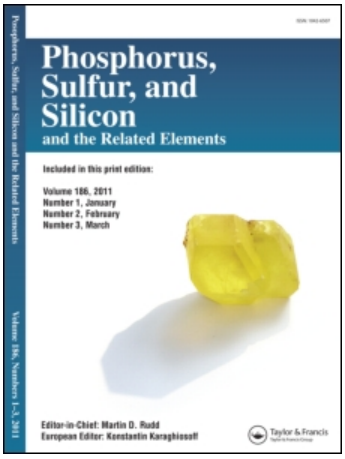

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A FACILE SYNTHETIC APPROACH TO DIMETHYL 2-ARYLAMINO-3-(TRIPHENYLPHOSPHORANYLIDENE) SUCCINATES FROM ELECTRON-POOR PRIMARY ARYLAMINES

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A one-step synthesis of dimethyl 2-arylamino-3-(triphenylphosphoranylidene)succinates in fairly good yields by the reaction of electron-poor primary arylamines, dimethyl acetylenedicarboxylate and triphenylphosphine is reported. The structures of these compounds were confirmed by UV, 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; electron-poor primary arylamines; ylides; vinylphosphonium salts

INTRODUCTION

Phosphorus ylides are important reagents in synthetic organic chemistry, especially in the synthesis of naturally occurring products, compounds with biological and pharmacological activity[1]. Phosphorus ylides are usually prepared by deprotonation of phosphonium salts. The phosphonium salts that are used most often are alkyltriphenylphosphonium halides, which can be prepared by the reaction of triphenylphosphine and an alkyl halide[2]. In recent years, we have established a one-pot method for the synthesis of stabilized ylides[3-5]. In this paper, we wish to describe the prepa-

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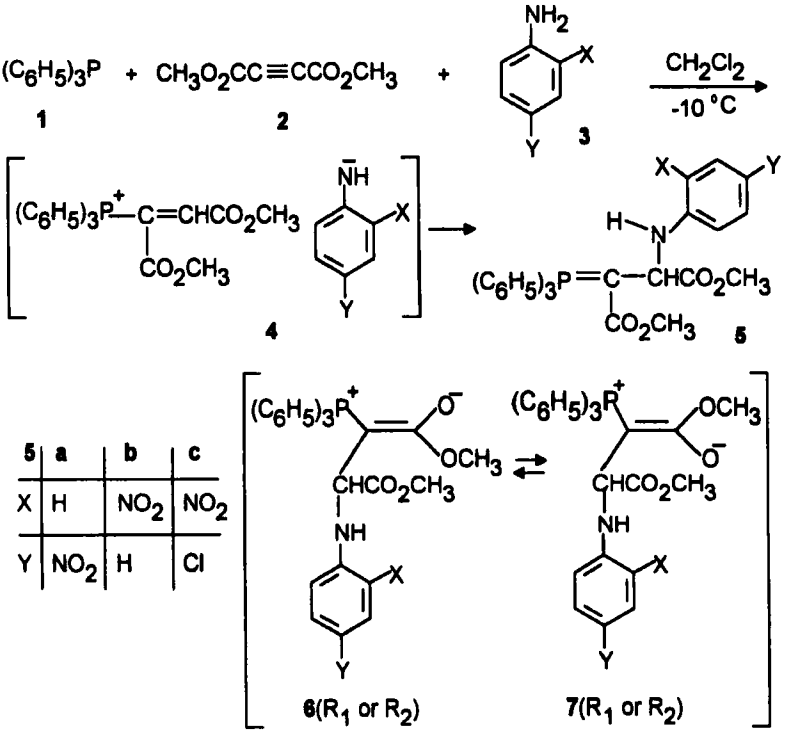
ration of dimethyl-2-arylamino-3-(triphenylphosphoranylidene)succinates in fairly good yields (Scheme 1).



SCHEME 1 R_1= major roramer and R_2=minor rotamer

RESULTS AND DISCUSSION

The ylide (**5**) may result from initial addition of triphenylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1 adduct, followed by attack of the amine anion on the vinyltriphenylphosphonium cation to form the stabilized phosphorane **5** (Scheme 1). We have also used aniline, diphenylamine and 3-nitroaniline in this reaction, but yields of the corresponding products **5** were very low. The weak acidity of these amines may be the factor in the reduction of yields.

