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COMPARATIVE CHEMICAL STUDIES OF THE BEHAVIOR OF 4-CYANO-1,2-DITHIOLES IN ANALOGY WITH 1,2,4-DITHIAZOLES TOWARD STABLE PHOSPHONIUM YLIDES

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COMPARATIVE CHEMICAL STUDIES OF THE BEHAVIOR OF 4-CYANO-1,2-DITHIOLES IN ANALOGY WITH 1,2,4-DITHIAZOLES TOWARD STABLE PHOSPHONIUM YLIDES

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The reaction of 5-*p*-chlorophenyl-4-cyano-1,2-dithiole-3-thione **2a** or its 3-carbonyl derivative **2b** with phosphonium ylides **1a** and **1b** afforded, in both cases, compounds **10a,b** and **13a,b**. In addition, compound **11a** or **11b** was also isolated from the first reaction (**2a** + **1a,b**). Reaction of **1c** with **2a** as with **2b** afforded compounds **10c** and **14**. The transformations **10a** and **11a** → **13a** as well as **10c** → **14** were also studied. Reaction of **2a** with fluorenylidene-triphenylphosphorane **1d** afforded, besides the expected olefin **10d**, the dithione **15**, while **2b** with **1d** yielded **10d** and the known ethylene compound **4**. Reduction of **15** by Cu powder yielded **4**. When the reactions of **2a** or **2b** with **1a–c** were performed in the presence of triethylamine, both the expected products **10a–c** and **22a–c** were obtained. The addition of triethylamine to the reaction mixture of **2a** or **2b** with **1d** did not affect the result.

Key words: 5-*p*-Chlorophenyl-4-cyano-1,2-dithioles, heterocyclic-*cis*-disulfides, phosphonium ylides, Wittig reaction.

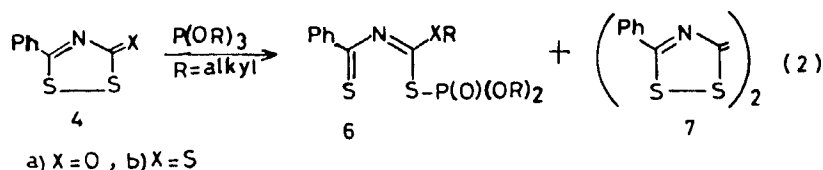
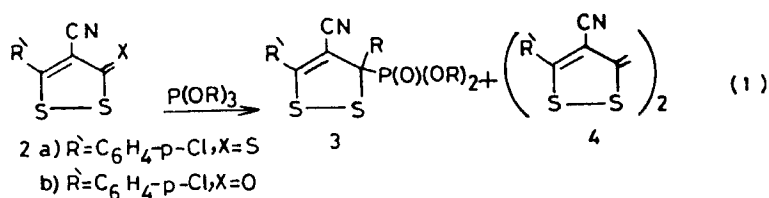
INTRODUCTION

In previous investigations, we reported that stable phosphonium ylides ($\text{Ph}_3\text{P}=\text{CHCOR}$, **1**) add to the weak S—S linkage in acyclic¹ and in heterocyclic^{2,3} *cis*-disulfides and the products rationalized as proceeding via 1:1 intermediates which can be envisaged as having anionic forms, contributing to their overall structures.

Later on, in a very recent work,⁴ we have observed that 5-*p*-chlorophenyl-4-cyano-1,2-dithiole **2a** behaves differently toward the nucleophilic phosphite esters in analogy with the behavior of the dithiazoles **5** toward the same reagent. Thus, while the phosphite-phosphorus attacks the S—S bond in **5** to give the phosphorothioates **6** [Equation (2)], it attacks the thiono-carbon in **2a** to give the phosphonates **3** [Equation (1)]. The dimeric products **4** and **7** were also obtained, respectively, from the above reactions, pointing out that the presence of the electron-withdrawing group (CN) substituent α to the thiocarbonyl group is responsible for the stabilization of the dithiole ring in **2**.⁴

In connection with this study, we now report our results that the dithioles **2a** and **2b**, easily prepared in high yields, are preferably attacked by the phosphonium ylides **1a–d** at the thiono- or the carbonyl group and/or the nitrile group rather than to be attacked at the S—S bond. Nevertheless, the broken of S—S linkage could only

