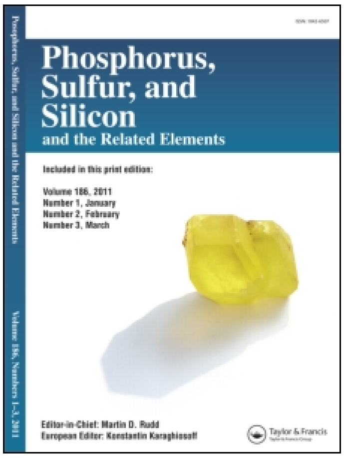

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ACIDITY AND REACTIVITY OF α-ARYLAZOPHENACYLTRIPHENYLPHOSPHONIUM BROMIDES

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ACIDITY AND REACTIVITY OF α-ARYLAZOPHENACYLTRIPHENYLPHOSPHONIUM BROMIDES

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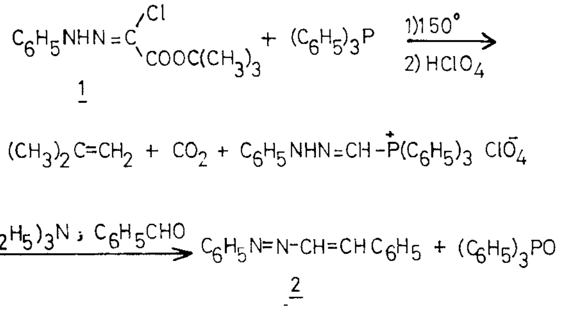
Two series of new compounds, i.e., α-arylazophenacyltriphenylphosphonium bromides **4** and the corresponding ylides **5** were prepared. Both **4** and **5** were found unreactive in Wittig-like reactions, possibly due to the high acidity of **4** and the low basicity of **5**. The pK_a values of **4** were determined in 80% (vol.) ethanol-water and were found to be correlated by the Hammett equation.

Our interest in the synthesis of arylazoalkenes of the type **6** and arylazoalkynes of the type **7** has prompted us to examine a recent report by Dalla Croce and Zaniboni.[1] These authors reported the synthesis of arylazoalkenes **2** from hydrazidoyl halides **1**. An example of their synthesis is shown in Scheme 1. We were interested to determine whether this reaction sequence (Scheme 1) could be employed to prepare **6** and **7**, with arylazophosphoranes of the type **5** as precursors of such compounds (Scheme 2).

RESULTS AND DISCUSSION

Hitherto undescribed arylazophenacyltriphenylphosphonium bromides **4** (Table I) were obtained by reaction of hydrazidoyl bromides **3** with triphenylphosphine in ethanol.[2] The corresponding phosphonium salts **4** were synthesized in excellent yields

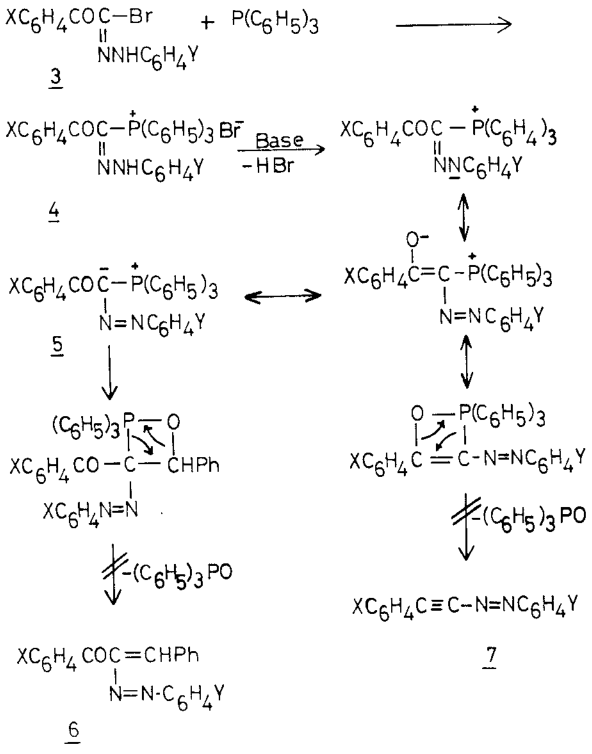


$$\underset{\mathbf{1}}{C_6H_5NHN{=}C\begin{matrix}^{Cl}\\ _{COOC(CH_3)_3}\end{matrix}} + (C_6H_5)_3P \xrightarrow[2)\,HClO_4]{1)\,150^\circ}$$

$$(CH_3)_2C{=}CH_2 + CO_2 + C_6H_5NHN{=}CH\text{-}\overset{+}{P}(C_6H_5)_3\ \overset{-}{ClO_4}$$

$$\xrightarrow{(C_2H_5)_3N\,;\ C_6H_5CHO} \underset{\mathbf{2}}{C_6H_5N{=}N\text{-}CH{=}CHC_6H_5} + (C_6H_5)_3PO$$

