

STUDIES OF THE REACTION OF TRIAMINOPHOSPHINES WITH α,β -UNSATURATED NITRILES

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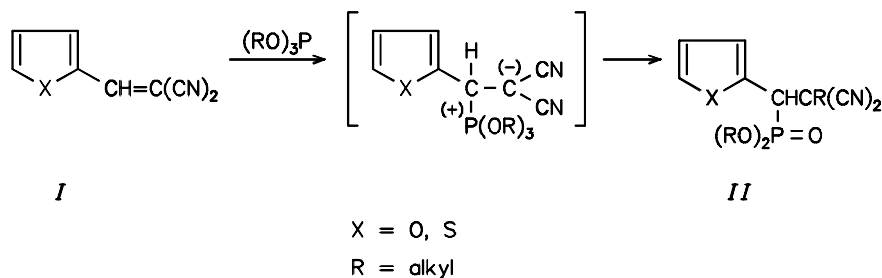
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Tris(dialkylamino)phosphines *IIIa* and *IIIb* react with furfurylidene malonitrile (*Ia*) and its thiophene analogue *Ib* to give a mixture of 1 : 1 adducts *IV* and *V*. Compounds *IV* have aminophosphonium dipolar ion structure, while compounds *V* are the ylide forms. The ratio of the products depends on the reaction conditions. Some reactions of *IV* and *V* are described.

As a continuation of the work^{1,2} on the reaction of trialkyl phosphites with α,β -unsaturated nitriles *I* the present investigation was done to compare the behaviour of tris(dialkylamino)phosphines $(R_2N)_3P$ and trialkyl phosphites $(RO)_3P$ toward the same species. It was shown^{1,2} that the phosphorus of the phosphites attacks the exocyclic ethylenic bond in *I* to give the phosphonate 1 : 1 adducts *II* (Scheme 1).

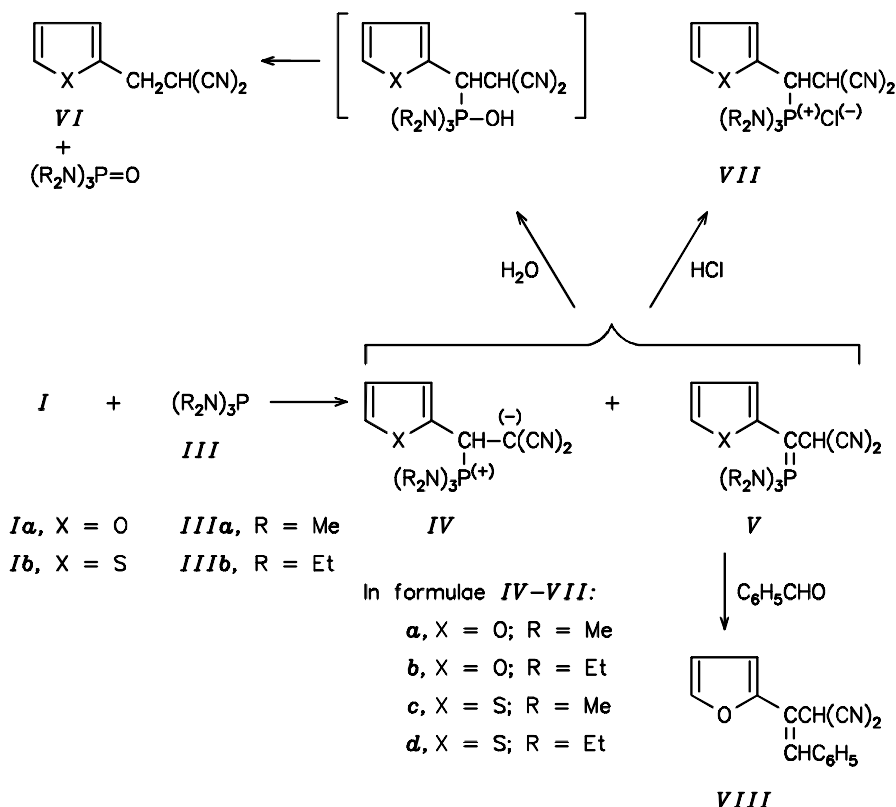
Furfurylidene malonitrile (*Ia*) or thienylylidene malonitrile (*Ib*) and tris(dimethylamino)phosphine (*IIIa*) or tris(diethylamino)phosphine (*IIIb*) in mole ratio 1 : 3 yielded, after 6 h in refluxing benzene, a crude product which generally precipitated out of the solution in $\approx 80\%$ yield. The resulting adduct can be isolated by fractional crystallization in two forms, one with ionic phosphorus (*IV*) in $\approx 43\%$ yield, and the other with C=P bond (*V*) in $\approx 28\%$ yield. Compounds *IV* were obtained as water-sensitive, red crystals, quite stable for 2 – 3 days. Compounds *V*, reddish brown crystals, were



