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CONJUGATED AZOALKENES. PART IX. NEW 1-AMINO-4-TRIPHENYLPHOSPHORANYLIDENE-5-OXO-2-PYRROLINES OR α,ß-UNSATURATED HYDRAZONES BY REACTION OF AZOALKENES WITH CARBOALKOXYMETHYLENE TRIPHENYLPHOSPHORANE

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Abstract - New 1-amino-4-triphenylphosphoranylidene-5-oxo-2-pyrrolines or α,ß-unsaturated hydrazones have been obtained in good yield under different reaction conditions by Wittig-type reaction of some conjugated azoalkenes with carboalkoxymethylene triphenylphosphorane. The isolation and characterization of 1,4-adduct intermediate showed that the reaction mechanism implicates only 1,6-zwitterionic intermediate without cycloadduct production, as usually suggested for the Wittig reaction. The crystal structure of one of 1-amino-4-triphenylphosphoranylidene-5-oxo-pyrrolines obtained has been elucidated by X-ray diffraction study, showing the resonance between the neutral and 1,4-dipolar form.

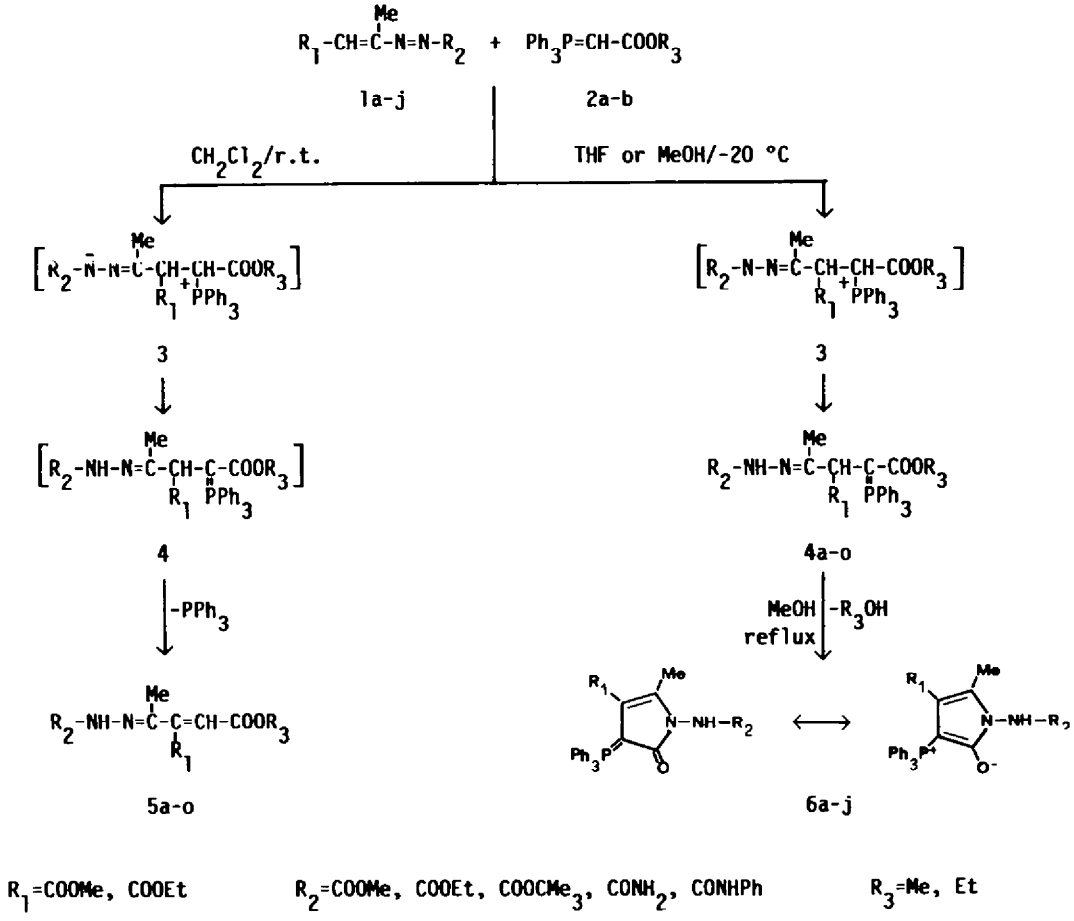
INTRODUCTION

In a previous paper some of us reported preliminary accounts on the little studied Wittig-type reaction of conjugated azoalkenes with phosphorus ylides.[1,2] In continuation of these investigations, we present here some interesting progress regarding the differences observed in the behaviour of the reaction between certain conjugated azoalkenes and carboalkoxymethylene triphenylphosphoranes, mainly depending on the reaction conditions. When the reaction was allowed to stand at room temperature in methylene chloride, α,ß-unsaturated hydrazones were directly formed, in accordance with our previous preliminary findings,[1] while new 1-amino-4-triphenylphosphoranylidene-5-oxo-2-pyrrolines were obtained in the case where the reaction was carried out in tetrahydrofuran or methanol at low

