

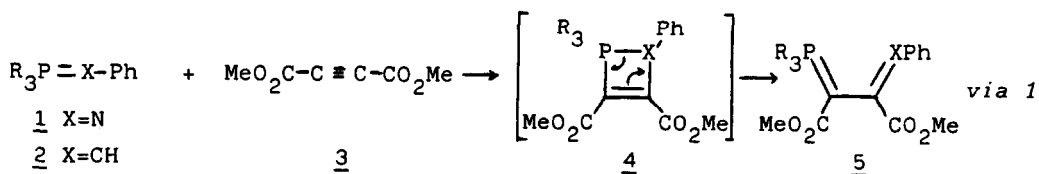
MECHANISTIC ASPECTS OF THE REACTION OF SOME PHOSPHONIUM
 YLIDES WITH ALKYL PROPYNOATES.

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SUMMARY: The reaction of alkoxycarbonylmethyltriphenylphosphonium ylides 1 with alkyl propynoates 3 in dichlormethane proceeds via [2+2] cycloaddition rather than Michael addition, to lead to stabilised phosphonium ylides.

In the course of our investigations into the reactivity of acetylenedicarboxylic acid esters 3 with phosphazenes 1 and the related iso-electronic phosphonium ylides 2, we have obtained stabilised phosphonium ylides 5, whose structures are consistent with those derived of a cyclic intermediate of the Wittig type 4, through a mechanism proposed for N-aryl phosphazenes 3 and triphenylphosphinalkylenes 4 in aprotic solvents long ago (via 1).

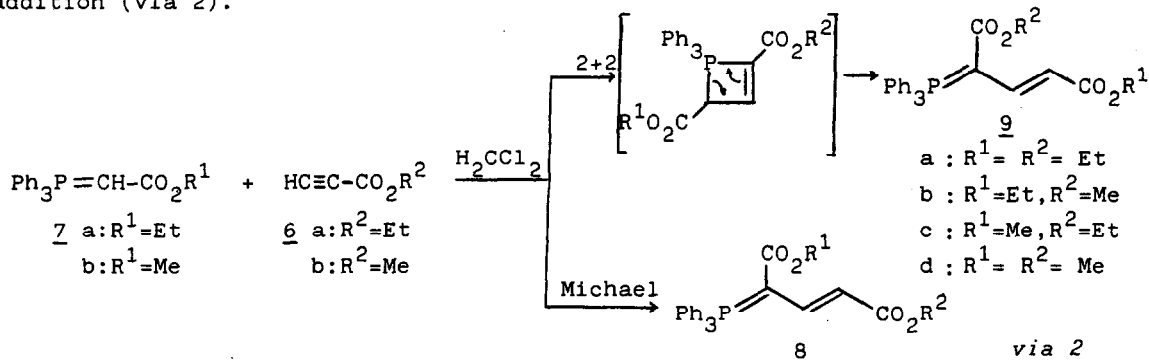


Moreover, alkyl propynoate 3 and dimethyl acetylenedicarboxylate (DMAD) show the same reactivity-type - cyclic intermediate- towards N-aryl trisamino phosphazenes 5 and often react similarly in cyclisation reactions 6 as well as in Michael additions.

The above mentioned results in the reaction of phosphonium ylides 2 and esters 3 prompted us to think that perhaps the acetylenic monoesters 3 could behave similarly, that is [2+2] cycloaddition followed by ring opening (via 1)

However, in previous communications⁸ it was reported that ethoxycarbonyl-methyltriphenylphosphonium ylide 7a adds to ethyl propynoate 6a in dichloromethane to afford the cross-conjugated phosphonium ylide 8a ($R^1 = R^2 = \text{Et}$) in a Michael addition fashion (via 2)

Here we wish to report that the reaction of compounds 7 with alkyl propynoate 6 progresses through a cyclic intermediate (via 1) rather than a Michael addition (via 2).



By the reported reaction⁸ (via 2), the elected phosphonium ylide and ester can not distinguish between the two processes (via 1 or 2), since both afford the same product ($R^1 = R^2 \rightarrow \underline{8} = \underline{9}$). However, different labelling in the ester groups of both the phosphonium ylides⁹ 7 and the propynoates 6 could permit the study of the products 8 and/or 9 ($R^1 \neq R^2$) through spectroscopic techniques. Such a study would reveal the product's structure and, hence, the mechanism.