SCHEME 1

formulated as methylenephosphoranes on the basis of spectral data presented below. Evidently, the unsaturated nitrile underwent 1,2-addition at carbon, but the resulting phosphonium betaine *IV* rearranged to the more stable ylide *V* (Scheme 2). Analogous proton shifts have been observed in the reaction of triphenylphosphine with maleic anhydride³, and of triaminophosphines with activated double bonds^{4,5}.

The composition and structure of *IV* were determined by elemental and molecular weight (MS) analyses. Also, their structure of phosphonium betaines is evident from the NMR data (Tables I and II). The ³¹P NMR spectra have a high-field resonance at $\delta \approx 38$ ppm, typical of *sp*²-hybridized phosphorus. The ¹H NMR spectrum of *IVa* (CD₃SOCD₃) showed the exocyclic methine proton as a doublet at δ 4.08 ppm with a rather large coupling constant (²*J*(H,P) = 24.5 Hz), which confirms the assigned structure *IV* and excludes the reverse addition product with a coupling constant in the range $\approx 10 - 13$ Hz. The six methyl groups attached to nitrogen gave one doublet at δ 2.58



SCHEME 2

ppm, $^3J(\text{H,P}) = 10.3$ Hz, i.e., the three dimethylamino groups are magnetically equivalent. The IR spectra of *IV* gave absorption bands at $\approx 2\,210$ (CN), $\approx 1\,610$ (C=C, thiophene) and at $1\,315$ and 860 cm^{-1} (P–N). On heating adducts *IV* above their melting points under reduced pressure, they regenerated the starting materials *I* and *III*. But, their refluxing in ethyl acetate for 3 h resulted in their rearrangement to give *V*, identified by melting points, mixed melting points and comparison of IR spectra.

On the other hand, structure of the isomeric by-products *V* is established by the elemental and spectral analyses (Tables I and II). The ^{31}P NMR shifts of *V* have, as expected, more positive shifts ($\delta \approx 63$ ppm) than *IV* as the electronegativity of P atom in *V* increased. ^1H NMR data of compounds *V* indicate that C atom α to P bears no H, since the methine proton appears as a doublet at $\delta \approx 4.6$ ($^3J(\text{H,P}) = 10$ Hz). Moreover, *V* showed an IR absorption band at $1\,385\text{ cm}^{-1}$ corresponding to C=P. Isolation of two stable forms, a dipolar ion with tetravalent phosphorus, and the other with pentacova-

TABLE I
Characteristic of compounds *IV* and *V*

Compound	M.p., °C (solvent)	Yield, %	Formula (M.w.)	Calculated/Found					M^+ m/z
				% C	% H	% N	% P	% S	
<i>IVa</i>	205 (CHCl ₃)	45	C ₁₄ H ₂₂ N ₅ OP (307.4)	54.71	7.22	22.79	10.07	–	307
				54.60	7.12	22.72	10.12		
<i>IVb</i>	178 (Me ₂ CO)	53	C ₂₀ H ₃₄ N ₅ OP (391.5)	61.36	8.75	17.89	7.91	–	391
				61.25	8.65	17.69	7.83		
<i>IVc</i>	165 (Me ₂ CO)	44	C ₁₄ H ₂₂ N ₅ PS (323.4)	51.99	6.86	21.66	9.58	9.91	323
				51.78	6.69	21.76	9.62	9.76	
<i>IVd</i>	140 (CHCl ₃)	48	C ₂₀ H ₃₄ N ₅ PS (407.6)	58.94	8.41	17.18	7.60	7.87	407
				58.86	8.33	17.20	7.54	7.78	
<i>Va</i>	245 (EtOAc)	28	C ₁₄ H ₂₂ N ₅ OP (307.4)	54.71	7.22	22.79	10.07	–	307
				54.65	7.15	22.71	10.14		
<i>Vb</i>	230 (EtOAc)	22	C ₂₀ H ₃₄ N ₅ OP (391.5)	61.36	8.75	17.89	7.91	–	391
				61.24	8.62	17.77	7.82		
<i>Vc</i>	192 (CHCl ₃)	23	C ₁₄ H ₂₂ N ₅ PS (323.4)	51.99	6.86	21.66	9.58	9.91	323
				51.82	6.81	21.55	9.62	9.82	
<i>Vd</i>	185 (Me ₂ CO)	18	C ₂₀ H ₃₄ N ₅ PS (407.6)	58.94	8.41	17.18	7.60	7.87	407
				58.76	8.32	17.22	7.52	7.76	