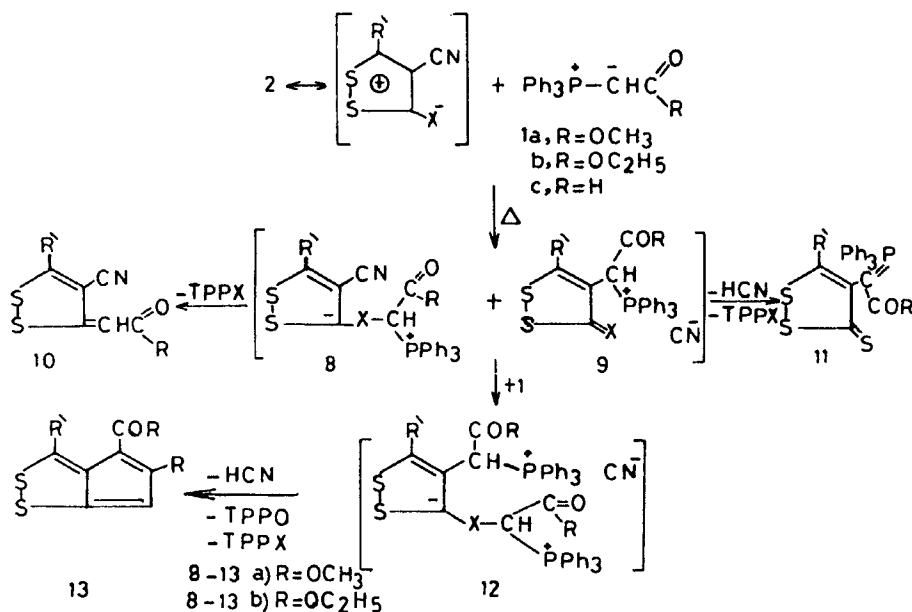
†To receive any correspondence.



be observed when the reactions were performed in the presence of a base (triethylamine).

RESULTS AND DISCUSSION

When the orange nitrile **2a** was allowed to react with two moles of methoxycarbonylmethylenetriphenylphosphorane **1a** in refluxing toluene for 10 h, three products **10a** (28%), **11a** (11%) and **13a** (14%) (Scheme I) were isolated from the product mixture. Triphenylphosphine sulfide and triphenylphosphine oxide were also isolated. The structure assignments for **10**, **11** and **13** were based on their spectroscopic and analytical data (see Tables I and II).



SCHEME 1

Elemental and mass spectral analyses of adduct **10a** corresponded to an empirical formula of $C_{13}H_8ClNO_2S_2$. Its IR spectrum revealed the presence of absorption bands at 2216 (CN), 1700 (C=O), 1632 (C=C) and 1266 (S—S). The 1H NMR spectrum of **10a** showed signals at δ 3.75 (s, 3H, OCH_3) and δ 6.45 ppm (s, 1H, =CH). In the MS of **10a**, the $m/z = 309 [M^+]$.

Adduct **11a** possessed an ylide phosphorane structure since it exhibited a positive shift in its ^{31}P NMR spectrum (δ 22.8 ppm, vs. 85% H_3PO_4). On the other hand, its IR spectrum indicates the absence of a stretching vibration at $\sim 2220\text{ cm}^{-1}$ which was assigned to the nitrile group in **2**. Other spectral data are fully in accord with the proposed structure **11** (cf. Tables I and II).

The last isolated product **13a** was obtained as brown crystals in ca 14% yield. Structural assignment for **13a** is based upon the following observations: (a) The mass spectrum of **13a** displayed a molecular ion peak at $m/z = 338 [M^+]$. (b) Its 1H NMR spectrum showed two singlets at δ 3.3 and 3.9 ppm whose peak area integrated to 6 protons, and are assigned to the two methoxyl groups (OCH_3). The aryl protons and the five membered ring proton appeared in the 7.28–7.77 ppm region. (c) In the IR spectrum of **13a**, the absorption band observed at 1246 cm^{-1} was assigned to the S—S linkage while the carbonyl ester appeared at 1723 cm^{-1} .

