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Abstract

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ARSENIC YLIDES STABILIZED BY ACYL SUBSTITUENTS

In recent years the properties of phosphorus ylides have been the subject of intensive study, especially in connection with their use in the Wittig reaction. However, a related class of compounds—arsenic ylides—has thus far remained in the background. Meanwhile, comparison of the reactivity of phosphorus and arsenic ylides and, in particular, of their behavior in the Wittig reaction is of considerable interest.

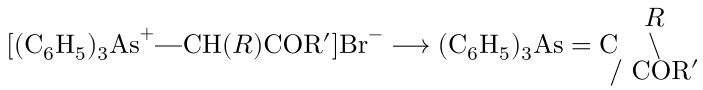
In 1958 Horner and Oediger described four stable arsenic ylides, obtained by condensation of triphenylarsonium dibromide with malonic acid nitrile and similar compounds in the presence of amines (^{1})

$$(C_6H_5)_3As = CXY \quad a)\ X = Y = CN; \quad b)\ X = Y = C_6H_5SO_2;$$

$$c)\ X = CN,\ Y = COOC_2H_5; \quad d)\ X = NO_2,\ Y = C_6H_5.$$

In Seyferth' s work (^{2}), certain reactions of triphenylarsoniummethylene were investigated. Finally, Johnson obtained the stable triphenylarsonium fluorenylide (^{3}), which reacts with aldehydes as a Wittig reagent. This exhausts the information on arsenic ylides available in the literature.

We describe here several arsenic ylides stabilized by the presence of an acyl group at the central carbon atom. These compounds were obtained by us from arsonium salts.



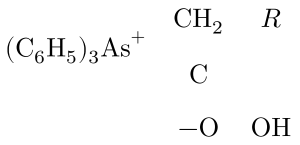
$$[(C_6H_5)_3As^{+}—CH(R)COR']Br^{-} \longrightarrow (C_6H_5)_3As = C \begin{matrix} R \\ \diagdown \\ / \ COR' \end{matrix}$$

(I) (II)

$$a)\ R = H,\ R' = OCH_3; \quad b)\ R = H,\ R' = CH_3;$$

$$c)\ R = H,\ R' = C_6H_5; \quad d)\ R = C_6H_5,\ R' = OCH_3.$$

Arsonium salts of the type $[(C_6H_5)_3As^+CH_2COR]X^-$, where $R = CH_3$, C_6H_5, OH, had already been described by Michaelis (^{4,5}). According to Michaelis, on treatment with alkalis they form betaines of the type

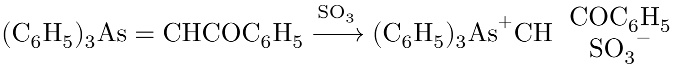


$$(C_6H_5)_3As^+ \begin{array}{ccc} CH_2 & & R \\ & C & \\ -O & & OH \end{array}$$

We were unable to obtain such betaines. (Ramirez and Dershowitz likewise could not repeat Michaelis' s experiments on obtaining analogous phosphorus betaines (^{6}).) When alkalis act on solutions of arsonium salts, no precipitate is formed. Passing dry ammonia through solutions of these salts in chloroform also leads neither to betaines nor to ylides (with the exception of 1d). The latter are formed in 50-60% yields upon treatment of arsonium salts with sodium amide in liquid ammonia or with sodium alcoholate in alcohol. In contrast to the compounds described by Michaelis, the arsenic ylides are insoluble in water, readily soluble in benzene, and have lower melting points. We have established that arsenic ylides and phosphorus ylides can be identified chromatographically in a thin layer of alumina. In this case the arsenic ylides are adsorbed more strongly than the corresponding phosphorus compounds (they have smaller R_f values). The ratio*

$$\frac{R_f \text{ arsenic}}{R_f \text{ phosphorus}} = 0.2 \text{ to } 0.9$$

(solvent—a mixture of benzene with acetone, 4:1). The compounds obtained are prone to electrophilic-addition reactions, as are phosphorus ylides. They can be sulfonated with dioxane sulfotrioxide to sulfobetaines (^{7}) and add bromine; they react smoothly with aldehydes with formation of unsaturated compounds and triphenylarsine oxide**

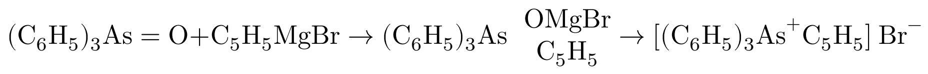


$$(C_6H_5)_3As = CHCOC_6H_5 \xrightarrow{SO_3} (C_6H_5)_3As^+CH \begin{array}{c} COC_6H_5 \\ SO_3^- \end{array}$$

$$(C_6H_5)_3As = CHCOC_6H_5 \xrightarrow{Br_2} [(C_6H_5)_3As^+CHBrCOC_6H_5]\ Br^-$$

