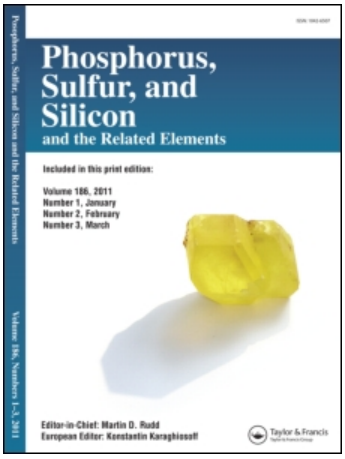

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An Efficient One-Pot Synthesis and Temperature Dependence of NMR Spectra of Nitrogen-Containing Phosphorus Ylides

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AN EFFICIENT ONE-POT SYNTHESIS AND TEMPERATURE DEPENDENCE OF NMR SPECTRA OF NITROGEN-CONTAINING PHOSPHORUS YLIDES

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The addition of triphenylphosphine to dialkyl acetylenedicarboxylates in the presence of trifluoroacetamide, a NH acid, leads to stable crystalline phosphorus ylides in exellent yields. These stable ylides exist as a mixture of two geometrical isomers as a result of restricted rotation around the carbon-carbon partial double bond, resulting from conjugation of the ylide moiety with the adjacent group.

Keywords: Acetylenic ester; trifluoroacetamide; triphenylphosphine; stabilized ylides

In recent years there has been increasing interest in the synthesis of organophosphorus compounds, i.e., those bearing a carbon atom bound directly to a phosphorus atom. This interest has resulted from the recognition of the value of such compounds for a variety of industrial, biological, and chemical synthetic uses.[1–8] As a result a large number of methods have apeared describing novel synthesis of organophos-phorus compounds. Phosphorus ylides are reactive intermediates, which take part in valuable reactions in the synthesis of organic products.

We present an efficient synthetic route to nitrogen-containing phosphorusylides **3** using of triphenylphosphine, dialkyl acetylenedicarboxylates **1**, and an electron-deficient amide,such as trifluoroacetamide **2** in good yields (Scheme 1).

RESULTS AND DISCUSSION

On the basis of the chemistry of trivalent phosphorus nucleophile[6,7] it is reasonable to assume that ylide **3** results from initial addition of

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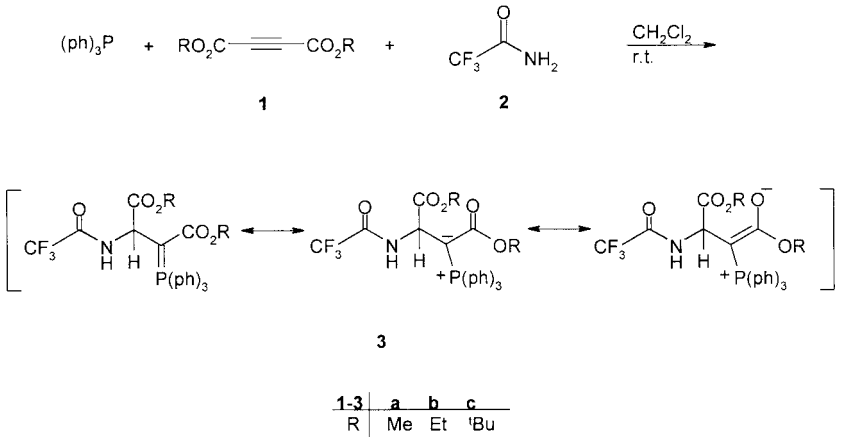


SCHEME 1

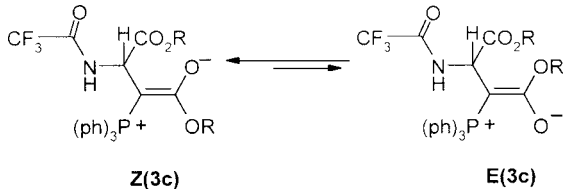
triphenylphosphine to the acetylenic ester and subsequent protonation of the reactive 1:1 adduct by trifluoroacetamide. Then the positively charged ion is attacked by the anion of NH-acids to form the stable ylide **3**.

The structures of compounds **3a–c** were deduced from their ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR and IR data.

The NMR spectra of ylides **3a–c** are consistent with the presence of two isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation about the partial double bond in (*E*)-3 and (*Z*)-3 geometrical isomers and is slow on the NMR time scale at ambient temperature.

