

## Kinetic Study of the Reaction Between Stabilized Arsonium Ylides and *p*-Nitrobenzaldehyde

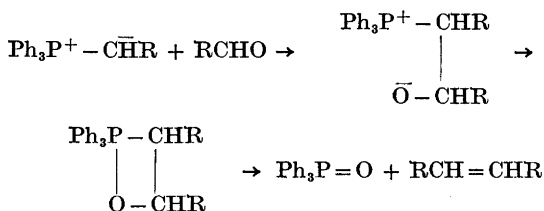
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The reaction of *p*-nitrobenzaldehyde with a series of stabilized arsonium ylides has been studied in benzene. Some rate measurements were also performed in dimethyl formamide, dimethyl sulphoxide, and in methanol. The reactivity of the ylides parallels their basicity, the most basic ylide also being the most reactive. The reaction is clearly second order, first order in each of ylide and aldehyde. The reaction shows little dependence on the polarity of the solvent. This finding does not appear to be consistent with the intermediacy of a betaine. The mechanism of the reaction is discussed.

Stabilized arsonium ylides react with aldehydes to give olefins and arsine oxide. The reaction between arsonium ylides and carbonyl compounds was discovered by Heffe<sup>1</sup> in 1937, and since that, several papers have appeared, dealing mainly with the synthetic applications of the reaction.<sup>2-7</sup> The mechanism of the reaction has been proposed<sup>2</sup> to be the same as that for the Wittig reaction of phosphonium ylides, where the reaction is thought to be initiated by a nucleophilic attack of the ylide carbanion on the carbonyl carbon, a betaine being formed. The betaine is then supposed to rearrange to a cyclic intermediate, which undergoes decomposition into olefin and phosphine oxide.<sup>8</sup>

In view of the increasing importance of phosphonium ylides in preparative organic chemistry, an investigation of the corresponding arsonium ylides



*Scheme 1.*

seemed to be of interest. Whereas the mechanism of the Wittig reaction of phosphonium ylides has been extensively investigated, there has been no attempt to correlate the structure of arsonium ylides with their reactivity in this reaction, and as far as the present author knows, no rate study has as yet been published.

A point of special interest is the proposed intermediacy of a betaine in this reaction. Evidence in favour of a betaine intermediate in the Wittig reaction of stabilized ylides was supposedly obtained from the rate increase, observed in certain polar solvents.<sup>9</sup> As shown by Rùchardt *et al.*,<sup>10</sup> the rate of the Wittig reaction of stabilized phosphonium ylides is, however, generally not increased in polar media. It was hoped that a study of the analogous arsonium ylides would give more convincing evidences in favour of a betaine intermediate, since the second step in the reaction (Scheme 1) is energetically less favourable when the ylide has arsenic as heteroatom. The present paper reports a kinetic study of the reaction between a series of stabilized arsonium ylides and *p*-nitrobenzaldehyde.

### EXPERIMENTAL

**Materials.** The arsonium ylides were prepared by the so-called "salt-method" on treatment of a solution of the appropriate arsonium salt with a suitable base. The arsonium salts were made from the respective arsines<sup>11</sup> on treatment with the appropriate  $\alpha$ -bromoketones, esters or amides, respectively. The arsonium ylides prepared during the present study are listed in Table 1, together with their melting points and analytical data.

**Synthesis of olefins.** The olefins needed as standard materials for determination of extinction coefficients were made from the appropriate ylides and *p*-nitrobenzaldehyde. The ylides were heated for a short time with an equivalent quantity of *p*-nitrobenzaldehyde in dry benzene. The expected olefins were always obtained in excellent yield. The identity of the compounds was established by m.p., IR and PMR spectra.

*trans*-4-Nitromethyleinnamate, recrystallized from ethanol, m.p. 160°, lit.<sup>15</sup> 162.

*trans*-4-Nitro-*N,N*-diphenyleinnamide, recrystallized from benzene, m.p. 171°.

4-Nitro-*trans*-chalcone was recrystallized from ethanol, m.p. 164°, lit.<sup>16</sup> 162.5°.

4-Nitro-benzylidenacetone, recrystallized from benzene, m.p. 112°, lit.<sup>17</sup> 110°.

4-Nitro-4'-phenyl-*trans*-chalcone was recrystallized from benzene, m.p. 212°.

4'-Methyl-4-nitro-*trans*-chalcone, recrystallized from ethanol, m.p. 162°, lit.<sup>18</sup> 161°.

4'-Bromo-4-nitro-*trans*-chalcone was recrystallized from benzene, m.p. 166°, lit.<sup>19</sup> 166°.

4,4'-Dinitro-*trans*-chalcone, recrystallized from benzene, m.p. 193°, lit.<sup>20</sup> 193–194°.

*p*-Nitrobenzaldehyde was recrystallized two times from ethanol, m.p. 106°, lit.<sup>21</sup> 106°.

Benzene was freed from thiophene by extraction with sulfuric acid. The product was then neutralized with sodium carbonate and washed with water. After drying over calcium chloride, the product was fractionated from sodium.

