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REACTIONS OF CARBETHOXYALKYLIDENETRIPHENYLPHOSPHORANES WITH ARYL AZIDES

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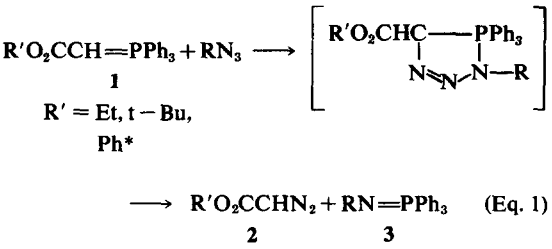
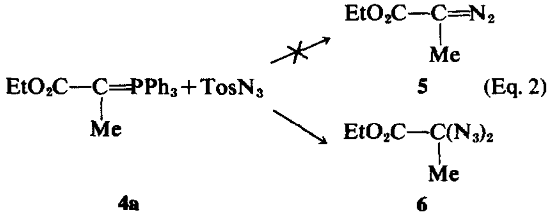
Abstract—The title reaction has been shown to give a complex mixture of products from which triazoles (**12** and **17**), maleates (**13**), fumarates (**14**), triphenylphosphine oxide (**15**), iminophosphoranes (**16**) and triazenes (**18**) have been isolated. Their formation is rationalized by two reaction paths, involving addition of the azide onto the C=C and C=P bonds of the ylide. Diazoesters **5** and **19**, which should result from C=P addition, were not isolated, but are believed to give rise to compounds **13**, **14** and **18**.

A number of recent papers are concerned with the reactions of azides with P-ylides stabilized by an ester function. Carboalkoxymethylenetriphenylphosphoranes (**1**) were found to react with a variety of azides, including tosyl azide,[1,2] acyl azides,[3] azidoformates,[4] P-azides,[3] and aryl azides,[3] to give diazoacetates (**2**) and iminophosphoranes (**3**) as the only isolated products. The reactions were shown to proceed by a concerted 1,3-dipolar cycloaddition of the azide onto the C=P bond of the ylide as shown in Eq. 1.[3]



Studies on the reactions of carbethoxyethylidenetriphenylphosphorane (**4a**) with azides brought about several conflicting reports in the literature. Harvey[1] described the reaction of **4a** with tosyl azide and reported the formation of ethyl 2-methyldiazoacetate (**5**) in 62% yield. This was later contested by two research groups[5] who attributed structure **6** (gem. bisazide) to the isolated product (Eq. 2).

A different pathway was observed for the reactions of **4a** with acyl azides and azidoformates. Concerted 1,3-dipolar addition of the azide onto the C=C bond of the ylide (enolate form) occurred in the first step of the reaction, followed by loss of $OPPh_3$ from the cyclic intermediate to give N-1 substituted 4-methyl-5-ethoxy-1,2,3-triazoles (**7**) (see Eq. 3).[3] The latter could only be isolated in a few cases, because they isomerized readily into the N-2 derivatives **8**, under the basic reaction conditions.[6] A recent paper by Zbiral and Stroh,[7] reporting the formation of vinyl azides **9** (*cis* and *trans*) from **4a** and acetyl azide by a Wittig-reaction, could not be repeated in our work.[6]



We also carried out the reactions of carbethoxybenzylidenetriphenylphosphorane (**4b**) with *p*-nitrobenzoyl azide and ethyl azidoformate, and isolated reaction products (**10**, **11** and $OPPh_3$) derived from the two modes of cycloaddition (see exp. section).

The diversity of reaction paths observed with **4a** and **4b** prompted us to investigate their reactions with aryl azides. Complex mixtures of products were obtained which were analyzed by NMR. The results are described in the present paper.

RESULTS AND DISCUSSION

When ylide **4a** was reacted with aryl azides under a variety of conditions, the NMR spectra of the crude mixtures indicated the presence of several products from which 1-aryl-4-methyl-5-ethoxy-1,2,3-triazole (**12**), diethyl α,β-dimethylmaleate (**13**) and diethyl α,β-dimethylfumarate (**14**) were unambiguously characterized. Their relative amounts were estimated by integration of the NMR Me sing-

