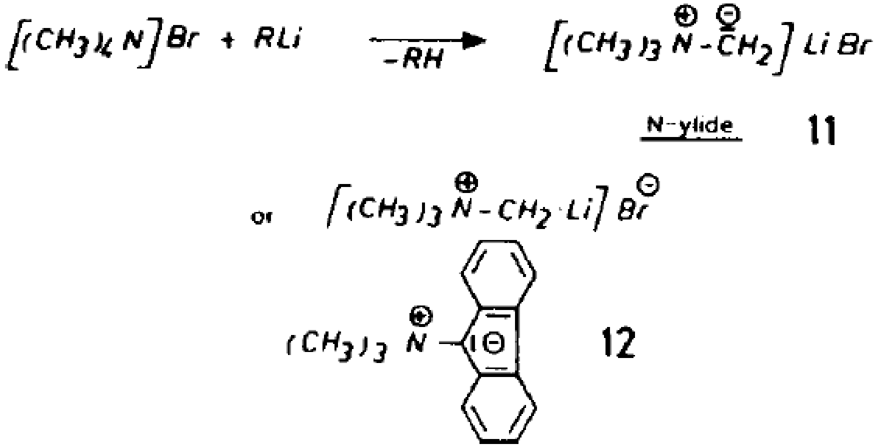


Fig. 10. Formation of Nylides (13).

When we extended this concept to the phosphonium salts, we found that they could be converted into the corresponding *P*-ylides even more readily than the analogous ammonium salts when treated with organolithium compounds (Fig. 11). The reason for the greater proton mobility is that phosphorus, unlike nitrogen, can expand its outer electron shell to a decet. This allows an energy-lowering resonance stability between the ylide and ylene forms.

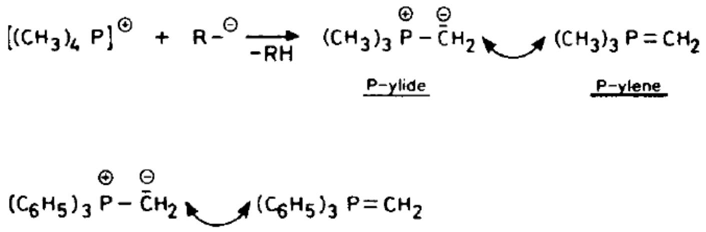


Fig. 11. Formation of *P*-ylides (17).

In the case of the *N*-ylide the semipolar nature of the N-C bond is demonstrated by its ability to add to benzophenone, forming the well-defined betaine (18) (Fig. 12). Now, if the same reaction was performed with triphenylphosphinemethylene, the expected betaine adductwas not obtained but, astonishingly, triphenylphosphine oxide and l,l-diphenylethylene (19). Evidently the initially produced betaine 13 - due to the ability of the central atom to expand its electron shell -formed the four-membered ring 14, which then decayed into two fragments as final products (20) and could not be isolated by itself (Fig. 13).

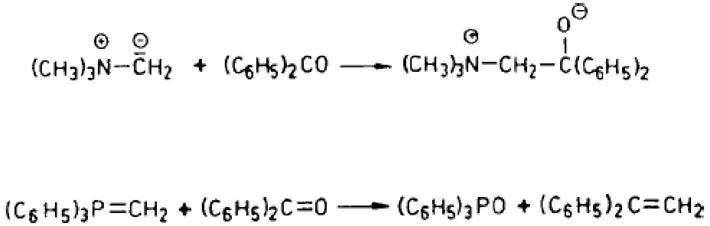


Fig. 12. Reactions with benzophenone (*18–20*).

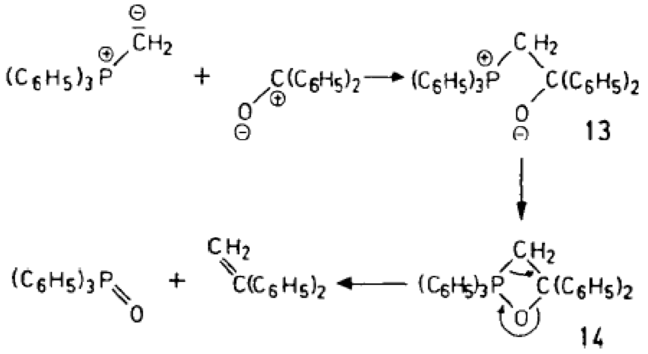


Fig. 13. Steps in the reaction of triphenylphosphinemethylene with benzophenone (25)

That the first step of the reaction is betaine formation was shown with the reaction of triphenylphosphinemethylene and benzaldehyde. In this case the betaine could be isolated as an intermediate product, and it decayed to triphenylphosphine oxide and styrene only on heating (20). This type of reaction (21) seemed to be of fundamental importance for preparative chemistry, and it also found industrial application (22). By these means it was possible to prepare vitamin A and β-carotene, among others. In the present

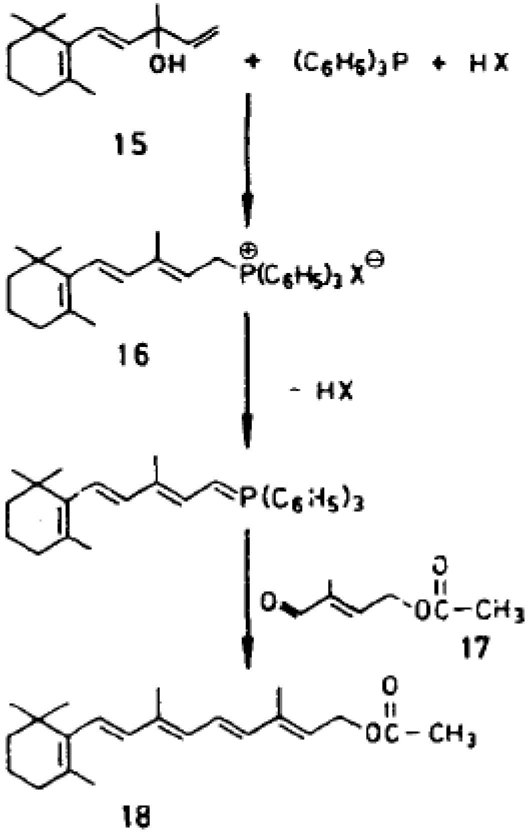


Fig. 14. Formation of vitamin A acetate (22).

