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REMARKS ON THE STRUCTURAL EVIDENCE OF HIGH REACTIVITY OF ARSONIUM YLIDES BEARING WITH AN ELECTRON-WITHDRAWING SUBSTITUENT

Meicheng Shao, Xianglin Jin and Youqi Tang
(Institute of Physical Chemistry, Peking University)

Qichen Huang and Yaozeng Huang
(Shanghai Institute of Organic Chemistry, Academia Sinica)

Summary. The crystal structures of benzoylmethylene triphenyl-arsorane, -phosphorane and triphenylarsine oxide have been studied so as to well account for the high reactivity of the title compounds.

Certain phosphonium ylides such as those with an electron-withdrawing substituent in the alkylidene moiety show considerably reduced nucleophilicity and in many cases will not react with carbonyl group. For example, Trippett and Walker(1) reported that neither carbethoxymethylene triphenylphosphorane nor cynomethylene triphenyl phosphorane could react with ketones whereas Ramirez and Dershowitz(2) reported that the benzoylmethylene triphenylphosphorane did not react with cyclohexanone and reacted with benzaldehyde only with difficulty. In contrast to the phosphonium ylides, Huang et al. found that the arsonium ylides bearing with an electron-withdrawing substituent ($COOCH_3$(3), COPh(4), CN(5) and $COCH_3$(6)) in alkylidene moeity reacted with ketones as well as aldehydes in moderate to excellent yields.

On the other hand, in contrast to carbomethoxymethylene triphenylphosphorane which did not react with crotonic ester, carbomethoxymethylene- and benzoylmethylene-triphenylarsorane reacted with acrylic, crotonic and α-methylacrylic esters, respectively to form derivatives of cyclopropane in moderate to excellent yields depending upon the esters used(7).

Furthermore the reactivities of carbomethoxymethylene and benzoylmethylene triphenylarsoranes and their corresponding phosphoranes toward perfluoropropylene oxide and perfluoro-olefins were compared, showing that the arsonium ylides are more reactive(8).

The high reactivity of arsonium ylides may be attributed to the overlap of the *p*-orbitals of carbon with *d*-orbitals of arsenic is less effective than with *d*-orbitals of phosphorus, therefore the " covalent canonical form (1a)" should make a smaller contribution to the overall structure of arsonium ylides than to that of the corresponding phosphonium ylides(9).

$$\underset{(\underline{1a})}{Ph_3As{=}CRR'} \longleftrightarrow \underset{(\underline{1b})}{Ph_3\overset{+}{As}{-}\overset{-}{C}RR'}$$

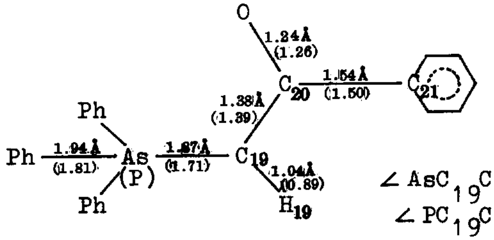
This paper deals with the studies of crystal structures of benzoylmethylene triphenyl-arsorane and -phosphorane so as to elucidate the difference in chemical behavior between these two ylides. In order to compare the bond pattern, the crystal structure of triphenylarsine oxide has also been studied.

Benzoylmethylene triphenylarsorane ($C_{26}H_{21}OAs$) crystalizes in space group C_{2h}^{4}—P2/n with a=19.317(5)Å, b=11.094(3)Å, c=19.825(7)Å, β=104.93(2)°, d=1.37g·cm^{-3}, Z=8(there are two molecules or 98 atoms in asymmetric unit of crystal), the ultimate discrepancy factor R=0.058. The structure was solved by means of SHELXTL program with a data set of 5372 independent reflections.

Benzoylmethylene triphenylphosphorane ($C_{26}H_{21}OP.1/2C_6H_6$) belongs in space group C_{2h}^{5}—P2_1/c, with a=13.274(2)Å, b=9.586(2)Å, c=18.554(2)Å, β=100.65(1)°, d=1.20g·cm^{-3}, Z=4, R=0.054, a total of 3538 independent reflections were collected. During the experiment, because benzene molecules escaped from crystal, the relative intensity of reference reflection fell from 1 to 0.26. The difficulty was overcome by a decay correction of intensities and the final structure obtained was very satisfactory.

