REACTIONS OF TETRACYANOETHYLENE WITH TER- AND PENTAVALENT PHOSPHORUS REAGENTS

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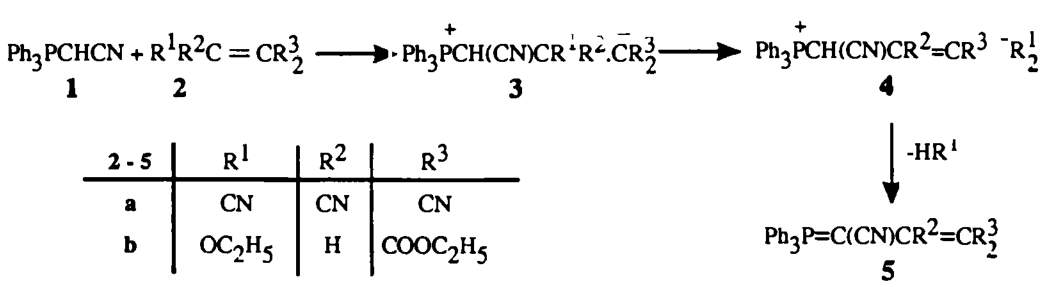
Abstract : The Wittig reaction of tetracyanoethylene **2a** with alkoxycarbonylmethylenetriphenylphosphoranes **7a,b** has been investigated and the reaction products **11** and **13** were isolated and identified. On the other hand, it was found that **2a** behaves differently toward dialkyl phosphonates **15a,b** from its behaviour toward trialkyl phosphites **18a,b** to give two types of phosphonate adducts **16** and **20**, respectively. Structures of the new products were elucidated on the basis of elemental and spectroscopic analyses.

Introduction

The nucleophilic character of phosphorus ylides has long been recognized and reactions of this class of compounds with a wide variety of electrophilic substrates have been reported (1-3). Among these, however, very little is known about the reactions of phosphorus reagents, generally, and phosphorus ylides, specifically, with unsaturated nitriles. Early, in 1962, Trippett (4) had shown that the reaction of cyanomethylenetriphenylphosphorane **1** with unsaturated nitriles **2** revealed a new pattern of attack by these reagents on activated carbon-carbon double bond. The initially observed intermediate **3** eleminates the electronegative group R^{1-}, e.g. CN^- or $C_2H_5O^-$, to form a phosphonium salt **4** which then loses R^1H to give the new stable phosphorane **5** (Scheme 1).



SCHEME 1

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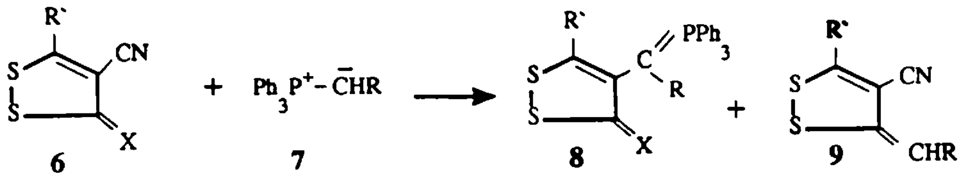
Moreover, the same result has, recently, been observed when we have found (5) that 5-p-chlorophenyl-4-cyano-1,2-dithioles **6** react, smoothly, with phosphonium ylides **7a,b** to give the substituted products **8** and **9** (Scheme 2).