Similarly, the reaction products of **2a** and ethoxycarbonylmethylenetriphenyl-

TABLE I
IR and 1H NMR data^a for the products **10**, **11**, **13–15** and **22**

| Compound | 1H (δ ppm) ^{b,c} | | | IR (cm^{-1}) | | | |
|------------|--------------------------------------|------------------|---|-------------------------|-------------|-------------------|------|
| | C—CH ₃ | OCH_3/OCH_2 | CH \neq CH | CN | C=O | C=C | S—S |
| 10a | | 3.75(s) | 6.45(s) | 2216 | 1700 | 1632 | 1266 |
| 10b | 1.3(t) | 4.25(q) | 6.3(s) | 2220 | 1715 | 1622 | 1255 |
| 10c | | | 5.8(d) ^d | 2210 | 1735 | 1647 | 1250 |
| 10d | | | $J_{HH} = 15.5$ | 2224 | | 1637 | 1246 |
| 11a | | 3.72(s) | | | 1723 | 1585 | 1305 |
| 11b | 1.37(t) | 4.23(q) | | | 1721 | 1587 | 1261 |
| 13a | | 3.3 & 3.9 (2s) | | | 1723 | | 1246 |
| 13b | 1.17 & 1.3 (2t) | 3.45 & 3.65 (2q) | | | 1714 | | 1250 |
| 14 | | | 5.75(d) $J_{HH} = 13.5$ | | 1735 | 1600 & 1630 (C=N) | 1255 |
| 15 | | | 7.2–8.5 (Ar-H) | 2230 | | | 1247 |
| 22a | | 3.4 & 3.7 (2s) | 3.95 & 5.72 (2s) | 2216 | 1700 & 1985 | 1622 | |
| 22b | 1.2 & 1.32 (2t) | 3.5 & 3.75 2q | 4.1 & 5.55 (2s) | 2224 | 1710 & 1715 | 1620 | 1250 |
| 22c | | | 4.2(d, $J_{HH} = 13.5$) 5.85, (d, $J_{HH} = 15$) | 2220 | 1737 & 1730 | 1742 | 1255 |

a) See experimental for details for 1H NMR and IR experiments. b) Coupling constant is recorded in Hertz.

c) Aryl- hydrogen protons for **10**, **11**, **13–15**, and **22** lie in the δ 7.35–7.75 ppm region. d) Aldehydic-proton for **10c**, **14** and **22c** lie in the δ , 9.2, 9.5 and 9.8 ppm, respectively, with $J_{HH} = -13 \rightarrow 15$ Hz.

TABLE II
Characteristic data of new compounds **10**, **11**, **13**–**15** and **22**