The 500 MHz ^{1}H NMR spectrum of **3c** at room temperature (25°C) exhibited two pairs of sharp singlets at 0.94 and 1.47 ppm and 1.43 and 1.45 ppm with an intensity of 3.7:1 for tertiarybutoxy groups of (*E*) and (*Z*) isomers. Increasing the temperature results in coalescence of the tertiarybutoxy resonances. At 60°C a fairly broad singlet was observed for the $OCMe_3$ group. This observation is attributed to the temperature dependent equilibrium between the geometric (rotational) isomers. From the spectrum it can be visualized that the dominant (major) isomer does have the most shielded tertiary butoxy group because of the anisotropic effects to phenyl groups. The methine proton appeared as a pair of symmetrical doublet of doublets with unequal intensities at 4.18 ppm ($^{3}J_{PH}$ 15.6 and $^{3}J_{HH}$ 8.3 Hz) and 4.25 ppm ($^{3}J_{PH}$ 14.8 and $^{3}J_{HH}$ 8.5 Hz) at 25°C. Raising the temperature also led to the gradual collapse of these peaks to a doublet of doublets. The NH proton observed as a pair of broad doublets of unequal intensities at 8.23 ppm ($^{3}J_{HH}$ 8.3 Hz)

and 7.92 ppm ($^3J_{HH}$ 8.5 Hz). The aromatic protons appear as a multiplet at 7.4–7.8 ppm. The ^{31}P $\{^1H\}$ NMR spectrum of **3c** exhibited two singlet peaks at δ 22 and 22.2 ppm and the ^{19}F NMR spectrum of **3c** also displayed two singlet peaks at −76.53 and −76.95 ppm in agreement with the presence of the two isomers *E* and *Z*. The ^{13}C NMR spectra of **3c** exhibited two doublets of unequal intensities at 42.69 ppm ($^1J_{PC}$ 130.8 Hz P=C) for the *Z*-isomer and 44.1 ppm ($^1J_{PC}$ 137.7 Hz P=C) for the *E*-isomer and two doublets at 53.44 ppm ($^3J_{PC}$ 18.3 Hz) and 52.23 ppm ($^3J_{PC}$ 18.8 Hz) for *Z* and *E*-isomers respectively.



SCHEME 2

Although the presence of the ^{31}P and ^{19}F NMR nuclei, complicates both ^1H and ^{13}C NMR spectra of **3c**, it helps in assignment of the signals by long-range coupling with ^1H and ^{13}C nuclei.

The ^1H, ^{13}C, ^{31}P, and ^{19}F NMR spectra **3a** and **3b** are similar to those of **3c**.

EXPERIMENTAL

Dialkyl acetylenecarboxylates, triphenylphosphin, and trifluoroacetamide were obtained from Fluka (Buchs, Switzerland) and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^1H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500, 125.8, 202.5 and 470.6 MHz respectively. IR spectra were recorded on a Shimadzu IR-470 spectrometer.

*General Procedure for Synthesis of dialkyl 2-[(2,2,2-trifluoroacetyl)-amino]-3-(1,1,1-triphenyl-γ^5-phosphanilidene) succinate (**3a–c**):* To a magnetically stirred solution of trifluoroacetamide (0.42 g, 2 mmol) and triphenylphosphine (2 mmol) in CH_2Cl_2 (8 ml) was added, dropwise a mixture of dialkyl acetylenedicarboxylates (2 mmol) in CH_2Cl_2(10 ml) at −10°C over 10 min. The mixture was allowed to warm to room temperature and stirred for 24 h. The solvent was removed under reduced pressure and the residue was purified by silica gel (Merck silica gel

230–400 mesh) column chromatography using hexane:ethyl acetate (1:4) as eluent.

