Methylene-triphenylarsorane (Triphenylarsonium Methylide)

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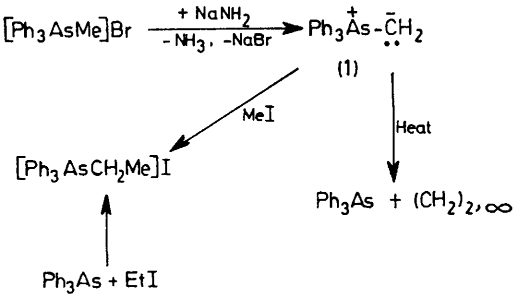
Summary Methylenetriphenylarsorane, Ph_3AsCH_2, has been isolated and characterized by analytical and spectroscopic methods.

ALTHOUGH the first arsonium ylide was prepared in 1902,[1] it was not assigned its correct formula until 1950.[2] Even now very few ylides of arsenic have been described[3-5] and, TABLE. ^1H and ^{13}C n.m.r. data of Ph_3AsCH_2, its arsonium salt precursor, and of related phosphorus compounds.[a]

	δ C$H_{3(2)}$/p.p.m.	δ $CH_{3(2)}$/p.p.m.	$^1J(^1H-^{13}C)$/Hz	Solvent
$\overset{+}{Ph_3AsMe}$ Cl^-	3·2,s	7·6,q	142·0	$CDCl_3$
$\overset{+}{Ph_3AsMe}$ Br^-	3·3,s	8·8,q	142·0	$CDCl_3$
$\overset{+}{Ph_3AsMe}$ I^-	3·2,s	9·9,q	142·0	$CDCl_3$
$\overset{+\ -}{Ph_3As\text{-}CH_2}$: (1)[b]	0·93,s	1·6,t	136·7	$C_6D_5CD_3$
$\overset{+}{Ph_3PMe}$ Br^-	3·17,d	11·4,dq	135	$CDCl_3$
$\overset{+\ -}{Ph_3P\text{-}CH_2}$:[c]	0·13,d	4·1,dt	153	C_6D_6

[a] Me_4Si standard. [b] The phenyl carbon atoms of (1) and the arsonium salts have the following chemical shifts; (1), 132·0 (*ortho*), 128·9 (*meta*), 130·5 (*para*), and 135·4 (C-1). (1) HBr salt: 131·2 (*ortho*), 129·8 (*meta*), 133·1 (*para*), and 120·7 (C-1). [c] Ref. 10.

with the exception of methylene- and trimethylsilylmethylene-trimethylarsorane,[6,7] only some carbonyl-stabilized ylides have been isolated.[8] Very little is known of the physical properties and general chemistry of arsonium ylides, in contrast with the large amount of information available on ylides of phosphorus and sulphur.

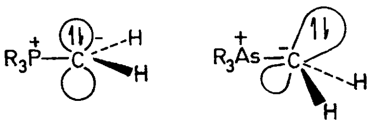


We have now isolated methylenetriphenylarsorane Ph_3AsCH_2 (1), the arsenic analogue of the classical Wittig reagent, Ph_3PCH_2. This species had been prepared by other workers and some of its reactions have been studied[3,9], but it could never be separated from solution with the byproducts of the synthetic procedure.

A solution of methyltriphenylarsonium bromide [1b] in dry tetrahydrofuran was treated with sodium amide for 1 h at at 20 °C then filtered under nitrogen, and evaporated *in vacuo*. Recrystallization from diethyl ether gave a *ca.* 50% yield of yellow crystals, m.p. 74 °C.†

Compound (1) is thermally unstable both in the solid state and in solution. Triphenylarsine, polymethylene, and ethylene have been identified as the only decomposition products. The reaction with MeI converts (1) into ethyltriphenylarsonium iodide, which was identical with a sample obtained from Ph_3As and EtI.

The n.m.r. spectrum of (1) (Table 1) shows that ^1J(CH) of the methyl group is only slightly reduced upon deprotonation of the arsonium cation, whereas this coupling constant is greatly increased in the corresponding phosphorus system.[10] In the phosphorus system, this change was supposed to be a consequence of an effective $sp^3 \rightarrow sp^2$ rehybridisation of the carbon atom upon ylide formation,[1] and this suggestion is borne out by the planar geometry found in recent *X*-ray results. For arsenic the bonding of the ylidic carbon seems to be virtually unchanged (sp^3),



and is therefore of pseudo-tetrahedral geometry. Similar results were obtained for the permethylated homologue.[7]

This result can be explained on the basis of markedly reduced π-bonding contributions in the arsenic series. *X*-Ray data on arsenic ylides should verify these assumptions by showing increased As–C distances and a non-planar geometry at the ylidic carbon. The much lower thermal stability of (1), with respect to the phosphorus ylide,[12] is also indicative of a different type of bonding, as is the pattern of chemical reactivity.[4]

We thank Dr. F. H. Köhler for obtaining the ^{13}C n.m.r. spectra, and Deutsche Forschungsgemeinschaft for financial support.

(*Received, 2nd June* 1975; *Com.* 613.)

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† Shorter or longer reaction times and lower or higher reaction temperatures lead either to much lower yields or to complete failure of the synthesis.

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