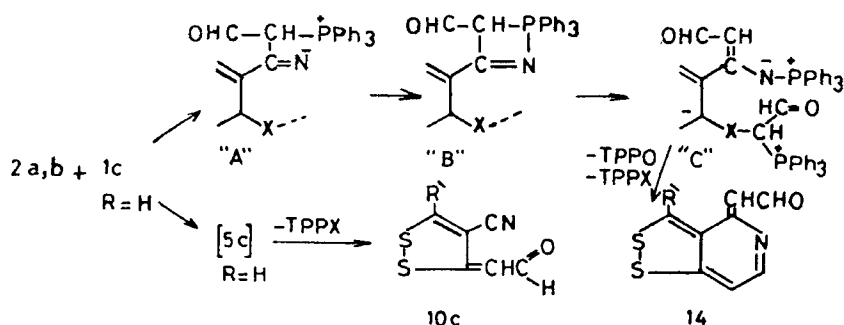
| Compound | Yield ^a (%) | m.p. (°C) (solvent) | Mol. form. (mol. wt.) | Found / required (%) | | | | | M ⁺ (m/z) |
|------------|---------------------------|--------------------------------------|--|----------------------|------|-------|------|-------|-------------------------|
| | | | | C | H | Cl | N/P | S | |
| 10a | 28 | 142-44 | C ₁₃ H ₈ ClNO ₂ S ₂ | 50.27 | 2.57 | 11.39 | 4.28 | 20.63 | 309 |
| | (25) ^b | C ₆ H ₆ | (309.81) | 50.4 | 2.6 | 11.44 | 4.52 | 20.7 | |
| 10b | 30 | 130-32 | C ₁₄ H ₁₀ ClNO ₂ S ₂ | 51.87 | 3.01 | 10.81 | 4.28 | 19.75 | 323 |
| | (28) | CH ₃ CN | (323.83) | 51.92 | 3.11 | 10.95 | 4.32 | 19.8 | |
| 10c | 33 | 98-100 | C ₁₂ H ₆ ClNOS ₂ | 51.44 | 2.01 | 12.62 | 4.86 | 22.86 | 279 |
| | (38) | (CH ₃) ₂ C(O) | (279.78) | 51.52 | 2.16 | 12.67 | 5.00 | 22.92 | |
| 10d | 18 | 175-77 | C ₂₃ H ₁₂ ClNS ₂ | 68.65 | 2.88 | 8.64 | 3.45 | 15.93 | 401 |
| | (20) | C ₆ H ₆ | (401.95) | 68.73 | 3.01 | 8.82 | 3.48 | 15.95 | |
| 11a | 11 | 115-17 | C ₃₀ H ₂₂ ClO ₂ S ₃ P | 62.61 | 3.75 | 6.02 | 5.48 | 16.53 | 315 ^c |
| | | (CH ₃) ₂ C(O) | (577.14) | 62.43 | 3.84 | 6.14 | 5.37 | 16.66 | |
| 11b | 10 | 93-95 | C ₃₁ H ₂₄ ClO ₂ S ₃ P | 63.08 | 3.88 | 5.95 | 5.39 | 16.36 | 329 ^c |
| | | p.e. | (591.17) | 62.98 | 4.09 | 5.99 | 5.24 | 16.27 | |
| 13a | 14 | 170-72 | C ₁₅ H ₁₁ ClO ₃ S ₂ | 52.61 | 3.17 | 10.27 | – | 18.86 | 338 |
| | (14) | CH ₂ Cl ₂ | (338.84) | 52.89 | 3.27 | 10.46 | – | 18.93 | |
| 13b | 12 | 163-65 | C ₁₇ H ₁₅ ClO ₃ S ₂ | 53.17 | 4.08 | 9.47 | – | 17.25 | 366 |
| | (13) | CH ₂ Cl ₂ | (366.9) | 55.55 | 4.12 | 9.66 | – | 17.48 | |
| 14 | 17 | 202-205 | C ₁₄ H ₈ ClNOS ₂ | 55.65 | 2.58 | 11.55 | 4.47 | 20.92 | 305 |
| | (10) | EtOAc | (305.82) | 54.86 | 2.63 | 11.59 | 4.58 | 20.97 | |
| 15 | 42 | 220-22 | C ₂₀ H ₈ Cl ₂ N ₂ S ₆ | 54.98 | 1.43 | 13.02 | 5.07 | 35.48 | 539 |
| | | CHCl ₃ | (539.61) | 44.34 | 1.49 | 13.14 | 5.19 | 35.65 | |
| 22a | 42 | 152-54 | C ₁₆ H ₁₂ ClNO ₄ S | 44.51 | 3.39 | 10.01 | 3.86 | 9.03 | 349 |
| | | CHCl ₃ | (349.82) | 54.91 | 3.45 | 10.13 | 4.00 | 9.17 | |
| 22b | 55 | 136-38 | C ₁₈ H ₁₆ ClNO ₄ S | 54.94 | 4.05 | 9.28 | 3.65 | 8.44 | 377 |
| | | C ₆ H ₆ | (377.86) | 57.07 | 4.27 | 9.38 | 3.71 | 8.48 | |
| 22c | 38 | 114-16 | C ₁₄ H ₈ ClNO ₄ S | 57.22 | 2.74 | 12.09 | 4.75 | 10.88 | 289 |
| | | p.e. | (289.75) | 57.86 | 2.78 | 12.24 | 4.83 | 11.06 | |

a) Yields are approximated. b) The yield between brackets is corresponding to the product which was isolated from the reaction of **2b** + **1a**-**d**. c) Compounds **11a**, **b** showed their ion peak at M⁺ = 262 (TPP).

phosphorane **1b** were assigned the analogous structures **10b**, **11b** and **13b** on the basis of comparable data (see Tables I and II).

Trials for conversion of **10a** and **11a** into **13a**, were undertaken. Heating **10a** or **11a** with 1 mole of **1a** in toluene for 18 h led, in each instance to the formation of **13a** (~42%), accompanied by triphenylphosphine oxide and/or triphenylphosphine sulfide elimination.

