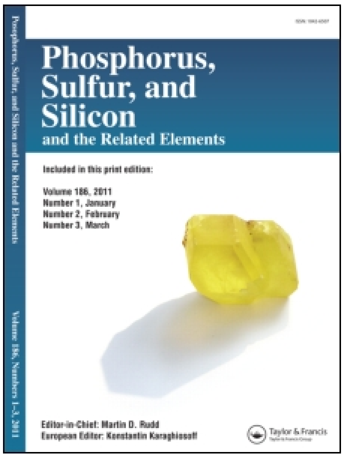

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Vinylphosphonium Salt Mediated Preparation of Substituted Imides and Furans from Benzoic Acid, 1,1,3,3-Tetramethylbutyl Isocyanide, and Acetylenic Esters

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Protonation of the reactive intermediates produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates by benzoic acid leads to vinyltriphenylphosphonium salts, which undergo complex reactions with 1,1,3,3-tetramethylbutyl isocyanide to produce corresponding substituted furans and imides in fairly good yields in a stereoselective manner.

Keywords Acetylenic ester; densely functionalized furan; electron-poor imide; phosphorus ylide; triphenylphosphine

INTRODUCTION

Organophosphorus compounds[1,2] have been extensively employed in organic synthesis as useful reagents as well as ligands in a number of transition metal catalysts.[3] Phosphorus ylides are a class of a special type of zwitterions, which bear strongly nucleophilic electron-rich carbanions. The electron distribution around the P^+-C^- bond and its consequent chemical implications has been probed and assessed through theoretical, spectroscopic, and crystallographic investigations.[4] They are excellent ligands and excel in their ligating functions with the unstabilized ylides because of their ambidentate and chemically differentiating character. Proton affinity of these ylides can be used as a molecular guide to assess their utility as synthetic reagents and their function as ligands in coordination and organometallic chemistry.[3,5]

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The nucleophilicity at the ylidic carbon is a factor of essential mechanistic importance in the use of these ylides as Wittig reagents. Phosphorus ylides are important reagents in synthetic organic chemistry, especially in the synthesis of naturally occurring products, and compounds with biological and pharmacological activity.[1,2] In recent years, we have established a one-pot method for the synthesis of stabilized ylides.[6–15]

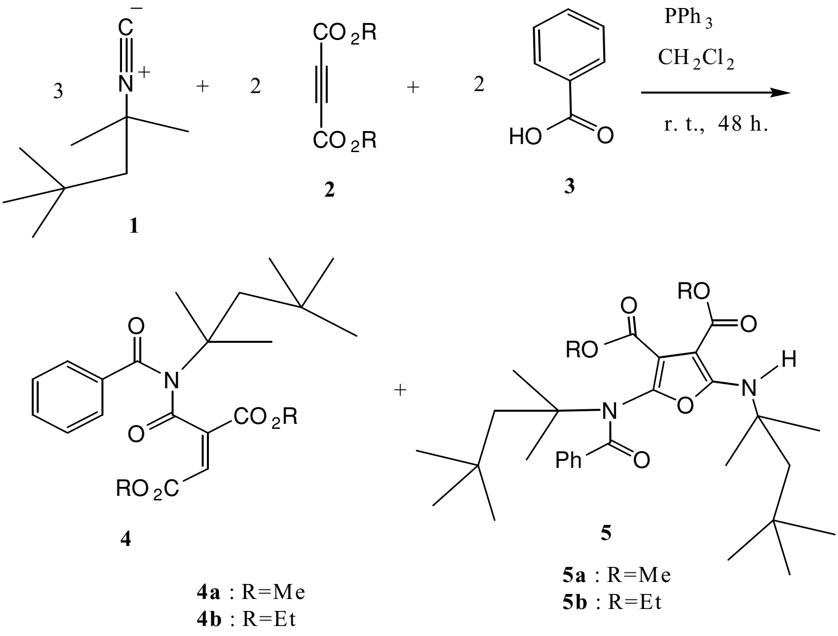
For several years acetylenic esters have attracted the attention of organic chemists and are reactive systems that can take part in many chemical syntheses,[16–18] almost as a Michael acceptor in the organic reactions.[16] In recent years, there has been increasing interest in the applications of acetylenic esters in the multicomponent[19–21] synthesis. Due to the atom economy, convergent character, and simplicity of one-pot procedures, multicomponent condensation reactions (MCRs) have an advantageous position among other reactions. The development of novel MCRs is receiving growing interest from industrial chemistry research groups and represents a challenge for organic chemists.[22–26] As part of our ongoing program to develop efficient and robust methods for the preparation of heterocyclic compounds,[27–37] we sought to develop a convenient preparation of densely functionalized furans **5** and imides **4** in fairly good yields in neutral conditions.