6a) R' = C_6H_4-p-Cl, X = S
6b) R' = C_6H_4-p-Cl, X = O

7-9a, R = $COOCH_3$
b, R = $COOC_2H_5$

SCHEME 2

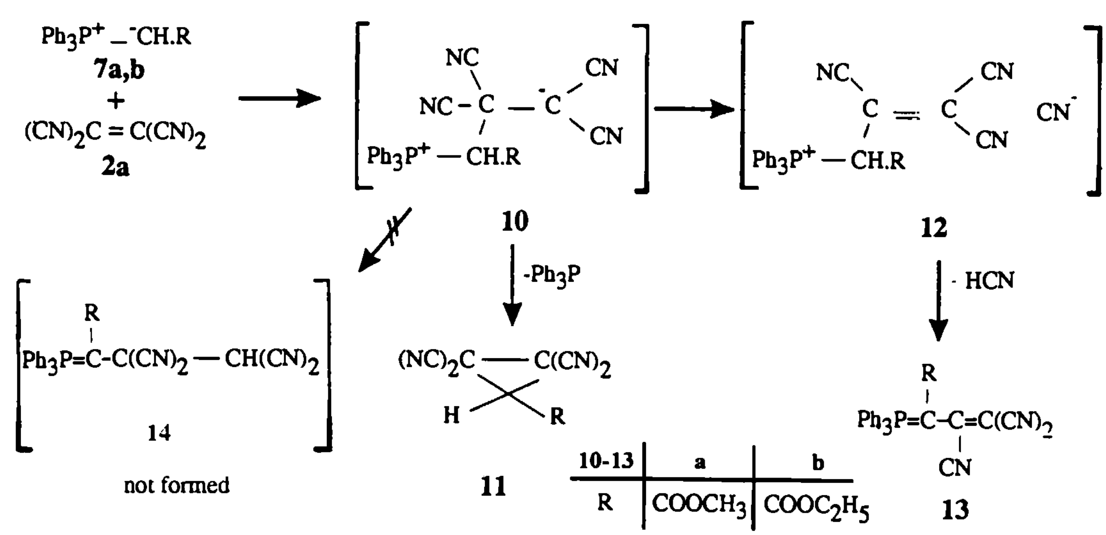
Our continuous interest in the behaviour of phosphonium ylides toward unsaturated nitriles (5,6) prompted us to re-examine the reactions of tetracyanoethylene **2a** with further phosphorus ylides **7a,b** and extended the scope to include a comparative study of the reactivity of compound **2a** toward dialkyl phosphonates **15a,b** and trialkyl phosphites **18a,b**.

Results and Discussion

1. Reactions of Tetracyanoethylene 2a and Phosphonium Ylides 7a,b

Tetracyanoethylene **2a** was found to react with methoxycarbonylmethylenetriphenylphosphorane **7a** in refluxing toluene to give a mixture of two main products (**11a** + **13a**) which could be separated by column chromatography. Triphenylphosphine was also isolated and identified.

The first product was obtained as yellow crystals in 33% yield and formulated as **11a** for the following reasons: (a) Elementary and mass spectral analyses for compound **11a** corresponded to an emperical formula $C_9H_4N_4O_2$ (200.163, m/z 200, M^+). (b) Its IR (KBr, cm^{-1}) spectrum revealed the absence of the strong band at



10-13	a	b
R	$COOCH_3$	$COOC_2H_5$

SCHEME 3

1645 assigned for conjugated C=C in **2a**. It showed bands at 2195 (CN), and 1735 (C=O, ester). In its ^{1}H-NMR spectrum (δ), the singlet at 3.65 is attributed to the methoxyl group, while the cyclopropane-methine proton resonated at 4.62 ppm (1H, CHR, s) (7,8).