NMR data show conclusively that the reaction between 7 and 6 proceeds via [2+2] cycloaddition rather than via simple Michael addition to yield stabilised phosphonium ylides 9. Thus, adduct 9b¹¹ ($R^1 = \text{Et}, R^2 = \text{Me}$), formed by reaction of 7a and 6b in dichloromethane¹², was characterised by NMR. Indeed, the ¹H NMR spectrum of 6b showed the absorption for the methoxy and ethoxy group at $\delta = 3.49(\text{OCH}_3)$ and $4.02(\text{OCH}_2)$, $1.14(\text{CH}_3)$ ppm respectively (see table) and the ¹³C NMR showed the methoxy carbon at $\delta = 49.7$ ppm as a well resolved doublet (⁴J_{PC} = 1.6 Hz.), while the methylene carbon of the ethoxycarbonyl group appeared as a narrow singlet at $\delta = 58.2$ ppm. Conversely, adduct 9c¹³ ($R^1 = \text{Me}, R^2 = \text{Et}$), obtained by treatment of 7b and 6a in dichloromethane¹², showed clearly different absorptions. Thus, the ¹H NMR presents the ethoxycarbonyl group with abnormally high-field shielding for the methyl group at $\delta = 0.86$ ppm due to diamagnetic coupling of the P-phenyl groups¹⁴. In ¹³C NMR its methoxy carbon appears at $\delta = 49.9$ ppm as a narrow singlet and its ethoxycarbonyl methylene signal at $\delta = 58.5$ ppm as a well resolved doublet, with ⁴J_{PC} = 1.2 Hz. Likewise, 9a and 9d are also consistent with this result (see Table).

Table of selected NMR spectroscopic data.

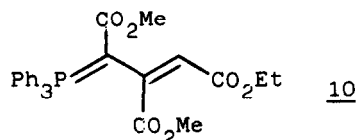
	$^1\text{H}(\text{DCCl}_3/\text{TMS})\delta(\text{ppm})^a$			$^{13}\text{C}(\text{DCCl}_3/\text{TMS})\delta(\text{ppm})^{a,b}$					$^{31}\text{P}(\text{DCCl}_3)\delta(\text{ppm})^{a,c}$
	OCH_2CH_3	OCH_2	OCH_3	OCH_2CH_3	OCH_2	OCH_3	C^{10}	C^{50}	
<u>9a</u>	1.14 0.85	4.02 3.95		14.3 14.6	58.2 58.3 (1.2) ^d		170.0 ^d (1.5) ^d	168.3 (15.2) ^e	24.4
<u>9b</u>	1.14	4.02	3.49	14.3	58.2	49.7 (1.6) ^d	169.8 ^d (1.5) ^d	168.5 (15.6) ^e	24.3
<u>9c</u>	0.86	3.94	3.55	14.3	58.5 ^d (1.2) ^d	49.9	170.3 ^d (1.5) ^d	167.7 (14.4) ^e	24.3
<u>9d</u>			3.48 3.56			49.6 (1.6) ^d 49.9	169.9 ^d (1.5) ^d	168.1 (14.9) ^e	24.2
<u>10</u>	1.14	4.03	3.31 3.35	14.2	59.3	49.2 (1.6) ^d 51.5	166.5	168.6 (15.6) ^e	18.0

a. Varian FT80 and Brücker WP 80 SY spectrometer; b. Numbering for 9 in ^{13}C -NMR

$\text{ROCO}-\overset{\overset{\text{C}^4}{\parallel}}{\text{C}^6}-\overset{\overset{2}{\text{C}}}{\text{CH}}-\overset{\overset{3}{\text{C}}}{\text{CH}}-\text{COOR}$; c. In DCCl_3 using H_3PO_4 85% as internal reference;
 PPh_3 d. $^4J_{\text{PC}}/\text{Hz}$.; e. $^2J_{\text{PC}}/\text{Hz}$.

Variable temperature ^1H NMR experiments confirmed completely the assignment of 9b and 9c. Thus, at 80 MHz. in hexadeuterioacetone, the methoxy singlet of 9b showed a broadening upon cooling which reached coalescence at 233K and similarly the ethoxy group of 9c also showed a coalescence at 233K showing that the methoxy and ethoxy are involved by the restricted rotation of the ylides 9b and 9c respectively, and are adjacent to them.

In the same way, when 7a was treated with DMAD in dichloromethane at room temperature, the stabilised phosphonium ylide 10¹⁵ was obtained. This compound is similar to that described by phosphoranes⁴ having hydrogen in the α position using aprotic solvents and whose formation was postulated by a cycloaddition (via 1).