With the addition of phenylsodium to triphenylboron, it could be demonstrated that boron can also act as tetracoordinate central atom (Fig. 15). Today this complex serves as an analytic reagent for the determination of potassium, rubidium, and cesium ions as well as for the quantitative determination and separation of ammonium and alkaloid salts.

$$(C_6H_5)_3B + C_6H_5\,Na \rightleftharpoons [(C_6H_5)_4B]Na$$

Fig. 15. Addition of phenylsodium to triphenylboron (*26*)

We called the complex salts with negatively charged central atom "ate" complexes for understandable reasons (23). They can be compared with the "onium" complexes, which were already known, as shown in Fig. 16. Because

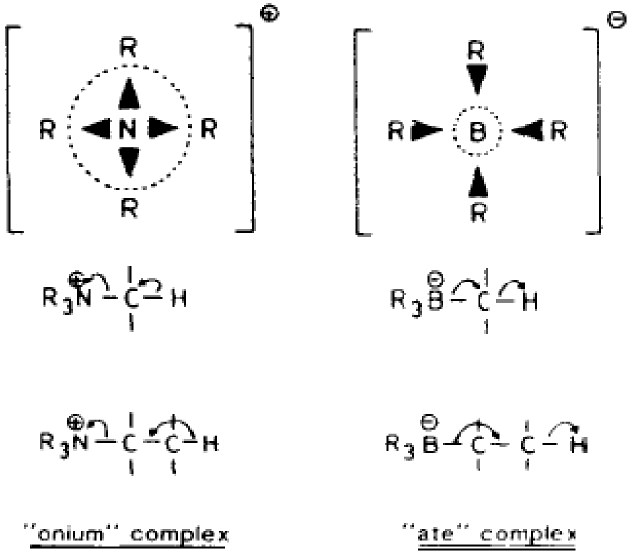
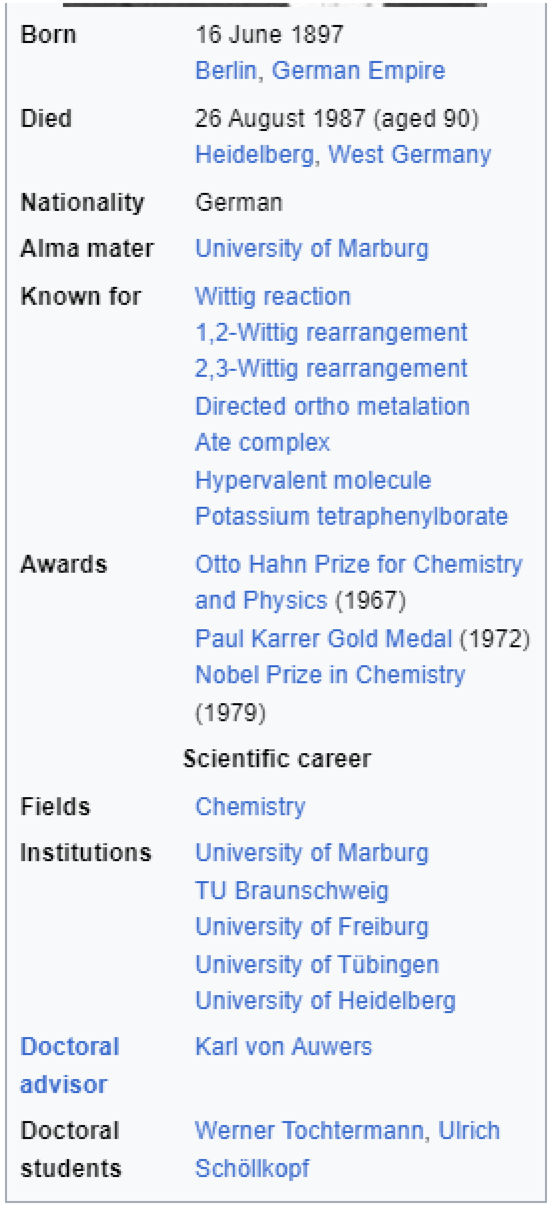


Fig. 16. Comparison of "onium" and "ate" complexes (23).

of the inductive effect of the central atom in onium complexes, all ligands R are cationically labilized and the hydrogen atoms at the neighboring carbon atoms are proton-mobile; however, in ate complexes all ligands at the central atom are anionically labilized and the hydrogen atoms at the neighboring carbon atoms are hydride-labile. This rule explains numerous reactions. I do not have time here to discuss its importance as a heuristic principle.

Thus I come to the end of my lecture. The excursion from diyls to ylides now ends at my idyll. With this I mean the conclusion of my research work as an emeritus, which allowed me to continue my work as a chemist free from the obligations of a teacher, and finally to devote myself completely to my interest in fine arts. I want to close my talk by offering cordial thanks to my collaborators. Without them my work could not have been accomplished.

Georg Wittig



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Known for	Wittig reaction 1,2-Wittig rearrangement 2,3-Wittig rearrangement Directed ortho metalation Ate complex Hypervalent molecule Potassium tetraphenylborate
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Doctoral advisor	Karl von Auwers
Doctoral students	Werner Tochtermann, Ulrich Schöllkopf

Thank you