SHORT PAPER

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A facile one-pot synthesis and temperature dependence of NMR spectra of stable heterocyclic phosphorus ylids

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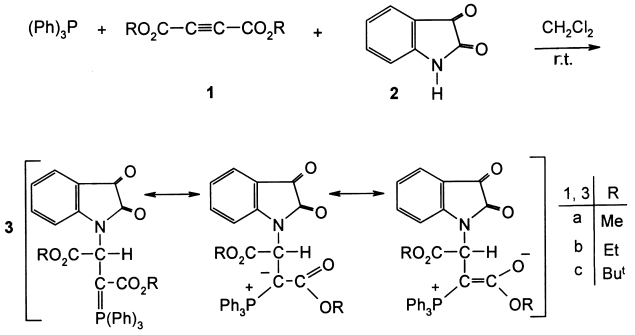
The addition of dialkyl acetylenedicarboxylates to isatin, a strong NH acid, in the presence of triphenylphosphine leads to stable crystalline phosphorus ylids in excellent yields and one of the three synthesised compounds **(3a)** exists as a mixture of two rotational isomers on the basis of variable temperature nmr spectroscopy.

Keywords: acetylenic esters, triphenylphosphine, NH-acids, organophosphorus compounds

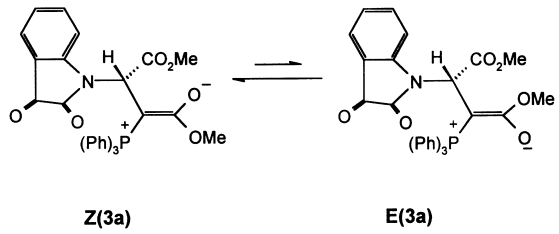
In recent years there has been increasing interest in the synthesis of organophosphorus compounds, *i.e.* those bearing a carbon atom bound directly to a phosphorus atom. This interest has resulted from the recognition of the value of such compounds for a variety of industrial and chemical synthetic uses. Phosphorus ylids are reactive systems, which take part in many reactions of value in the synthesis of organic products.[1-8]

We have already described the synthesis of a group of these systems using triphenylphosphine, dialkyl acetylenedicarboxylates and a carbon acid.[5] With the purpose of preparation of phosphorus ylids using NH acids, we performed the reaction of isatin (**2**) with triphenylphosphine and dialkyl acetylenedicarboxylates (**1**).



On the basis of the well established chemistry of trivalent phosphorus nucleophiles it is reasonable to assume that phosphorus ylid **3** resulted from the initial addition of triphenylphosphine to the acetylenic ester and a subsequent protonation of the 1:1 adduct by NH acid, isatin. Then the positively charged ion is attacked by the anion of the amide to form phosphorane **3**.

The structures of compounds **3a–c** were deduced from their elemental analysis and their ^{1}H, ^{13}C and ^{31}P NMR and IR spectral data. Of special interest are the strong carbonyl absorption bands at 1609–1734 cm^{-1} for all the compounds. We have examined the proton NMR spectrum of **3a** in $CDCl_3$ at various temperatures. The 500 MHz ^{1}H NMR spectrum of **3a** at room temperature (25°C) exhibited two pairs of sharp singlets at δ 3.09, 3.78 ppm and δ 3.67, 3.76 ppm with an intensity ratio of 4:1. As the temperature was increased, these collapsed to two singlets at δ 3.09 and 3.78 ppm. This observation is attributed to the temperature dependent equilibrium between the geometric (rotational) isomers, *E* and *Z* **(3a)**, *i.e.* the result of restricted rotation. The coalescence temperature was about 65°C. At 75°C only two singlets are observed for the methoxy groups and no further dynamic NMR effect was observed up to 90°C. From the spectrum it is clear that the dominant (major) isomer, in fact, does have the most shielded methoxy group, because of the anisotropic effects of phenyl groups. The methine proton appeared as a pair of symmetrical doublets of unequal intensity centred at δ 5.30 and 5.23 ppm ($^3J_{PH}$ 16.2 and 17.9 Hz, respectively), at 25°C. Raising the temperature also led to the gradual collapse of this quartet to a doublet. This collapse is attributed to the same temperature dependent equilibrium between *E* and *Z* **(3a)** isomers. The ^{31}P NMR spectrum of **3a** also exhibited two single peaks at δ 22.62 and 19.92 ppm in agreement with the presence of two isomers, *E* and *Z*.



The aromatic protons appear as a multiplet at δ 7.08–7.84 ppm. The ^{13}C NMR spectrum of **3a** displayed 18 distinct resonances (eight of which are doublets) for each isomer (**3a**–*E*/*Z*). Althogh the presence of the ^{31}P nucleus complicates both the ^{1}H and ^{13}C NMR spectra of **3a**, it helps in assignment of the signals by long-range coupling with ^{1}H and ^{13}C nuclei.