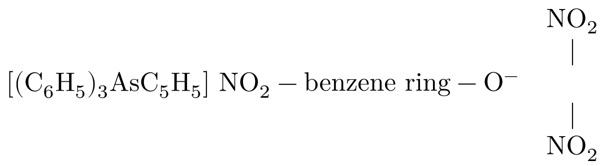
$$(C_6H_5)_3As = CHCOC_6H_5 \xrightarrow{C_6H_5CHO} C_6H_5CH = CHCOC_6H_5 + (C_6H_5)_3AsO$$

Arsenic ylides are apparently more reactive substances than their phosphorus analogues. They decompose more rapidly on storage (especially in the light) and can be obtained from salts only under significantly more severe conditions than phosphorus ylides (the ease of ylide formation usually corresponds to their stability and low reactivity). We also attempted to obtain triphenylarsine cyclopentadienylide by two routes: by the action of cyclopentadienylmagnesium bromide on triphenylarsine dibromide, and also on triphenylarsine oxide. In the first case the Grignard reagent reduced the bromide to triphenylarsine; in the second, triphenylcyclopentadienylarsonium was obtained in good yield.



$$(C_6H_5)_3As = O + C_5H_5MgBr \rightarrow (C_6H_5)_3As \begin{matrix} OMgBr \\ C_5H_5 \end{matrix} \rightarrow [(C_6H_5)_3As^{+}C_5H_5]\ Br^{-}$$

$$[(C_6H_5)_3As^{+}C_5H_5]\ Br^{-} \rightarrow [(C_6H_5)_3AsC_5H_5]\ BF_4^{-}$$



$$[(C_6H_5)_3AsC_5H_5]\ NO_2 - \text{benzene ring} - O^{-} \begin{matrix} NO_2 \\ | \\ \\ | \\ NO_2 \end{matrix}$$

However, the action of bases on the cyclopentadienyl arsonium salt does not lead to formation of an ylide: the salt either remains unchanged or is hydrolyzed. This result was unexpected for us, since triphenylphosphine cyclopentadienylide is very stable ([8]); moreover, Johnson described triphenylarsine fluorenylide ([3]). The only product that we succeeded in isolating from the interaction of triphenylstibine dibromide with cyclopentadienylmagnesium bromide was pentaphenylstibine ([8]). (In addition, there are formed—resinous products were isolated.) The initially formed dicyclopentadienyltriphenylstibine probably then disproportionates and resinifies.

$$(C_6H_5)_3SbBr_2 + 2C_5H_5MgBr \rightarrow [(C_6H_5)_3Sb(C_5H_5)_2]$$

$$\downarrow$$

$$(C_6H_5)_5Sb + [(C_5H_5)_5Sb]$$

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* We give the values of $\frac{R_f \text{ arsenic}}{R_f \text{ phosphorus}}$ for various ylides: IIa–0.18; IIb–0.69; IIv–0.88; IIg–0.79.

** The behavior of arsenic ylides in the Wittig reaction will be reported in a separate communication.

Experimental Part

1. Synthesis of arsonium salts. Alkyltriphenylarsonium salts are formed in good yields upon several days' interaction of triphenylarsine with α-brominated ketones or esters in benzene solution (^{4,5}) or in chloroform. Triphenyl-α-phenylcarbomethoxymethylarsonium bromide (*I*) is described for the first time. Yield 60%, m.p. 117-118° (from CH_3NO_2—THF).

$$\begin{aligned} C_{27}H_{24}AsO_2Br.\quad & \text{Found, \%: C 60.25, 60.47; H 4.46, 4.69} \\ & \text{Calculated, \%: C 66.61; H 4.50} \end{aligned}$$

2. Preparation of arsenic ylides. Method A. To a solution of sodium amide (from 0.016 mole of sodium) in 100 ml of liquid ammonia at −78°, 0.016 mole of the arsonium salt was added in portions; the solution was stirred for 20 min, after which the ammonia was gradually removed without access of moisture. The residue was washed several times with hot benzene, the benzene extracts were combined, the benzene was distilled off to a small volume, petroleum ether was added, and the mixture was cooled for several hours at 0°. The precipitated ylide was filtered off.

Method B. To a cold solution of the arsonium salt in a minimal amount of absolute methanol, a solution of an equivalent amount of sodium methylate in methyl alcohol was added dropwise. The methanol was distilled off in vacuo to dryness. Further treatment was analogous to method A.

Method C. A stream of dry ammonia was passed for 1 h into a solution of 1 g of the salt in a minimal amount of chloroform. The solution was filtered, washed with water, and the chloroform was removed in vacuo. Further work-up was ordinary. According to our observations, this is the most convenient method for obtaining stable phosphorus ylides, especially triphenylphosphine-benzoylmethylene. Of the arsenic ylides, only ylide (*II*) was obtained by us in this way.

