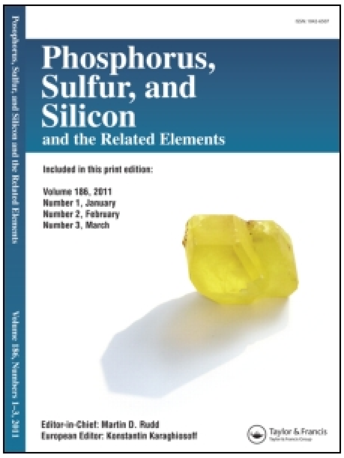

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Wafaa M. Abdou

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Synthesis and Characteristics of Novel Thiazoie and Dithiazole Derivatives. Reactions of Acyclic- and Heterocyclic *Cis*-Disulfides with Some Nucleophilic Phosphorus Reagents

WAFAA M. ABDOU

National Research Centre, Dokki, Cairo, Egypt

The behavior of phosphorus ylides such as alkoxycarbonyl-and β-ketoalkylidenephosphoranes toward different types of acyclic and cyclic *cis*-disulfides has been investigated whereby several substituted-thiazoles, dithiazoles, thioles and dithioles as well as different types of dimeric products were isolated and identified.

Keywords: acyclic- and heterocyclic *cis*-disulfides; phosphorus ylides

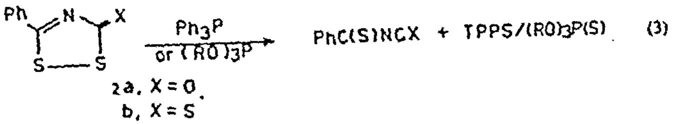
INTRODUCTION

Disulfides and their derivatives constitute a class of compounds of wide interest for both biological and chemical behavior studies. It has been reported that organic disulfides of general formula R-S-S-R (R= alkyl or aryl) react with trialkyl phosphites and sodium dialkyl phosphonates to give phosphorothioate esters[1,2] (eqs.1 and 2).

$$\text{R-S-S-R} + (\text{RO})_3\text{P} \longrightarrow \text{RSP}(\text{OR})_2 + \text{R-S-R} \quad (1)$$

$$\text{R-S-S-R} + (\text{RO})_2\text{P(O)Na} \longrightarrow \text{RSP(O)}(\text{OR})_2 + \text{NaSR} \quad (2)$$

On the other hand, it has been reported[3] that heterocyclic *cis*-disulfides, 5-phenyl-*3H*-1,2,4-dithiazole-3-one **2a** and its thione derivative **2b** react with trialkyl phosphites to give thioacyl isocyanate (or isothiocyanate) along with the corresponding trialkyl thiophosphate (eq. 3).The work detailed here involves a study on the interactions

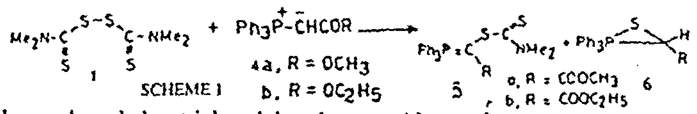


of the acyclic disulfide: tetramethylthiuram disulfide 1 and several types of heterocyclic *cis*-disulfides which contain this moiety in combination with function groups bearing a greater or lesser decrease of electronegativity such as 2a,b and 5-*p*-chlorophenyl-4-cyano-1,2-dithiole-3-thione 3a and its -3-one derivative 3b with phosphorus ylides of type 4. The biological evaluation of the new products seem to be interest.

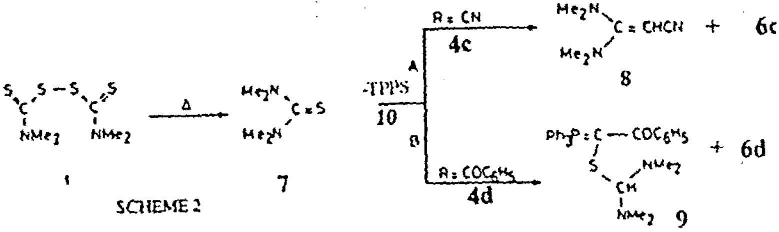
RESULTS AND DISCUSSION

I-*Reaction of Disulfide* 1 *and Phosphorus Ylides.*[4]

Treatment of 1 with one equiv. of 4a,b in boiling tetrahydrofuran for 6 h gave the substituted ylides 5a,b (65%) and the episulfides 6a,b (~20%) as depicted in Scheme 1. Conversely, 1 reacts with cyano-4c or benzoyl-methylenetriphenylphosphorane 4d to give compounds 6c,d (~12%) along with 8 (33%) or 9 (28%), respectively, were isolated obviously, through an initial decomposition of 1 to tetraalkylthiourea7, carbon disulfide and sulfur,[5] followed by thiocarbonyl olefination by the Wittig reagent 4c or 4d (Scheme 2).