lent phosphorus, from a reaction of $(R_2N)_3P$ with α -diketones was previously reported^{6,7}.

Effort was devoted to optimize the yields of the products of the reaction of nitriles *I* with aminophosphine *IIIa*. Thus, the reaction of *I* and *IIIa* was carried out in several solvents of different polarity (benzene, acetonitrile and ethyl acetate) maintaining the general conditions as in the first experiment (Table III). From the data shown in Table III, it is obvious that nitriles *I* react with aminophosphine *IIIa* in low-boiling polar solvent to give preferentially the betaine species *IV* and diminish its conversion to

TABLE II
IR, 1H NMR and ^{31}P NMR data for compounds *IV* and *V*

Compound	IR ($\tilde{\nu}$, cm^{-1}) ^a			^{31}P NMR δ , ppm	1H NMR (δ , ppm) ^{b,c}			
	C \equiv N	N-P	N=P		CH ₃ N CH ₃ C	NCH ₂	HC-P	HC-CN
<i>IVa</i>	2 220	1 310, 860	–	38.64	2.58 d $^3J(H,P)$ 10.3	–	4.08 d $^2J(H,P)$ 24.5	–
<i>IVb</i>	2 210	1 305, 875	–	38.25	1.37 t $^3J(H,P)$ 10.0	3.37 q $J(H,H)$ 6.0	4.20 d $^2J(H,P)$ 24.0	–
<i>IVc</i>	2 220	1 310, 865	–	42.73	2.54 d $^3J(H,P)$ 10.5	–	4.02 d $^2J(H,P)$ 22.4	–
<i>IVd</i>	2 220	1 325, 875	–	42.84	1.35 t $^3J(H,P)$ 11.2	3.34 q $J(H,H)$ 6.2	4.31 d $^2J(H,P)$ 21.8	–
<i>Va</i>	2 215	–	1 385	64.20	2.47 d $^3J(H,P)$ 9.7	–	–	4.83 d $^3J(H,P)$ 9.7
<i>Vb</i>	2 210	–	1 380	64.28	1.31 t $^3J(H,P)$ 12.2	3.25 q $J(H,H)$ 6.2	–	4.6 d $^3J(H,P)$ 10.5
<i>Vc</i>	2 220	–	1 390	65.50	2.49 d $^3J(H,P)$ 9.5	–	–	4.52 d $^3J(H,P)$ 9.5
<i>Vd</i>	2 215	–	1 380	63.57	1.32 t $^3J(H,P)$ 10.2	3.24 q $J(H,H)$ 6.5	–	4.48 d $^3J(H,P)$ 10.2

^a IR spectra also showed bands around $1\ 610\ cm^{-1}$ (C=C, furan or thiophene); ^b coupling constant in Hz; ^c furan and thiophene, δ 6.4 – 7.8.

the more stable form *V*. On the other hand, it was demonstrated that the use of a higher-boiling solvent (even polar) leads to the predominance of the C=P form.

Exposure of *IV* or *V* to air or quenching the crude reaction products with water resulted in their conversion to *VI* (Scheme 2). Hexamethylphosphortriamide was also identified in solution, ^{31}P NMR $\delta = +24$ ppm. The structure assignment of *VI* is based on molecular weight determination and ^1H NMR spectrum (3.26 d, 2 H, $J(\text{H,H}) = 8$ (CH_2) and 3.91 t, 1 H, $J(\text{H,H}) = 8$ (CH)).

