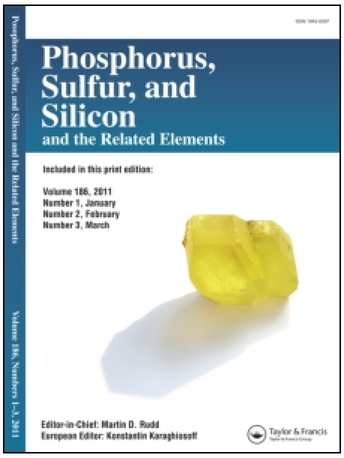

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THE REACTIONS OF TRIPHENYLPHOSPHINE ALKYLENES WITH 3(2-THIENYL)ACRYLONITRILES

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*Ethyl 3-(2-thienyl)acrylocyanoacetate (**1b**) reacts with ester ylide phosphoranes **2a,b** in toluene, containing triethylamine, affording the Michael addition products **7a,b** and the cyclopropanes **6a,b** and **8a,b**. The reaction of **1b** with keto ylide **2c** in ethyl acetate containing benzoic acid in addition to the ylide **7c** the pyran **12** was obtained. On the other hand, (cyanomethyl)triphenylphosphonium chloride (**13**) reacts, under the phase-transfer catalysis conditions, with **1b** to give the cyclopropane derivative **15** whereas with **1a**, the new ylide **16** along with the propene derivative **17** were obtained.*

Keywords: Acrylonitriles; alkylidenephosphoranes; Michael addition; substitution reaction; Wittig reaction

INTRODUCTION

Recently,[1] it has been shown that the phosphoryl carbanions [Horner-Wittig reagents, $(EtO)_2P(O)CH_2R$] react with 3-(2-thienyl)acrylonitrile (**1a**) and ethyl 3-(2-thienyl)acrylocyanoacetate (**1b**) to give different phosphorylated cyclic and acyclic systems, depending on the nature of the α-substituent of the reagent and the basicity of the reaction medium employed. The investigation also has indicated that **1b** behaves differently from **1a** toward the phosphoryl carbanions, whereupon the ester function of the substituted acrylonitrile **1b** was involved in some reactions. In an earlier study,[2] we reported that the reaction of the nitrile **1a** with the conventional Wittig reagents **2a–c** resulted to mainly the corresponding (1:1) phosphorus ylides **3** along with the ethylene derivatives

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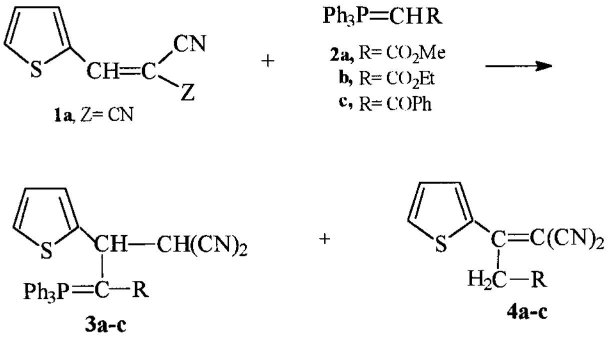


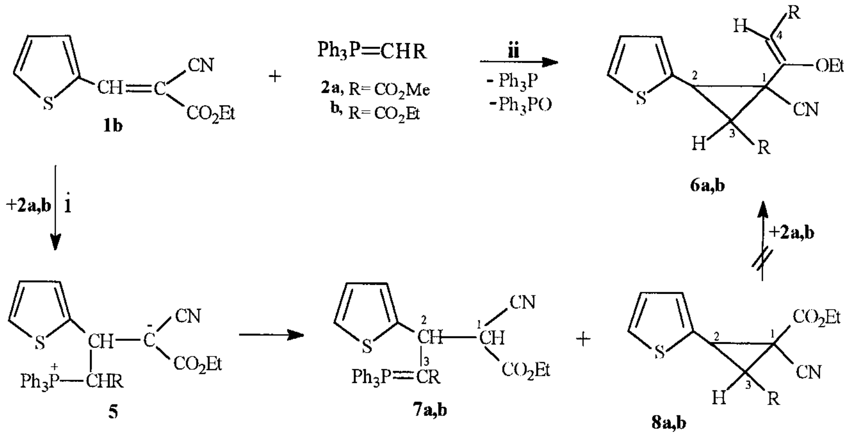
SCHEME 1

4 as a minor products (Scheme 1). Similar reactions also were studied[3,4] and in all cases,[1–4] an initial Michael addition occurred at the exocyclic ethylene bond in this class of compounds, regardless of the type of the phosphorus carbanion used.