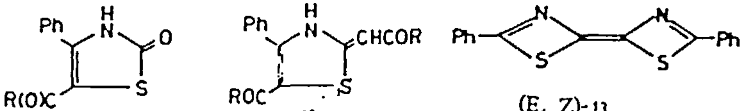
SCHEME 1



SCHEME 2

II-*Reaction of Cyclic cis-Disulfide* 2a *with Phosphorus Ylides.*[6]

Treatment of **2a** with **4a** and **4b** at 25 °C gave the thiazole derivatives **11a,b** (~45%) and **12a,b** (~13%), whereas with **4e** (R= CH_3) in ethyl acetate, the thiazole analog **12c** (70%) was only obtained (Scheme 3). Conversely, the reaction of **2a** with the ylides **4d** (R= C_6H_5) or **4f** (R= H) yielded in both cases the dimeric product **13** (~66%).

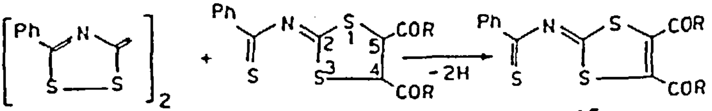


11 12 (E, Z)-13

SCHEME 3

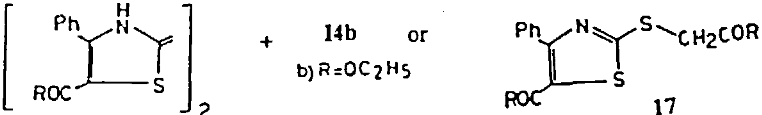
III-*Reaction of the Dithiazole* 2b *with Phosphorus Ylide.*[7]

In a systematic study, the reaction of *cis*-disulfide **2b** with **4a** in boiling THF afforded 1,3-dithiole derivative **14a** (53%) and the dimeric product *E*13A(20%). However, compound **14a** could be oxidized by N-bromosuccinimide to the known dithiole **15**[9] (Scheme 4).



13A 14a SCHEME 4 15

When **2b** was treated with ylides **4b** (R= OC_2H_5) and **4e** (R= CH_3), the dimeric compounds **16a,b** (62%) along with the disubstituted 1,3-dithiole **14b** (27%, with **4b**) or **17** (44%, with **4e**).



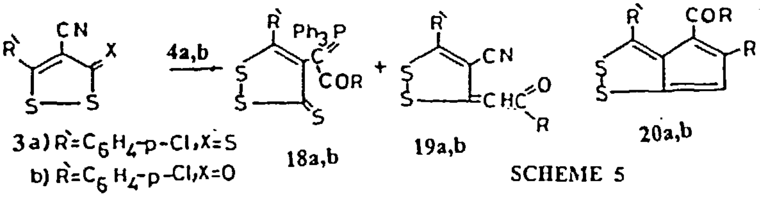
16a,b

14b or b) R=OC2H5

17 , R=CH3

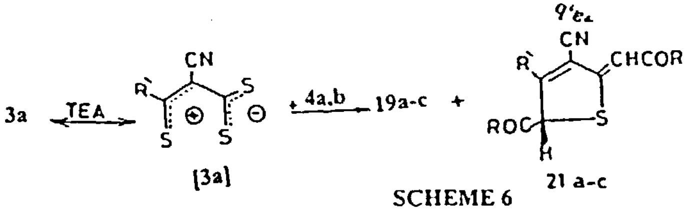
IV-*Reactions of the Dithiole* 3a,b *with Phosphorus Ylides.*[9]

Treatment of the nitrile **3a** with **4a** and **4b** gave the new ylides **18a,b** (~11%) along with the dithioles **19a,b** (~26%) and **20a,b** (~13%). Heating **18a** or **19a** with **4a** led to the formation of **20a** (Scheme 5).



SCHEME 5

Likewise, the reaction of **3b** with **4a** and **4b** results again in the formation of comparable products **19a,b** and **20a,b**, nevertheless compounds analogous to **18** were not isolated from these reactions. Carrying out the latter reactions (**3a,b** + **4a,b**) in the presence of a base (triethylamine) yielded the expected products **19a,b** (~22%) and the substituted thioles **21a,b** (~48%) (Scheme 6).



SCHEME 6

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