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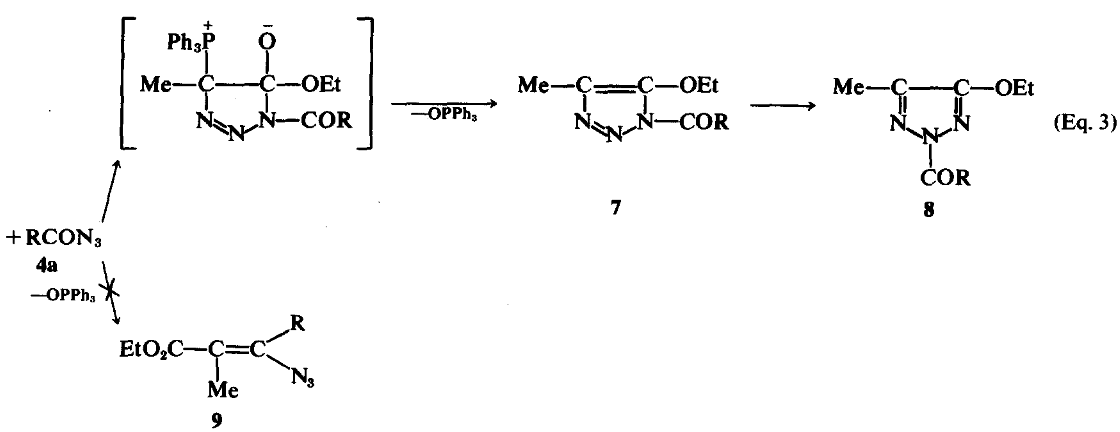
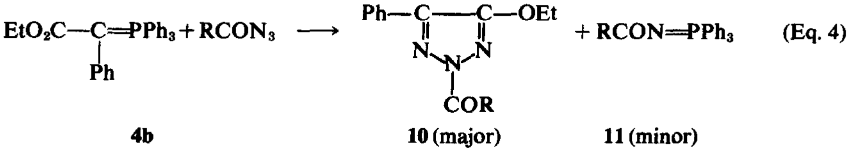
*The reaction of **1** (R' = Ph) with *p*-nitrobenzoyl azide was studied in this laboratory and furnished, after 4 hr at 20°, compounds **2** (R' = Ph, 100% by NMR) and **3** (R' = Ph, 34% isolated, m.p. 205–206·5°).





let absorptions. Besides compounds **12–14**, triphenylphosphine oxide (**15**) and aryliminotriphenylphosphorane (**16**) were also isolated in the pure state. The results are summarized in Table 1.

The less basic ylide **4b** was also treated with aryl azides and yielded 1-aryl-4-phenyl-5-ethoxy-1,2,3-triazole (**17**), 1-aryl-3-carbethoxybenzylidenetriazene (**18**), triphenylphosphine oxide (**15**) and aryliminotriphenylphosphorane (**16**). A rough estimation of the relative amounts of compounds **17** and **18** could be made from the NMR spectra of the crude reaction mixtures by integration of the CH_3—CH_2— triplet absorptions. The results are listed in Table 2.

Table 1. Product distribution in the reaction of **4a** with 1 equiv. of aryl azide

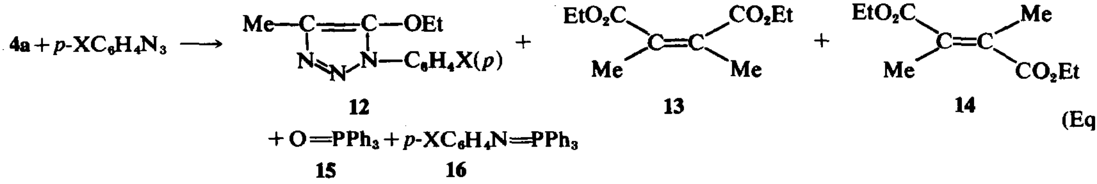
X	Reaction conditions (solvent, temp., time)	% **4a** unreacted *a*	% **12** *a*	% **12** *b*	% **13** *a*	% **13** *b*	% **14** *a*	% **14** *b*	% of other Me peaks at ~ τ8	% **15** *b*	% **16** *b*
NO_2	CH_2Cl_2, 20°, 3 hr	6	73	35					21[c]	30	29
	$CDCl_3$, 20°		80		6		12				
	C_6H_6, 75°	11	78		4		7				
	CCl_4, 75°	19	62		7		10				
Br	CCl_4, 80°, 1 hr	46	30	9	6		9		9	35	15
H	CCl_4, 80°, 8 hr	22	38	16	10	—[d]	24	—[d]	5	—[d]	—[d]

[a]Determined by NMR; [b]Isolated; [c]This value also includes compounds **13** and **14**; [d]A sample of pure product was isolated.