In continuation of our interest in this area, we now report our results on the reactions of stabilized ester-**2a**,**b** and keto-**2c** ylide phosphoranes with acrylonitrile **1b**. The reactions between (cyanomethylene)triphenylphosphorane (**14**) and **1a**,**b** as well as some transformations of the products obtained are also reported.

RESULTS AND DISCUSSION

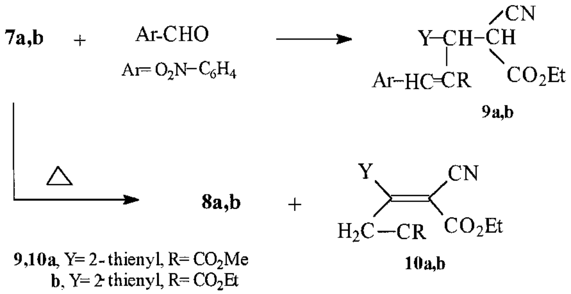
Acrylonitrile **1b** on treatment with (methoxycarbonylmethylene)-triphenylphosphorane (**2a**) (2 molar amounts) in boiling toluene, the educts remained practically unchanged, even after 3 days. Conversely, the reaction completed when it was carried out in the presence of triethylamine. Separation of the product mixture by column chromatography yielded the new ylide **7a** (18%) together with the cyclopropane derivatives **6a** (22%) and **8a** (28%). Similarly treatment of **1b** with (ethoxycarbonylmethylene)triphenylphosphorane for 3 days at reflux, ylide **7b** (15%) along with the cyclopropane derivatives **6b** (26%) and **8b** (29%) were obtained (Scheme 2). However, when **1b** was treated with an equimolar amount of **2a** under the same reaction conditions, products **7a** (20%), **6a** (10%), and **8a** (25%) were obtained along with unchanged nitrile **1b** (25%). Further reaction of ylides **7a**,**b** with aromatic aldehyde (O_2N–C_6H_4CHO-*p*) led to the formation of Wittig products **9a**,**b** in good yields (~65%) (Scheme 3). Elemental analyses, molecular weight measurements (MS), IR, and NMR spectroscopy elucidate the structures of the new products.



SCHEME 2

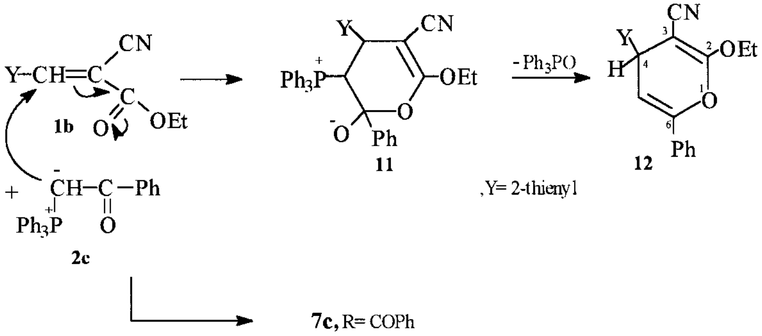
Respective mechanism for the formation of the products **6–8** from the reaction of **2a**,**b** with **1b** involves two routes. 1) Michael addition reaction of the ylides **2a**,**b** on the more electrophilic site of the exocyclic ethylenic linkage in **1b** yields the resonance hybrid **5**.[1–4] The intermediate **5** stabilizes itself through the migration of the proton-α- to the positive phosphorus atom-to the electron rich carbanionic center, yielding the ylide **7**. In addition, the dipolar form **5** might undergo an elimination reaction-ejection of triphenylphosphine-producing the cyclopropane **8**.[5] 2) The ylide **2**, concurrently, attacks both the activated carbon-carbon double bond and the ester-carbonyl group, to give the product **6** with concomitant loss of triphenylphosphine and triphenylphosphine oxide. For similar reactions, cyclopropane derivatives have also been reported in the literature,[6] on treatment of oxobutenoate with alkylidene phosphoranes. Furthermore, the attack at the carbonyl ester rather than the nitrile group in the cyanoacetate moiety is a documented process.[7] In favor of Scheme 2, the product **8a** (as a representative example) is recovered, practically unchanged, when heated with **2a** in boiling toluene containing TEA, even for 2 days. Nevertheless, heating the ylide **7a**,**b** in ethyl acetate for 24 h at the reflux temperature afforded the respective cyclopropane **8** and the olefin **10** (Scheme 3). Repeating the latter reaction in the presence of one mole equivalent of **2** led to the same result whereupon **8** and **10** were obtained.

