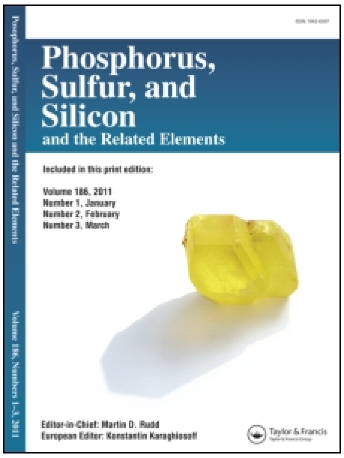

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REACTION OF PHOSPHORANES WITH CINNAMONITRILES. A NOVEL SYNTHESIS OF α-SUBSTITUTED PHOSPHONIUM YLIDES

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Reaction of phosphoranes with cinnamonitriles. Synthesis of α-substituted-β-arylacrylic acids via the Witting reaction.

Keywords: Arylidenemalononitrile; cyclopropane derivatives; phosphoranes

The alkylation of phosphonium ylides[1–5] is an important route to more complex ylides which are often unavailable by other methods.[6] Our interest in carbon-carbon bond formation by arylidene exchange[7] led us to investigate the alkylation of phosphoranes with cinnamonitriles, and to explore the synthetic utility of the products of this reaction. Carbethoxymethylenetriphenylphosphorane **1** and benzylidenemalononitrile **2** were found to react readily with excellent yield to give an addition product having the molecular formula $C_{32}H_{27}N_2O_2P$ without elimination of by-product. Five isomeric forms **3–7** are possible for this addition product (Scheme 1). The structure of ylide **4** was established to represent the reaction product based on its spectroscopic data. The IR spectrum revealed broad absorption band at $\nu = 2220 - 2222\ \mathrm{cm}^{-1}$ characteristic for two CN groups.[8] If the reaction product is the cyclic isomer form **7** it would have one sharp CN absorption. The ^1H and ^{13}C NMR spectra for a molecule with structure **4** support the proposed structure. Thus, ^1H NMR spectrum ($CDCl_3$) showed besides the aromatic signals a doublet of doublets at 3.22 ppm with coupling constant $J_{H,H}$