SCHEME 1



SCHEME 2

TABLE I

Synthesized phosphonium salts **4**

Compd.			M.p.,[a]	Mol. formula	Br, %		
No.	*X*	*Y*	°C	(Mol. wt.)	Calcd.	Found	pK_a
4a	H	H	194	$C_{32}H_{26}BrN_2OP$[b] (565.45)	14.13	14.00	4.70 ± 0.04
4b	4-CH_3	H	184	$C_{33}H_{28}BrN_2OP$[c] (579.48)	13.79	13.61	4.65 ± 0.06
4c	4-OCH_3	H	208	$C_{33}H_{28}BrN_2O_2P$ (595.48)	13.42	13.20	4.36 ± 0.07
4d	4-Cl	H	200	$C_{32}H_{25}BrClN_2OP$ (599.90)	13.32	13.51	4.19 ± 0.06
4e	3-Cl	H	212	$C_{32}H_{25}BrClN_2OP$ (599.90)	13.32	13.10	4.06 ± 0.01
4f	4-NO_2	H	208	$C_{32}H_{25}BrN_3O_3P$ (610.45)	12.09	12.91	3.59 ± 0.08
4g	H	4-CH_3	204	$C_{33}H_{28}BrN_2OP$ (579.48)	13.79	13.49	4.86 ± 0.01
4h	H	4-Br	208	$C_{32}H_{25}Br_2N_2OP$ (644.35)	24.80	24.61	4.08 ± 0.03
4i	H	4-NO_2	209	$C_{32}H_{25}BrN_3O_3P$ (610.45)	13.09	13.29	2.90 ± 0.04

[a] With decomposition.

[b] Anal. Found (Calcd.): C, 67.17 (67.97); H, 4.82 (4.63) %. Mass spectrum, m/e (rel. intensity, %): 565 (0.1), 262 (100), 303 (19.8), 222 (0.2), 105 (57.8), 117 (0.2), 91 (0.1), 77 (31.8).

[c] Anal. Found (Calcd.): C, 68.00 (68.40); H, 4.95 (4.87) %. Mass spectrum, m/e (rel. intensity, %): 579 (0.1), 262 (19.8), 212 (0.8), 133 (0.9), 106 (11.2), 105 (100), 77 (44.4).

TABLE II

Synthesized ylides **5**

Compd. No.	*X*	*Y*	M.p., °C	Mol. formula (Mol. wt.)	*N*, % Calcd.	Found
5a	H	H	165	$C_{32}H_{25}N_2OP^a$ (484.54)	5.78	5.71
5b	4-CH_3	H	152	$C_{33}H_{27}N_2OP^b$ (498.57)	5.62	5.60
5c	4-OCH_3	H	172	$C_{33}H_{27}N_2O_2P$ (514.56)	5.44	5.22
5d	4-Cl	H	153	$C_{32}H_{24}ClN_2OP$ (518.98)	5.39	5.17
5g	H	4-CH_3	145	$C_{33}H_{27}N_2OP$ (498.57)	5.62	5.41
5h	H	4-Br	128	$C_{32}H_{24}BrN_2OP$ (563.44)	4.97	4.72
5i	H	4-NO_2	177	$C_{32}H_{24}N_3O_3P^c$	7.94	7.90

[a] Anal. Found (Calcd.): C, 79.15 (79.32); H, 5.24 (5.20) %. Mass spectrum, m/e (rel. intensity, %): 484 (0.1), 262 (100), 105 (43.9), 77 (42.0).

[b] Anal. Found (Calcd.): C, 79.25 (79.50); H, 5.40 (5.45) %. Mass spectrum, m/e (rel. intensity, %): 498 (0.1), 262 (88.3), 133 (3.7), 105 (100), 106 (9.1), 91 (11.7), 77 (49.8).