Dimethyl sulphoxide was fractionated from calcium hydride, b.p. 70°/10, lit.<sup>10</sup> 71°/11.

A pure product of dimethyl formamide was used as received (Fluka *puriss*).

**Rate measurements.** The rates of reaction of the ylides with *p*-nitrobenzaldehyde were determined by following the ultraviolet absorption of the reaction solution at the absorption maximum of the olefin formed. The concentration of olefine was calculated from the equation:

$$X = \frac{Ef - (\epsilon_1 A_0 + \epsilon_2 B_0)d}{(\epsilon_3 + \epsilon_4 - \epsilon_1 - \epsilon_2)d}$$

where

*E* = extinction of the reaction mixture,

*f* = dilution before the measurements were done,

$\epsilon_1$ ,  $\epsilon_2$ ,  $\epsilon_3$  and  $\epsilon_4$  = molar extinction coefficients of ylide, *p*-nitrobenzaldehyde, olefin and the respective arsine oxide,

Table 1. Physical data of ylides  $R_3As=CHCOX$ .

Compound	R	X	m.p.	Recryst. from	C (Found)	C (Calc.)	H (Found)	H (Calc.)	Base
1	Ph	OMe	160°, lit. <sup>12</sup> 133–140°	Benzene/petrol ether	66.93	66.67	5.05	5.06	MeO <sup>-</sup>
2	Ph	NPh <sub>2</sub>	157–158°	Benzene	74.60	74.56	5.20	5.08	MeO <sup>-</sup>
3	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	Ph	Oily subst.	Benzene/ether	67.02	67.70	5.31	5.29	MeO <sup>-</sup>
4	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	Ph	167–169°	Benzene/petrol ether	74.52	74.83	5.75	5.85	OH <sup>-</sup>
5	Ph	Me	142°, lit. <sup>13</sup> 123°	Benzene/ether	69.21	69.61	5.26	5.21	MeO <sup>-</sup>
6	Ph	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	145–146°, lit. <sup>14</sup> 150–151°	Benzene/ether	73.68	73.97	5.17	5.29	MeO <sup>-</sup>
7	Ph	<i>p</i> -PhC <sub>6</sub> H <sub>4</sub>	161–162°	Benzene	76.59	76.80	5.08	5.04	MeO <sup>-</sup>
8	Ph	Ph	170°, lit. <sup>13</sup> 170°	Benzene	73.50	73.58	5.01	4.99	MeO <sup>-</sup>
9	Ph	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	161–163°, lit. <sup>14</sup> 155–156°	Benzene/ether	62.15	62.05	4.02	4.00	MeO <sup>-</sup>
10	Ph	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	117° (dec.), lit. <sup>14</sup> 110–120°	Acetone/ether	66.60	66.53	4.61	4.30	MeO <sup>-</sup>

$A_0$  = initial concentration of ylide, and

$B_0$  = initial concentration of aldehyde.

The rate constants were calculated according to the equation:

$$kt = \frac{2.303}{A_0 - B_0} \log \frac{A_0(B_0 - x)}{B_0(A_0 - x)}$$

*Determination of ylide basicity.* The order of the basicity of the ylides was established by using the "umylidierung" method of Bestmann.<sup>22</sup> His method was slightly modified, however. Equimolar quantities of ylide and triphenylfluorenyl phosphonium bromide dissolved in methylene dichloride were mixed, and the equilibrium concentrations of the two ylides were determined by measuring the absorption of the reaction solution at the absorption maximum of triphenylphosphine fluorenylide at 384 m $\mu$ . The basicity of the ylides (Table 1) increases in the order  $10 < 9 < 8 < 7 < 6 < 5 < 4 < 3 < 2 < 1$ . The  $pK_a$  of the ylides 10, 9, 8, and 6 have been determined in 50 % ethanol by Nesmeyanov *et al.*<sup>14</sup> and were found to be 6.67, 7.95, 8.52, and 8.97, respectively. Aksnes and Songstad<sup>24</sup> reported  $pK_a$  of 8 to be 8.55, and that of 9 to be 8.00.

## RESULTS AND DISCUSSION

The experimental data from the present study show that the mechanism of the reaction between stabilized arsonium ylides and *p*-nitrobenzaldehyde undoubtedly is very similar to that of the Wittig reaction. As can be seen from the rate data summarized in Table 2, the more reactive ylides are also

Table 2. Rate data for the reaction of stabilized arsonium ylides ( $R_3As=CHCOX$ ) with *p*-nitrobenzaldehyde.