(**3a**): white crystal m.p. 150–151°C, yield 90%; IR (KBr) (υ_{max}, cm^{-1}): 1630, 1735 and 1745 (C=O), 3450 (NH); ^1H NMR (500 MHz, $CDCl_3$) (**3a**-*z*, 73%): δ_H 3.16 and 3.72 (6H, 2s, 2OCH), 4.70 (1H, dd, $^3J_{PH}$ 14.4 Hz and $^3J_{HH}$ 8.7 Hz, CH) 7.50–7.75 (15H, m, arom), 8.34 (1H, d, $^3J_{HH}$ 8.7 Hz, NH); (**3a**-*E*, 27%): δ_H 3.58 and 3.72 (6H, 2s, 2OCH), 4.56 (1H, dd, $^3J_{PH}$ 14.4 Hz and $^3J_{HH}$ 8.7 Hz, CH) 7.50–7.75 (15H, m, arom), 8.34 (1H, d, $^3J_{HH}$ 8.7 Hz, NH); ^{13}C NMR (125.77 MHz, $CDCl_3$) (**3a**-*z*): δ_C 42.65 (d, $^1J_{PC}$ 130.1 Hz, P=C), 49.3 and 52.66 ($2OCH_3$), 52.73 (d, $^2J_{PC}$ 18.04 Hz, P=C–CH), 116.07 (q, $^1J_{FC}$ 287.9 Hz, CF_3), 125.6 (d, $^1J_{PC}$ 92.7 Hz, C_{ipso}), 128.8 (d, $^2J_{PC}$ 12.4 Hz, C_{ortho}), 132.4 (d, $^4J_{PC}$ 2.4 Hz, C_{para}), 133.75 (d, $^3J_{PC}$ 9.8 Hz, C_{meta}), 155.91 (q, $^2J_{FC}$ 36.85 Hz, C=O amide), 170.50 (d, $^2J_{PC}$ 12.83 Hz, C=O ester), 172.28 (d, $^3J_{PC}$ 6.92 Hz, C=O ester); (**3a**-*E*): δ_C 43.34 (d, $^1J_{PC}$ 138.2 Hz, P=C), 50.21 and 52.6 ($2OCH_3$), 52.08 (d, $^2J_{PC}$ 17.46 Hz, P=C–CH), 119.07 (q, $^1J_{FC}$ 287.9 Hz, CF_3), 125.6 (d, $^1J_{PC}$ 93.4 Hz, C_{ipso}), 128.8 (d, $^2J_{PC}$ 12.4 Hz, C_{ortho}), 132.4 (d, $^4J_{PC}$ 2.4 Hz, C_{para}), 133.75 (d, $^3J_{PC}$ 9.8 Hz, C_{meta}), 155.91 (q, $^2J_{FC}$ 36.85 Hz, C=O amide), 169.82 (d, $^2J_{PC}$ 12.8 Hz, C=O ester), 172.28 (d, $^3J_{PC}$ 6.92 Hz, C=O ester); ^{31}P {^1H} NMR (202.46 MHz) (**3a**-*Z*): δ_P 22.03 (Ph_3P=C); (**3a**-*E*): δ_P 22.23 (Ph_3P=C).

(**3b**): white crystal m.p 158–160°C, yield 85%; IR (KBr) (υ_{max}, cm^{-1}): 1628, 1730 and 1740 (C=O), 3447 (NH); ^1H NMR (500 MHz, $CDCl_3$) (**3b**-*z*, 74.5%): δ_H 0.46 and 1.23 (6H, 2t, $^3J_{HH}$ 7.1 Hz, $2CH_3$) 3.71 and 4.18 (4H, 2q, $^3J_{HH}$ 7.1 Hz, $2OCH_2$), 4.45 (1H, dd, $^3J_{PH}$ 14.49 Hz and $^3J_{HH}$ 8.61 Hz, CH) 7.50–7.75 (15H, m, arom), 8.34 (1H, d, $^3J_{HH}$ 8.7 Hz, NH); (**3b**-*E*, 25.5%): δ_H 1.19 and 1.27 (6H, 2t, $^3J_{HH}$ 7.1 Hz, $2CH_3$), 4.12–4.23 (4H, m, $2OCH_2$), 4.45 (1H, dd, $^3J_{PH}$ 14.49 Hz and $^3J_{HH}$ 8.61 Hz, CH) 7.50–7.75 (15H, m, arom), 8.36 (1H, d, $^3J_{HH}$ 8.6 Hz, NH); ^{13}C NMR (125.77 MHz, $CDCl_3$) (**3b**-*Z*): δ_C 13.88 and 14.11 ($2CH_3$), 42.39(d, $^1J_{PC}$ 130.1 Hz, P=C), 52.71 (d, $^2J_{PC}$ 18.11 Hz, P=C–CH), 52.88 and 61.59 ($2OCH_2$), 116.09 (q, $^1J_{FC}$ 287.5 Hz, CF_3), 126.29 (d, $^1J_{PC}$ 92.82 Hz, C_{ipso}), 128.72 (d, $^2J_{PC}$ 12.2 Hz, C_{ortho}), 132.33 (d, $^4J_{PC}$ 2.4 Hz, C_{para}), 133.84 (d, $^3J_{PC}$ 9.94 Hz, C_{meta}), 155.92 (q, $^2J_{FC}$ 36.85 Hz, C=O amide), 170.04 (d, $^2J_{PC}$ 12.71 Hz, C=O ester), 171.7 (d, $^3J_{PC}$ 6.92 Hz, C=O ester); (**3a**-*E*): δ_C 14.18 and 14.92 ($2CH_3$), 43.38 (d, $^1J_{PC}$ 138.0 Hz, P=C), 52.10 (d, $^2J_{PC}$ 17.67 Hz, P=C–*C*H), 58.35 and 61.59 ($2OCH_2$), 116.1 (q, $^1J_{FC}$ 287.5 Hz, CF_3), 125.68 (d, $^1J_{PC}$ 92.69 Hz, C_{ipso}), 128.81 (d, $^2J_{PC}$ 12.2 Hz, C_{ortho}), 132.33 (d, $^4J_{PC}$ 2.4 Hz, C_{para}), 133.84 (d, $^3J_{PC}$ 9.9 Hz, C_{meta}), 155.51 (q, $^2J_{FC}$ 36.85 Hz, C=O amide), 169.39 and 169.54 (2C=O, ester), ^{31}P {^1H} NMR (202.46 MHz) (**3b**-*Z*): δ_P 22.01 (Ph_3P=C); (**3b**-*E*): δ_P 23.12(Ph_3P=C).