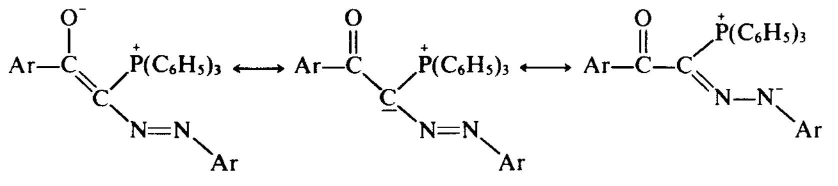
[c] Anal. Found (Calcd.): C, 72.45 (72.58); H, 4.44 (4.57) %.

(85–90%). The expected structures of these salts were in agreement with their elemental and spectral (mass, ir, and pmr) analyses (see Experimental and Tables I–III).

Treatment of **4** with sodium ethoxide in ethanol gave the corresponding new ylides **5** in almost quantitative yields (Table II). Mass spectral data and elemental analyses substantiated the structures of the ylides prepared. When such ylides were heated in ethanol in the presence or absence of potassium hydroxide or sodium ethoxide, they were recovered unchanged and in no experiment the corresponding arylazoalkynes **7** could be obtained.

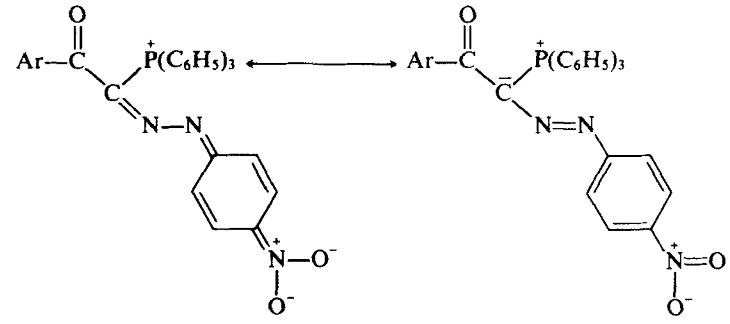
After this result, the reaction of **5** with aldehydes was investigated. When **5a** was refluxed for four hours with benzaldehyde in ethanol, no reaction was observed and **5a** was recovered unchanged. The same result was obtained when this experiment was repeated in the presence of triethylamine, potassium hydroxide, or sodium ethoxide. Also, when a mixture of the phosphonium salt **4a** and benzaldehyde in ethanol was refluxed for four hours in the presence of sodium ethoxide, the only product obtained was the ylide **5a**.

The above results indicate that the arylazo ylides of the type **5** are unreactive in Wittig-like reactions. This chemical inertness may be due to the possible high degree of resonance stabilization of such ylides. Such a stabilization would reduce the nucleophilicity of **5** necessary for an attack on the carbonyl carbon atom of aldehydes to give **6** and inhibit self-decomposition into **7**. This rationalization seems to be substantiated by the infrared spectra of **5** which revealed the absence of the carbonyl bands exhibited by the corresponding phosphonium salts **4**.



5

There is one exception, however. The *p*-nitro ylide, **5i**, shows a weak carbonyl frequency at ~1665 cm^{-1}. This indicates at least some contribution from the resonance structures containing a carbonyl group:



Nevertheless, even the ylide **5i** does not react with benzaldehyde in a Wittig-like reaction under conditions described above for the parent ylide **5a**.

To cast more light on this problem, the relative basicities of the ylides **5** were determined by potentiometric titration of **4** and **5** and compared with those of **8** and **9**, respectively, because it was reported that the nucleophilicities of various ylides parallel their basicities.[3] In 80% (vol.) ethanol-water, all phosphonium salts **4** behave as acids and the ylides **5** as weak bases. The effective pK_a's of the compounds studied are listed in Table I. It should be noted that the pK_a data obtained by potentiometric titration of **5** with hydrochloric acid agree well with the data obtained by titration of **4** with potassium hydroxide. The data indicate that arylazophenacyltriphenylphosphonium salts **4** are more acidic than the parent phenacyltriphenylphosphonium bromides **8**. For example, the pK_a values of **4a** ($X = H$) and **8a** ($X = H$) are 4.40 and 6.00, respectively.[4,5] This finding is compatible with the relatively strong resonance stabilization of the arylazo group.

