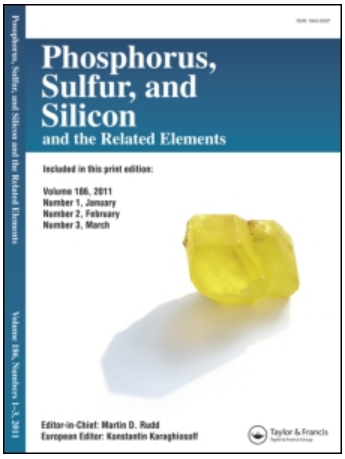


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# Action of Nucleophilic Phosphorus Reagents on Heterocyclic *cis*-Disulfides

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As a contribution to previous studies of the reaction of phosphorus nucleophiles with heterocyclic *cis*-disulfides,[1,2] the reactivity of trialkyl phosphites **2** toward 5-p-chlorophenyl-4-cyano-1,2-dithiol-3-thione **1a**, 5-phenyl-1,2,4-dithiazol-3-thione **1b** and its 3-carbonyl derivative **1c** has now been investigated.

The reaction of the thione **1a** (0.01 mol) with trimethyl, triethyl or triisopropyl phosphites **2a-c** was found to proceed in the absence of solvent at 100 °C for ~10 h. Chromatographic separation of the reaction mixture produced two crystalline products **8** and **9**. The parallel trialkyl thiophosphate was also identified ($^{31}$P NMR) in the product-mixture in each case. Reaction of **1a** with **2a** produced in addition to **8a** and **9**, another crystalline yellow product assigned structure **7** (R=$CH_3$) (see table A).

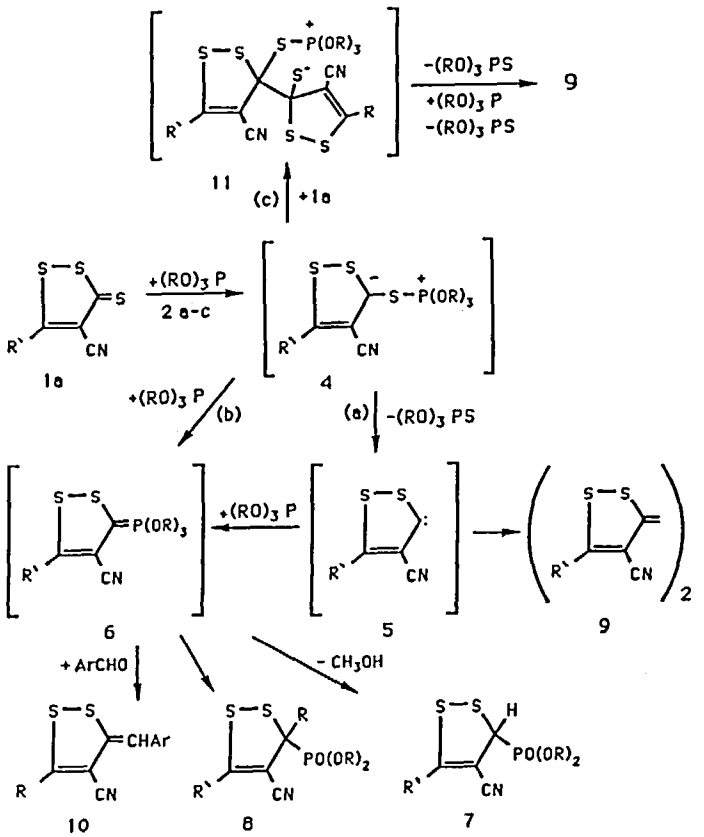
**Table A : Reaction conditions and the products of the reaction of 1a with 2a-c.**

| Educt | Reaction Time (h) | Reaction products Compound (yield, %)[a] | | | |
|---|---|---|---|---|---|
| **1a** + **2a** | 10 | **7** (15) | **8a** (28) | **9** (15) | |
| **1a** + **2b** | 10 | – | **8b** (45) | **9** (16) | |
| **1a** + **2c** | 8 | – | **8c** (52) | **9** (20) | |
| **1a** + **2a** + ArCHO | 8 | **7** (10) | **8a** (15) | **9** (<5) | **10** (35) |

a) yields are approximated.

Reasons for phosphonate structures **7** and **8** are: a) Satisfactory elemental analyses and molecular weight determinations (MS) were obtained for all new compounds. b) Their $^{31}$P NMR spectra have chemical shifts at δ 28-30 ppm (vs. 85% $H_3PO_4$). c) In the $^1$H NMR spectrum of **8a**, the methyl protons appear as a doublet at δ 1.96 ppm with $^2J_{HP}$ = 10.5 Hz. The presence of –C–$CH_3$ group was supported by a signal at δ 19.6 ppm in the $^{13}$C NMR spectrum and a signal at δ 35.8 ppm (C.$CH_3$), a value which coincides with a chemical shift for the ring sp$^3$-carbon atom bearing a methyl group. The $^1$H NMR of **7** lacked the signal due to the –C–$CH_3$ group, instead another doublet appeared at δ 4.45 ppm with $^2J_{HP}$=18.2 Hz, which attributed to the ring-methine proton.

* To receive any correspondence.




4-11, R` and R as in 1a and 2; Ar = $C_6H_5$

Scheme 1

d) The IR spectra of 7 and 8 showed -S-S- absorption band at 1275 $cm^{-1}$. Finally, on carrying out the above reaction in the presence of benzaldehyde, it yielded the phosphonates 7 (10%) and 8a (15%), the dimeric product 9 (<5%) and 3-benzylidene derivative 10 as a major product (35% yield), which was identified by elemental analysis, mass and $^{13}C$ NMR spectroscopy.