temperature to produce the 1,4-adduct intermediate, which was then treated with methanol under reflux. The isolation and characterization of this common intermediate, as well as the usefulness of its conversion into two different reaction products and, particularly, the unknown cyclic ketotriphenylphosphoranylidene aminopyrroline derivatives, are also discussed.

RESULTS AND DISCUSSION

Conjugated azoalkenes (**1a-j**) easily react with carboalkoxymethylene triphenylphosphorane (**2a-b**) at room temperature under magnetic stirring in methylene



Scheme

chloride to give directly the α,ß-unsaturated hydrazone derivatives (**5a-o**) in good yield and triphenylphosphine in almost quantitative yield (see Scheme). In this case the disappearance of the two reagents is concomitant with the gradual appearance of the two products (monitored by silica gel tlc).

Yields, and melting points of the α,ß-unsaturated hydrazone derivatives **5a-o** are listed in Table 1.

In such conditions, the reaction probably takes place by nucleophilic attack from the carbanion of the 1,2-dipolar form in resonance with carboalkoxymethylene triphenylphosphorane[2,3] ($Ph_3P{=}CH\text{-}COOR_3 \longleftrightarrow Ph_3P^{+}\text{-}CH^{-}\text{-}COOR_3$) (**2a-b**) to the azo-ene system of conjugated azoalkene (**1a-j**), in accordance with our previous investigations on analogous matter and that reported below.[4,5] This attack results in the 1,4-conjugate addition (Michael-type) of carboalkoxycarbonylmethylentriphenylphosphonium ylide to the azo-ene system (**4**), <u>via</u> the 1,6-zwitterionic intermediate (**3**) without further cycloaddition as usually suggested for the Wittig reaction.[2,6] The hydrazone derivative (**5a-o**) smoothly arises from this intermediate by the facile loss of triphenylphosphine.

Table 1 - Yield, and melting points of the α,ß-unsaturated hydrazone derivatives **5a-o**.

Hydrazone (5)	R_1	R_2	R_3	Yield[a] (%)	Mp[b] (°C)
5a	COOMe	COOMe	Me	73	171-173
5b	COOMe	COOMe	Et	82	168-171
5c	COOMe	COOEt	Me	90	125-127
5d	COOEt	COOMe	Me	80	126-128
5e	COOEt	COOMe	Et	78	135-137
5f	COOEt	COOEt	Me	88	117-119
5g	$COOCMe_3$	COOMe	Me	70	137-139
5h	$COOCMe_3$	COOMe	Et	80	128-131
5i	$COOCMe_3$	COOEt	Me	72	119-121
5j	$CONH_2$	COOMe	Me	73	174-176
5k	$CONH_2$	COOMe	Et	70	178-181
5l	$CONH_2$	COOEt	Me	78	181-183
5m	CONHPh	COOMe	Me	70	184-186
5n	CONHPh	COOEt	Me	76	150-152
5o	CONHPh	COOEt	Et	72	158-160

[a]Yield of pure isolated product. [b]Melting points are uncorrected.

The carbon-carbon double bond conjugated with the activating carbon-nitrogen double bond produced from this reaction represents a useful system in the transformation and the synthesis of organic molecules (i.e. by means of Michael-type and 1,4-conjugate additions, (4+2) and (3+2) cycloadditions etc.).[4,5,7] Furthermore, the relevant α-olefinated carbonyl compounds may be readily obtained from cleavage of the hydrazone derivatives by one of the numerous procedures reported in literature for this purpose.[8]

In the case where the reaction is carried out in tetrahydrofuran or methanol (see Experimental) at -20 °C, the 1,4-adduct intermediate (**4a-o**) generally precipitates rapidly as mixture of isomers,[9] exhibiting no further significant reaction in these conditions, and can be easily collected (otherwise the solvent can be removed by evaporation under reduced pressure). By heating the methanolic solution of this intermediate under reflux, 1-amino-4-triphenylphosphoranylidene-5-oxo-2-pyrroline derivative (**6a-j**) was obtained in good yield (see Scheme).[10]

Procedures (see Experimental), yields, and melting points of the 1,4-adducts **4a-o** are listed in Table 2. Yields, and melting points of the 1-amino-4-triphenylphosphoranylide-

Table 2 - Procedures, yields, and melting points of the 1,4-adducts **4a-o**.