The structural products (**10**, **11** and **13**) indicated two positions in **2** are susceptible to nucleophilic attack. The first position relates to attack at the thiocarbonyl group. The initial thiophilic addition is assumed^{5,6} in many other reactions involving nucleophilic reagents and thiocarbonyl group activated by α electron-withdrawing substituent. This addition afforded the reactive 1:3 dipolar intermediate **8a** (Scheme I). Desulfuration with formation of triphenylphosphine sulfide gave the Wittig



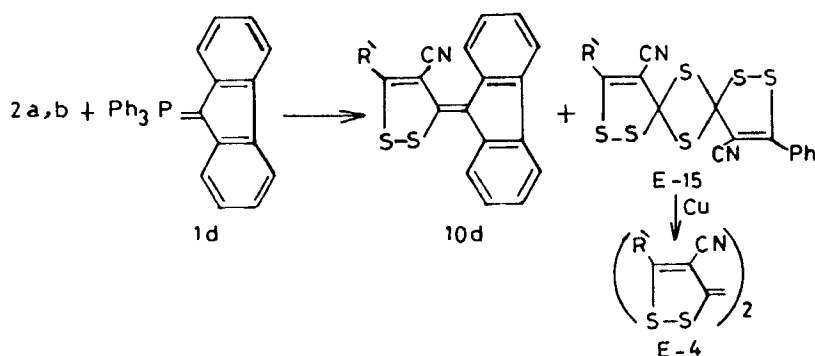
SCHEME II

product **10a**. The second site of attack is concerned with addition of the Wittig reagent to the activated carbon-carbon double bond (C4) with elimination of CN^- to form the phosphonium salt **9**.⁷ Stabilization of **9** was attained by two kinds of pathways: path (a) results from a loss of HCN to give the phosphorane **11**. The second pathway (b) is the reaction of the phosphonium salt **9**, initially formed, with a second ylide species **1a** to give the biphosphonium intermediate **12a**. The further transformations of betaine **12a** afforded compound **13a** via intramolecular Wittig reaction⁸ and ring closure with elimination of HCN, triphenylphosphine sulfide and triphenylphosphine oxide. However, the intermediate **12a** can also be formed from the olefin **10** or from its precursor intermediate **8**, i.e. all of these reactions can compete (Scheme I).

The reaction of **2a** with formylmethylenetriphenylphosphorane **1c** represents another, even more interesting variation of the Wittig reaction (Scheme II). As in the case with ylides **1a** and **1b** the primary condensation product **10c** (33%) seems to be predominant, while products analogous to compounds **11** and **13** were not isolated from this reaction, instead, compound **14** was obtained in 17% yield. Structure **10c** was deduced from correct elemental analysis, IR, ^1H and mass spectroscopic data (cf. Tables I and II).

The structure of the other isolated product **14** was assigned from elemental analysis, IR, ^1H NMR and mass spectral data. Elemental and mass spectral analyses for compound **14** corresponded to an empirical formula of $\text{C}_{14}\text{H}_8\text{ClNOS}_2$. The ^1H NMR of **14** revealed the presence of a singlet at 6.25 ppm corresponding to the methylene $=\text{CH}$ -proton. The aromatic and the quinoline protons appeared as a multiplet at 7.6–7.85 ppm (m, Ar-H, 6H) while the aldehydic proton appeared at 9.2 ppm (d, ^1H , $J_{\text{HH}} = 13.5$ Hz, $\text{C}(\text{O})\text{H}$). The IR spectrum of **14** showed the absence of CN absorption band and, instead, it showed a new band at 1630 cm^{-1} attributed to $\text{C}=\text{N}$.