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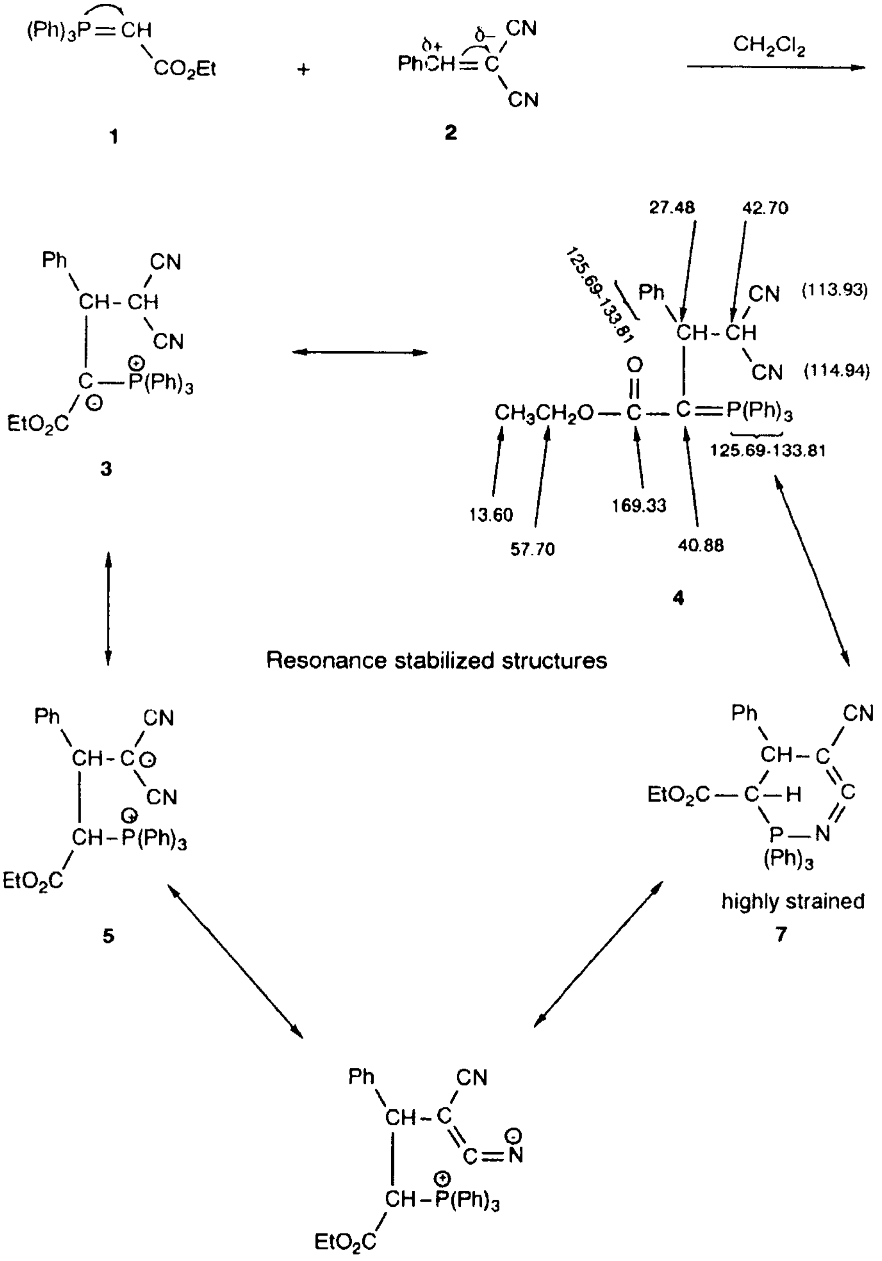
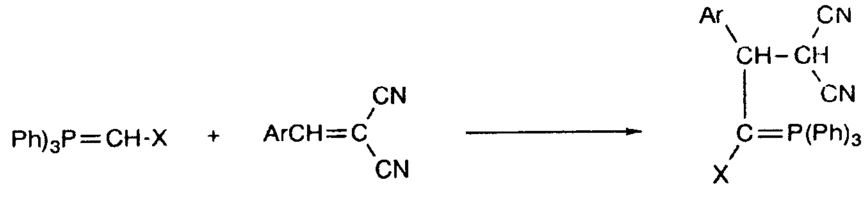
*Corresponding author.



1
2
CH2Cl2
3
4
5
7
27.48
42.70
125.69-133.81
(113.93)
(114.94)
125.69-133.81
13.60
57.70
169.33
40.88
Resonance stabilized structures
highly strained



8 **9** **10**

8,9 and 10

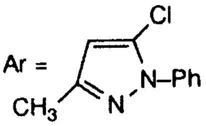
a, X = CO_2Me Ar = Ph

b, X = COPh Ar = Ph

c, X = CO_2Et Ar = p–$NO_2C_6H_4$

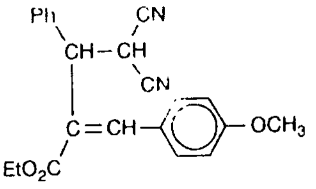
d, X = CO_2Et Ar = 2–furyl

e, X= CO_2Et Ar =



= 4.2 and $J_{H,P}$ = 18.7 Hz for the β-CH methine proton. Also, a highly deshielded doublet at δ = 5.26 ppm is assigned to the methine proton for the malonyl moiety. The isomers **5**,**6** and **7** would be expected to show a multiplet with high J_{HP} value for the methine protons α to the phosphorus atom ^{13}C NMR data support the proposed structure (cf. structure 4). To generalize our synthetic methodology, we obtain **10a–e** via reaction of ylides **8a–e** with arylidenemalononitrile **9a–e** (Scheme 2).