1,4-Adduct (**4**)	Procedure	R_1	R_2	R_3	Yield[a] (%)	Mp[b] (°C)
4a	A	COOMe	COOMe	Me	95	107-109
4b	A	COOMe	COOMe	Et	90	140-142
4c	A	COOMe	COOEt	Me	88	119-121
4d	A	COOEt	COOMe	Me	92	115-118
4e	A	COOEt	COOMe	Et	95	104-106
4f	A	COOEt	COOEt	Me	90	101-103
4g	A	$COOCMe_3$	COOMe	Me	70	110-113
4h	A	$COOCMe_3$	COOMe	Et	68	108-110
4i	A	$COOCMe_3$	COOEt	Me	72	117-119
4j	B	$CONH_2$	COOMe	Me	70	179-181
4k	B	$CONH_2$	COOMe	Et	75	167-168
4l	B	$CONH_2$	COOEt	Me	72	137-139
4m	B	CONHPh	COOMe	Me	65	134-136
4n	B	CONHPh	COOEt	Me	68	128-130
4o	B	CONHPh	COOEt	Et	70	123-125

[a]Yield of pure isolated product. [b]Melting points are uncorrected.

Table 3 - Yield, and melting points of the pyrroline derivatives **6a-j**.

Pyrrolines (**6**)	R_1	R_2	Yield[a] (%)	Mp[b] (°C)
6a	COOMe	COOMe	75	198-201
6b	COOMe	COOEt	72	208-211
6c	COOEt	COOMe	78	214-215
6d	COOEt	COOEt	70	219-221
6e	$COOCMe_3$	COOMe	74	192-195
6f	$COOCMe_3$	COOEt	76	144-147
6g	$CONH_2$	COOMe	67	222-225
6h	$CONH_2$	COOEt	65	232-235
6i	CONHPh	COOMe	60	210-212
6j	CONHPh	COOEt	68	130-132

[a]Yield of pure isolated product. [b]Melting points are uncorrected.

ne-5-oxo-2-pyrroline derivatives **6a-j** are listed in Table 3.

Under these latter conditions, the type of attack and behaviour of the addition of carboalkoxymethylene triphenylphosphorane (**2a-b**) to the azo-ene system of conjugated azoalkene (**1a-j**) remains the same as originally described[1] to give the common 1,4-adduct intermediate (**4a-o**), which can be isolated from the reaction in tetrahydrofuran or methanol at low temperature and, upon dissolution in methylene chloride, affords the α,ß-unsaturated hydrazones. When the same intermediate is treated with methanol under reflux, it prefers to undergo an internal nucleophilic attack by the nitrogen of the C=N group on the carbon atom of the ester group resulting in ring closure, in a similar way to our previous findings on the formation of 1-aminopyrrole derivatives.[3,4] Indeed, it is noteworthy that in several previous investigations only ketones led to a similar ring closure, while esters, as well as amides, failed to react.[4,5,11,12] This represents the first case in which we have observed such internal cyclization process ascribable to an ester. Kinetic investigations are in progress in order to clarify the different reaction pathways observed.

Moreover, the latter procedure is interesting, as 1-amino-4-triphenylphosphoranylidene-5-oxo-2-pyrrolines represent a class of unknown organic compounds.[13]

As there were some difficulties in the molecular structure determination of the products **6** by usual spectral technologies, including chemical shift assignments by high field ^1H and ^{13}C NMR spectroscopy and, in order to unambigously confirm the cyclic structures, an X-ray diffraction study of the compound **6c** was carried out. The

stereochemistry of the molecule is shown in Figure and is in good agreement with our previous finding on this matter.[5,11b,14]