It is evident that β -ketoalkylenetriphenylphosphorane **1c** does not effect a replacement of the nitrile group, but instead it leads to a product in which phosphorus-nitrogen bond is formed. Thus, 2 moles of **1c** reacts with **2a** to give the intermediate "A," followed by ring closure to the dihydrophosphazete "B" which further by opening the four membered ring leads to the iminophosphorane "C." Intramolecular Wittig-type attack of the crowded intermediate "C," as in the former case, affords the quinoline derivative **14** via the usual ring closure and extrusion



SCHEME III

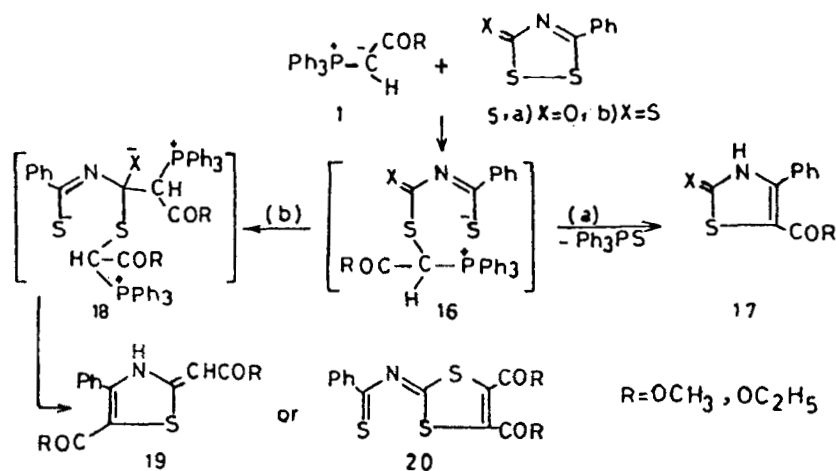
of triphenylphosphine sulfide and triphenylphosphine oxide. Such a mechanism was previously reported for the reaction of activated acetylenes^{9,10} and activated nitriles^{11,12} with some phosphonium ylides. When **10c** was allowed to react with 1 mole of **1c**, it yielded **14** in 13.6% yield.

Treatment of **2a** with fluorenylidene triphenylphosphorane **1d** in refluxing toluene for 20 h and separation of the reaction mixture by column chromatography gave the Wittig condensation product **10d** (18%) and the dithione **15** (22%) (see Tables I and II). These are the only products formed regardless of the ratio of the reactants employed. In addition to analysis and molecular weight determination, the structure of **15** was confirmed by conversion of this compound to the ethylene **4** when it was refluxed with freshly reduced copper powder in xylene. This is a characteristic reaction for the dithione compounds.^{13,14} Compounds **15** and **4** were assigned E-isomers since **4** is consistent with melting point and spectral data given in the previous study⁴ for the same dimeric product, which was isolated from the reaction of trialkyl phosphites with the same substrates.

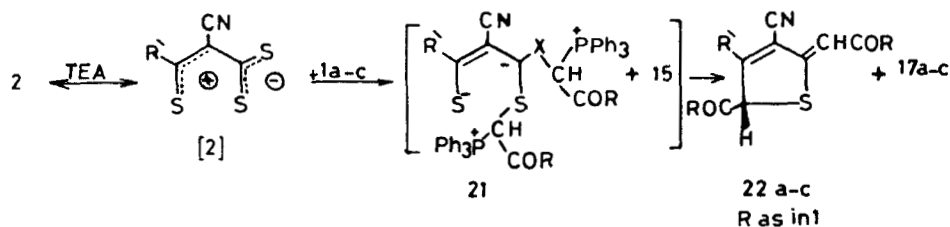
Obviously, fluorenylidene triphenylphosphorane, in which the negative charge is delocalized throughout the fluorene nucleus, and thus reduce the reactivity, can not react further with the nitrile group. In addition, formation of the dimeric product **15** reminds of the tendency of this class of compounds, heterocyclic *cis*-disulfides, for dimerization during their reactions with other nucleophiles.^{2-4,15,16}

Extension of the investigation to the reaction of 5-*p*-chlorophenyl-4-cyano-1,2-dithiol-3-one **2b** with the same ylides **1a-d** was also investigated as described for **2a**, whereas we found that the reaction of **2b** with **1a** and **1b** results again in the formation of comparable products **10a** and **13a** as well as **10b** and **13b**, respectively, nevertheless compounds analogous to **11** were not isolated from these reactions (**2b** + **1a,b**). Similarly, **1c** reacted with **2b**, as with **2a**, to afford **10c** and **14**. However, there is a very little difference in yields (see Table II). Identification of the products was based upon direct comparison of mps and IR spectra. On the other hand, reaction of **2b** with **1d** afforded **10d** and the ethylene compound **4**.