Moreover, *IVa* and/or *Va* could be converted into the stable phosphonium salt *VIIa* by anhydrous hydrogen chloride in methylene chloride solution. The elemental analysis showed that one mol HCl had combined with one mol *IVa* or *Va*. The ^{31}P NMR shift of *VIIa* (δ 52.5 ppm) is consistent with the fact⁴ that the ^{31}P NMR resonances of triamino-phosphine ylides occur, in contrast to triphenylphosphine ylides, at higher magnetic fields than the resonance of corresponding phosphonium betaines or phosphonium salts. ^1H NMR spectrum of *VIIa* is also in accordance with the assigned structure. It shows the exocyclic protons (2 H) as two doublets: CH α to P is centered at δ 4.2 ($^2J(\text{H,P}) = 23.5$ Hz), while CH β to P is centered at δ 4.55 ppm ($^3J(\text{H,P}) = 10.5$ Hz).

Furthermore, we have also investigated whether *V* would undergo reaction with benzaldehyde in the Wittig reaction⁸. Such a reaction would be expected to lead to the formation of hexamethylphosphortriamide and an alkene. Indeed, when a mixture of *Va* and benzaldehyde was heated in ethyl acetate for 8 h, ^{31}P NMR spectroscopy indicated the formation of P=O ($\delta = +24$ ppm) and the olefinic product *VIII* was isolated. Its structure assignment is based on mass, infrared and ^1H NMR data. Compound *VIII* had the molecular formula $\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}$ and $m/z = 234$ (M^+). Its IR spectrum showed a new band at $1\ 618\ \text{cm}^{-1}$ corresponding to C=C. Also, it had absorption bands at $2\ 230$ (CN) and $1\ 600$ (arom.) cm^{-1} . Its ^1H NMR spectrum (CDCl_3) had signals at δ 4.05 d, 1 H,

TABLE III
Yields of compounds *IV* and *V* in the reaction of nitriles *I* with tris(dimethylamino)phosphine (*IIIa*)

Compound	Solvent	Time, h	Yield, %	
			<i>IV</i>	<i>V</i>
<i>Ia</i>	Benzene	6	43	28
<i>Ia</i>	CH_3CN	10	65	10
<i>Ia</i>	EtOAc	5	–	75
<i>Ib</i>	Benzene	6	40	25
<i>Ib</i>	CH_3CN	10	60	12
<i>Ib</i>	EtOAc	5	–	78

$J(\text{H,H}) = 4$ (CHCN); 5.65 d, 1 H, $J(\text{H,H}) = 4$ (=CH-Ar); 6.2 – 8.15 m, 9 H (furan and arom.).

Summarizing, it seems clear that the relative stability of compounds with quintuply and quadruply bonded phosphorus, obtained from the reaction of trivalent phosphorus compounds, $(\text{RO})_3\text{P}$ or $(\text{R}_2\text{N})_3\text{P}$ with α,β -unsaturated nitriles may vary significantly with the structure of both reagents^{1,2,7-11}. Moreover, we showed that additions of triaminophosphines to activated double bond are readily accomplished whereby the products can be treated in a variety of ways (thermolysis, hydrolysis, acidolysis and Wittig reaction) which increases the synthetic use of the phosphorus reagents.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra ($\tilde{\nu}$ in cm^{-1}) were recorded in KBr pellets, using Perkin-Elmer Infracord Spectrophotometer Model 197 (Grating). The ^1H NMR spectra were measured in CDCl_3 on Varian Spectrometers at 90 MHz, using TMS as an internal reference; δ are given in ppm, J in Hz; ^{31}P NMR spectra were recorded with a Varian FT-80 Spectrometer (vs 85% H_3PO_4). The mass spectra were run at 70 eV on Kratos MS-50 equipment provided with a data system. Elemental analyses were carried out at the microanalysis laboratory of National Research Centre, Cairo. All the reactions were performed under nitrogen.

Reaction of α,β -Unsaturated Nitriles *Ia*, *Ib* with Triaminophosphines *IIIa*, *IIIb*. General Procedure

To a stirred suspension of nitrile *Ia* (ref.¹²) or *Ib* (ref.¹³) (0.01 mol) in dry benzene (30 ml) a solution of *IIIa* or *IIIb* (0.015 mol) in 25 ml of benzene was added at room temperature and the reaction mixture was refluxed for ≈ 6 h. Benzene was removed under reduced pressure and the residue was triturated with boiling methylene chloride. Crystallization of the residue from suitable solvents afforded products *V*. Evaporation of CH_2Cl_2 solution to dryness and crystallization of the residual substance from the proper solvent (see Table I) yielded compounds *IV*. For yields, melting points, and physical and analytical data, see Table I. The reactions in acetonitrile or ethyl acetate were carried out in the same way (Table III).