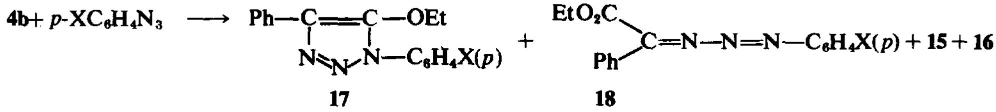
Table 2. Product distribution in the reaction of **4b** with aryl azides in benzene solution

X	Reaction conditions (ratio **4b** : azide, temp., time in days)	% **4b** unreacted *a*	% **4b** unreacted *b*	% **17** *a*	% **17** *b*	% **18** *a*	% **18** *b*	% of other Me peaks at ~ 8·5	% **15** *b*	% **16** *b*
NO_2	1 : 1, 20°, 20	46		11	1	43			3	
	1 : 1, 80°, 3		22				25			30
	1 : 2, 80°, 3			9	1	91	26			29
Br	1 : 1, 80°, 10	43	37	10		20		27		
	1 : 2, 80°, 45			20	—[c]	80				
H	1 : 1, 80°	39		17		44				

[a]Determined by NMR; [b]Isolated; [c]A sample of pure product was isolated.



(Eq. 5)



(Eq. 6)

The formation of compounds **13**, **14** and **18** deserves comment. The isolation of substantial amounts of iminophosphoranes (**16**) in the two reaction series indicates that cycloaddition of the azide not only occurred onto the C=C bond of the ylide (to give **12**, **15** and **17**) but also onto the C=P bond. The other expected reaction products, namely the diazoesters **5** and **19** respectively, have not been isolated nor detected by IR and NMR. It is, however, not surprising that the unstable ethyl 2-methyldiazoacetate (**5**) would have decomposed under the reaction conditions to give olefins **13** and **14**, presumably via an azine (Eq. 7).[8] Unlike **5**, diazocompound **19** apparently reacted with a second molecule of azide to yield triazene **18** (Eq. 8). This view is consistent with the observation that the yield of **18** strongly increased by increasing the initial azide concentration (see Table 2). The alternative possibility that the diazocompound **19** first would undergo decomposition to a carbene, followed by reaction with the azide is excluded by the fact that electrophilic carbenes are known to attack the α-nitrogen atom of azides, yielding imines instead of triazenes.[9]

A comparison of the yields of triazoles **12** and **17** in Tables 1 and 2 points to the conclusion that ylide **4a** allows more addition to occur on the C=C bond than does ylide **4b**. This trend was also observed for the reactions of **4a**,**b** with acyl azides and azidoformates (see Eq. 3 and 4) and can be attributed to an increased C=C bond character of ylide **4a**.[10] Triazole formation also seems to be favored over iminophosphorane formation by the use of electronegative substituted azides; i.e. $RCON_3 > p\text{-}NO_2C_6H_4N_3 > p\text{-}BrC_6H_4N_3 > C_6H_5N_3$.

EXPERIMENTAL

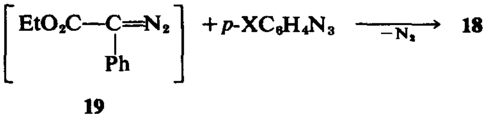
All m.p.'s were obtained on a Leitz apparatus and are uncorrected. IR spectra were taken on a Perkin-Elmer 521 spectrometer. NMR spectra were recorded with a Varian A-60 spectrometer using TMS as an internal reference. Carbethoxyethylidenetriphenylphosphorane (**4a**) was prepared as reported,[11] m.p. 160–162°; IR (KBr) 1625, (CH_2Cl_2) 1610 cm^{-1}.

Synthesis of carbethoxybenzylidenetriphenylphosphorane (**4b**). BuLi (0·08 mole) was added to a stirred suspension of benzyltriphenylphosphonium chloride (0·08 mole) in dry benzene (200 ml) under N_2. Then a benzene soln of ethyl chloroformate (0·04 mole in 50 ml) was added dropwise till decoloration of the red soln. The ppt was filtered and the mother liquor was evaporated to dryness. The residue was crystallized from EtOAc and furnished ylide **4b** in 47–55% yield, m.p. 142–143·5°; IR (KBr) 1595, (CH_2Cl_2) 1625 cm^{-1}.