Triphenylarsine-carbomethoxymethylene (IIa). Yield by method A 50%, by method B 62%. M.p. 181-183° (from benzene + petroleum ether). $\lambda_{\max}$265 mμ ($\lg\varepsilon$3.73).

$$\begin{aligned} C_{21}H_{19}AsO_2.\quad & \text{Found, \%: C 66.69, 66.43; H 4.78; 5.03} \\ & \text{Calculated, \%: C 66.15; H 5.05} \end{aligned}$$

Triphenylarsine-benzoylmethylene (*II*). Yield by method A 66%, method B 55%. M.p. 154-156° (from benzene + petroleum ether). $\lambda_{\max}$255 mμ ($\lg\varepsilon$4.32), $\lambda_{\max}$310 mμ ($\lg\varepsilon$3.72).

$$\begin{aligned} C_{26}H_{21}AsO.\quad & \text{Found, \%: C 73.65, 73.64; H 5.38, 5.25} \\ & \text{Calculated, \%: C 73.64; H 5.01} \end{aligned}$$

Triphenylarsine-acetylmethylene (II). Yield by method B 60%. Melting point before recrystallization 171-175°; after recrystallization from benzene, m.p. 165-166°. $\lambda_{\max} 270$ mμ (lg ε3.56).

$C_{21}H_{19}AsO$. Found, %: C 69.27, 69.17; H 5.33; 5.39
Calculated, %: C 69.62; H 5.30

Triphenylarsine-α-phenyl-carbomethoxymethylene (II). Yield by method C 55%. M.p. 156-158° (from a benzene–petroleum ether mixture).

$C_{27}H_{23}AsO_2$. Found, %: C 71.65, 71.55; H 5.34, 5.30
Calculated, %: C 71.42; H 5.13

3. Reactions of triphenylarsine-benzoylmethylene.

Sulfurization of triphenylarsinebenzoylmethylene. This was carried out with dioxane sulfotrioxide in accordance with the previously published procedure (7). The yield of sulfobetaine was about 86%, m.p. 246-248° (from nitromethane).

Found, %: C 62.06, 61.95; H 3.91, 3.92; S 7.16, 6.90
$C_{26}H_{21}AsSO_4$. Calculated, %: C 61.91; H 4.19; S 6.35

Bromination of triphenylarsine-benzoylmethylene. To a solution of 0.5 g of the ylide in 10 ml of chloroform, in the cold, the calculated amount of bromine in carbon tetrachloride was added dropwise (0.19 g of bromine). Ether precipitated 0.68 g of the brominated product with m.p. 165-167°, yield ~100%. After reprecipitation with benzene from chloroform, m.p. 168-169°.

Found, %: C 52.67, 52.45; H 3.62, 3.47
$C_{26}H_{21}AsOBr_2$. Calculated, %: C 52.48; H 3.70

4. Synthesis of triphenyl-cyclopentadienyl-arsonium salts. To a solution of the Grignard reagent prepared from 7.5 g of ethyl bromide and 1.44 g of magnesium in 50 ml of ether, 7.0 g of cyclopentadiene in 40 ml of ether was added over 15 min, and the mixture was heated for 30 min. Then, over the course of 40 min, a solution of triphenylarsine oxide (6.0 g) in hot benzene was introduced, and the mixture was left for 12 h at 20°. The benzene-ether solution was decanted; 30 ml of water and 20 ml of conc. hydrobromic acid were added to the viscous residue. The resulting solution was heated with activated charcoal and filtered. The aqueous solution was washed many times with chloroform; the chloroform solution was dried with magnesium sulfate, the solvent was removed in vacuo, and the remaining glassy mass was triturated with a small amount of abs. acetone; the crystals were separated and washed with abs. ether. The yield of triphenylcyclopentadienylarsonium bromide was almost quantitative; however, the sample could not be brought to analytical purity. From the bromide, the fluoroborate and picrate were obtained; unlike the bromide, these are poorly soluble in water. Triphenylcyclopentadienylarsonium fluoroborate, m.p. 294-298° (from $(CH_3)_2CO + CH_3OH$).

Found, %: C 60.82, 60.99; H 4.33, 4.41; F 16.28, 16.65
$C_{23}H_{20}AsBF_4$. Calculated, %: C 60.31; H 4.40; F 16.60

Triphenylcyclopentadienylarsonium picrate, m.p. 185-186° (from CH_3OH).

Found, %: C 58.01, 58.08; H 3.58, 3.71; N 7.17, 7.17
$C_{29}H_{22}N_3O_7As$. Calculated, %: C 58.05; H 3.70; N 7.00

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Note: Figure translations are in progress. See original paper for figures.