Triphenylarsine oxide ($C_{18}H_{15}OAs$) belongs in space group C_{2h}^{5}—P2_1/c with a=6.320(4)Å, b=28.28(2)Å, c=9.221(5)Å, β=116.08°, d=1.45g·cm^{-3}, Z=4, R=0.060, 2564 independent reflections. The structure was solved by direct method.

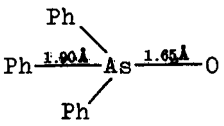
A general aspect of configuration and main bond parameters is shown as follows:



$\angle AsC_{19}C_{20}$=114.6°

$\angle PC_{19}C_{20}$=121.1°

Arsonium (phosphonium) ylide



Triphenylarsine oxide

In the structures atoms As(P), C_{19}, C_{20}, C_{21} and O are coplanar, As(P), C_{19}, C_{20}, and O participating in conjugate system.

In arsonium ylide, the bond length of As-C_{19} (1.87Å) is approximately the mean value of bond length of single bond (1.98Å) and that of double bond (1.78Å), while in phosphonium ylide, the bond length of P-C_{19} (1.71Å) also lies between that of single bond (1.87Å) and double bond (1.67Å) but

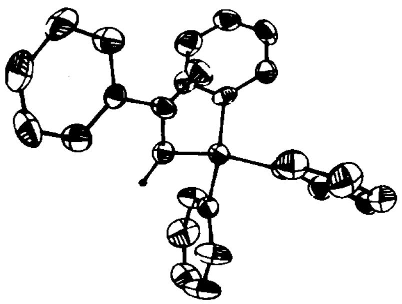


Fig. 1 Configuration of $Ph_3AsCHCOPh$ Molecule 1

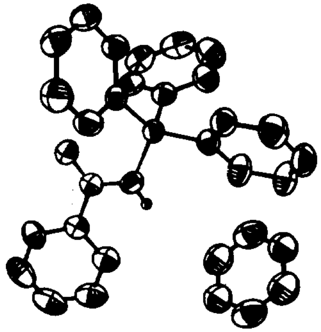


Fig. 2 Configuration of $Ph_3PCHCOPh \cdot 1/2C_6H_6$ Molecule

the latter is remarkably close to double bond length. The bond of C_{19}-C_{20} in either arsonium or phosphonium ylide possesses double bond character.

The bond length of As-O in triphenylarsine oxide is very short possessing high multiple bond character. We anticipate that accompanying the σ bond along the x axis, two d-p π bonds may be formed by using the outer d_{xy} and d_{xz} orbitals and the excitation energy of the electrons to outer d orbitals may be compensated by the chemical energy of the formation of multiple bonds. This may well account for easy degradation of ylides to form triphenylarsine oxide. We think, it is also true for the phosphonium ylides.

In either arsonium or phosphonium ylide, the methylene carbon is capable to participate at most in one d-p π bond, leading to the transformation of ylene structure to ylide structure. Thus, the multiple bond character of As(P)-C decreases, and the bond length is that of single and double bond in between, causing As(P)-C to gain ionic character. It is probably the structural basis of Wittig reaction.

In either ylide, the bond of C_{19}-C_{20} possesses striking double bond character. We suggested that this interesting phenomenon is partly due to the decrease of As(P)-C multiple bond character and related charge transfer, and partly due to the inductive effect of the electronegative oxygen atom through the conjugated carbon chain. These two factors work in concert to cause the π electrons more or less to localize at the potential trap between C_{19} and C_{20}. Thus the energy of the molecule lies at the most favourable condition. Obviously, when a ylide has an electron withdrawing group capable of effectively participating in conjugation at the methylene moiety, its stability increases.

The multiple bond character of As-C is lower than that of P-C, or in other words, As-C bond possesses higher ionic character, therefore the structural analysis gives a direct evidence that the arsonium ylides are more reactive than the corresponding phosphonium ylides.

The difference of chemical behaviors of arsonium and phosphonium ylides and the origin of the ionic character of As(P)-C mainly depends upon the participation of outer d orbital bond formation and the gaps of energy levels between nd and np or ns orbitals. The outer d orbital of phosphorus needs less excitation energy and thus P-C bond of phosphonium ylide is able to maintain higher composition of multiple bond.

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Note: A complete list of refined co-ordinates and thermal parameters of three crystal structures as well as data of bond distances, bond angles and relevant plane equations have been simutaneously sent to Cambridge Crystallographic Data Centre (C. C. D. C.).

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