It was of interest to explore the synthetic utility of the alkylated phosphorane **4**. In particular, α-substituted ylides should lead to β-arylacrylic acids having an α-substituent with a reactive nucleus, such as the malonyl moiety. Compounds of this type are not easily available by other methods. When the alkylated ylide **4** was allowed to react with anisaldehyde, the Witting reaction occurred readily with elimination of triphenylphosphine oxide to give a product having molecular formula $C_{22}H_{20}N_2O_3$. Three isomeric forms **11–13** are possible for this condensation product. The structure of the cyclopentane derivative **13** was established by elemental analyses and spectroscopic methods. Thus, the ^1H NMR spectrum shows, in addition to the methyl group and aromatic signals, a broad signal at δ = 3.60 ppm assigned to the NH_2 unit. This signal disappears upon addition of deuterium oxide to the NMR sample suggestive of a facile



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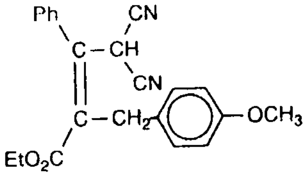

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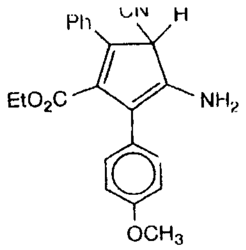
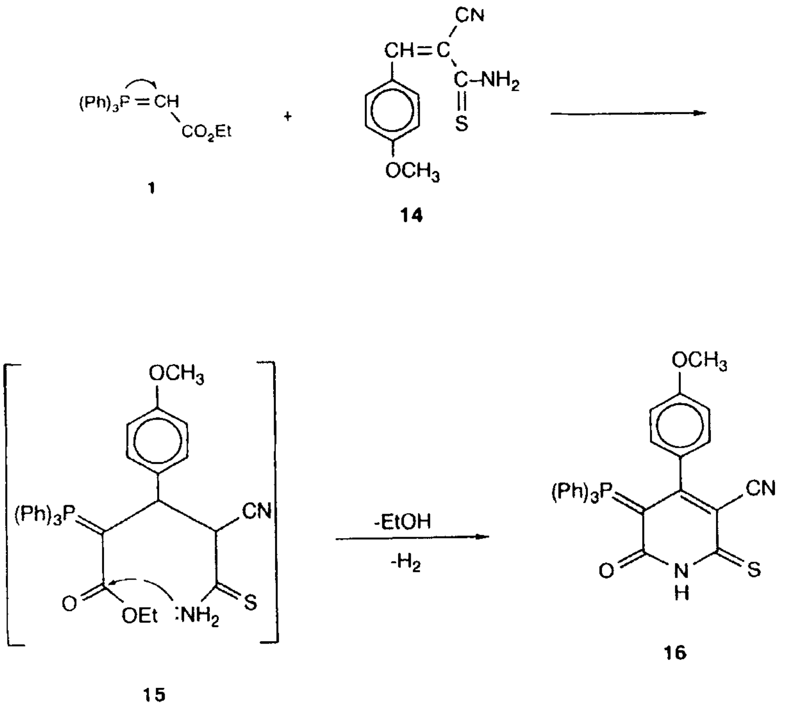


13

hydrogen/deuterium exchange. Also, the IR spectrum shows two bands for NH_2 at ν = 3400, 3300 cm^{-1}. To our knowledge this is the first reported formation of cyclopentadiene derivatives from Witting reaction of simple cinnamonitrile.

The pyridine thione **16** was obtained in resonable yield upon reaction of carbethoxymethylenetriphenylphosphorane **1** with arylidenecyanothioacetamide **14**. The mass spectrum of **16** revealed a molecular formula $C_{31}H_{23}N_2O_2PS$. Also, the IR and ^1H NMR spectral data are in agreement with the proposed structure **16**. The reaction is believed to proceed via **15** as intermediate.