RESULTS AND DISCUSSION

Protonation of the reactive intermediates produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates **2** by benzoic acid **3** leads to vinyltriphenylphosphonium salts **7**, which undergo complex reactions with 1,1,3,3-tetramethylbutyl isocyanide **1** to produce corresponding densely functionalized furans **5** and imides **4** in fairly good yields in neutral conditions (Schemes 1 and 2). The reaction proceeds smoothly and cleanly under reaction conditions, and no side reactions were observed. The reactions were completed in 48 h, and densely functionalized furans **5** were observed as major products (Table I). In this reaction, triphenylphosphine acts as a catalyst. In the absence of the triphenylphosphine,[25,26] the reactions were completed after 72 h in CH_2Cl_2 at room temperature with imides **4** observed as major products (Table I).[25,26] The ^1H NMR ($CDCl_3$) spectra of compounds **4** show the presence of one estereoisomer (***E***) for each imides **4**. ***Z*** isomers of the imides **4** were not isolated. It seems that ***Z*** isomers **12** are more reactive than ***E*** isomers toward formation of adduct **13** with 1,1,3,3-tetramethylbutyl isocyanide **1** and act as intermediate in the formation of furans **5** (Scheme 2). The reaction is stereoselective.

TABLE I Synthesis of Imides 4 and Furans 5 (see Scheme 1)

Entry	Products	In the presence of PPh_3 (r. t., 48 h.): Total isolated yield % (**4** + **5**); Ratio of **4:5**		In the absence of PPh_3 (r. t., 72 h.): Total isolated yield % (**4** + **5**); Ratio of **4:5**	
1	**4a/5a**	91;	31:69	80;	90:10
2	**4b/5b**	85;	30:70	75;	83;17