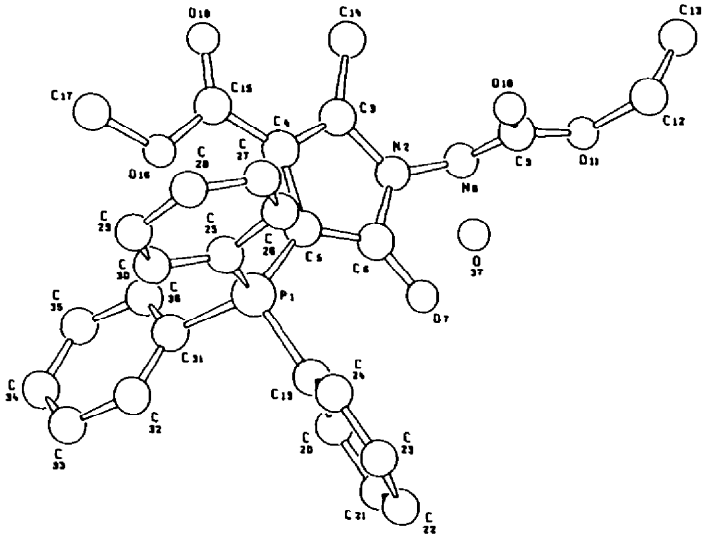


Figure. X-Ray crystal structure of the compound **6c** with the atom numbering system used in the crystallographic analysis.

It is noteworthy that the bond distances between all the atoms of the ring are very similar ranging from 1.367 Å for C(3)-C(4) to 1.464 Å for C(4)-C(5). This is in accordance with the pyrrolic[5,11b,14a,14b] rather than the pyrrolinic structure.[5,14c] Moreover, the sum of the bond angles around the heteroatom N(2) is close to 360°, confirming sp^2 hybridization for this atom. Finally, the sum of the bond angles involving the atoms of the heterocycle is close to 540°, indicating very small deviations from the plane for the atoms of the five-membered ring. All these facts suggest that for this compound the 1,4-dipolar canonical form, analogous to zwitterionic phosphorus betaine intermediate in the Wittig reaction,[2] is an important contributing structure to the resonance hybrid (see Scheme). Diffractometric data and MNDO calculations exclude any chemical bond between P(1) and O(7) atoms, analogous to the four-membered cyclic phosphorane intermediate of the Wittig reaction.[2] Failure to form the four membered ring is principally ascribable to the double bond between C(5) and C(6) atoms that results in a distance between P(1) and O(7) atoms of nearly 3.3 Å.

EXPERIMENTAL

Alkoxycarbonylazoalkenes (R_2=COOMe, COOEt, $COOMe_3$),[15] and aminocarbonylazoalkenes (R_2=$CONH_2$,

CONHPh)[16] (**1a–j**) were synthesized as previously reported and in accordance with the respective references. Carbomethoxy- and carboethoxymethylene triphenylphosphorane (**2a–b**) were commercial material (Aldrich) and were used without further purification. The characterization of triphenylphosphine was made in comparison with authentical commercial specimen (Farmitalia-Carlo Erba). Mps were determined in capillary tubes with a Büchi apparatus, and are uncorrected. The products often decompose at melting point. IR spectra were obtained in Nujol mull with a Perkin-Elmer 298 spectrophotometer. ^{1}H NMR spectra at 60 MHz were recorded on a Varian EM-360L spectrometer in DMSO-d_6 or $CDCl_3$. Chemical shifts (δ) are reported in ppm downfield from internal TMS. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; D_2O ex, D_2O exchange. Merck precoated silica gel $60F_{254}$ plates (0.25 mm) were employed for analytical thin-layer chromatography (TLC), Merck silica gel PF_{254} plates (2.0 mm) for preparative TLC, and silica gel Kieselgel 60 (0.063–0.200 mm) for column chromatography. All the compounds prepared showed a satisfactory elemental analysis (C±0.35, H±0.30, N±0.30).

General procedure for the synthesis of the α,β-unsaturated hydrazone derivatives 5a–o. To a stirred solution of carboalkoxymethylene triphenylphosphorane (**2**) (1 mmol), dissolved in methylene chloride (1.5 ml), was added dropwise a solution of conjugated azoalkene (**1**) (1 mmol) dissolved in methylene chloride (1.5 ml), and the mixture was stirred (1 h) at room temperature until the azoalkene completely disappeared (monitored by silica gel TLC). The crude product was purified by chromatography on a silica gel column (elution with methylene chloride and methylene chloride-ethyl acetate mixtures). The product **5** was further purified by crystallization from ethyl acetate-petroleum ether (b.p. 40–60 °C).

5a: IR 3280, 1755, 1725, 1635, 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.92 (3H, s), 3.65 (3H, s), 3.70 (3H, s), 3.82 (3H, s), 5.95 (1H, s), 8.38 (1H, br s, D_2O ex) ppm.