Com- pound	R	X	Rate constant (l mol <sup>-1</sup> s <sup>-1</sup> )	Solvent	Reaction temp.	Activation energy (kcal/mol)	$\Delta S^*$ (e.u.)	Shift of methine proton ( $\delta$ ppm)
1	Ph	OMe	~ 160	C <sub>6</sub> H <sub>6</sub>	25.0°			3.15
2	Ph	NPh <sub>2</sub>	~ 40	C <sub>6</sub> H <sub>6</sub>	25.0°			3.11
3	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	Ph	10.5 ± 0.1	C <sub>6</sub> H <sub>6</sub>	25.0°			4.08
4	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	Ph	8.3 ± 0.1	C <sub>6</sub> H <sub>6</sub>	25.0°			4.60
5	Ph	Me	6.5 ± 0.1	C <sub>6</sub> H <sub>6</sub>	25.0°			3.98
6	Ph	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	5.70 ± 0.05	C <sub>6</sub> H <sub>6</sub>	25.0°	5.0	-40.5	4.68
			4.50 ± 0.05	C <sub>6</sub> H <sub>6</sub>	17.2°			
			7.40 ± 0.05	C <sub>6</sub> H <sub>6</sub>	35.0°			
			1.20 ± 0.05	DMF	25.0°			
			2.70 ± 0.02	DMSO	25.0°			
7	Ph	<i>p</i> -PhC <sub>6</sub> H <sub>4</sub>	4.5 ± 0.1	C <sub>6</sub> H <sub>6</sub>	25.0°			4.78
8	Ph	Ph	4.0 ± 0.1	C <sub>6</sub> H <sub>6</sub>	25.0°			4.71
9	Ph	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	0.86 ± 0.01	C <sub>6</sub> H <sub>6</sub>	25.0°			
10	Ph	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	0.087 ± 0.002	C <sub>6</sub> H <sub>6</sub>	25.0°			4.83

the more basic ones and *vice versa*. The same reactivity sequence is reported from studies of analogous phosphonium ylides.<sup>23</sup> There is also a fair correlation between the chemical shift of the methine proton of the ylides and their reactivity with *p*-nitrobenzaldehyde. Such a trend was expected, since the higher

electron density on the carbanion of the more reactive ylides ought to be reflected in the chemical shift of the methine proton.

A Hammett plot for the *p*-phenacylidene substituents in the ylides 3, 5, 6, 9, and 10 versus  $\sigma$  gave a  $\rho$  value of  $-2.2$  (Fig. 1). The reaction of the ylide 6

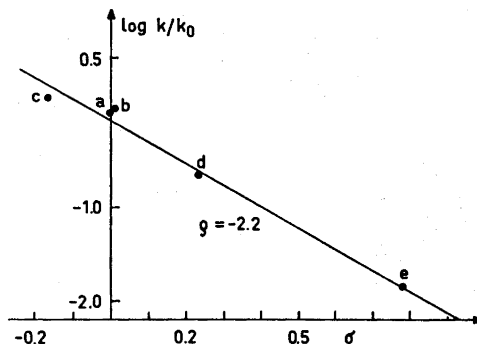


Fig. 1. Dependence of reactivity on  $\sigma$  in the reaction between  $\text{Ph}_3\text{As}=\text{CH}-\text{CO}-\text{C}_6\text{H}_4-\text{X}-p$  and  $p\text{-NO}_2\text{C}_6\text{H}_4\text{CHO}$  in benzene at  $25^\circ$ . X is as follows: (a), H; (b),  $\text{C}_6\text{H}_5$ ; (c),  $\text{CH}_3$ ; (d), Br; (e),  $\text{NO}_2$ .

is five times faster in benzene than in dimethyl formamide, and two times faster in benzene than in dimethyl sulphoxide. The reaction in methanol is faster than in benzene, but quantitative measurements could not be made due to the instability of the ylide in this solvent. The decreased reactivity in the more polar solvents dimethyl sulphoxide and dimethyl formamide as compared to the relatively unpolar benzene is not consistent with formation of a betaine in the first step of the reaction. From studies of the Wittig reaction of stabilized ylides it has been argued<sup>9</sup> that the effect of solvent polarity upon this reaction is in agreement with increased charge localisation in the transition state. The work of Rüchardt *et al.*<sup>10</sup> shows, however, that the Wittig reaction is very little affected by the polarity of the solvent. In fact, the tendency seems to be just the same as in the reaction of the arsonium ylide, *i.e.* a slower rate of reaction in more polar solvents.

The strong rate increase in the Wittig reaction observed in methanol as compared to benzene<sup>9</sup> might be due to the hydrogen bonding abilities of the former solvent, and not primarily to the higher polarity. The relatively small rate increase observed in chloroform may also be attributed to hydrogen bonding, since chloroform contains an active hydrogen atom. Since there is no evidence of betaines in the reactions of stabilized phosphonium or arsonium ylides with carbonyl compounds, it seems unnecessary to postulate such intermediates in the present reactions. The observed solvent effects may thus be better explained, if it is assumed that a concerted mechanism is operative, where a neutral pentacovalent four-membered transition state is formed in one step, without any intermediacy of a betaine. A synchronized reaction mechanism must be expected to lower the activation entropy, and explains also the large negative entropies of activation (Table 2). It may also explain the very low activation energies observed in these reactions. The observed substituent effects and catalysis by hydrogen bonding solvents may also be equally well compatible with a concerted mechanism.

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