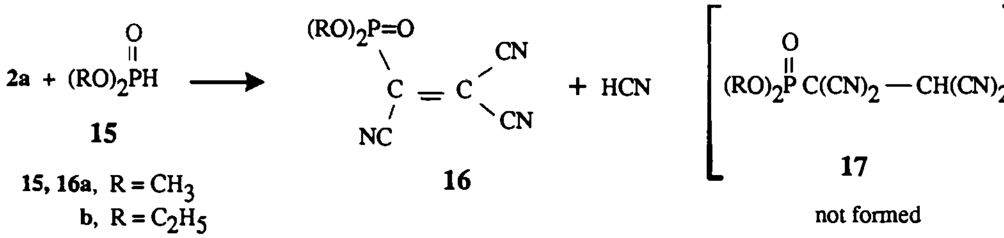
The second product was obtained as brown substance in 38% yield and assigned the ylide structure **13a** on the basis of the elemental analysis, IR, and mass spectral data. (a) The ^{31}P-NMR spectrum of **13a** showed a positive shift at δ 23.6 ppm which is in the region characteristic for this class of compounds (9). (b) Its ^{1}H-NMR spectrum showed a singlet at δ 3.8 was ascribed to the methoxyl group in **13a**, meanwhile, the aromatic protons (15H) appeared as a multiplet in the δ 7.52-8 ppm region. (c) The IR (KBr, cm^{-1}) of **13a** showed absorption bands at 2195 (CN), 1730 (C=O, ester) 1657 (C=C), 1500 (C=P) and at 1415 (P-C, phenyl).

Similarly, the reaction products of **2a** and **7b** were assigned analogous structures **11b** and **13b** on the basis of comparable spectroscopic arguments.

The mechanism proposed to account for the formation of **11** and **13** from the reaction of **2a** and phosphonium ylides **7a,b** is shown in Scheme 3. Initial nucleophilic attack by the carbanion centre in the ylide on the activated carbon-carbon double bond gives a resonance hybride like **10** (Scheme 3). Even though **10** may be reasonably (R is an electron-withdrawing group) (10) stabilizes through proton migration, giving rise to a new ylide **14**, nevertheless, it is partly stabilized by elemination of triphenylphosphine to afford the cyclopropane derivative **11** (7,10) and partly *via* elemination of HCN to yield the new phosphoranes, **13**. The latter mechanism (**2a** → **13**) parallels the reaction course had been previously reported by Trippett (4) for the reaction of **2a** and cyanomethylenetriphenylphosphorane **1** (Scheme 1).

2. *Reactions of 2a and Dialkyl Phosphonates 15a,b*

The behaviour of tetracyanoethylene **2a** toward dimethyl phosphonate **15a** and diethyl phosphonate **15b** was also studied. Thus, the reaction of **2a** with dimethyl phosphonate **15a** was completed by refluxing the reactants in CH_2Cl_2 for 4 h. It yielded a brown crystalline material to which structure **16a** was assigned for the following reasons: (a) Compatible elementary analysis and molecular weight determination (MS) for **16a** corresponded to $C_7H_6N_3O_3P$. (b) The phosphonate structure in the product **16a** was established by a signal at 27.82 ppm in the ^{31}P-NMR spectrum (DMSO). (c) Its IR spectrum (KBr) showed absorption bands (cm^{-1}) at 2213 (CN), 1650 (C=C), 1241 (P=O, free) and at 1030 (P-O-CH_3) (8). (c) The ^{1}H-NMR spectrum of **16a** showed signals at δ 3.35 and 3.45 ppm (6H, 2d, each with $^3J_{HP} = 12.5$ Hz) due to the methoxyl groups attached to phosphorus. However, the presence of the ethylenic (C=C) absorption band in the IR spectrum and the lack of a signal due to a methide proton [P-C(CN)$_2$-CH(CN)$_2$, cf., **17**] in the ^{1}H-NMR spectrum of **16a** as well as the



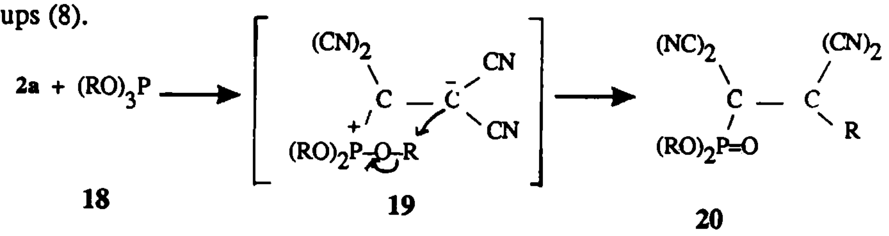
SCHEME 4

molecular ion peak in its mass spectrum confirm the assigned structure **16a** and rule out the other alternative structure **17**.