5b: IR 3285, 1760, 1720, 1625, 870 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.30 (3H, t, J=7.0 Hz), 1.97 (3H, s), 3.80 (3H, s), 3.88 (3H, s), 4.22 (2H, q, J=7.0 Hz), 6.08 (1H, s), 8.57 (1H, br s, D_2O ex) ppm.

5c: IR 3240, 3160, 1745, 1720, 1695, 1630, 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.32 (3H, t, J=7.0 Hz), 1.88 (3H, s), 3.58 (3H, s), 3.62 (3H, s), 4.20 (2H, q, J=7.0 Hz), 5.80 (1H, s), 8.47 (1H, br s, D_2O ex) ppm.

5d: IR 3235, 3140, 1750, 1725, 1695, 1635, 880 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.30 (3H, t, J=7.0 Hz), 1.98 (3H, s), 3.77 (3H, s), 3.90 (3H, s), 4.20 (2H, q, J=7.0 Hz), 6.10 (1H, s), 8.88 (1H, br s, D_2O ex) ppm.

5e: IR 3335, 3080, 1750, 1725, 1705, 1615, 890 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.33 (6H, t, J=7.0 Hz), 1.98 (3H, s), 3.88 (3H, s), 4.19 (2H, q, J=7.0 Hz), 4.22 (2H, q, J=7.0 Hz), 6.08 (1H, s), 8.75 (1H, br s, D_2O ex) ppm.

5f: IR 3230, 3140, 1740, 1720, 1695, 1635, 865 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.27 (3H, t, J=7.0 Hz), 1.35 (3H, t, J=7.0 Hz), 1.90 (3H, s), 3.63 (3H, s), 4.08 (2H, q, J=7.0 Hz), 4.25 (2H, q, J=7.0 Hz), 5.90 (1H, s), 8.57 (1H, br s, D_2O ex) ppm.

5g: IR 3255, 3170, 1750, 1735, 1715, 1630, 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.48 (9H, s), 1.92 (3H, s), 3.62 (3H, s), 3.75 (3H, s), 5.88 (1H, s), 8.75 (1H, br s, D_2O ex) ppm.

5h: IR 3330, 3240, 3130, 3100, 1745, 1715, 1695, 1630, 890 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.28 (3H, t, J=7.0 Hz), 1.38 (9H, s), 1.96 (3H, s), 3.87 (3H, s), 4.20 (2H, q, J=7.0 Hz), 6.05 (1H, s), 8.50 (1H, br s, D_2O ex) ppm.

5i: IR 3225, 3150, 1745, 1725, 1695, 1630, 870 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.50 (9H s), 1.52 (3H,

t, J=7.0 Hz), 1.88 (3H, s), 3.48 (3H, s), 4.25 (2H, q, J=7.0 Hz), 5.92 (1H, s), 8.05 (1H, br s, D_2O ex) ppm.

5j: IR 3490, 3345, 3190, 3090, 1730, 1715, 1695, 1630, 860 cm^{-1}; ^1H NMR (DMSO-d_6) 1.98 (3H, s), 3.60 (3H, s), 3.67 (3H, s), 6.01 (2H, br s, D_2O ex), 6.03 (1H, s), 9.75 (1H, br s, D_2O ex) ppm.

5k: IR 3470, 3330, 3240, 3100, 1745, 1715, 1695, 1625, 860 cm^{-1}; ^1H NMR (DMSO-d_6) 1.25 (3H, t, J=7.0 Hz), 2.05 (3H, s), 3.77 (3H, s), 4.14 (2H, q, J=7.0 Hz), 6.19 (2H, br s, D_2O ex) 6.20 (1H, s), 10.00 (1H, br s, D_2O ex) ppm.

5l: IR 3490, 3350, 3190, 3090, 1730, 1715, 1695, 1630, 860 cm^{-1}; ^1H NMR (DMSO-d_6) 1.20 (3H, t, J=7.0 Hz), 1.95 (3H, s), 3.58 (3H, s), 4.12 (2H, q, J=7.0 Hz), 6.08 (2H, br s, D_2O ex), 6.09 (1H, s), 9.72 (1H, br s, D_2O ex) ppm.

5m: IR 3375, 3220, 3100, 1725, 1685, 1680, 1620, 875 cm^{-1}; ^1H NMR ($CDCl_3$) 2.08 (3H, s), 3.67 (3H, s), 3.87 (3H, s), 5.67 (1H, s), 6.80-7.43 (5H, m), 7.87 (1H, br s, D_2O ex), 10.01 (1H, br s, D_2O ex) ppm.