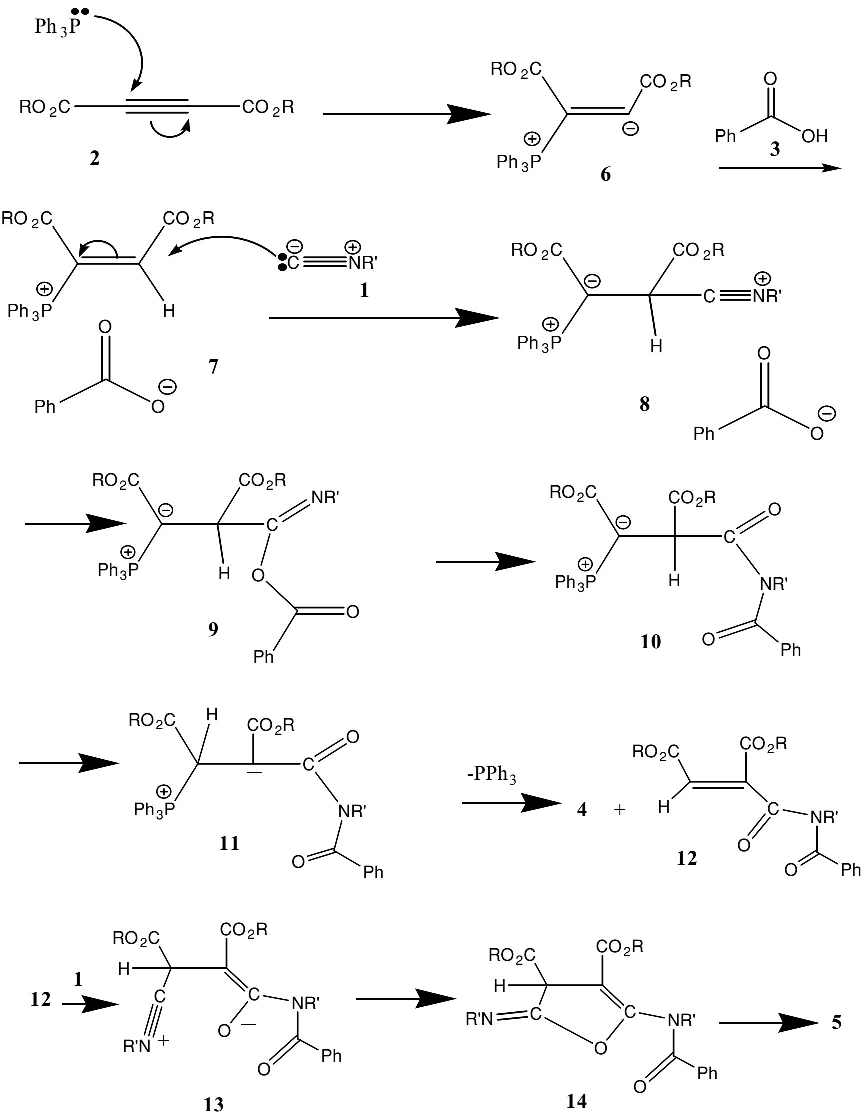


SCHEME 1

The mechanism of the reaction between the triphenylphosphine, 1,1,3,3-tetramethylbutyl isocyanide (**1**) dialkyl acetylenedicarboxylates (**2**), and benzoic acid (**3**) has not been established experimentally. However, a possible explanation is proposed in Scheme 2. The structures of the products were deduced from their IR, ^1H NMR, and ^{13}C NMR spectra (see the Experimental section).

CONCLUSIONS

In summary, we have found a new and efficient method for preparing electron-poor imides (**4**) and fully substituted furans (**5**) from



R = Me, Et ; R' = 1,1,3,3-tetramethylbutyl

SCHEME 2

triphenylphosphine, 1,1,3,3-tetramethylbutyl isocyanide (**1**) dialkyl acetylenedicarboxylates (**2**), and benzoic acid (**3**) in neutral conditions (Scheme 1, Scheme 2, and Table I). We believe the reported method offers a simple and efficient route for the preparation of electron-poor imides (**4**) and fully substituted furans (**5**) (Scheme 1). Its ease of work-up and fairly good yields make it a useful addition to modern synthetic methodologies.Other aspects of this process are under investigation.

EXPERIMENTAL

^{1}H (250.13 MHz) and ^{13}C (62.90 MHz) NMR measurements were recorded on a Brucker 250 spectrometer in $CDCl_3$ with tetramethylsilane as internal standard. IR spectra were measured on a Mattson-1000 FTIR spectrophotometer. Starting materials and solvents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. Flash chromatography columns were prepared from Merck silica gel powder.

General Procedure for the Preparation of Compounds 4a–b and 5a–b

To a magnetically stirred solution of triphenylphosphine (0.262 g, 1 mmol) and benzoic acid **3** (0.28 g, 2 mmol) in dry CH_2Cl_2 (1 ml) was added dropwise a solution of **2** (2 mmol) in CH_2Cl_2 (2 mL) at -10°C over 15 min. The mixture was allowed to warm to room temperature and to it was added dropwise a solution of 1,1,3,3-tetramethylbutyl isocyanide **1** (3 mmol) in CH_2Cl_2 (1 mL) over 10 min. The mixture was stirred for 48 h. The solvent was removed under reduced pressure, and the viscous residue was purified by flash column chromatography (silica gel; light petroleum ether-ethyl acetate). Characterization data are given in the next section.