These results suggest that the phosphonium ylides obtained have structure 9 and, therefore, that the reaction progresses preferably through cycloaddition. In this context, it was recently reported¹⁶ that phosphonium ylides having hydrogen in the α position react with methyl 2-perfluoroalkynoates in dichloromethane to produce acyclic precursors of polysubstituted benzenoids.

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9. Compounds 7a and 7b have similar basicity¹⁰
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11. Spectral data for 9b: δ_{H} (80MHz, DCCl_3) = 1.14 (t, 3H, OCH_2CH_3), 3.49 (s, 3H, OCH_3), 4.02 (q, 2H, OCH_2), 6.13 (dd, 1H, $^3J_{\text{HH}} = 14.7$ Hz., $^4J_{\text{PH}} = 0.5$ Hz., =CH), 7.04 (dd, 1H, $^3J_{\text{HH}} = 14.7$ Hz., $^3J_{\text{PH}} = 17.3$ Hz., =CH), 7.48-7.85 (m, 15H, ArH). δ_{C} (20MHz, DCCl_3) = 14.3 (OCH_2CH_3), 49.7 (d, $^4J_{\text{PC}} = 1.6$ Hz., OCH_3), 58.0 (d, $^1J_{\text{PC}} = 121.9$ Hz., C_4), 58.2 (OCH_2), 101.5 (d, $^3J_{\text{PC}} = 15.2$ Hz., C_2), 122.6-133.6 (Car), 144.7 (d, $^2J_{\text{PC}} = 15.6$ Hz., C_3), 168.5 (d, $^2J_{\text{PC}} = 15.6$ Hz., C_5), 169.8 (d, $^4J_{\text{PC}} = 1.5$ Hz., C_1) δ_{P} (32 MHz., DCCl_3) = 24.3 ppm.
12. Under the reaction conditions 10% of the 8b isomer was obtained, this being 18% in the case of 8c corresponding to 9c.
13. Spectral data for 9c: δ_{H} (80 MHz., DCCl_3) = 0.86 (t, 3H, OCH_2CH_3), 3.55 (s, 3H, OCH_3), 3.94 (q, 2H, OCH_2), 6.3 (dd, 1H, $^3J_{\text{HH}} = 14.7$ Hz., $^4J_{\text{PH}} = 0.5$ Hz., =CH), 7.05 (dd, 1H, $^3J_{\text{HH}} = 14.7$ Hz., $^3J_{\text{PH}} = 17.3$ Hz., =CH), 7.45-7.8 (m, 15 H, ArH). δ_{C} (20 MHz, DCCl_3) = 14.3 (OCH_2CH_3), 49.9 (OCH_3), 58.0 (d, $^1J_{\text{PC}} = 119.7$ Hz., C_4), 58.5 (d, $^4J_{\text{PC}} = 1.2$ Hz., OCH_2), 101.5 (d, $^3J_{\text{PC}} = 14.8$ Hz., C_2), 123.7-134.4 (Car), 146.0 (d, $^2J_{\text{PC}} = 15.0$ Hz., C_3), 167.7 (d, $^2J_{\text{PC}} = 14.4$ Hz., C_5), 170.74 (d, $^4J_{\text{PC}} = 1.5$ Hz., C_1). δ_{P} (32 MHz., DCCl_3) = 24.3 ppm.
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15. Spectral data for 10: δ_{H} (80 MHz, DCCl_3) = 1.14 (t, 3H, OCH_2CH_3), 3.31 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 4.03 (q, 2H, OCH_2), 6.15 (d, $^4J_{\text{PH}} = 0.6$ Hz., =CH), 7.15- 7.95 (m, 15H, ArH), δ_{C} (20 MHz, DCCl_3) = 14.2 (OCH_2CH_3), 47.4 (d, $^1J_{\text{PC}} = 125.1$ Hz., C_4), 49.2 (d, $^4J_{\text{PC}} = 1.5$ Hz., OCH_3), 51.1 (OCH_3), 59.3 (OCH_2), 121.2 (d, $^3J_{\text{PC}} = 10.1$ Hz., C_2) 123.6-133.5 (Car), 142.6 (d, $^2J_{\text{PC}} = 15.2$ Hz., C_3), 166.5 (C_1), 168.6 (d, $^2J_{\text{PC}} = 15.6$ Hz., C_5), 170.6 (d, $^3J_{\text{PC}} = 3.8$ Hz., CO). δ_{P} (32 MHz, DCCl_3) = 18.0 ppm.
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