Reactions of **4b** *with acyl azides.* When equimolar amounts (0·005 mole) of ylide **4b** and *p*-nitrobenzoyl azide were reacted in CH_2Cl_2 (2 ml) at room temp. for 1 month, the NMR spectrum indicated the presence of the corresponding triazole **10** and iminophosphorane **11** in a ratio of 85 : 15%. They were isolated in 54 and 3% respectively by fractional crystallization from ether.

Similarly, when **4b** (0·005 mole) was allowed to react with one equiv of ethyl azidoformate in benzene (10 ml) at 50° for 10 days, the corresponding triazole **10** and iminophosphorane **11** were present by NMR in a ratio of 70 : 30%, and further isolated in 36 and 0·3% respectively by fractional crystallization from ether. Several crops of pure triphenylphosphine oxide were also obtained in the two reactions.

$$2\left[\mathrm{EtO_2C{-}\underset{Me}{C}{=}N_2}\right]_{\mathbf{5}} \xrightarrow[-N_2]{} \left[\mathrm{EtO_2C{-}\underset{Me}{C}{=}N{-}N{=}\underset{Me}{C}{-}CO_2Et}\right] \xrightarrow[-N_2]{} \mathbf{13}+\mathbf{14} \qquad \text{(Eq. 7)}$$



$$\left[\mathrm{EtO_2C{-}\underset{Ph}{C}{=}N_2}\right]_{\mathbf{19}} + p\text{-}XC_6H_4N_3 \xrightarrow[-N_2]{} \mathbf{18} \qquad \text{(Eq. 8)}$$

Compound **10** ($R = p$-$NO_2C_6H_4$) had m.p. 149–150° (ether); IR (KBr) 1703, 1533, 1523, 1324, 1305, 1287, 908 and 846 cm^{-1}; NMR ($CDCl_3$) τ1·63 (*s*, 4H), 1·70–2·00 (m, 2H), 2·37–2·58 (m, 3H), 5·39 (q, 2H, J = 7 Hz) and 8·44 (t, 3H, J = 7 Hz). Found: C, 60·35; H, 4·10; N, 16·55; O, 18·90. Calc. for $C_{17}H_{14}N_4O_4$ (338) C, 60·35; H, 4·14; N, 16·57; O, 18·93.

2-Carbethoxy-4-phenyl-5-ethoxy-1,2,3-triazole (**10**, R = OEt) had m.p. 104·5–105° (ether); IR (KBr) 1769, 1558, 1541, 1490, 1482, 1418, 1343, 1332, 1311, 1298, 1291, 1215, 1037, 954 and 857 cm^{-1}; NMR ($CDCl_3$) τ1·79–2·07 (m, 2H), 2·45–2·70 (m, 3H), 5·42 (q, 2H, J = 7 Hz), 5·45 (q, 2H, J = 7 Hz), 8·49 (t, 3H, J = 7 Hz) and 8·51 (t, 3H, J = 7 Hz). Found: C, 59·80; H, 5·90; N, 16·35; O, 18·45. Calc. for $C_{13}H_{15}N_3O_3$ (261) C, 59·77; H, 5·75; N, 16·09; O, 18·39.

Reaction of **4a** *with* p-*nitrophenyl azide.* Equimolar amounts of ylide and azide were allowed to react under the conditions given in Table 1. The solvent was removed on a rotary evaporator and the residue fractionally crystallized from MeOH (to give **12** and **16**) and aqueous MeOH (to give **12** and/or **15**).

Compound **12** (X = NO_2) was recrystallized from MeOH, m.p. 124·5–126°; IR (KBr) 3084, 2983, 1603, 1582, 1518, 1489, 1334, 1320, 1264, 1095, 846 and 842 cm^{-1}; NMR ($CDCl_3$) τ1·52–2·05 (two d, 4H), 5·72 (q, 2H, J = 7 Hz), 7·59 (s, 3H) and 8·60 (t, 3H, J = 7 Hz). Found: C, 53·20; H, 4·80; N, 22·60; O, 19·35. Calc. for $C_{11}H_{12}N_4O_3$ (248) C, 53·22; H, 4·84; N, 22·58; O, 19·35.