3,3`-bi(1,2-dithiol-3H-ylidene) 9 was obtained as orange crystals, mp. 196 °C, m/e = 475 ($M^+$), calcd. = 475.46. The principle spectral features of 9 are its absorption at $\upsilon_{max}$ $cm^{-1}$ 2215 (CN), 1275 (-S-S-) and 1622 (C = C).

The structure of 3,3`-bi(1,2-dithiol-3H-ylidene) 9 was presumed to be (E)- isomer since it is previously reported [3, 4] that Z-alkenes having electron - withdrawing group (CN, cf. 4 and 11, Scheme 1) substituent α to the thiocarbonyl group of the substrate, isomerizes to the thermodynamically more stable E-isomer.

Scheme 1 presents the three kinds of pathways had been observed from the thiocarbonyl group in 1a which is adjacent to α electron-withdrawing group (-CN)

substituent. Thus, the initial thiophilic addition is assumed, involving trialkyl phosphite and the thiocarbonyl group. The evoluted thiophilic addition product 4 can undergo desulfuration with formation of carbene 5 [path (a)]. Reaction of 5 with a second equivalent of phosphite [path (b)] or the substrate **1a** [path (c)] leads to the resulting products 8 and 9, respectively. Formation of 7 was explained *via* the protonation-arbuzov type dealkylation of the ylide intermiate 6.

On the other hand, when **1b** or **1c** was allowed to react with trialkyl phosphites **2a-c** under the same experimental conditions used with **1a**, the reaction course takes another way to give **14a-f**, **16** and the parallel trialkyl thiophosphate or trialkyl phosphate, respectively, (Scheme 2). This result is contrary to the previously reported[5] observations that, only, thioacyl isothiocyanates or thioacyl isocyanates and the corresponding thiophosphate were the reaction products, for the same reactions. Moreover, addition of benzaldehyde to the reactants **1b** or **1c** and trialkyl phosphite did not affect the result.

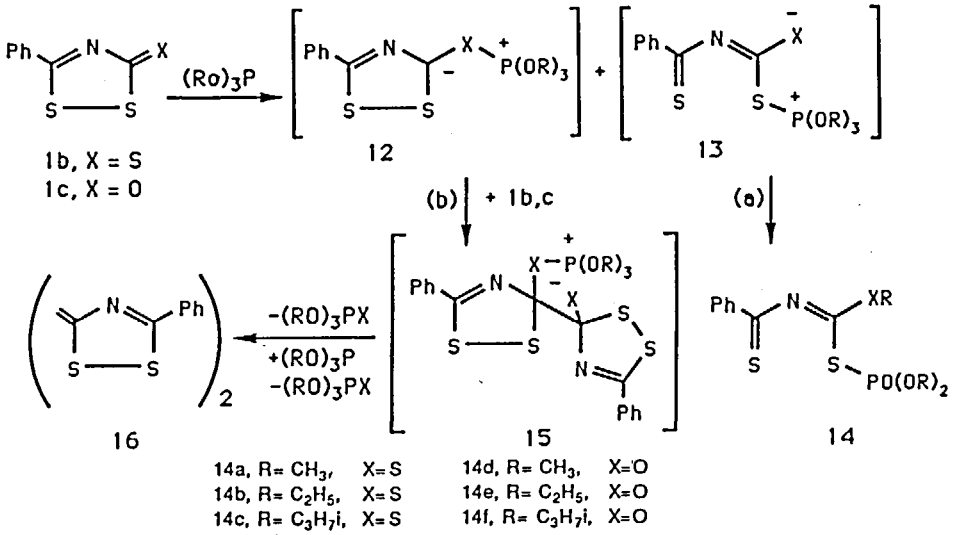


**Table B : The reaction of 1,2,4-dithiazoles 1b and 1c with trialkyl phosphites 2a-c.**

| Product | X | R | Mp °C | Yield[a] (%) | Product | X | R | Mp °C | Yield[a] (%) |
|---|---|---|---|---|---|---|---|---|---|
| **14a** | S | $CH_3$ | 83[b] | 33 | **14d** | O | $CH_3$ | 66[d] | 38 |
| **14b** | S | $C_2H_5$ | 109[b] | 47 | **14e** | O | $C_2H_5$ | 71[d] | 44 |
| **14c** | S | $C_3H_7$-i | 113[c] | 55 | **14f** | O | $C_3H_7$-i | 81[d] | 48 |

a) Yields are approximated. b) From ether / light petroleum ether (b.r. 40-60 °C).
c) From cyclohexane. d) From pentane.

Structural assignment for O,O-dialkyl S-phosphorothioate **14** was based on microanalyses and spectroscopic interpretations (MS, IR, $^1H$, $^{31}P$ and $^{13}C$ NMR spectra), e.g., $^{31}P$ NMR chemical shifts for **14** are $\delta \sim 22.5$ ppm.




Scheme 2

The identity of 3,3`-bi(5-phenyl-3H-1,2,4-dithiazol-3-ylidene) **16** was confirmed by comparison with authentic specimen.[2] However, we were unable to assigne the (E)- or the (Z)-structure for the dimeric product **16** since the already available spectroscopic data can not decisively differentiate between the two isomers. X-ray crystallographic analysis will be undertaken and the data will be published in the forthcoming communication.

A possible explanation for the course of the reaction of **1b** and **1c** with trialkyl phosphites is shown in Scheme 2. We presumed the enhanced ability of -S-S-linkage to be disrupted due to the absence of the electron- withdrawing group substituent from

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