An unexpected result was obtained in the case of applying (benzoylmethylene)triphenylphosphorane on **1b**. In addition to the analogous ylide **7c** 3-cyano-2-ethoxy-6-phenyl-4H-4-(2-thienyl)pyran (**12**) was obtained as the major product. Cyclopropane analog was not observed in this reaction. The reaction did not proceed in toluene containing TEA,



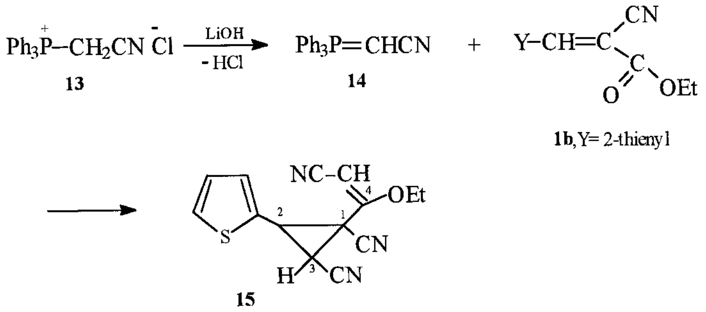
SCHEME 3

as previously described for **2a**,**b** whereas in ethyl acetate containing a catalytic amount of benzoic acid the reaction was completed. Elemental analysis and exact mass measurement of **12** showed the empirical formula to be $C_{18}H_{15}NO_2S$ (309). The spectroscopic data are also in agreement with the assigned structure. The formation of **12** is suggested to start with the attack by the carbanion center in **2c** to the active exocyclic methide carbon in **1b** giving rise to the intermediate **11**. Further elimination of triphenylphosphine oxide affords the pyran derivative **12** (Scheme 4). An analogous reaction is reported to proceed between the same ylide and quinone methides, with concomitant formation of triphenylphosphine oxide.[7]



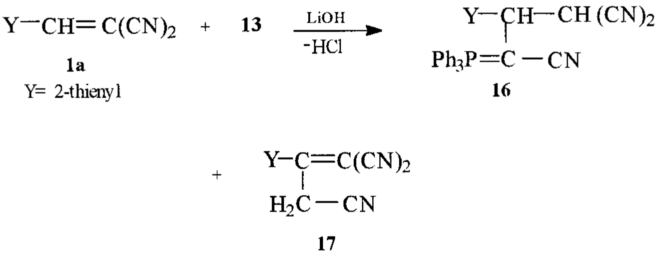
SCHEME 4

Next, the reaction between (cyanomethylene)triphenylphosphorane (**14**) and **1b** as well as **1a** was investigated. Treatment of the ylide **14**, prepared in situ from the corresponding phosphonium salt **13**, with the cyanoacetate **1b** yielded the cyclopropane derivative **15** (48%), as the sole reaction product (Scheme 5).



SCHEME 5

On the other hand, the malonitrile **1a** reacted the phosphonium salt **13**, under the same prevailing conditions, giving the ylide **16** and the known[1] propene derivative **17** (Scheme 6). Compound **17** was found to be identical with the product previously[1] isolated from the reaction of the nitrile **1a** with the Horner-Wittig reagent counterpart [$(EtO)_2P(O)CH_2CN$]. Furthermore, the reaction and the products that have been described in Scheme 6 parallel to Scheme 1, previously reported.[2]



SCHEME 6

In summary, the results of the earlier[1,2] and the present investigation allow interesting observations to be drawn. 1) Notwithstanding, the initial step in the reactions of the α,β-unsaturated nitriles **1a**,**b** with α-phosphoryl- and α-phosphorane carbanions involves the Michael addition of the synthon at the exocyclic methide carbon in **1a**,**b**, the sequel of the initial step vary markedly, according to the nature of the α-substituent in the educts and the reaction conditions. 2) The results also showed that the behavior of **1b** with either the Wittig or the Wittig-Horner reagents are in great disparity with that of the malonitrile analog **1a**. The latter result is, however, attributable to the involvement of the ester function of the substituted acrylonitrile **1b** in the reactions. 3) The unexpected behavior of **1b** toward the keto ylide **2c** leading to the pyran **12** represents a facile and direct approach for incorporating two heterocyclic moieties of anticipated biological activities in one and the same molecule.

EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer spectrophotometer model 297 (Grating) using KBr disc. The ^{1}H and ^{13}C NMR spectra were run on a Varian Gemini 200 (200 MHZ) instrument, using TMS as an internal reference. The ^{31}P NMR spectra were recorded relative to external H_3PO_4 (85%) with a Varian CFT-80 instrument. The mass spectra were performed at 70 eV on an MS-50 Kratos (A.E.I.) spectrometer provided with data system. The appropriate precautions in handling moisture-sensitive compounds were observed. Light petroleum refers to the fraction 40–60°C.