(**3c**): white crystal m.p. 155–157°C, yield 87%; IR (KBr) (ν_{max}, cm^{-1}): 1630, 1726 and 1738 (C=O), 3417 (NH); ^1H NMR (500 MHz, $CDCl_3$) (**3e**-*Z*, 73%): δ_H 0.94 and 1.47 (18H, 2s, $2CMe_3$) 4.25 (^1H, dd, $^3J_{PH}$ 14.8 Hz and $^3J_{HH}$ 8.46 Hz, CH) 7.45–7.73 (15H, m, arom), 8.28 (1H, d, $^3J_{HH}$ 8.4 Hz, NH); (**3c**-*E*, 27%): δ_H 1.43 and 1.45 (18H, 2s, $2CMe_3$), 4.18 (^1H, dd, $^3J_{PH}$ 15.59 Hz and $^3J_{HH}$ 8.28 Hz, CH) 7.50–7.75 (15H, m, arom), 7.92 (^1H, d, $^3J_{HH}$ 8.2 Hz, NH); ^{13}C NMR (125.77 MHz, $CDCl_3$) (**3c**-*Z*): δ_C 28.09 and 28.27 ($2CMe_3$), 42.69 (d, $^1J_{PC}$ 130.8 Hz, P=C), 53.44 (d, $^2J_{PC}$ 18.3 Hz, P=C–CH), 77.69 and 81.39 ($2OCMe_3$), 116.17 (q, $^1J_{FC}$ 288.14 Hz, CF_3), 126.82 (d, $^1J_{PC}$ 92.57 Hz, C_{ipso}), 128.53 (d, $^2J_{PC}$ 12.2 Hz, C_{ortho}), 132.17 (d, $^4J_{PC}$ 2.6 Hz, C_{para}), 133.92 (d, $^3J_{PC}$ 9.81 Hz, C_{meta}), 155.67 (q, $^2J_{FC}$ 36.47 Hz, C=O amide), 169.5 (d, $^2J_{PC}$ 11.9 Hz, C=O ester), 170.79 (d, $^3J_{PC}$ 7.8 Hz, C=O ester); (**3e**-*E*): δ_C 28.27 and 28.88 ($2CMe_3$), 44.10 (d, $^1J_{PC}$ 137.6 Hz, P=C), 52.23 (d, $^1J_{PC}$ 18.8 Hz, P=C–CH), 77.85 and 81.52 ($2OCMe_3$), 116.17 (q, $^1J_{FC}$ 288.14 Hz, CF_3), 128.62 (d, $^1J_{PC}$ 92.44 Hz, C_{ipso}), 128.62 (d, $^2J_{PC}$ 12.2 Hz, C_{ortho}), 132.17 (C_{para}), 133.92 (d, $^1J_{PC}$ 9.8 Hz, C_{meta}), 155.17 (q, $^2J_{FC}$ 36.34 Hz, C=O amide), 169.58 (C=O ester), 170.59 (d, $^3J_{PC}$ 7.6 Hz, C=O ester), $^{31}P\{^1H\}$ NMR (202.46 MHz) (**3e**-*Z*): δ_P 22.01 (Ph_3P=C): (**3b**-*E*): δ_P 23.12 Ph_3P=C).

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