On the same ground, compound **2a** was allowed to react with diethyl phosphonate **15b** to give a phosphonate adduct formulated as **16b** (see experimental).

3- Reaction of 2a and Trialkyl Phosphites 18a,b.

On the other hand, the reaction of tetracyanoethylene **2a** with trimethyl phosphite **18a** and triethyl phosphite **18b** proceeded, smoothly, in CH_2Cl_2 to give products (> 80% yield for which structures **20a,b** were, respectively, assigned. Evidences for structure **20** are: (a) The ^{31}P-NMR spectra of **20** showed chemical shifts around δ 26.5 ppm indicating they are phosphonates (9). (b) Satisfactory elementary analyses and molecular weight determinations (MS) were recorded for both products. (c) The IR spectrum (KBr, cm^{-1}) of **20a**, taken as an example, showed the presence of absorption bands at 2213 (CN), 1245 (P=O, free), and at 1044 (P-O-CH_3) (8). Moreover, the strong ethylenic C=C absorption band present in the IR spectrum of **2a** at 1645 cm^{-1} was absent in the spectrum of **20a**. (d) Its ^{1}H-NMR ($CDCl_3$, δ) revealed protons of the $P(O)(OCH_3)_2$ groups (6H) as two doublets ($^3J_{HP}$ = 13 Hz) at 3.6 and 3.75 ppm. It also showed a doublet (3H, $^4J_{HP}$ = 4.5 Hz) at δ 1.75 ppm which coincides with a chemical shift expected for a methyl group on sp^3-carbon atom containing two electron - withdrawing groups (8).



SCHEME 5

17 - 19a, R = CH_3
b, R = C_2H_5

A mechanism that accounts for formation of adducts **20a,b** from the reaction of tetracyanoethylene **2a** with trialkyl phosphites **18a,b** is depicted in Scheme 5. This involves an initial nucleophilic attack on **2a** by P(III) reagent to afford the C-phosphonium betaine **19**, which undergoes then intramolecular group translocation to yield the new phosphonate structure **20** according to the 1 : 2 addition pattern. However, this result is along the line we have, recently, explored (6, 11) for C-alkylation of unsaturated nitriles by trialkyl phosphites.

Conclusion

Significanly, the three reactions reported here are indicative of the broad reaction spectrum of which the nucleophilic phosphorus reagents are cabable. Moreover, it has been shown from the present and the previous results (4, 5), that alkylidenephosphoranes react with unsaturated nitriles in a manner rather different from the already known (2, 10) with conjugated carbon-carbon double bond. Furthermore, although tetracyanoethylene **2a** reacts with trialkyl phosphites as is frequently observed (11) with unsaturated nitrile, anomalous behaviour, however, was shown toward dialkyl phosphonates, whereby substitution reaction occurred to give the phosphonate products **16** (Scheme 4).

Experimental Part

All melting points are uncorrected. The IR spectra were recorded in KBr, with Perkin-Elmer Infracord Spectrometer, 157 G. The ^{1}H-NMR spectra were run on Varian Spectrometer at 90 MHz, using TMS as an internal reference. ^{31}P-NMR spectra were recorded with a Varian FT-80 Spectrometer (vs. 85% H_3PO_4). The mass spectra were performed at 70 eV on MS-50 Kratos (A.E.I) Spectrometer provided with data system.

The appropriate precautions in handling moisture - senstive compounds were observed. Solvents were dried by standard techniques, including high vacuum procedures.

Reagents: Trialkyl phosphites were purified by treatment with sodium ribbon followed by fractional distillation. Dialkyl phosphonates were freshly distilled. Alkylidenephosphoranes **7a,b** were prepared by an established method (12). Tetracyanoethylene **2a** is commercially available from Aldrish company.