I. Action of Phosphorus Ylides 2a and 2b on Acrylonitrile 1b

No reaction was observed when **1b** and 2 molar amounts of **2a** (or **2b**) were refluxed in toluene even after 3 days whereupon **1b** and **2a** (or **2b**) were recovered, practically unchanged, in ∼90% yield.

General Procedure

A stirred solution of ethyl 3-(2-thienyl)acrylocyanoacetate (**1b**)[8] (0.8 g, 3.88 mmol) and (methoxycarbonylmethylene)triphenylphosphorane (**2a**) (2.7 g, 7.76 mmol) in dry toluene (20 mL) containing triethylamine (TEA, 0.5 ml) was boiled under reflux for 3 days. The product mixture was evaporated on silica gel under reduced pressure, and applied to a silica gel column using hexane containing increasing amounts of ethyl acetate as eluents whereby compounds **8a**, **7a**, and **6a** were eluted respectively.

Ethyl methyl 1-cyano-2-(2-thienyl)cyclopropane-1,3-dicarboxylate (**8a**) was obtained (up to 7:3, *v/v*) as yellow crystals (300 mg, 28%), m.p. 147–148°C (CH_2Cl_2); $C_{13}H_{13}NO_4S$ (279.32): calcd.: C 55.90, H 4.69, N 5.01, S 11.48; found: C 55.98, H 4.77, N 4.93, S 11.37; NMR ($CDCl_3$); δ_H 1.23 (t, 3H, $J_{HH} = 7.2$ Hz, O.C.C**H**$_3$), 3.61, 3.77 (2d, 2 × 1H, $J_{HH} =$ 11.5 Hz, C-2-**H** & C-3-**H**), 3.89 (s, 3H, OC**H**$_3$), 4.36 (q, 2H, $J_{HH} = 7.2$ Hz, O.C**H**$_2$CH$_3$), 7.16, 7.66, 7.87 (m, 3 × 1H, Het-**H**); δ_C 14.4 (O.C.**C**H$_3$), 30.4, 32.3 (**C**-2 & **C**-3), 54.8 (O**C**H$_3$), 62.5 (O**C**H$_2$ CH$_3$), 110.6 (**C**N), 122.3, 124.5, 126.2 (**C**-4, **C**-3, **C**-5, Het-**C**), 137.6 (**C**-2, thienyl), 160.5, 162.8 (2 × C(O), esters) ppm; MS: m/z (%) = 279 (M^+, 20), 264 (11), 252 (100), 249 (17), 222 (21), 194 (4), 179 (20), 166 (13), 96 (48); IR: $\nu = 2218$ (CN), 1722, 1715 (2 × C(O), esters) cm^{-1}.

Ethyl methyl [1-cyano-2-(2-thienyl)propanylid-3-ene]triphenylphosphorane-1,3-dicarboxylate (**7a**) was obtained (3:7, *v/v*) as yellow flakes (376 mg, 18%); m.p. 172–174°C ($CHCl_3$); $C_{31}H_{28}NO_4PS$ (541.62): calcd.: C 68.34, H 5.21, N 2.59, P 5.72, S 5.92; found: C 68.84, H 5.28, N 2.49, P 5.66, S 5.84; NMR ($CDCl_3$): δ_H 1.22 (t, 3H, $J_{HH} = 7.3$ Hz, O.C.C**H**$_3$), 3.45 (dd, 1H, $J_{HH} = 10.3$, $J_{HP} = 3.8$ Hz, C-2-**H**), 3.86 (s, 3H, O.C.C**H**$_3$), 4.03 (q, 2H, $J_{HH} = 7.3$ Hz, OC**H**$_2$CH$_3$), 4.25 (dd, 1H, $J_{HH} = 10.3$, $J_{HP} = 2.2$ Hz, C-1-**H**), 7.25–7.92 (m, 18 H, Ar-**H** & Het-**H**); $\delta_P = 28.6$ ppm; MS: m/z (%) = 541 (M^+, 12), 526 (9), 511 (4), 514 (28), 262 (10), 252 (100), 251 (12), 222 (14), 194 (8), 166 (16), 96 (35); IR: $\nu = 2220$ (CN), 1720_w (2 × C=O, esters), 1675, 1445 (C=PPh$_3$) cm^{-1}.

