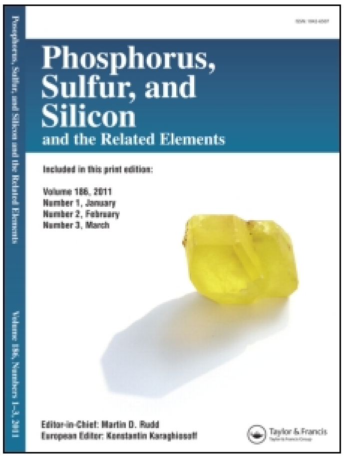

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ONE-STEP, THREE-COMPONENT SYNTHESIS OF DIALKYL 2-(IMIDO-*N*-YL)-3-(TRIPHENYLPHOSPHORANYLIDENE) BUTANEDIOATES

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ONE-STEP, THREE-COMPONENT SYNTHESIS OF DIALKYL 2-(IMIDO-*N*-YL)-3-(TRIPHENYLPHOSPHORANYLIDENE) BUTANEDIOATES

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A one-step synthesis of dialkyl 2-(imido-*N*-yl)-3-(triphenylphosphoranylidene)butanedioates in fairly good yields by the reaction of imides, dialkyl acetylenedicarboxylates and triphenylphosphine is reported. The structures of these compounds were confirmed by IR, MS and ^{1}H, ^{31}P and ^{13}C NMR spectroscopy, and elemental analyses. The NMR spectra indicated that the compounds ($CDCl_3$ as solvent) contained two rotamers with unequal population for each ylide.

Keywords: Triphenylphosphine; acetylenic esters; imides; ylides; vinylphosphonium salts

Phosphorus ylides have found use in a wide variety of reactions of interest to synthetic chemists, especially in the synthesis of naturally occurring products, compounds with biological and pharmacological activity[1]. The most general method for the synthesis of phosphorus ylides is the dehyrohalogenation of corresponding phosphonium salts by bases[2]. We have recently described[3] the synthesis of dialkyl [indane-1,3-dione-2-ylidene] alkoxysuccinates **1** (Fig. 1) from the reaction of triphenylphosphine, dialkyl acetylenedicarboxylates, alcohols, and ninhydrin using an intermolecular Wittig reaction[4,5]. For the purpose of preparation of dialkyl [indane-1,3-dione-2-ylidene] imidosuccinates, such as **2** (Fig. 1), we conducted the reaction of succinimide, dimethyl acetylenedicarboxylate, triphenylphosphine, and ninhydrin. This reaction did not afford the corresponding compound **(2)** even at reflux temperature (toluene as solvent) after 24 h. TLC indicated that the solution contained ylide **7a** and unreacted ninhydrin (Scheme 1).

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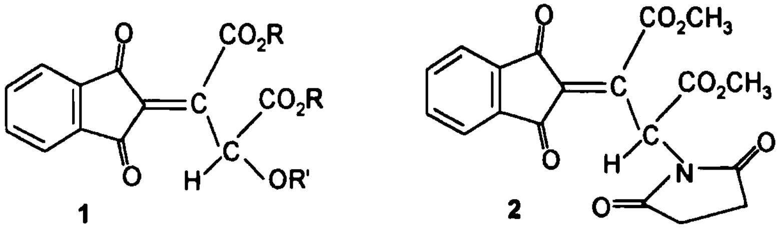
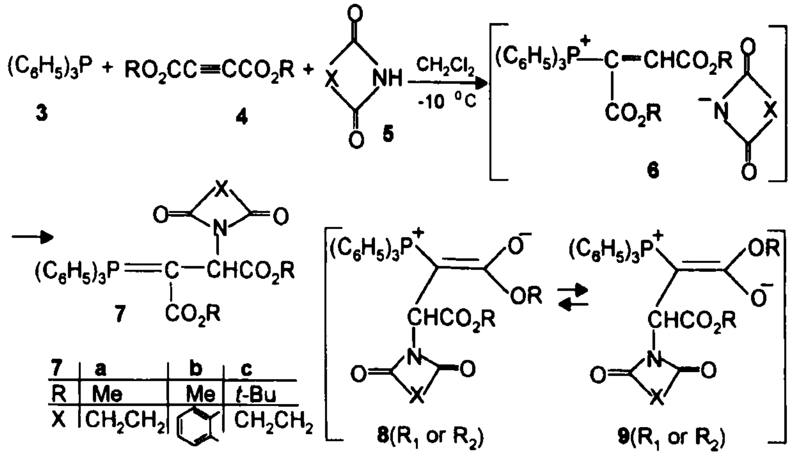


FIGURE 1

The ylide (**7**) may result from initial addition of triphenylphosphine **3** to the acetylenic ester **4** and concomitant protonation of the 1:1 adduct, followed by attack of the imide anion on the vinyltriphenylphosphonium cation to form highly stabilized phosphorane **7**. Steric and dipole-dipole intractions between the imide group of phosphorane **7** and indane-1,2,3-trione, may result in reduction of the reactivity of ylides (Scheme 1).