The ^{1}H and ^{13}C NMR spectra of **3b** and **3c** show that only one isomer *(E)* exists in each case, probably, because of steric hindrance between the bulky ester groups and the triphenylphosphine group, rotation about C=C bond is hindered, and only the *E* isomer exists. The ^{1}H and ^{13}C NMR spectra of these isomers are similar to those of **3a**, except for the ester groups, which exhibited characteristic resonance with appropriate chemical shifts.

In conclusion, the procedure that we have described here, may be an acceptable method for the preparation of phosphoranes with variable functionalities. Functionalized heterocyclic phosphorus ylids **3a-c** may be considered as potentially useful synthetic intermediates.

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Experimental

Dialkyl acetylenedicarboxylates, triphenylphosphine and isatin were obtained from Fluka (Buchs, Switzerland) and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. ^{1}H, ^{13}C and ^{31}P NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500, 125.8 and 202.5 MHz, respectively. IR spectra were recorded on a Shimadzu IR-470 spectrometer.

General procedure for synthesis of dialkyl 2-(N-isatin)-3- (triphenylphosphoranilidene)butanedioate(**3**)**:** To a magnetically stirred solution of triphenylphosphine (0.524 g, 2 mmol) and isatin (0.294 g, 2 mmol) in CH_2Cl_2 (6 ml) was added, dropwise, a mixture of dialkyl acetylenedicarboxylate (2 mmol) in CH_2Cl_2 (4 ml) at –10°C over 10 min. The reaction mixture was then allowed to stand at room temperature and stirred for 24 hr.

The solvent was removed under reduced pressure and the viscous residue was purified by silica gel (Merck silica gel 60, 230–400 mesh) column chromatography using ethyl acetate-hexane. The solvent was removed under reduced pressure and the product was obtained from recrystallisation from ether–pentane.

(3a): Yellow solid, m.p. 110°C, yield 75%; IR (KBr) (ν_{max}, cm^{-1}): 1733, 1635 and 1609 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$)(**3a**–*Z*): δ_H 3.09 and 3.78 (6 H, 2 s, 2 OCH3), 5.30 (1 H, d, $^{3}J_{PH}$ 16.21 Hz, CH), 7.08–7.84 (19 H, m, arom); (**3a**–*E*): δ_H 3.67 and 3.76 (6 H, 2 s, 2 OCH_3), 5.23 (1 H, d, $^{3}J_{PH}$ 17.95 Hz, CH), 7.08–7.84 (19 H, m, arom); ^{13}C NMR (125.77 MHz, $CDCl_3$) (**3a**–*Z*:) δ_C 38.02 (d, $^{1}J_{PC}$ 122.66 Hz, P=C), 49.43 and 52.80 (2 OMe), 54.79 (d, $^{2}J_{PC}$ 15.48 Hz, P=C-*CH*), 115.51, 123.21, 124.34, 138.48 (4 CH, isatin), 118.03 (N-C=C), 125.67 (d, $^{1}J_{PC}$ 91.69 Hz, C_{ipso}), 129.07 (d, $^{3}J_{PC}$ 12.20 Hz, C_{meta}), 132.52 (d, $^{4}J_{PC}$ 2.39 Hz, C_{para}), 133.38 (d, $^{2}J_{PC}$ 9.81 Hz, C_{ortho}), 150.45 (N-*C*=C), 156.77(C=O, amide), 169.65 (d, $^{2}J_{PC}$ 12.20 Hz, C=O ester), 170.73 (d, $^{3}J_{PC}$ 14.97, C=O ester), 184.46 (C=O, ketone); (**3a**–*E*): δ_C 38.72 (d, $^{1}J_{PC}$ 132.06 Hz, P=C), 50.62 and 52.59 (2 OMe), 54.97 (d, $^{2}J_{PC}$ 15.58 Hz, P=C-*CH*), 115.4, 123.12, 124.63 and 38.1 (4 CH, isatin), 118.31 (N-C=*C*), 125.04 (d, $^{1}J_{PC}$ 91.81 Hz, C_{ipso}), 128.54 (d, $^{3}J_{PC}$ 12.07 Hz, C_{meta}), 132.14 (d, $^{4}J_{PC}$ 2.5 Hz, Cpara), 133.46 (d, $^{2}J_{PC}$ 11.70 Hz, C_{ortho}), 150.77 (N-C=C), 157.05 (C=O, amide), 169.85 (d, $^{2}J_{PC}$ 12.6 Hz, C=O ester), 170.73 (d, $^{3}J_{PC}$ 14.96, C=O ester), 184.14 (C=O, ketone); ^{31}P NMR (202.46 MHz) (**3a**–*Z*) δ_P 22.62[$(Ph)_3P$=C]; (**3a**–*E*): δ_P 19.92 [$(Ph)_3P$=C]; (Found: C, 69.2; H, 4.74; N, 2.45. $C_{32}H_{26}NPO_6$ requires C, 66–69; H, 4.75; N, 2.54%).