The NMR spectra indicated that solutions of compound **5** ($CDCl_3$as solvent) contained two rotamers (**6** and **7**) in unequal population. The rota-

meric 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 **5a-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 542, 542 and 576, respectively.

In summary, we have developed a convenient, one-pot method for preparing stabilized ylides (**5a-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 a 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 dimethyl-2-arylamino-3-(triphenylphosphoranylidene)succinates (5a-c)

To a magnetically stirred solution of triphenylphosphine **1** (0.262 g, 1 mmol) and **3** (1 mmol) in CH_2Cl_2 (5 ml) was added dropwise a mixture of **2** (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 ethyl acetate-methanol (1:1). Crystals of **5** were collected by filtration.

Selected data for dimethyl 2-(4-nitroanilino)-3-(triphenylphosphoranylidene)succinates (5a)

Pale yellow crystals, m. p. 180.9–181.7°C, yield 57.5%. UV (ethanol 95%) (λ_{max} / nm, logε): 232, 3.91; 388, 3.80. IR (KBr) (ν_{max}, cm^{-1}): 3408;

3070; 2953; 1742; 1626; 1603; 1441; 1317. ^{1}H NMR ($CDCl_3$, major rotamer (R_1) 70% and minor rotamer (R_2) 30%) δ_H: 3.15 (R_1), 3.69 (R_1), 3.61 (R_2) and 3.69 (R_2) (6H, 4s, $4OCH_3$); 4.41 (R_1, dd, $^3J_{PH}$=15.1 Hz and $^3J_{HH}$=7.1 Hz) and 4.21 (R_2,, dd, $^3J_{PH}$=18.0 Hz and $^3J_{HH}$=7.2 Hz) (1H, P=C- CH); 6.0–6.2 (3H, m, *ortho*-CH and NH, NHAr); 7.5–8.0 (17H, m, arom.).^{13}C NMR ($CDCl_3$) δ_C: 42.44 (R_1, d, $^1J_{PC}$ =125.1 Hz) and 43.73 (R_2, d, $^1J_{PC}$ =126.4 Hz) (P=C); 49.41 (R_1), 52.46 (R_1), 52.39 (R_2) and 52.46 (R_2) ($4OCH_3$); 55.50 (R_1, d, $^2J_{PC}$ =14.9 Hz) and 55.06 (R_2, d, $^2J_{PC}$ =15.2 Hz) (P=C-^{13}C); 111.49–152.36 (fairly complex, arom.); 170.23 (R_1, d, $^2J_{PC}$ =12.3 Hz), 173.57(R_1, d, $^3J_{PC}$ =7.2 Hz), 169.81 (R_2, d, $^2J_{PC}$ =12.4 Hz) and 175.61 (R_2, d, $^3J_{PC}$ =8.1 Hz) (4CO of esters). ^{31}P NMR ($CDCl_3$) δ_P: 21.63 (R_1) and 22.87 (R_2). MS (m/z, %): 542 (M^+, 2); 484(40); 483(28); 452(18); 451(14); 406(36); 405(32); 262(100); 183(68); 108(36); 92(6); 77(15); 65(9); 59(10). Analysis: Calc. for $C_{30}H_{27}N_2O_6P$(542.53): C, 66.42; H, 5.02; N, 5.16%. Found: C, 66.4; H, 4.9; N, 5.1%.

Selected data for dimethyl 2-(2-nitroanilino)-3-(triphenylphosphoranylidene)succinates (5b)