EXPERIMENTAL

All melting points are uncorrected. Carboethoxy methylene, carbomethoxymethylene and benzoyl-methylene triphenylphosphoranes were prepared according to established procedures.[1–3] IR spectra were recorded from KBr pellets on a Pa 9712 IR spectrophotometer. ^1H NMR spectra were recorded on a Varian EM-360 (60 MHz) and Jeol (270 MHz) with DMSO-d_6 and $CDCl_3$ as solvents and TMS as internal reference. ^{13}C NMR spectra were measured on a Jeol (68.5 MHz) spectrometer. Chemical shifts are expressed as δ units (ppm) with shifts down field from the reference. Analytical data were obtained from the Microanalytical data unit at Cairo University. The mass spectra were recorded on a Kratos (75 ev) MS spectrometer.

Reaction of cinnamonitriles with phosphonium ylides (4,10a–e and 16): General procedure

To a solution of cinnamonitriles (0.01 mol) in dry dichloromethane (30 ml), the appropriate Wittig reagent (0.01 mol) was added. The reaction mixture was stirred overnight. The solvent was then evaporated under vacuum. The remaining residue was washed with chloroform and petroleum ether (40–60°) several times. The solid product so formed was crystalized from the suitable solvent.

3,3-Dicyano-1-Ethoxycarbonyl-2-Phenylpropan-1-Ylidentriphenylphosphorane (4)

White crystals, yield 4.36 g (87%), m.p. 160°C crystallization solvent $CHCl_3$-petrolum ether (40–60). IR(KBr); 2220–2222 (CN), 1660 (C=O), 1615 (C=C); ^1H NMR ($CDCl_3$); δ = 0.41 (t, 3H, CH_3); 3.22 (dd, 1H, CH $J_{H,H}$ = 4.2, $J_{H,P}$ = 18.7 Hz); 3.68 (q, 2H, CH_2); 5.26 (d, 1H, CH, $J_{H,H}$ = 4.2); 7.07–7.36 (m, Ph protons and $CHCl_3$); 7.47–7.79 (m, 15H, 3 Ph protons); ^{13}C NMR (cf. structure 4) MS, m/z = 502 (M^+). Anal. Calcd. for $C_{32}H_{27}N_2O_2P$: C, 76.49; H, 5.37; N, 5.50. Found: C, 76.5; H, 5.4; N, 5.4.

3,3-Dicyano-1-Methoxycarbonyl-2-Phenylpropan-1-Ylidentriphenylphosphorane (10a)

White crystals, yield 3.90 (80%), m.p. 165°C crystallization solvent $CHCl_3$-cyclohexane IR(KBr): 2220 (CN), 1665 (C = O); ^1H NMR ($CDCl_3$) δ = 3.41 (dd, 1H, CH, $J_{H,H}$ = 4.0, $J_{H,P}$ = 18.6 Hz); 3.59 (s, 3H, CH_3); 5.26 (d, $1H_2$ CH $J_{H,H}$ = 4.1); 7.10–7.42 (m, Ph protons and $CHCl_3$); 7.48–7.79 (m, 15H, 3Ph protons); Ms, m/z = 488 (M^+). Anal. Calcd. for $C_{31}H_{25}N_2O_2P$: C, 76.22; H, 5.12; N, 5.73. Found: C, 76.3; H, 5.1; N, 5.8.

3,3-Dicyano-1-Benzoyl-2-Phenylpropan-1-Ylidentriphenylphosphorane (10b)

White crystals, yield 4.37 g (82%), m.p. 150°C crystallization methanol. IR (KBr): 2220, 2180 (CN), 1675 (C=O). ^1H NMR (insoluble). Ms, m/z = 534 (M^+). Anal. Calcd. for $C_{36}H_{27}N_2OP$: C, 80.89; H, 5.05; N, 5.24. Found: C, 80.9; H, 5.1; N, 5.3.