(3b): Orange powder, m.p. 106°C, yield 83%; IR (KBr) (ν_{max}/cm^{-1}): 1733, 1626 and 1609 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.5 and 1.3 (6 H, 2 t, $^{3}J_{HH}$ 9 Hz, 2 CH_3), 3.75 and 4.3 (4 H, 2 q, $^{3}J_{HH}$ 9 Hz, 2 OCH_2), 5.3 (d, $^{2}J_{PC}$ 18 Hz, CH), 7–8 (19 H, m, arom); ^{13}C NMR (125.77 MHz, $CDCl_3$): δ_C 13.8 and 14.1 (2 CH_3), 37.3 (d, $^{1}J_{PC}$ 122.2 Hz, P=C), 57.98 (d, $^{2}J_{PC}$ 15 Hz, P=C-*CH*), 61.42 and 62.0 (2 OCH_2), 115.44, 122.97, 124.0 and 138.32 (4 CH, isatin), 117.88 (N-C=C), 125.78 (d, $^{1}J_{PC}$ 91.21 Hz, C_{ipso}), 128.86 (d, $^{3}J_{PC}$ 11.85 Hz, C_{meta}), 132.38 (d, $^{4}J_{PC}$ 2.3 Hz, C_{para}), 133.34 (d, $^{2}J_{PC}$ 10.04 Hz, C_{ortho}), 150.3 (N-*C*=C), 156.77 (C=O, amide), 169.3 (d, $^{2}J_{PC}$ 12.51 Hz, C=O ester), 170.37 (d, $^{3}J_{PC}$ 14.95 Hz, C=O ester), 184.5 (C=O, ketone); (Found: C, 69.9; H, 5.1; N, 2.34. $C_{34}H_{30}NPO_6$ requires C, 70.46; H, 5.22; N, 2.42%).

(3c): Yellow powder, m.p. 135–137°C, yield 95%; IR(KBr) (ν_{max}/cm^{-1}): 1734, 1630 and 1610 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1 and 1.6 (18 H, 2 S, 2 CMe_3), 5.1 (1 H, d, $^{3}J_{PH}$ 18 Hz, CH), 7–8.2 (19 H, m, arom); $_{13}C$ NMR (125.77 MHz) δ^C 28.18 and 28.36 (s, 2 CMe_3), 37.10 (d, $^{1}J_{PC}$ 121.92 Hz, P=C), 55.44 (d, $^{2}J_{PC}$ 16.02 Hz, P=C-*CH*), 77.73 and 81.35 (2 CMe_3), 115.65, 122.97, 124.16 and 138.46 (4 CH, isatin), 117.95 (N-C=*C*), 126.24 (d, $^{1}J_{PC}$ 91.18 Hz, C_{ipso}), 128.83 (d, $^{3}J_{PC}$ 12.07 Hz, C_{meta}), 132.36 (d, $^{4}J_{PC}$ 2.52 Hz, C_{para}), 133.53 (d, $^{2}J_{PC}$ 9.68 Hz, C_{ortho}), 150.75 (N-*C*=C), 156.86 (C=O, amide), 168.78 (d, $^{2}J_{PC}$ 11.57 Hz, C=O ester), 169.03 (d, $^{3}J_{PC}$ 14.34 Hz, C=O ester), 184.93 (C=O, ketone); (Found: C, 71.77 H, 5.95;N, 2.08. $C_{38}H_{38}NPO_6$ requires C, 71.80 H, 6.03;N, 2.20%).

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References

1 H.R. Hudson, in *The Chemistry of Organophosphorus Compounds, Vol. 1. Primary, Secondary and Tertiary Phosphines, Polyphosphines and Heterocyclic Organophosphorus (III) Compounds*, (F.R. Hartley Ed:), Wiley, New York, 1990, pp. 386-472.
2 R. Engel, *Synthesis of Carbon-Phosphorus Bonds*, CRC Press, Boca Raton, FL, 1988.
3 H.H. Wasserman, C.M. Baldino and S. J. Coats, *J. Org. Chem.* 1995, **60**, 8231.
4 H.J. Bestmann and O. Vostrowsky, *Topics Curr. Chem.* 1983, **109**, 86.
5 I. Yavari and R. Baharfar, *Tetrahedron Lett*, 1998, **39**, 1051; *J. Chem. Res. (S)*, 1997, 146.
6 K.M. Pietrusiewiz and M. Zablocka, *Chem. Rev.* 1994, **94**, 1375.
7 O.I. Kolodiazhnyi, *Russ. Chem. Rev*. 1997, **66**, 225.
8 I. Yavari, M.T. Maghsoodlou, H. Djahaniani and N. Hazeri, *J. Chem. Res. (S)*, 1999, 216-217.