Thermal Treatment of *IVa*

Betaine *IVa* (0.2 g) was heated to 240 °C for one hour in a cold finger sublimator, under reduced pressure (657 Pa). The reaction vessel was left to cool and ethanol (3 ml) was added. The crystals which separated were recrystallized from ethanol to give nitrile *Ia* which was identified by melting point, mixed melting point and comparison of the IR spectra¹².

Conversion of *IVa* into *Va*

A solution of *IVa* (0.2 g) was refluxed in ethyl acetate (25 ml) for 3 h. The reaction mixture was evaporated to dryness and the residual substance was crystallized from chloroform to give *Va* (0.17 g, 86%), identified by melting point, mixed melting point, and comparison of the IR spectra.

Reaction of *IVa* or *Va* with Water

A solution containing *IVa* or *Va* (0.2 g) in benzene (4 ml) was added dropwise to water (20 ml) with vigorous stirring. Removal of the volatile components under reduced pressure (60 °C, 2 105 Pa) gave

an oil which was shown to contain only hexamethylphosphortriamide (^{31}P NMR $\delta = +24$ ppm) and *Vla*. The former was removed by distillation at $60\text{ }^\circ\text{C}/0.657\text{ Pa}$ whereby the latter remained; yield 59 mg (62.3%), m.p. $62 - 64\text{ }^\circ\text{C}$ (hexane). For $\text{C}_8\text{H}_6\text{N}_2\text{O}$ (146.1) calculated: 65.75% C, 4.12% H, 19.17% N; found: 65.55% C, 4.07% H, 19.03% N. IR spectrum (KBr): 2 225 (CN), 1 610 (C=C, furan). ^1H NMR spectrum (CDCl_3): 3.26 d, 2 H, $J(\text{H,H}) = 8$ (CH_2); 3.91 t, 1 H, $J(\text{H,H}) = 8$ (CH); 6.4 – 7.8 m, 3 H (furan). Mass spectrum, m/z : 146 (M^+ , 100%).

Reaction of *Va* with Hydrogen Chloride

A stirred suspension of *Va* in CH_2Cl_2 (20 ml) was cooled to $0 - 5\text{ }^\circ\text{C}$ and treated with anhydrous HCl gas to saturation. The red solution became yellow; after 15 min the solvent was removed at 2 368 Pa. The solid (224 mg, 90%) of the aminophosphonium salt *VIIa* was obtained, m.p. $183\text{ }^\circ\text{C}$ (ethanol). For $\text{C}_{14}\text{H}_{23}\text{ClN}_5\text{OP}$ (343.8) calculated: 48.90% C, 6.74% H, 10.31% Cl, 20.37% N, 9.01% P; found: 48.86% C, 6.35% H, 10.08% Cl, 20.25% N, 9.27% P. ^1H NMR spectrum (CDCl_3): 4.2 dd, 1 H $^2J(\text{H,P}) = 23.5$, $J(\text{H,H}) = 13.5$ (CH–P); 4.55 dd, 1 H, $^3J(\text{H,P}) = 10.5$, $J(\text{H,H}) = 13.5$ (C–CH); 6.4 – 7.8 m, 3 H (furan). ^{31}P NMR spectrum (CDCl_3): 52.5. Mass spectrum, m/z : 343 (M^+ , 55%).

Wittig Reaction of Compound *Va*

A solution of *Va* (0.2 g) in ethyl acetate (25 ml) was heated under reflux with benzaldehyde (2 ml) for 8 h. The precipitate formed on cooling was washed with cold benzene and then recrystallized from benzene to give *VIII* (100 mg, 67%), m.p. $176\text{ }^\circ\text{C}$. For $\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}$ (234.3) calculated: 76.91% C, 4.30% H, 11.96% N; found: 76.82% C, 4.18% H, 11.09% N. IR spectrum (KBr): 2 230 (CN), 1 618 (C=C), 1 600 (arom.). ^1H NMR spectrum (CDCl_3): 4.05 d, 1 H, $J(\text{H,H}) = 4$ (CHCN); 5.65 d, 1 H, $J(\text{H,H}) = 4$ (C=CH–Ph); 6.2 – 8.15 m, 9 H (furan and arom.). Mass spectrum, m/z : 234 (M^+ , 100%).

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