5n: IR 3370, 3200, 3090, 1745, 1720, 1695, 1630, 860 cm^{-1}; ^1H NMR ($CDCl_3$) 1.40 (3H, t, J=7.0 Hz), 2.18 (3H, s), 3.78 (3H, s), 4.43 (2H, q, J=7.0 Hz), 6.13 (1H, s), 6.87-7.67 (5H, m), 8.12 (1H, br s, D_2O ex), 10.52 (1H, br s, D_2O ex) ppm.

5o: IR 3390, 3360, 3200, 3100, 1740, 1715, 1685, 1625, 865 cm^{-1}; ^1H NMR ($CDCl_3$) 1.33 (3H, t, J=7.0 Hz), 1.42 (3H, t, J=7.0 Hz), 2.18 (3H, s), 4.22 (2H, q, J=7.0 Hz), 4.35 (2H, q, J=7.0 Hz), 6.12 (1H, s), 6,93-7.40 (5H, m), 8.07 (1H, br s, D_2O ex), 10.25 (1H, br s, D_2O ex) ppm.

General procedures for the synthesis of the 1,4-adducts 4a-o. **Procedure A.** To a stirred solution of carboalkoxymethylene triphenylphosphorane (**2a-b**) (1 mmol), dissolved in tetrahydrofuran (4 ml), at -20 °C was added a solution of the conjugated azoalkene (**1a-f**) (1 mmol) dissolved in tetrahydrofuran (2 ml). **Procedure B.** To a stirred solution of carboalkoxymethylene triphenylphosphorane (**2a-b**) (1 mmol), dissolved in methanol (1.5 ml), at -20 °C was added a solution of the conjugated azoalkene (**1g-j**) (1 mmol) dissolved in methanol (4 ml). In both cases, the azoalkene disappearance (monitored by silica gel TLC) led to the incipient formation of a precipitate. The reaction was allowed to stand until the complete precipitation (1-20 h) of the product, which was collected under reduced pressure and washed with cyclohexane. In the case of **4j-l**, the product precipitated after evaporating the methanol to half volume under reduced pressure, followed by cooling in refrigerator. The crude product **4** shows satisfactory purity and, frequently, further attempts of purification by crystallization may induce some degradation.

4a: IR 3460, 3425, 3210, 1740, 1725, 1440, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) 2.08 and 2.20 (3H, 2s), 3.10 and 3.58 (3H, 2s), 3.41 and 3.53 (1H, 2s), 3.65 and 3.70 (3H, 2s), 3.78 (3H, s), 7.27-7.90 (16H, m) ppm.

4b: IR 3460, 3210, 1735, 1700, 1440, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) 0.55 (3H, t, J=7.0 Hz), 2.05 and 2.17 (3H, 2s), 3.33 and 3.43 (1H, 2s), 3.47-4.63 (8H, m), 7.20-8.13 (16H, m) ppm.

4c: IR 3440, 3390, 3260, 3170, 1730, 1710, 1440, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) 1.25 (3H, t, J=7.0 Hz), 2.07 and 2.17 (3H, 2s), 3.07 and 3.53 (3H, 2s), 3.60 and 3.67 (1H, 2s), 3.77 (3H, s), 7.27-7.97 (16H, m) ppm.

4d: IR 3460, 3390, 3255, 3160, 1710, 1740, 1440, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) 1.30 (3H, t, J=7.0 Hz), 2.05 and 2.17 (3H, 2s), 3.08 and 3.55 (3H, 2s), 3.42 and 3.50 (1H, 2s), 3.65 and 3.70 (3H, 2s), 4.25 (2H, q, J=7.0 Hz), 7.15-7.93 (16H, m) ppm.

4e: IR 3420, 3250, 3150, 1735, 1705, 1440, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) 0.45 (3H, t, J=7.0 Hz), 1.28 (3H, t, J=7.0 Hz), 2.03 and 2.13 (3H, 2s), 3.30 and 3.55 (1H, 2s), 3.77-4.47 (4H, m), 7.33-8.00 (16H, m) ppm.

4f: IR 3450, 3380, 3250, 1735, 1705, 1435, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) 1.25 (3H, t, J=7.0 Hz), 1.28 (3H, T, J=7.0 Hz), 2.07 and 2.16 (3H, 2s), 3.07 and 3.54 (3H, 2s), 3.40 and 3.50 (1H, 2s), 4.05-4.35 (4H, m), 7.17-7.97 (16H, m) ppm.