1-Cyano-2-(2-thienyl)-1(methyl-1-ethoxyethylene-2-carboxylate)cyclopropane-3-carboxylic acid methyl ester (**6a**) was obtained (pure AcOEt) as yellow crystals (285 mg, 22%), m.p. 188–190°C ($CHCl_3$); $C_{16}H_{17}NO_5S$ (335.39): calcd.: C 57.30, H 5.11, N 4.17, S 9.56; found: C 57.37, H 5.19, N 4.06, S 9.46; ^{1}H NMR ($CDCl_3$): $\delta = 1.07$ (t, 3H, $J_{HH} = 6.8$ Hz, CH$_2$C**H**$_3$), 3.58 (d, 1H, $J_{HH} = 8.8$ Hz, C-3-**H**), 3.77–4.13 (m, 9H, C-1-**H** & 2 × OC**H**$_3$ & OC**H**$_2$), 6.28 (s, 1H, C=C**H**), 7.23–7.86 (m, 3H, Het-**H**) ppm; MS: m/z (%) = 335 (M^+, 13), 320 (26), 308 (100), 305 (7), 278 (41), 250 (11), 222 (3), 191 (24), 146 (13), 96 (29); IR: $\nu = 2195$ (CN), 1725_w [2 × C(O)], 1618 (C=C) cm^{-1}.

Similarly, the reaction of (ethoxycarbonylmethylene)triphenylphosphorane (**2b**) with **1b** was carried out under reflux in toluene containing TEA for 3 days thereby the procedure and the workup are the same (with **2a**) using the same amounts. The product residue was chromatographed with hexane/AcOEt to give **8b**, **7b**, and **6b** respectively.

Diethyl 1-cyano-2-(2-thienyl)cyclopropane-1,3-dicarboxylate (**8b**) was obtained (up to 6:4, *v/v*) as yellow crystals (328 mg, 29%), m.p. 141–143°C ($CHCl_3$); $C_{14}H_{15}NO_4S$ (293.35): calcd.: C 57.32, H 5.15, N 4.77, S 10.93; found: C 57.41, H 5.21, N 4.72, S 10.86; NMR ($CDCl_3$): $\delta_H = 0.85$, 1.16 (2t, 2 × 3H, $J_{HH} = 7.3$ Hz, 2 × O.C.C**H**$_3$), 3.58, 3.75 (2d, 2 × 1H, $J_{HH} = 11.5$ Hz, C-2-**H** & C-3-**H**); 3.87–4.12 (2q (m), 2 × 2H, 2 × OC**H**$_2$CH$_3$), 7.14, 7.66, 7.88 (m, 3 × 1H, Het-**H**); $\delta_C = 14.42$, 16.7 (C.**C**H$_3$, esters), 31.6, 33.5 (**C**-2 & **C**-3), 62.5, 63.1 (2 × OCH$_2$, esters), 109.2 (**C**N), 122.6, 124.4, 126.8 (**C**-4, **C**-3, **C**-5, Het-**C**), 135.6 (**C**-2, thienyl), 159.7, 162.4 (2 × C(O), esters) ppm; MS: m/z (%) = 293 (M^+, 11), 278 (24), 266 (100), 263 (6), 236 (11), 208 (9), 180 (18), 193 (16), 96 (41); IR: $\nu = 2220$ (CN), 1720, 1705 (2 × C(O), ester) cm^{-1}.

Diethyl-[1-cyano-2(2-thienyl)propanylid-3-ene]triphenylphosphorane-1,3-dicarboxylate (**7b**) was obtained (3:7, *v/v*) as yellow flakes (322 mg, 15%); m.p. 156–158°C ($CHCl_3$); $C_{32}H_{30}NO_4PS$ (555.65): calcd.: C 69.17, H 5.44, N 2.52, P 5.57, S 5.77; found: C 69.25, H 5.51, N 2.43, P 5.51, S 5.66; NMR ($CDCl_3$): $\delta_H = 1.12$, 1.27 (2t, 2 × 3H, $J_{HH} = 6.8$ Hz, 2 × O.C.C**H**$_3$), 3.56 (dd, 1H, J_{HH} = 11.3, J_{HP} = 3.3 Hz, C-2-**H**), 3.95–4.08 (2q, 2 × 2H, J_{HH} = 6.8 Hz, 2 × OC**H**$_2$CH$_3$), 4.42 (d, 1H, J_{HH} = 11.3, J_{HP} = 2.5 Hz, C-1-**H**), 7.25–7.83 (m, 18 H, Ar-**H** & Het-**H**); δ_P = 30.3 ppm; MS: m/z (%) = 555 (M$^+$, 12), 540 (7), 528 (21), 525 (6), 266 (100), 262 (21), 238 (13), 210 (10), 185 (8), 96 (30); IR: ν = 2198 (CN), 1720$_w$ (2 × C=O, esters), 1674, 1460 (C=PPh$_3$) cm^{-1}.