$XC_6H_4COCH_2\overset{+}{P}(C_6H_5)_3\ Br^-$ $\qquad$ $XC_6H_4CO\overset{-}{C}H\overset{+}{P}(C_6H_5)_3$

8 **9**

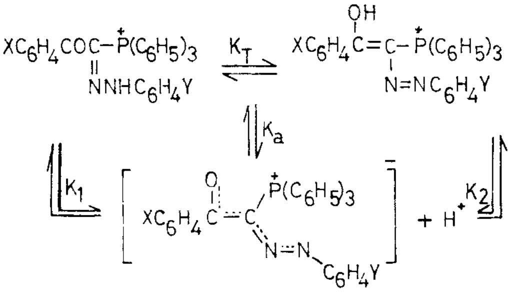
The results in Table I show that, at least to some extent, the basicity of **5** is influenced by the substituents in the aroyl and *N*-aryl moieties. When the pK_a values for **4a**-**4f** were plotted against the Hammett substituent constants, σ_X, a good straight line was obtained. Similarly, a plot of the pK_a values of **4a** and **4g**-**4i** *vs.* σ_Y was linear. The corresponding regression lines for these correlations are given by Eqs. (1) and (2), respectively. The magnitude of the value of 2.01 found for the effect of the substituents upon the aroyl moiety

$$pK_a = 4.44 - 1.09\,\sigma_X;\ r = 0.997,\ s = \pm 0.04 \qquad (1)$$

$$pK_a = 4.06 - 2.01\,\sigma_Y;\ r = 0.997,\ s = \pm 0.07 \qquad (2)$$

(r = correlation coefficient; s = standard deviation)

is close to the value of 2.3 reported for substituted phenacyltriphenylphosphonium bromides **8**.[6] These linear correlations indicate that the phosphonium salts **4a**-**4i** exist predominantly in one tautomeric form, i.e., the keto-hydrazone tautomer (NH) (Scheme 3). If the azo-hydroxy tautomer (OH) coexisted in equilibrium with the keto-hydrazone form (NH), good correlations would not be observed.[7] This is because for such an equilibrium (Scheme 3), the overall acid dissociation K_a is re-



SCHEME 3

lated to the dissociation constants K_1 and K_2 of the NH and OH forms, respectively, and to the tautomeric constant K_T by Eqs. (3) and (4). According to these equations, a linear relationship between pK_a and σ_X should be observed only if $K_1 = K_2$. In general, the values of K_1 and K_2 are different because of the ionization of the NH and OH groups, respectively. The assignment of the tautomeric NH structure for **4** is compatible with the spectral data of the compounds examined. Thus, the infrared spectra of the compounds contain a weak hydrazone NH band at about 3420 ± 10 cm^{-1}, and a carbonyl band near 1640 ± 10 cm^{-1}, respectively. Both the NH and CO bands were absent in the spectra of the ylides **5a–5h**. The electronic absorption spectra of **4** are typical of hydrazones.[8,9] Each of the compounds studied exhibits two intense maxima ($\log \epsilon > 4$) near 350 and 400 nm (Table III).

$$K_a = K_1/(1 + K_T) \tag{3}$$

$$K_a = K_2K_T/(1 - K_T) \tag{4}$$

In conclusion, the results obtained in this study suggest that α-arylazo-derivatives of α-aroyl halides do not exhibit chemical reactivity characteristic of their α-carbalkoxy analogs.

TABLE III

Spectral data for the phosphonium salts **4** and the ylides **5**

Compd. No.	C_2H_5OH λ_{max}, nm ($\log \epsilon$)	KBr, cm^{-1} $\tilde{\nu}_{C=O}$	$\tilde{\nu}_{N-H}$	δ ($CDCl_3$), ppm
4a	350 (4.6), 400 (4.4)	1640	3420	[a]
5a	355 (4.4), 400 (4.2)	—	—	
4b	355 (4.0), 410 (4.0)	1630	3380	10.2 (bs, 1H), 2.27 (s, 3H)
5b	355 (5.1), 400 (4.9)	—	—	2.30 (s, 3H)
4c	355 (4.3), 410 (4.3)	1630	3400	10.18 (bs, 1H), 3.65 (s, 3H)
5c	360 (4.1), 400 (4.0)	—	—	3.64 (s, 3H)
4d	350 (4.1), 390 (4.1)	1630	3400	[a]
5d	360 (4.3), 390 (4.2)	—	—	
4e	350 (4.0), 390 (4.0)	1640	3380	[a]
4f	350 (4.1), 445 (4.2)	1635	3420	[a]
4g	350 (3.9), 400 (3.8)	1630	3400	10.2 (bs, 1H), 2.30 (s, 3H)
5g	355 (4.3), 400 (4.1)	—	—	2.26 (s, 3H)
4h	350 (4.2), 400 (4.2)	1630	3400	[a]
5h	355 (4.2), 390 (4.1)	—	—	
4i	350 (4.3), 400 (4.1)	1640	3380	[a]
5i	361 sh (3.9), 445 (4.4)	1665 (w)	—	