4g: IR 3460, 3250, 3150, 1740, 1700, 1440, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) 1.50 (9H, s), 2.02 and 2.10 (3H, 2s), 3.07 and 3.53 (3H, 2s), 3.33 and 3.50 (1H, 2s), 3.67 (3H, s), 7.20-7.97 (16H, m) ppm.

4h: IR 3450, 3240, 3150, 1735, 1730, 1700, 1440, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) 0.42 (3H, t, J=7.0 Hz), 1.50 (9H, s), 2.05 and 2.13 (3H, 2s), 3.37 and 3.57 (1H, 2s), 3.60-4.00 (5H, m), 7.23-7.93 (16H, m) ppm.

4i: IR 3450, 3250, 3150, 1735, 1705, 1440, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) 1.25 (3H, t, J=7.0 Hz), 1.50 (9H, s), 2.05 and 2.13 (3H, 2s), 3.03 and 3.53 (3H, 2s), 3.33 and 3.45 (1H, 2s), 4.14 (2H, q, J=7.0 Hz), 7.23-7.93 (16H, m) ppm.

4j: IR 3470, 3390, 3290, 3230, 3150, 1725, 1690, 1435, 1100 cm^{-1}; ^1H NMR (DMSO-d_6) 1.92 and 2.00 (3H, 2s), 2.92 and 3.10 (3H, 2s), 3.36 (1H, m), 3.56 and 3.73 (3H, 2s), 5.67 (2H, br s, D_2O ex), 7.20-7.80 (15H, m), 8.70 and 8.80 (1H, 2 br s, D_2O ex) ppm.

4k: IR 3470, 3380, 3290, 3230, 3150, 1720, 1685, 1435, 1100 cm^{-1}; ^1H NMR (DMSO-d_6) 0.37 (3H, t, J= 7.0 Hz), 1.97 and 2.04 (3H, 2s), 3.30-3.83 (6H, m), 5.77 (2H, br s, D_2O ex), 7.30-7.90 (15H, m), 8.83 and 8.95 (1H, 2 br s, D_2O ex) ppm.

4l: IR 3470, 3380, 3300, 3240, 3150, 1735, 1680, 1435, 1100 cm^{-1}; ^1H NMR (DMSO-d_6) 1.25 (3H, t, J=7.0 Hz), 1.96 and 2.04 (3H, 2s), 3.17-3.57 (4H, m), 4.05 (2H, q, J=7.0 Hz), 5.73 (2H, br s, D_2O ex), 7.40-7.83 (15H, m), 8.80 and 8.90 (1H, 2 br s, D_2O ex) ppm.

4m: IR 3460, 3380, 3200, 3090, 1740, 1705, 1690, 1440, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) 2.10 and 2.22 (3H, 2s), 3.10 and 3.57 (3H, 2s), 3.42 and 3.50 (1H, 2s), 3.73 (3H, s), 6.90-7.96 (21H, m), 8.70 (1H, br s, D_2O ex) ppm.

4n: IR 3450, 3390, 3200, 3090, 1735, 1705, 1690, 1440, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) 1.32 (3H, t, J=7.0 Hz), 2.10 and 2.20 (3H, 2s), 3.08 and 3.55 (3H, 2s), 3.30 and 3.38 (1H, 2s), 4.20 (2H, q, J=7.0 Hz), 6.75-7.95 (21H, m), 8.37 (1H, br s, D_2O ex) ppm.

4o: IR 3660, 3450, 3380, 3200, 3110, 1730, 1690, 1450, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) 0.42 (3H, t, J=7.0 Hz), 1.30 (3H, t, J=7.0 Hz), 2.13 and 2.22 (3H, 2s), 3.08 and 3.24 (1H, 2s), 3.67 (2H, q, J=7.0 Hz), 4.20 (2H, q, J=7.0 Hz), 6.87-7.95 (21H, m), 8.38 (1H, br s, D_2O ex) ppm.

General procedure for the synthesis of the 1-amino-4-triphenylphosphoranylidene-5-oxo-2-pyrroline derivatives 6a-j. A solution of 1,4-adduct (**4a-o**) (1 mmol), dissolved in methanol (5 ml), was heated under reflux for 8 h. The mixture was cooled at -20 °C for 4 h. The product **6** crystalized was collected under reduced pressure and washed with cyclohexane. The product **6** shows satisfactory purity and can be purified further by crystalization with methanol.

6a: IR 3610, 3550, 3130, 1795, 1745, 1705, 1085 cm^{-1}; ^1H NMR ($CDCl_3$) 2.32 (3H, s), 2.97 (3H, s), 3.51 (3H, s), 7.00-7.70 (15H, m), 7.90 (1H, br s, D_2O ex) ppm.