1-Cyano-2-(2-thienyl)-1-(ethyl 1-ethoxyethylene-2-carboxylate)cyclopropane-3-carboxylic acid ethyl ester (**6b**) was obtained (pure AcOEt) as yellow crystals (364 mg, 26%), m.p. 180–182°C (CHCl$_3$); $C_{18}H_{21}NO_5S$ (363.44): calcd.: C 59.49, H 5.82, N 3.85, S 8.82; found: C 59.57, H 4.78, N 3.77, S 8.73; ^{1}H NMR (CDCl$_3$): δ = 1.07–1.23 (m, 9H, 3 × C.C**H**$_3$), 3.63 (d, 1H, J_{HH} = 8.8 Hz, C-3-**H**), 3.96–4.21 (m, 7H, 3 × OC**H**$_2$ & C-2-**H**), 6.21 (s, 1H, C=C**H**), 7.23–7.81 (m, 3H, Het-**H**) ppm; MS: m/z (%) = 363 (M$^+$, 18), 348 (29), 336 (100), 333 (5), 306 (43), 278 (9), 250 (5), 205 (19), 160 (9), 96 (31); IR: ν = 2183 (CN), 1731$_w$ [2 × C(O)], 1622 (C=C) cm^{-1}.

(B). The reaction between equimolar amounts of compounds **1b** and **2a** under the same reaction conditions described above gave unchanged nitrile **1b** (ca. 25%). Further elution afforded again compounds **8a** (25%), **7a** (20%), and **6a** (10%).

Wittig Reaction of Ylides 7a,b

To a stirred solution of **7a** or **7b** (0.5 g, ~0.9 mmol) in ethyl acetate (10 mL) *p*-nitrobenzaldehyde (150 mg, 1 mmol) was added, and the reaction mixture was refluxed for 48 h. After the evaporation of the solvent, the residue was chromatographed by hexane/AcOEt to give firstly (6:4, *v/v*) triphenylphosphine oxide, followed by the second fraction (2:8, *v/v*), which afforded the Wittig product **9a** or **9b** in ~45% yield.

Olefin **9a**, m.p. 225°C (ethyl alcohol); $C_{20}H_{18}N_2O_6S$ (414.45) calcd.: C 57.96, H 4.38, N 6.76, S 7.74; found: C 57.92, H 4.45, N 6.68, S 7.62; ^{1}H NMR (CDCl$_3$): δ = 1.23 (t, 3H, CH$_2$C**H**$_3$), 3.57, 3.71 (2d, 2 × 1H, J_{HH} = 10 Hz, C-1-**H** & C-2-**H**), 4.07 (m, 5H, OC**H**$_2$ & OC**H**$_3$), 6.73 (s, 1H, C=C**H**), 7.25–7.89 (m, 7H, Ar-**H** & Het-**H**) ppm; MS: m/z (%) = 414 (M$^+$, 24), 399 (9), 387 (33), 384 (17), 378 (7), 351 (100), 321 (35), 293 (7), 265 (21), 234 (23), 220 (13), 96 (37); IR: ν = 2190 (CN), 1720$_w$, [2 × C(O)], 1615 (C=C, exocyclic) cm^{-1}.

Olefin **9b**, m.p. 196–198°C (ethyl alcohol); $C_{21}H_{20}N_2O_6S$ (428.47): calcd.: C 58.87, H 4.71, N 6.54, S 7.48; found: C 58.93, H 4.77, N 6.44, S 7.39; ^{1}H NMR (CDCl$_3$): δ = 1.22, 1.24 (2t, 2 × 3H, 2 × O.C.C**H**$_3$), 3.61, 3.75 (2d, 2 × 1H, J_{HH} = 9.5 Hz, C-1-**H** & C-2-**H**), 4.13 (m, 2 × 2H, 2 × OC**H**$_2$); 6.68 (s, 1H, C=C**H**), 7.25–7.89 (m, 7H, Ar-**H** & Het-**H**) ppm; MS: m/z (%) = 428 (M$^+$, 13), 413 (9), 401 (28), 398 (12), 392 (21), 365 (100), 335 (29), 307 (16), 279 (25), 234 (19), 220 (9), 96 (39); IR: $\nu = 2200$ (CN), 1720_w, [2 × C(O)], 1618 (C=C, exocyclic) cm^{-1}.

***Action of Heat on the Ylides* 7a,b**: A solution of the ylide **7a** or **7b** (0.4 g) in toluene (10 mL) was heated under reflux for 24 h. After the removal of the solvent, the residue was chromatographed by hexane/AcOEt to give two fractions.

***(A) with* 7a:** The first fraction (7:3, *v/v*) afforded yellow crystals of the cyclopropane **8a** (37 mg, 18%), m.p. 146–148°C (CH_2Cl_2), identical with the material has previously obtained.