[a] All compounds exhibit an aromatic proton multiplet signal in their ^1H nmr spectra between 6.9 and 8.3 ppm.

EXPERIMENTAL

The spectra were recorded on the following instruments; nmr, a Varian T 60A spectrometer; ir, a Perkin Elmer 257 grating spectrophotometer; mass, a Perkin Elmer RMU-6E spectrometer (ionization energy 70 eV); uv, a Cary 17 recording spectrophotometer. Melting points were obtained using an electrothermal melting point apparatus (Gallenkamp) and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by the microanalytical laboratory of the University of Cairo, Giza, Egypt. Hydrazidoyl bromides were prepared from phenacyldimethylsulfonium bromide and *N*-nitrosoacetanilide as previously described.[2]

Phosphonium salts, **4a–4i**.

A hydrazidoyl bromide (0.005 mole) and triphenylphosphine (1.3 g, 0.005 mole) were refluxed in ethanol (25 ml) for 2 h, the reaction mixture was cooled and diluted with ether to precipitate the product. The solid was collected, washed with ether, and crystallized from ethanol-ether. The compounds prepared and their physical properties are listed in Tables I and III.

Phosphonium ylides, **5a–5h**.

To a stirred solution of sodium ethoxide in ethanol [prepared by dissolving metallic sodium (0.11 g, 0.005 mole) in ethanol (20 ml)], a phosphonium salt was added. The salt dissolved and, after 1 h at room temperature, the corresponding ylide precipitated. It was collected and crystallized from ethanol. The synthesized ylides are listed in Tables II and III.

Reaction of ylides with aldehydes.

Equimolecular quantities of the phosphonium ylide **5a** and benzaldehyde (0.005 mole each) were refluxed in ethanol for 4 h, cooled, and the solid was collected and crystallized from ethanol. Compound **5a** was recovered unchanged. The same result was obtained when this experiment was repeated in the presence of triethylamine or potassium hydroxide, the only isolated product being the ylide **5a**.

Reaction of phosphonium salts with potassium hydroxide.

A mixture of the phosphonium salt **4a** (1 g), 5% methanolic potassium hydroxide (40 ml) and water was refluxed for 2 h. The mixture was cooled, diluted with water, and the solid formed was collected. Crystallization from ethanol yielded yellow crystals, m.p. 165°C, mixed m.p. with **5a** showed no depression.

Measurement of pK$_a$*'s.*

The acid dissociation constants of **4a–4i** were determined potentiometrically in 80% (vol.) ethanol-water at 25°C according to the usual procedure.[10] An Extech digital pH-meter type 671 fitted with an Orion combination glass electrode type 91–06 was used to record the pH values. The instrument was calibrated by two standard Beckman buffer solutions with pH 4.01 and 10.00. The pH-meter readings B were converted to hydrogen ion concentration $[H^+]$ by means of the Eq. (5):[11]

$$-\log [H^+] = B + \log U_H \tag{5}$$

where $\log U_H = -0.4$ is the correction factor for the solvent composition and ionic strength μ for which B is read at 25°C.

Approximately 0.5 to 1.0 mole of the desired phosphonium salt was dissolved in 25 ml of 80% (vol.) ethanol-water and titrated potentiometrically with $0.1N$ potassium hydroxide (prepared in the same solvent mixture). The ylide solutions were titrated with $0.1N$ hydrochloric acid. Both the salt and the ylide gave essentially identical potentiometric curves, i.e., the titration is reversible. The pK_a values were calculated from the titration data from Eq. (6):

$$K_a = \frac{(a\, T_L + [H^+])\,[H^+]}{T_L\,(1 - a) - [H^+]} \tag{6}$$

where *a* is the molar ratio of the base (acid) added to the compound, and T_L is the total concentration of the acid (ylide).

ACKNOWLEDGMENT

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