Orange crystals, m. p. 83.1–84.7°C; yield 51.2%. UV(ethanol 95%) (λ_{max} / *nm*, log ε): 268, 3.93; 427, 3.70. IR(KBr) (ν_{max}, cm^{-1}): 3380; 3060; 2949; 1749; 1614; 1562; 1437; 1314. ^{1}H NMR ($CDCl_3$, major rotamer (R_1) 60% and minor rotamer (R_2) 40%) δ_H: 3.15 (R_1), 3.63 (R_1), 3.65 (R_2) and 3.68 (R_2) (6H, 4s, $4OCH_3$); 5.25 (R_1, d, $^3J_{PH}$=19.0 Hz) and 4.38 (R_2, d, $^3J_{PH}$=18.0 Hz) (1H, P=C- CH); 6.29 (R_1, br s) and 6.08 (R_2, br s)(1H, NH); 6.5–8.7 (19H, m, arom.). ^{13}C NMR ($CDCl_3$) δ_C: 42.83 (R_1, d, $^1J_{PC}$ =124.8 Hz) and 43.75 (R_2, d, $^1J_{PC}$=134.7 Hz) (P=C); 49.43 (R_1), 52.01 (R_1), 49.56 (R_2) and 53.03 (R_2) ($4OCH_3$); 55.86 (R_1, d, $^2J_{PC}$ =13.3 Hz) and 54.63 (R_2, d, $^2J_{PC}$ =13.6 Hz) (P=C-^{13}C); 115.18 (R_1) and 115.07 (R_2)(C6 of NHAr, arom.); 119.01–144.21 (fairly complex, arom.); 170.33 (R_1, d, $^2J_{PC}$ =11.9 Hz), 173.38 (R_1, d, $^3J_{PC}$=3.3 Hz) 170.16 (R_2, d, $^2J_{PC}$ =13.6 Hz) and 172.51 (R_2, d, $^3J_{PC}$ =4.2 Hz) (4CO of esters). ^{31}P NMR ($CDCl_3$) δ_P: 20.72 (R_1) and 22.49 (R_2). MS (m/z, %): 542 (M^+, 1); 484(31); 483(20); 452(10); 451(9); 406(40); 405(38); 262(100); 183(65); 108(33); 92(5); 77(12); 65(7); 59(11). Analysis: Calc. for $C_{30}H_{27}N_2O_6P$(542.53): C, 66.42; H, 5.02; N, 5.16%. Found: C, 66.6; H, 5.1; N, 5.0%.

Selected data for dimethyl-2-(4-chloro-2-nitroanilino)-3-(triphenylphosphoranylidene)succinates (5c)

Orange crystals, m. p. 107.4–108.9°C; yield 55.7%. UV(ethanol 95%) (λ_{max} / *nm*, log ε): 272, 3.86; 441, 3.62. IR (KBr) (ν_{max}, cm^{-1}): 3400; 3040; 2953; 1742; 1626; 1568; 1441; 1356. ^{1}H NMR ($CDCl_3$, major rotamer (R_1) 59% and minor rotamer (R_2) 41%) δ_H: 3.16 (R_1), 3.62 (R_1), 3.64 (R_2) and 3.67 (R_2) (6H, 4s, $4OCH_3$); 5.26 (R_1, d, $^3J_{PH}$=21.6 Hz) and 4.35 (R_2, d, $^3J_{PH}$=18.2 Hz) (1H, P=C- CH); 6.48 (R_1, br s) and 6.04 (R_2, br s)(1H, NH); 6.8–8.7 (18H m, arom.). ^{13}C NMR ($CDCl_3$) δ_C: 42.64 (R_1, d, $^1J_{PC}$ =124.3 Hz) and 43.62 (R_2, d, $^1J_{PC}$ =125.5 Hz) (P=C); 49.53 (R_1), 52.55 (R_1), 50.79 (R_2) and 52.38 (R_2) ($4OCH_3$); 55.99 (R_1, d, $^2J_{PC}$ =12.1 Hz) and 55.40 (R_2, d, $^2J_{PC}$=13.8 Hz) (P=C-^{13}C); 117.29 (R_1) and 115.82 (R_2)(C6 of NHAr, arom.); 125.10–142.64 (fairly complex, arom.); 170.37 (R_1, d, $^2J_{PC}$ =12.8 Hz), 173.07 (R_1, d, $^3J_{PC}$ =5.3 Hz), 169.83 (R_2, d, $^2J_{PC}$ =12.3 Hz) and 171.49 (R_2, d, $^3J_{PC}$ =4.9 Hz) (4CO of esters). ^{31}P NMR ($CDCl_3$) δ_P: 20.57 (R_1) and 22.44 (R_2). MS (m/z, %): 576 (M^+, 1); 520(9); 519(7); 518(29); 517(23); 488(4); 487(3); 486(12); 485(10); 442(13); 441(11); 440(41); 439(35); 262(100); 183(62); 128(2); 126(6); 108(30); 59(12). Analysis: Calc. for $C_{30}H_{26}ClN_2O_6P$(576.98): C, 62.45; H, 4.54; N, 4.86%. Found: C, 62.3; H, 4.6; N, 4.7%.

Acknowledgements

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