Dimethyl (E)-2-{[benzoyl(1,1,3,3-tetramethylbutyl)-amino]carbonyl}-2-butenedioate 4a

Viscous yellow oil, IR (KBr) ($\upsilon_{\max}$, cm^{-1}): 1738 (OCNCO), 1669 (CO_2Me), 1600 (C=C), 1546 and 1454 (Ph), 1369, 1253, 1200 and 1123 (C–O).^{1}H NMR (250.13 MHz, $CDCl_3$): δ_H 0.99 (9 H, s, CMe_3), 1.55 (6 H, s, CMe_2), 2.30 (2 H, s, CH_2), 3.54 (3 H, OMe), 3.70 (3 H, s, OMe), 6.28 (1 H, NH), 7.30 (2 H, dd, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 7.5$ Hz, 2 CH_{meta} of C_6H_5), 7.45 (1 H, t, $^3J_{HH} = 7.7$ Hz, CH_{para} of C_6H_5), 7.68 (2 H, d, $^3J_{HH} = 7.7$ Hz, 2 CH_{ortho} of C_6H_5). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ_C 22.59 ($\mathit{C}Me_3$), 28.23 (CH_3 of CMe_2), 31.66 (CH_3 of CMe_3), 50.44 (CH_2), 52.21 (OMe), 52.53 (OMe), 64.91 (C of CMe_2), 128.15 (2 CH_{meta} of C_6H_5), 128.43 (2 CH_{ortho} of C_6H_5), 130.38 (C=*C*H), 134.03 (CH_{para} of C_6H_5), 136.04 (C_{ipso} of C_6H_5), 140.99 (*C*=CH), 161.68 (PhCON*C*O), 162.77 (CO_2Me), 163.53 (CO_2Me), 175.11 (Ph*C*ON).

Diethyl (E)-2-{[benzoyl(1,1,3,3-tetramethylbutyl)-amino]carbonyl}-2-butenedioate 4b

Viscous yellow oil, IR (KBr) (υ_{max}, cm^{-1}): 1730 (OCNCO), 1676 (CO_2Me), 1610 (C=C), 1553 and 1469 (Ph), 1376, 1261, 1200 and 1161 (C—O).^{1}H NMR (250.13 MHz, $CDCl_3$): δ_H 1.07 (9 H, s, CMe_3), 1.25 (3 H, t,$^3J_{HH} = 7.2$ Hz, CH_3), 1.28 (3 H, t,$^3J_{HH} = 7.2$ Hz, CH_3), 1.65 (6 H, s, CMe_2), 2.38 (2 H, s, CH_2), 4.11 (2 H, q,$^3J_{HH} = 7.2$ Hz, OCH_2CH_3), 4.22 (2 H, q,$^3J_{HH} = 7.2$ Hz, OCH_2CH_3), 6.33 (1 H, s, NH), 7.40 (2 H, dd, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 7.5$ Hz, $2CH_{meta}$ of C_6H_5), 7.54 (1 H, t, $^3J_{HH} = 7.4$ Hz, CH_{para} of C_6H_5), 7.78 (2 H, d, $^3J_{HH} = 7.4$ Hz, 2 CH_{ortho} of C_6H_5).^{13}C NMR (62.90 MHz, $CDCl_3$): δ_C 13.76 (CH_3CH_2), 14.08 (CH_3CH_2), 28.59 (CMe_3), 31.58 (CH_3 of CMe_2), 31.77 (CH_3 of CMe_3), 50.41(CH_2), 61.49 (OCH_2), 62.18 (OCH_2), 65.12 (C of CMe_2), 128.45 (2 CH_{meta} of C_6H_5), 128.77 (2 CH_{ortho} of C_6H_5), 130.41 (C=CH), 134.00 (CH_{para} of C_6H_5), 136.40 (C_{ipso} of C_6H_5), 141.74 (C=CH), 162.15 (PhCONCO), 162.63 (CO_2Me), 163.41 (CO_2Me), 175.39 (PhCON).

Dimethyl 2-[Benzoyl(1,1,3,3-tetramethylbutyl)amino]-5-(1,1,3,3-tetramethylbutylamino)-3,4-furandicarboxylate 5a