The second fraction (3:7, *v/v*) gave orange crystals of *ethyl methyl 1-cyano-2-(2-thienyl)prop-1-ene-1,3-dicarboxylate* (**10a**) (88 mg, 43%), m.p. 155–156°C (MeCN); $C_{13}H_{13}NO_4S$ (279.32): calcd.: C 55.90, H 4.69, N 5.01, S 11.48; found: C 55.96, H 4.78, N 5.10, S 11.35; ^1H NMR ($CDCl_3$): $\delta = 1.12$ (t, 3H, O.CH_2**CH_3**), 2.73 (s, 2H, 3-C**H_2**), 3.88–3.98 (m, 5H, OC**H_2** & OC**H_3**), 7.2, 7.58, 7.94 (m, 3H, Het-**H**) ppm; MS: m/z (%) = 279 (M^+, 30), 264 (13), 252 (100), 249 (13), 222 (20), 194 (5), 179 (22), 166 (13), 96 (49); IR: $\nu = 2222$ (CN), 1731, 1718 [2 × C(O], 1618 (C=C, exocyclic) cm^{-1}.

***(B) with* 7b**: The first fraction (6:4, *v/v*) afforded yellow crystals of **8b** (42 mg, 26%), m.p. 141–142°C ($CHCl_3$), identical with the one obtained before.

The second fraction (3:7, *v/v*) yielded orange crystals of *diethyl 2-(2-thienyl)prop-1-ene-1,3-dicarboxylate* (**10b**) (59 mg, 28%), m.p. 147–148°C (MeCN); $C_{14}H_{15}NO_4S$ (293.35): calcd.: C 57.32, H 5.51, N 4.77, S 10.93; found: C 57.39, H 5.26, N 4.71, S 10.88; ^1H NMR ($CDCl_3$): $\delta =$ 1.17–1.2 (m (2t), 6H, 2 × C.C**H_3**), 2.78 (s, 2H, C**H_2**), 4.11 (m (2q), 4H, 2 × O.C**H_2**), 7.24–7.86 (m, 3H, Het-**H**) ppm; MS: m/z (%) = 293 (M^+, 10), 278 (4), 266 (100), 263 (9), 208 (9), 180 (21), 193 (10), 96 (38); IR: $\nu =$ 2195 (CN), 1730, 1715 (2 × C=O), 1610 (C=C, exocyclic) cm^{-1}.

Repeating the above reaction in the presence of equimolar amount of the ylide **2** led to the same result yielding **8** (~15) and **10** (~32%).

***Action of the Ylide* 2a *on the product* 8a**: The reaction between compound **8a** (0.3 g) and one quiv. of the ylide **2a** in boiling toluene (10 mL), containing TEA, for 2 days was carried out and the product mixture was worked up as usual to give yellow crystals (~0.25 g, 90%) and proved to be unchanged **8a** (m.p., mixed m.p., and comparative IR spectra). No identification (TLC) for **6a** in the product mixture was observed.

II. Action of Phosphorus Ylide 2c on Acrylonitrile 1b

A stirred solution of compound **1a** (0.8 g, 3.88 mmol) and (benzoylmethylene)triphenylphosphorane (**2c**) (1.52 g, 4 mmol) in dry toluene

(30 mL) containing TEA (0.5 ml) was refluxed for 4 days whereupon no reaction was occurred (TLC). Repeating the reaction in boiling ethyl acetate containing benzoic acid (0.5 g) for 3 days afforded compounds **12** and **7c**, respectively, after the usual workup.

3-Cyano-2-ethoxy-6-phenyl-4H-4-(2-thienyl)pyran (**12**) was obtained (1:1, *v/v*, AcOEt/EtOH) as red crystals (490 mg, 41%), m.p. 238–240°C (EtOH); $C_{18}H_{15}NO_2S$ (309.39): calcd.: C 69.88, H 4.88, N 4.53, S 10.36; found: C 69.81, H 4.95, N 4.42, S 10.27; ^{1}H NMR (d$_6$-DMSO): $\delta = 0.99$ (t, 3H, $J_{HH} = 6.8$ Hz, O.C.C**H**$_3$), 3.76 (q, 2H, O.C**H**$_2$CH$_3$), 4.66 (s, 1H, C-4-**H**), 7.24–8.22 (m, 9H, Ph-**H**, Het-**H** & C-5-**H**); MS: m/z (%) = 309 (M$^+$, 32), 294 (10), 282 (100), 281 (58), 236 (17), 189 (33), 96 (40); IR: $\nu = 2195$ (CN) cm^{-1}.