It should be noted that the presented behavior of the Wittig reagents **1a-d** toward 4-cyano-1,2-dithioles **2a** and **2b** is in marked disparity with the behavior of the same reagents toward 1,2,4-dithiazoles **5a** and **5b**. In the latter case, the phosphonium ylides **1** reacted with **5a,b**, mainly at the S—S bond to give the intermediates **16** which can either afford **17** [Scheme IV, path (a)], or react further with



SCHEME IV



SCHEME V

a second ylide molecule to lead finally to new thiazoles **19** or dithiole derivatives **20** [Scheme IV, path (b)] depending on the substituents and the reaction conditions employed. Two different types of dimeric products were also isolated from these reactions depending on the kind of the substrates.^{2,3}

In view of the previous reports,^{3,17,18} that weak bases affect the cleavage of S—S bond, it was of interest to study the reactions of **2a** with **1a–c** in refluxing toluene containing triethylamine. Separation of the reaction mixture by column chromatography gave the expected products **10a–c** and the substituted thioles **22** (Scheme V). Products analogous to compounds **11**, **13** or **14** which are derived from the attack of **1** at the nitrile group were not isolated from these reactions. Structure **22** was deduced from correct elemental analysis, IR, ¹H NMR and mass spectroscopic data (cf. Tables I and II). Isolation of **22** from the latter reaction can be explained by invoking catalytic action of triethylamine which enhances the ability of the strained S—S linkage to be disrupted with formation of the thiole **22** via the intermediate **21**.

CONCLUSION

In view of all the facts mentioned in the present and the previous^{2–4} studies, it can be seen that the nature of the α substituent to the carbonyl- or the thiocarbonyl

group in **2a,b** and **5a,b** plays a decisive role in their reactions with nucleophilic phosphorus compounds such as trialkyl phosphites⁴ and Wittig reagents.^{2,3} The present approach has a built-in advantage of being able to implement wide variations in the substituents at C3 and C4 of heterocyclic cis-disulfide moiety. The results of the present work also show marked resemblance between **2a** and **2b** in their chemical behavior toward phosphonium ylides under similar conditions. The findings, also, support the assumption that the basic medium stimulate the course of the reaction at the S—S bond.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were run on a Perkin-Elmer Infracord Spectrometer model 197 (Grating) in KBr. The ¹H NMR spectra were measured in CDCl₃ on a Bruker Spectrometer Model WH-90 and the chemical shifts were recorded in δ , ppm relative to TMS. The ³¹P NMR spectra were carried out on a Varian CFT 20 Spectrometer (vs. external 85% H₃PO₄). The mass spectra were run at 70 eV on Kratos MS-50 equipment provided with a data system. Elemental analyses were carried out at the Microanalytical Laboratory, National Research Centre, Cairo.

Reaction of 2a with 1a and 1b: *General procedure.* To a solution of **1a**¹⁹ or **1b**¹⁹ (10 mmol) in 30 ml toluene, a solution of **2a**²⁰ (1.4 g, ~5 mmol) in 30 ml of the same solvent was added. The reaction mixture was refluxed for 8–10 h (TLC). The product mixture was evaporated on silica gel under reduced pressure and applied to a silica gel column with petroleum ether containing increasing amounts of chloroform and then with pure chloroform to give:

- The fractions up to 9:1 v/v eluted colorless needles of triphenylphosphine sulfide (ca 77%), mp 162°C (ethyl alcohol).
- The fractions up to 8:2 v/v yielded a yellow product which was recrystallized from the appropriate solvent (see Table II) to give yellow crystals shown to be **10a** or **10b**, respectively.
- The fractions up to 7:3 v/v gave a yellow product which was, recrystallized from the appropriate solvent (see Table II) to give yellow crystals identified as **11a** or **11b**, respectively.
- The fractions up to 6:4 v/v afforded colorless crystals of triphenylphosphine oxide (75%) mp 156°C (benzene).
- Elution with CHCl₃ gave a brown **13a** or **13b**, respectively, which was recrystallized from the appropriate solvent. Percentage yields, physical and analytical data for compounds **10a,b**, **11a,b** and **13a,b** are given in Tables I and II.