3,3-Dicyano-1-Ethoxymethyl-2-p-Nitrophenylpropan-1-Ylidentriphenylphosphorane (10c)

Yellow crystals, yield 4.10 g (75%), m.p. 167°C crystallization from $CHCl_3$-petroleum ether (40–60) 1:1. IR (KBr): 2225 (CN), 1605 (C=O). ^1H NMR (Deuterated acetone): δ = 0.48 (t, 3H, CH_3), 3.41 (dd, 1H, CH $J_{H,H}$ = 4.2, J_{HP} = 18.3 Hz); 3.62 (q, 2H, CH_2); 5.51 (d, 1H, CH $J_{H,H}$ = 4.2); 7.40–8.22 (m, 14H, aromatic protons). Ms, m/z = 547 (M^+). Anal. Calcd. for $C_{32}H_{26}N_3O_4P$: C, 70.20; H, 4.75; N, 7.67. Found: C, 70.1; H, 4.8; N, 7.7.

3,3-Dicyano-1-Ethoxymethyl-2-Furylpropan-1-Yidentriphenylphosphorane (10d)

White crystals, yield 3.78 g (77%), m.p. 150°C crystallization solvent benzene-petroleum ether (40–60). IR (KBr): 2220 (CN), 1620 (C=O). ^1H NMR (DMSO). 1.10 (t, 3H, CH_3); 3.72 (dd, 1H, CH, $J_{H,H}$ = 4.2, $J_{H,P}$ = 17.5 Hz); 4.21 (q, 2H, CH_2); (5.40 (d, 1H, CH $J_{H,H}$ = 4.1); 6.51–6.81 (m, 2H, furyl protons); 7.41–7.81 (m, 16H, 3Ph protons and 1H furyl protons). Anal. Calcd. for $C_{30}H_{25}N_2O_3P$: C, 73.17; H, 5.08; N, 5.69. Found: C, 73.2; H, 5.0; N, 5.6.

3,3-Dicyano-1-(Ethoxymethyl-2-(5-'Chloro-3'-Methyl-1'-Phenylpyrazole-4'-yl)Propan-1-Ylidentriphenylphosphorane (10e)

Pale yellow crystals, yield 4.82 g (80%), m.p. 106°C. Crystallized from benzene/cyclohexane 1:1. IR (KBr). 2225–2222 (CN), 1660 (C=O). ^1H NMR (insoluble). Ms, m/z = 617 (M^+). Anal. Calcd. for $C_{36}H_{30}ClN_4O_2P$: C, 70.07; H, 4.86; N, 9.08. Found: C, 69.9; H, 4.9; N, 8.8.

Ethyl 4-Amino-5-p-Anisyl-3-Cyano-2-H-2-Phenylcyclopentane-1-Carboxylate (13)

To a solution of alkylated ylide **4** (0.0 mol) [prepared by the previous method] in dry dichloromethan (25 ml), anisaldehyde (0.01 mol) was added. The reaction mixture was stirred overnight. The solvent was evaporated under vacuum and the residue was washed several times with cyclohexane untill all the triphenylphosphine oxide removed. The residue was crystallized from pt. ether (40–60°C) as yellow crystals, m.p. 157°C, yield (85%). IR (KBr) 3400–3300 (NH_2), 2225 (CN); 1715 (C=O). ^1H NMR (Deuterated acetone): δ = 0.51 (t, 3H, CH_3), 3.42 (s, 3H, CH_3); 3.60 (br, exceh., 2H, NH_2); 3.81 (q, 2H, CH_2); 5.1 (s, 1H, CH); 6.81–7.32 (m, 10H, 2Ph protons).

4-p-Anisyl-5-Cyano-1,6-Dihydro-2-oxo-6-Thioxopyridine-3-Ylidentriphenylphosphorane (16)

Prepare according to the general procedure: Pale yellow crystalls, yield 3.72 g (72%), m.p. 135°C. Crystallized from 1:1 $CHCl_3$/n-hexane; I(KBr) 2220 (CN), 1675 (C = O), 1600 (C=C); ^1H NMR ($CDCl_3$) δ = 3.71 (s, 3H, CH_3); 6.41–7.80 (m, 19H, aromatic protons); 11.51 (br, 1H, NH). Ms, m/z = 518 (M^+). Anal. Calcd. for $C_{31}H_{23}N_2O_2SP$: C, 71.81; H, 4.44; N, 5.40. Found: C, 72.0; H, 4.4; N, 5.5.

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