Ethyl [2-(2-thienyl)-3-benzoylpropanylidene]triphenylphosphorane-1,1-cyanoacetate (**7c**) was obtained (2:8, *v/v*, AcOEt/EtOH) as reddish brown crystals (400 mg, 18%), m.p. 181–183°C (EtOH); $C_{36}H_{30}NO_3PS$ (587.69): calcd.: C 73.57, H 5.14, N 2.38, P 5.27, S 5.46; found: C 73.66, H 5.04, N 2.24, P 5.22, S 5.39; NMR (d$_6$-DMSO) $\delta_H = 1.14$ (t, 3H, $J_{HH} = 6.6$ Hz, O.C.C**H**$_3$), 3.58 (dd, 1H, $J_{HH} = 10.5$, $J_{HP} = 3.8$ Hz, C-2-**H**), 4.04 (q, 2H, $J_{HH} = 6.6$ Hz, OC**H**$_2$), 4.45 (dd, 1H, $J_{HH} = 10.5$, $J_{HP} = 2.3$ Hz, C-1-**H**), 7.24–8.01 (m, 23 H, Ph-**H** & Het-**H**); $\delta_P = 22.53$ ppm; MS: m/z (%) = 587 (M$^+$, 18), 572 (3), 560 (23), 298 (100), 270 (29), 262 (13), 207 (29), 96 (37); IR: $\nu = 2216$ (CN), 1720 (C=O, ester), 1682 (C=O, benzoyl), 1672, 1443 (C=PPh$_3$) cm^{-1}.

III. Action of Phosphorus Ylide 14 on 1b and 1a

General Procedure

A solution of cyanomethylenephosphomium chloride (**13**) (7.76 mmol) and the acrylonitriles **1b**,**a** (3.88 mmol) in absolute ethanol (40 mL) was stirred for 15 min. Freshly prepared aqueous lithium hydroxide (0.5 N, 10 mL) was added in one portion to the mixture, and the two-phase system was stirred at room temperature until the consumption of the starting acrylonitrile (for 72 h for **1b** and for 24 h for **1a**). The mixture was then extracted with $CHCl_3$ (2 × 50 mL). The combined extracts were washed with water (25 mL), dried, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel by using hexane containing an increasing amounts of ethyl acetate.

A. The reaction with **1b** (0.8 g, 3.88 mmol) gave 1-(cyanomethylvinylether)-1,3-dicyano-2-(2-thienyl)cyclopropane (**15**) (AcOEt, eluent) as orange crystals (0.5 g, 48%), m.p. 142–144°C (CH_2Cl_2/light petroleum); $C_{14}H_{11}N_3OS$ (269.33): calcd.: C 62.43, H 4.12, N 15.60, S 11.90; found: C, 62.54; H, 4.07; N, 15.54; S, 11.82; ^{1}H NMR (DMSO-d$_6$): $\delta = 1.14$ (t, 3H, $J_{HH} = 7$ Hz, C.C**H**$_3$), 3.51 (d, 1H, $J_{HH} = 8.8$ Hz, C-2-**H**), 3.95 (2H, q, OC**H**$_2$), 4.42 (d, 1H, J_{HH} = 8.8 Hz, C-3-**H**), 5.74 (s, 1H, =C**H**CN), 7.28–7.94 (m, 3H, Het-**H**); MS: m/z (%) = 269 (M$^+$, 62), 254 (5), 272 (76), 260 (100), 245 (36), 233 (65), 188 (13), 96 (23); IR: ν = 1987, 1995–2005 (3 × CN), 1618 (C=C, exocyclic) cm^{-1}.

B. The reaction with **1a**[9] (0.8 g, 5 mmol) gave two fractions. The first fraction (up to 4:1, *v*/*v*, hexane/AcOEt) afforded yellow substance, recrystalized from benzene, and identified as 1,1,3-tricyano-2-(2-thienyl)prop-1-ene (**17**) (230 mg, 23%), m.p.: 118–120°C [lit.[1], m.p.: 168–170°C]; MS: m/z (%) = 199 (M$^+$, 55); requires 199.234.

The second fraction yielded a reddish brown substance, recrystallized from chloroform to give **16** (855 mg, 37%); m.p. 179–182°C; $C_{28}H_{20}N_3PS$ (462.38): calcd.: C 72.73, H 4.54, N 9.09, P 6.70, S 6.93; found: C 72.66, H 4.46, N 9.04, P 6.77, S 6.82; NMR (d$_6$-DMSO): δ_H 3.42 (d of d, 1H, $^1J_{HP}$ = 10.5 Hz, C-2-**H**); 3.68 (d of d, 1H, J_{HH} = 7.2 Hz, C-1-**H**); 7.23–8.02 (m, 18 H, Ph-**H**, Het-**H**); δ_P = 24.8 ppm; MS: m/z (%) = 462 (M$^+$, 23), 435 (18), 381 (6) 370 (11), 262 (10), 161 (100), 96 (33); IR: $\nu = 2222_w$ (3 × CN), 1645, 1535 (C=P) cm^{-1}.

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