Viscous yellow oil, IR (KBr) (υ_{max}, cm^{-1}): 3485 (NH), 1730 (CO_2Me), 1669 (CO_2Me), 1576 CON), 1215 (C—O).^{1}H NMR (250.13 MHz, $CDCl_3$): δ_H 1.04 (9 H, s, CMe_3), 1.11 (9 H, s, CMe_3), 1.40 (3 H, s, CMe_2), 1.50 (3 H, s, CMe_2), 1.52 (3 H, s, CMe_2), 1.54 (3 H, s, CMe_2), 1.60 (2 H, s, CH_2), 1.90 (1 H, d, $^2 J_{HH} = 15.0$ Hz, CH_2), 1.75 (1 H, d, $^2J_{HH} = 15.0$ Hz, CH_2), 3.63 (3 H, s, OMe), 3.75 (3 H, s, OMe), 7.07 (1 H, s, NH), 7.22 (2 H, d, $^3J_{HH} = 7.0$ Hz, 2 CH_{ortho} of C_6H_5), 7.27 (1 H, t, $^3J_{HH} = 7.0$ Hz, CH_{para} of C_6H_5), 7.44 (2 H, t, $^3J_{HH} = 7.5$ Hz, 2 CH_{meta} of C_6H_5).^{13}C NMR (62.90 MHz, $CDCl_3$): δ_C 28.11 (CMe_3), 28.79 (CMe_3), 30.01 (CH_3 of CMe_2), 30.18 (CH_3 of CMe_2), 31.44 (CH_3 of CMe_3), 31.66 (CH_3 of CMe_3), 31.73 (CH_2), 49.33 (CMe_2), 50.90 (CMe_2), 51.80 (OMe), 53.01 (OMe), 56.18 (CH_2), 65.69 (CH_2), 85.59 (C4 of furan), 114.76 (C3 of furan), 127.28 (CH_{para} of C_6H_5), 127.62 (2 CH_{ortho} of C_6H_5), 129.83 (2 CH_{meta} of C_6H_5), 138.32 (C_{ipso} of C_6H_5), 139.89 (C5 of furan), 159.02 (C2 of furan), 163.62 (CO_2Me), 165.13 (CO_2Me), 172.20 (NCO).

Diethyl 2-[Benzoyl(1,1,3,3-tetramethylbutyl)amino]-5-(1,1,3,3-tetramethylbutylamino)-3,4-furandicarboxylate 5b

Viscous yellow oil, IR (KBr) (υ_{max}, cm^{-1}): 3492 (NH), 1746 (CO_2Me), 1684 (CO_2Me), 1569 (CON), 1230 (C—O).^{1}H NMR (250.13 MHz, $CDCl_3$): δ_H 1.03 (9 H, s, CMe_3), 1.10 (9 H, s, CMe_3), 1.18 (3 H, t, $^3J_{HH} = 7.0$ Hz, CH_3), 1.29 (3 H, t, $^3J_{HH} = 7.0$ Hz, CH_3), 1.40 (3 H, s, CMe_2), 1.51 (3 H, s, CMe_2), 1.55 (6 H, s, CMe_2), 1.60 (2 H, m, CH_2), 1.71 (2 H, d, $^1J = 15.0$

Hz, CH_2), 1.86 (2 H, d, $^1J = 15.0$ Hz, CH_2), 4.11 (3 H, m, OEt), 4.32 (3 H, m, OEt), 7.02 (1 H, s, NH), 7.12 (2 H, d, $^3J_{HH} = 7$ Hz, 2 CH_{ortho} of C_6H_5), 7.26 (1 H, t, $^3J_{HH} = 7$ Hz , CH_{para} of C_6H_5), 7.46 (2 H, t, $^3J_{HH} = 7.5$ Hz , 2 CH_{meta} of C_6H_5).^{13}C NMR (62.90 MHz, $CDCl_3$): δ_C 14.04 (CH_3), 14.17 (CH_3), 28.12 (CMe_3), 28.94 (CMe_3), 30.03 (CH_3 of CMe_2), 30.20 (CH_3 of CMe_2), 31.45 (CH_3 of CMe_3), 31.62 (CH_3 of CMe_3), 31.65 (CH_2), 49.35 (CMe_2), 52.98 (CMe_2), 56.11 (OEt), 59.57 (OEt), 61.17 (CH_2), 65.67 (CH_2), 85.91 (C4 of furan), 115.2 (C3 of furan), 127.42 (CH_{para} of C_6H_5), 127.59 (2 CH_{ortho} of C_6H_5), 129.77 (2 CH_{meta} of C_6H_5), 138.22 (C_{ipso} of C_6H_5), 139.07 (C5 of furan), 158.88 (C2 of furan), 164.75 (CO_2Me), 165.13 (CO_2Me), 172.13 (NCO).

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