1. Reaction of Tetracyanoethylene 2a with Phosphonium Ylides 7a,b

A mixture of 1.3 g (0.01 mol) of **2a** and 0.013 mol of ylide **7a** or **7b** in 50 ml of toluene was refluxed for 10-12 h (TLC). After cooling to the room temperature, the reaction mixture was evaporated to dryness in the presence of silica gel (5g). The mixture was then added to a column, previously charged with silica gel in petroleum ether. The column was developed with petroleum ether containing increasing amounts of chloroform and then with pure ethyl alcohol. The fraction with 100% petroleum ether eluted colourless needles, mp 80 °C (~45% yield) of triphenylphosphine.

The fraction up to 7:3 v/v gave compound **11a** or **11b**

11a was obtained as yellow crystals (660 mg, 33%), mp 153-155 °C (pentane). Anal. Calcd. for $C_9H_4N_4O_2$ (200.163) : C 54.00, H 2.01, N 27.99. Found: C. 53.87, H 1.96, N 27.75. IR (KBr, cm^{-1}): 2195 (CN), 1735 (C=O, ester). ^{1}H-NMR (CDC_{13}): δ 3.65 (3H, OCH_3, s), 4.62 (1H, CHR, s). MS: m/z 200 [M$^+$, 22%].

Compound **11b** was obtained as orange crystals (630 mg, 30%), mp 201-203 °C (acetonitrile). Anal. Calcd. for $C_{10}H_6N_4O_2$ (214.19): C 56.07, H 2.82, N 26.16. Found: C 55.87, H 2.76, N 26.03. IR (KBr) cm^{-1}: 2200 (CN), 1715 (C=O, ester). ^{1}H-NMR ($CDCl_3$): δ 0.95 (3H, $C.CH_3$, t), 4 (2H, OCH_2, q), 4.57 (1H, CHR, s). MS: m/z 214 [M$^+$, 25%].

Elution with 100% ethyl alcohol afforded **13a** or **13b**

13a was obtained as brown crystals (1.7 g, 38%), mp 218-220 °C ($CHCl_3$). Anal. Calcd. for $C_{26}H_{18}N_3O_2P$ (435.43): C 71.72, H 4.16, N 12.11, P 6.69. Found: C 71.54, H 4.02, N 11.98, P 6.77. IR (KBr) cm^{-1}: 2195 (CN), 1730 (C=O, ester), 1657 (C=C), 1500 (C=P), 1415 (P-C, Phenyl). ^{1}H-NMR (DMSO) δ: 3.8 (3H, OCH_3, s), 7.52-7.8 ppm (15H, Ar-H, m). ^{31}P-NMR (DMSO): δ 23.6 ppm. MS: m/z 462 [M$^+$, <5%].

Compound **13b** was obtained as brown crystals (1.9 g, 42%), mp 250-253 °C (ethyl alcohol). Anal. Calcd. for $C_{27}H_{20}N_3O_2P$ (449.46): C 72.15, H 4.48, N 9.35, P 6.88. found : C 72.02, H 4.41, N 9.17, P 6.96. IR (KBr) cm^{-1}: 2210 (CN), 1715 (C=O, ester), 1665 (C=C). ^{1}H-NMR (DMSO) δ: 0.87 (3H, $C.CH_3$, t), 4.12 (2H, OCH_2, q), 7.5-7.85 ppm (15 H, Ar-H, m). ^{31}P-NMR (DMSO): δ 22.75 ppm. MS: m/z 476 [M$^+$, <5%].

2. Reaction of Tetracyanoethylene 2a and Dialkyl Phosphonates 15a,b

A mixture of the titled compound **2a** (1.3 g, 0.01 mol) and dimethyl or diethyl phosphonate **15a,b**, respectively, (4 ml) was refluxed in CH_2Cl_2 for 4-6 h (TLC). After removal of the volatile materials, *in vacuo*, the residue was triturated twice with light petroleum, then recrystallized from the appropriate solvent to give **16a** or **16b**, respectively.