SCHEME 1 R1= major roramer and R2=minor rotamer

The NMR spectra indicated that solutions of compound **7** ($CDCl_3$ as solvent) contained two rotamers (**8** and **9**) in unequal population. The rotameric signals did not coalesce at 60 °C. The relative precentages of rotamers in $CDCl_3$ for each ylide (**7**) (Scheme 1) were determined from their ^1H NMR spectra[6–8]. The structures **7a-c** were deduced from their elemental analyses and their ^1H, ^{13}C and ^{31}P NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at *m/z* of 503, 551 and 587, respectively.

In summary, we have developed a convenient, one-pot method for preparing highly stabilized ylides (**7a-c**) utilising *in situ* generation of the phosphonium salts. Other aspects of this process are under investigation.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. UV spectra were recorded on a Shimadzu UV-2100 spectrophothometer. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^1H, ^{13}C and ^{31}P NMR spectra were measured with BRUKER DRX-500 AVANCE spectrometer at 500, 125 and 202.44 MHz, respectively. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV.

General procedure for the preparation of dialkyl 2-(imido-N-yl)-3-(triphenylphosphoranylidene)butanedioates (7a-c)

To a magnetically stirred solution of triphenylphosphine **3** (0.262 g, 1 mmol) and **5** (1 mmol) in CH_2Cl_2 (5 ml) was added dropwise a mixture of **4** (1 mmol) in CH_2Cl_2 (5 ml) at −10°C over 15 min. The mixture was allowed to warm up to room temperature. The solvent was removed under reduced pressure and the residue was crystallized from hexane-diethyl ether (1:1). White crystals of **7** were collected by filtration.

Selected data for dimethyl 2-(succinimido-N-yl)-3-(triphenylphosphoranylidene)butanedioate (7a)

White crystals, m.p. 198.5–198.8°C, yield 66.5%. UV(ethanol 95%) (λ_{max} / nm, logε): 203, 3.31. IR (KBr) (ν_{max}, cm^{-1}): 3061; 2953; 1749; 1711; 1657; 1441. ^1H NMR ($CDCl_3$, major rotamer (R_1) 56% and minor rotamer (R_2) 44%) δ_H: 2.5–2.6 (4H, m, CH_2CH_2); 3.08 (R_1), 3.69 (R_1), 3.57 (R_2)

and 3.68 (R_2) (6H, 4s, $4OCH_3$); 4.66 (R_1, d, $^3J_{PH}$=15.6 Hz) and 4.70 (R_2, d, $^3J_{PH}$=17.5 Hz) (1H, P=C- CH); 7.5–7.8 (15H, m, arom.). ^{13}C NMR ($CDCl_3$)) δ_C: 28.41 (CH_2CH_2); 36.84 (R_1, d, $^1J_{PC}$ =130.8 Hz) and 38.55 (R_2, d, $^1J_{PC}$ =139.4 Hz) (P=C); 49.43 (R_1), 53.18 (R_1), 50.90 (R_2) and 52.96 (R_2) ($4OCH_3$); 55.74 (R_1, d, $^2J_{PC}$ =17.9 Hz) and 55.33 (R_2, d, $^2J_{PC}$ =17.5 Hz) (P=C-^{13}C); 126.3–135.7 (fairly complex, arom.); 176.72 (NC=O); 171.36 (R_1, d, $^2J_{PC}$ =10.8 Hz), 176.69(R_1, d, $^3J_{PC}$ =8.4Hz), 169.42 (R_2, d, $^2J_{PC}$ =12.8Hz) and 177.60 (R_2, d, $^3J_{PC}$ =11.2Hz) (4CO of esters). ^{31}P NMR ($CDCl_3$) δ_P: 23.53 (R_1) and 23.31 (R_2). MS (m/z, %): 503 (M^+, 4); 444(46); 262(100)' 183(85); 108(50); 77(18). Analysis: Calc. for $C_{28}H_{26}NO_6P$(503.15): C, 66.80; H, 5.20; N, 2.78%. Found: C, 66.26; H, 5.16; N, 2.74%.