Reaction of 2a with 1c: To a solution of **2a** (1.4 g, ~5 mmol) in 30 ml toluene, a solution of **1c**²¹ (3 g, ~10 mmol) in 30 ml toluene was added. The reaction mixture was refluxed for 15 h. After the reaction was completed (TLC) the solvent was distilled off and the residue was chromatographed as previously described. The column was developed with hexane, containing increasing amounts of chloroform to give:

- The fractions up to 9:1 v/v yielded TPPS (72%), mp 162°C.
- The fractions up to 8:2 v/v afforded a yellow substance which was recrystallized from the proper solvent (see Table II) to give **10c**.
- The fractions up to 6:4 v/v eluted TPPO (78%), mp 156°C.
- The fractions up to 5:5 v/v gave brown substance **14** which was recrystallized from ethyl acetate. Percentage yields, physical and spectral data of compounds **10c** and **14** are listed in Tables I and II.

Conversion of 10a and 11a to 13a and 10c to 14: A mixture of **10a** or **11a** (200 mg) and one mole equiv. of the parallel ylide **1a** in dry toluene (40 ml) was refluxed for 18–20 h; the volatile materials were evaporated, *in vacuo*. The residue was collected and recrystallized from the appropriate solvent (see Table II) to give compound **13a**, in ~42% yield. The identity of **13a** was established by mp, mixed mps and comparative IR spectral determinations with the corresponding reference sample. Unidentified materials, TPPO and unchanged substances were also isolated. In the same manner, **10c** was converted to **14** in 13.6% yield.

Reaction of 2a with 1d: A mixture of **2a** (1.4 g, ~5 mmol) and **1d**²² (2.2 g, ~5 mmol) in toluene (50 ml) was refluxed for 20 h. The reaction mixture was worked up in the same way and the column chromatography was developed by toluene containing increasing amounts of ethyl acetate. The fractions up to 9:1 v/v yielded colorless needles of TPPS (75%), mp 162°C.

The fraction up to 5:5 v/v afforded a yellow product which was, recrystallized from benzene to give **10d** as yellow crystals.

The fractions up to 3:7 v/v gave yellow crystals, shown to be **15**. The results of **10d** and **15** are summarized in Tables I and II.

Conversion of 15 to 4: 0.2 g of **15** was refluxed in 20 ml of dry xylene with 0.9 g of freshly reduced copper powder for 6 h. The inorganic and volatile materials were removed to give a semi-solid substance which solidified after being triturated with a cold pentane to afford a yellow substance mp 190–92°C, proved to be the ethylene **4**, previously reported,⁴ (mixed melting points and comparative spectral data). Mass spectrum: $m/z = 475$ (M^+ , 33%).

Reaction of 2a with 1a–d in the presence of triethylamine: Reaction of **2a** with **1a**, **1b** or **1c** was performed in refluxed tetrahydrofuran containing 0.5 ml of triethylamine, similar to the general procedure, with the same amounts. After evaporation of the volatile materials *in vacuo*, **10a** (25.3%) and **22a** (42.3%) or **10b** (22.7%) and **22b** (55.2%) or **10c** (18.8%) and **22c** (38.7%) were obtained, respectively, by column chromatography (silica gel/light petroleum with increasing amounts of chloroform). Physical, elemental analyses and spectral data for **22a**, **22b** and **22c** were presented in Tables I and II.

Carrying out the reaction of **2a** and **1d** in refluxing THF containing 0.5 ml TEA, did not affect the previous reaction products **10d** and **15** or their percentage yields.

Reaction of 2b with 1a–d: Reaction of **2b** with **1a**, **1b** or **1c** was performed in refluxing toluene for 12–15 h (TLC). Working up of the reaction mixture, elution and separation of the products were accomplished in the manner as described for the reaction of **2a** with **1a**, **1b**, or **1c**. Identification of the products exactly matched the compounds isolated in reaction of **2a** with the parallel ylide **1a**, **1b** or **1c**.

Reaction of **2b** with **1d** afforded **10d** and **4** (48%) instead of **10d** and **15**. Percentage yields of the isolated products are given in Table II.

Reaction of **2b** with **1a,b** did not afford analogous compounds to **11a,b**, whereas it yielded only **10a,b** and **13a,b**.

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