The phosphonate **16a** was obtained as brown crystals (1.4 g, 68%) mp 283-285 °C (acetone-ether). Anal. Calcd. for $C_7H_6N_3O_3P$ (211.13): C 39.82, H 2.86, N 19.9, P 14.67. Found: C 39.74, H 2.83, N 19.85, P 14.82. IR (KBr) cm^{-1}: 2213 (CN), 1650 (C=C), 1241 (P=O, free), 1030 (P-O-CH_3). ^1H-NMR (DMSO) δ: 3.35 and 3.45 ppm [6H, $(OCH_3)_2$, 2d, $^3J_{HP} = 12.5$ Hz]. ^{31}P-NMR (DMSO): δ 27.82 ppm. MS: m/z 211 [M^+. 28%].

Compound **16b** was obtained as brown crystals (1.7 g, 73%), mp 268-270 °C (acetone-ether). Anal. Calcd. for $C_9H_{10}N_3O_3P$ (239.18): C 45.2, H 4.21, N 17.57, P 12.95. Found: C 45.13, H 4.16, N 17.39, P 12.8. IR (KBr) cm^{-1}, 2200 (CN), 1640 (C=C), 1245 (P=O, free), 1050 cm^{-1} (P-O-C_2H_5). ^1H-NMR (DMSO) δ: 1.25 (6H, OC.CH_3, t, $J_{HP} = 13$ Hz), 3.95 (4H, OCH_2, qt, $^3J_{HP} = 13$ Hz). ^{31}P-NMR (DMSO): δ 29.32 ppm MS: m/z 239 [M^+, 55%].

3. Reaction of Tetracyanoethylene 2a with Trialkyl Phosphites 18a,b

To a stirred suspension of **2a** (1.3 g, 0.01 mol) in 30 ml of dry CH_2Cl_2 at 0-5 °C was added a solution of trimethyl phosphite or triethyl phosphite **18a, b**, respectively, (0.03 mol) in the same solvent (5 ml). After being warmed to r.t. (3 h), the reaction mixture was stirred for 48 h. The precipitated materials so formed was collected, dried and recrystallized from the suitable solvent to yield **20a** or **20b**, respectively.

Compound **20a** was obtained as yellow crystals (2 g, 83%), mp 153-155°C (cyclohexane). Anal. Calcd. for $C_9H_9N_4O_3P$ (252.18): C 42.86, H 3.59, N 22.22, P 12.28. Found: C 42.69, H 3.52, N 22.08, P 12.35. IR (KBr) cm^{-1}: 2213 (CN), 1245 (P=O, free), 1044 cm^{-1} (P-O-CH_3). ^1H-NMR ($CDCl_3$) δ: 1.75 (3H, C.CH_3, d, J_{HP}= 3.5 Hz), 3.6, 3.75 ppm (6H, $POCH_3$, 2d, $^3J_{HP}$= 13 Hz). ^{31}P-NMR ($CDCl_3$): δ 26.5 ppm. MS: m/z 252 [M^+, 44%).

Compoound **20b** was obtained as orange crystale 2.5, 85%). mp 128-130 °C (acetonitrile). Anal. Calcd. for : $C_{12}H_{15}N_4O_3P$ (294.264): C 48.98, H 5.14, N 19.04, P 10.52. Found: C 48.85, H 5.02, N 18.79, P 10.3. IR (KBr) cm^{-1}: 2206 (CN), 1244 (P=O, free), 1162 (P-O-C_2H_5). ^1H-NMR ($CDCl_3$) δ: 0.8 (3H, C.C.CH_3, t), 1.35 (6H, OC.CH_3, d of t, $^3J_{HP} = 11.5$ Hz), 3.65 (2H, C.CH_2, q), 4.12 (4H, $POCH_2$, qt, $^3J_{HP} = 11.5$ Hz). ^{31}P-NMR ($CDCl_3$): δ 25.84 ppm. MS: m/z 294 [M^+, 33%].

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