Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

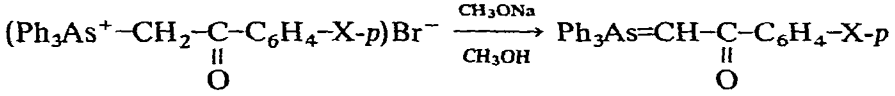
NOTE

COMPARISON OF BASICITY OF SOME ARSONIUM AND PHOSPHONIUM YLIDES

NIC. A. NESMEYANOV, V. V. MIKULSHINA AND O. A. REUTOV
Department of Chemistry, University of Moscow, Moscow B234 (U.S.S.R.)

(Received January 10th. 1968)

In our previous work[1,2] it was observed that arsonium ylides can be prepared from arsonium salts only on treatment with essentially more effective bases than is necessary for their phosphonium analogs. This report deals with the quantitative comparison of the basicity of some arsonium and phosphonium ylides. We have synthesized several new triphenylarsinebenzoylmethylenes with various substituents in the *para*-position of the benzoyl group.



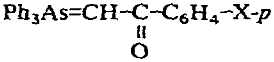
$$(Ph_3As^+{-}CH_2{-}\underset{\overset{\|}{O}}{C}{-}C_6H_4{-}X\text{-}p)Br^- \xrightarrow[CH_3OH]{CH_3ONa} Ph_3As{=}CH{-}\underset{\overset{\|}{O}}{C}{-}C_6H_4{-}X\text{-}p$$

I a–f II a–f

(a, X = H) (c, $X = CH_3$) (e, X = Br)
(b, $X = OCH_3$) (d, X = Cl) (f, $X = NO_2$)

TABLE 1

TRIPHENYLARSINEMETHYLENES



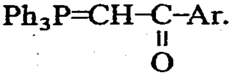
$Ph_3As{=}CH{-}\underset{\overset{\|}{O}}{C}{-}C_6H_4{-}X\text{-}p$

Compound		Yield (%)	M.p. (°C)	Analysis[a] C	H	As	Br
IIa	$C_{26}H_{21}AsO$	70	167–169	73.45 (73.59)	4.84 (4.93)	17.80 (17.65)	
IIb	$C_{27}H_{23}AsO_2$	82	145–146	71.39 (71.34)	5.16 (5.10)	16.57 (16.50)	
IIc	$C_{27}H_{23}AsO$	70	150–151	73.86 (73.98)	5.26 (5.29)	17.03 (17.09)	
IId	$C_{26}H_{20}AsOCl$	50	156–157	68.29 (68.04)	4.44 (4.39)	—	
IIe	$C_{26}H_{20}AsOBr$	68	155–156	62.42 (62.05)	4.08 (4.00)	—	15.89 (15.88)
IIf	$C_{26}H_{20}AsNO_3$	53	110–112	66.51 (66.53)	4.53 (4.29)	—	

[a] Calculated values in parentheses.

The yields, melting points and analyses of these compounds are given in Table 1.

The frequencies in the IR spectra (in Nujol) which characterize the conjugated bond system $As{=}CH{-}C{=}O$, fluctuate between 1505 and 1525 cm^{-1} and are thus similar to the corresponding frequencies of $Ph_3P{=}CH{-}\underset{\underset{O}{\|}}{C}{-}Ar$.



$Ph_3P{=}CH{-}C({=}O){-}Ar$

We have determined the pK_a of the series of conjugate acids of the ylides by potentiometric titration (in 0.1 N KCl solution in 50% by volume ethanol at 21°, based on three titration points).

The greater the electronegativity of the substituent X, the greater is the acidity of the arsonium salts (in other words, the basicity of the ylides decreased) and this is evident from the following experimental data*.

Substituent X	OCH_3	CH_3	H	Cl	Br	NO_2
pK_a	9.16	8.97	8.52	8.02	7.95	6.67

The effect of the substituents agrees well with the Hammett equation, the constants being $\rho = 2.38$ and $r = 0.994$. Figure 1 illustrates the dependence of the pK_a of arsonium ylides (curve I, our data) on σ, and that of the analogous phosphonium ylides under similar conditions (curve II, based on the data of Kabachnik *et al.*[3]*).

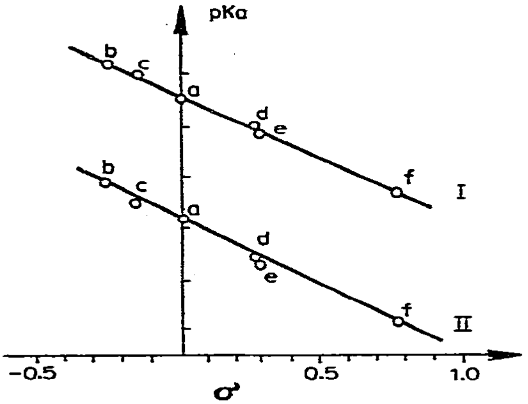


Fig. 1. Dependence of pK_a on σ. (I), $Ph_3As{=}CH{-}\underset{\underset{O}{\|}}{C}{-}C_6H_4{-}X\text{-}p$; (II), $Ph_3P{=}CH{-}\underset{\underset{O}{\|}}{C}{-}C_6H_4{-}X\text{-}p$. X is as follows: (a), H; (b), OCH_3; (c), CH_3; (d), Cl; (e), Br; (f), NO_2.

Arsonium ylides are obviously essentially more basic (200–230 times) than the analogous phosphonium compounds.

Thus arsenic plays a smaller part than phosphorus in the distribution of the negative charge. This is due to a lesser electronegativity of arsenic and perhaps to a greater diffusion of the 4d-orbitals, which prevents their effective overlapping with the 2p-orbitals of carbon.

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* The data do not include corrections for activities.

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