Reaction of **4a** *with* p-*bromophenyl azide.* Ylide **4a** (0·02 mole) was reacted with 1 equiv of azide in CCl_4 (100 ml) at 80° for 1 hr. Removal of solvent and addition of ether furnished several crops, containing **4a**, **15** and/or **16**. The residue was distilled under reduced pressure and yielded **12** (X = Br), m.p. 57·5–58 (*n*-pentane); IR (KBr) 3000, 1600, 1581, 1506, 1350, 1276, 1006 and 827 cm^{-1}; NMR ($CDCl_3$) τ2·42 (s, 4H), 5·88 (q, 2H, J = 7 Hz), 7·65 (s, 3H) and 8·69 (t, 3H, J = 7 Hz). Found: C, 46·95; H, 4·15; Br, 27·60; N, 15·10; O, 5·80. Calc. for $C_{11}H_{12}BrN_3O$ (282): C, 46·81; H, 4·25; Br, 28·37; N, 14·89; O, 5·67.

Reaction of **4a** *with phenyl azide.* Equimolar amounts (0·06 mole) of **4a** and phenyl azide were allowed to react in CCl_4 (300 ml) at 80° to completion. Crystallization from ether yielded unreacted **4a**, in addition to **15** and/or **16**. The residue was fractionally distilled *in vacuo* and furnished five fractions containing **12**, **13**, **14**, **16**, aniline and an unknown compound in varying proportions.

The first three fractions were combined and subjected to column chromatography on silica gel ($CHCl_3$) to give compounds **13** (contaminated with aniline) and **14**, which were characterized by NMR ($CDCl_3$): **13**, τ5·77 (q, 4H, J = 7 Hz), 8·07 (s, 6H) and 8·72 (t, 6H, J = 7 Hz); **14**, τ5·73 (q, 4H, J = 7 Hz), 7·93 (s, 6H) and 8·69 (t, 6H, J = 7 Hz).

Compound **12** (X = H) was obtained pure (16%) from the 5th fraction by redistillation, and was characterized by comparison with reported data.[12]

Reaction of **4b** *with* p-*nitrophenyl azide.* Ylide **4b** and azide were allowed to react under the conditions given in Table 2. The solvent was removed under reduced pressure and the residue fractionally crystallized from ether to give **4b**, **17**, **18**, **15** and **16**.

Compound **17** (X = NO_2) was recrystallized from ether, m.p. 122–123·5°; IR (KBr) 1614, 1596, 1519, 1500, 1376, 1357, 1347, 1338, 977 and 852 cm^{-1}; NMR ($CDCl_3$) τ1·38–1·95 (two d, 4H), 1·87–2·12 (m, 2H), 2·33–2·40 (m, 3H), 5·92 (q, 2H, J = 7 Hz) and 8·70 (t, 3H, J = 7 Hz). Found: C, 61·97; H, 4·35; N, 17·85. Calc. for $C_{16}H_{14}N_4O_3$ (310): C, 61·93; H, 4·52; N, 18·06.

Compound **18** (X = NO_2) was recrystallized from ether, m.p. 134·5–136° (dec.); IR (KBr) 3105, 2977, 1732, 1586, 1566, 1499, 1441, 1339, 1326, 1223, 1198, 1044, 1026, 1014, 859 and 692 cm^{-1}; NMR ($CDCl_3$) τ1·47–2·31 (two d, 4H), 1·80–2·08 (m, 2H), 2·27–2·61 (m, 3H), 5·46 (q, 2H, J = 7 Hz) and 8·59 (t, 3H, J = 7 Hz). Found: C, 59·97; H, 4·18; N, 17·47; O, 19·55. Calc. for $C_{16}H_{14}N_4O_4$ (326): C, 59·89; H, 4·29; N, 17·18; O, 19·63.

Reaction of **4b** *with* p-*bromophenyl azide.* Ylide **4b** (0·01 mole) was reacted with azide in benzene soln (50 ml) to completion. The solvent was replaced by ether in order to isolate unreacted **4b**. The residue was chromatographed on silica gel and yielded a mixture of **17** and *p*-bromoaniline. Crystallization from *n*-pentane furnished pure **17** (X = Br), m.p. 96–97°; IR (KBr) 1591, 1494, 1378, 1013, 981, 829 and 699 cm^{-1}; NMR ($CDCl_3$) τ1·74–1·96 (m, 2H), 2·13 (s, 4H), 2·25–2·52 (m, 3H), 5·95 (q, 2H, J = 7 Hz) and 8·57 (t, 3H, J = 7 Hz).

The iminophosphoranes **16** isolated in this work were characterized by comparison with authentic samples prepared by the method of Staudinger.[13]

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