6b: IR 3640, 3445, 3140, 1755, 1740, 1680, 1435, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) 0.47 (3H, t, J=7.0 Hz), 2.30 (3H, s), 3.47 (2H, q, J=7.0 Hz), 3.48 (3H, s), 7.00-7.70 (15H, m), 8.37 (1H,

br s, D_2O ex) ppm.

6c: IR 3600, 3520, 3110, 1740, 1725, 1685, 1440, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) 1.15 (3H, t, J=7.0 Hz), 2.33 (3H, s), 2.95 (3H, s), 3.85 (2H, q, J=7.0 Hz), 7.00-7.77 (16H, m) ppm.

6d: IR 3460, 3140, 3110, 1740, 1680, 1440, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) 0.70 (3H, t, J=7.0 Hz), 1.20 (3H, t, J=7.0 Hz), 2.42 (3H, s), 3.56 (2H, q, J=7.0 Hz), 4.12 (2H, q, J=7.0 Hz), 7.25-7.92 (16H, m) ppm.

6e: IR 3420, 3150, 1740, 1720, 1675, 1440, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) 1.47 (9H, s), 2.37 (3H, s), 3.03 (3H, s), 7.00-8.00 (16H, m) ppm.

6f: IR 3440, 3135, 3070, 1730, 1680, 1435, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) 0.64 (3H, t, J=7.0 Hz), 1.40 (9H, s), 2.33 (3H, s), 3.54 (2H, q, J=7.0 Hz), 6.84-8.10 (16H, m) ppm.

6g: IR 3450, 3380, 3200, 1715, 1670, 1650, 1645, 1105 cm^{-1}; ^1H NMR (DMSO-d_6) 2.25 (3H, s), 2.87 (3H, s), 5.92 (2H, br s, D_2O ex), 7.27-7.87 (15H, m), 8.25 (1H, br s, D_2O ex) ppm.

6h: IR 3490, 3400, 3200, 1715, 1680, 1640, 1435, 1105 cm^{-1}; ^1H NMR (DMSO-d_6) 0.54 (3H, t, J=7.0 Hz), 2.30 (3H, s), 3.42 (2H, q, J=7.0 Hz), 5.82 (2H, br s, D_2O ex), 7.13-7.83 (15H, m), 8.30 (1H, br s, D_2O ex) ppm.

6i: IR 3680, 3490, 3300, 3200, 1720, 1710, 1675, 1440, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) 2.43 (3H, s), 3.07 (3H, s), 6.40-6.93 (5H, m), 7.25-8.00 (15H, m), 8.67 (1H, br s, D_2O ex), 8.75 (1H, br s, D_2O ex) ppm.

6j: IR 3650, 3280, 3200, 3140, 1685, 1680, 1440, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) 0.70 (3H, t, J=7.0 Hz), 2.48 (3H, s), 3.59 (2H, q, J=7.0 Hz), 6.40-6.97 (5H, m), 7.17-7.97 (15H, m), 8.63 (1H, br s, D_2O ex), 8.75 (1H, br s, D_2O ex) ppm.

X-Ray analysis of compound 6c. Intensity data were collected by a CAD4 diffractometer using $\omega/2\vartheta$ scan, ϑ range $2.5° \leq \vartheta \leq 25°$, Mok radiation λ=0.7107 Å. (Mok α)=1.09 cm^{-1}, F000=548.0. The unit-cell parameters were determined by a least square refinement on diffractometer angles for 25 automatically centered reflections $8° \leq \vartheta \leq 14°$. Of 3822 independent reflections, 1779 having I 2.5 σ(I) were considered unobserved.

Crystal data of compound 6c. $C_{28}H_{27}N_2O_5P.H_2O$, MW= 520.49, triclinic, space group P1, a=9.566(3) Å, b=11852 (4) Å, c=13.538 54) Å, V=1314 $Å^3$, Z=2, D_c=1.31 g cm^{-3}.

Structure determination and refinement. The structure was solved by direct methods and refined anisotropically by full-matrix least-squares analysis using the SHELX program packages.[17] Methyl and phenyl (1.395 Å) groups were refined as rigid bodies. The hydrogen atoms were calculated geometrically when they were not found in the Fourier difference syntheses but not refined. The final R was 0.060. Final difference Fourier map excursions 0.56 to -0.33 $Å^{-3}$. The atomic co-ordinates for this work are available on request from the director of the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this paper.

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