Selected data for dimethyl 2-(phethalimido-N-yl)-3-(triphenylphosphoranylidene) butanedioate (7b)

White crystals, m. p. 182.3–182.9°C; yield 64.6%. UV(ethanol 95%) (λ_{max} / *nm*, log ε): 205, 2.60; 219, 2.63. IR(KBr) (υ_{max}, cm^{-1}): 3031; 2937; 1760; 1718; 1649; 1440. ^{1}H NMR ($CDCl_3$, major rotamer (R_1) 51% and minor rotamer (R_2) 49%) δ_H: 3.16(R_1), 3.74(R_1), 3.63(R_2) and 3.71 (R_2) (6H, 4S, $4OCH_3$); 4.78 (R_1, d, $^3J_{PH}$ =15.8Hz) and 4.82 (R_2, d, $^3J_{PH}$ =17.7 Hz) (1H, P=C-CH); 7.4–7.7(19H, m, arom.). ^{13}C NMR ($CDCl_3$) δ_C: 37.73 (R_1, d, $^1J_{PC}$ =130.6 Hz) and 39.41 (R_2, d, $^1J_{PC}$ =138.9 Hz) (P=C); 49.54 (R_1), 53.30(R_1), 53.02 (R_2) and 54.78 (R_2) ($4OCH_3$); 55.41 (R_1, d, $^2J_{PC}$ =17.3 Hz) and 54.78 (R_2, d, $^2J_{PC}$ =16.8 Hz) (P=C-^{13}C); 123.4–134.1 (fairly complex, arom.); 168.02 (NC=O); 169.74 (R_1, d, $^2J_{PC}$ =2.4Hz), 171.99(R_1, d, $^3J_{PC}$ =6.7 Hz), 169.65(R_2, d, $^2J_{PC}$ =2.6 Hz) and 171.94 (R_2, d, $^3J_{PC}$ =6.4Hz) (4CO of esters). ^{31}P NMR ($CDCl_3$) δ_P: 24.17 (R_1) and 23.87 (R_2). MS(m/z,%): 551 (M^+, 2); 492(20); 262(100); 230(28); 183(77); 147(23); 108(50); 76(40). Analysis: calc. for $C_{32}H_{26}NO_6P$(551.15): C, 69.69; H, 4.74; N, 2.53%. Found: C, 69.72; H, 4.88; N, 2.52%.

Selected data for di-tert-butyl-2-(succinimido-N-yl)-3-(triphenylphosphoranylidene) butanedioate (7c)

White crystals, m. p. 189.3–189.6 °C; yield 63.4%. UV(ethanol 95%) (λ_{max} / *nm*, log ε): 202,3.27. IR (KBr) (υ_{max}, cm^{-1}): 3068; 2976; 1789: 1711; 1664; 1394. ^{1}H NMR ($CDCl_3$, only one of the two rotamers was observed) δ_H: 0.93 and 1.51 (18H, 2s $2O(CH_3)_3$); 2.4–2.6(4H, m,

CH_2CH_2); 4.48(^{1}H, d, $^3J_{PH}$ = 17.2Hz, P=C-CH); 4.7–7.8(15H, m, arom.). ^{13}C NMR($CDCl_3$) δ_C: 28.62 and 30.04(2OC($^{13}CH_3)_3$); 28.41(CH_2-CH_2); 35.94(d, $^1J_{PC}$ =131.5 Hz, P=C); 57.14(d, $^2J_{PC}$=17.6Hz, P=C-^{13}C); 77.41 and 81.44(2O$^{13}C(CH_3)_3$); 128.1–134.1(fairly complex, arom.) 168.23(d, $^2J_{PC}$ =12.5 Hz, C=O of ester); 169.72(d, $^3J_{PC}$ =12.8 Hz, C=O of ester); 176. 72(C=O of imide). ^{31}P NMR($CDCl_3$) δ_P: 22.79. Ms(m/z, %): 587(M$^+$, 5); 486(30); 430(63); 386(25); 262(100); 183(60); 108(45); 57(83). Analysis: Calc. for $C_{34}H_{38}NO_6P$(587.15): C, 69.50; H, 6.51; N, 2.38% found: C, 69.35; H, 6.55; N, 2.28%.

Acknowledgements

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