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STUDIES OF PHOSPHORUS YLIDES WITH TETRAMETHYLTHIURAM DISULFIDE

WAFAA M. ABDOU,* and EL-SAYED M.A. YAKOUT
National Research Centre, Dokki, Cairo, Egypt.

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ABSTRACT: In contrast to the behaviour of the entitled disulfide (**1**) toward Wittig reagents (**2a, b**), which undergoes direct and simple nucleophilic displacement reactions giving **7a, b, 8** and **9** as the final products, an extensive decomposition occurred when the same disulfide was treated with ylides **2c, d**, furnishing the adducts **7c, d, 8** and **12** or **14**, respectively. The given structures were based upon analytical, chemical and spectroscopic results.

Key words: Organic disulfides; tetramethylthiuram disulfide, Wittig reaction, thiaphosphirans.

INTRODUCTION

Disulfides and their derivatives constitute a class of organic compounds of wide medical and biological importance. They are known to possess therapeutic values in controlling diseases, such as pneumonea;[1] useful as fungicides[2, 3] and seed protectants[3] as well as being utilized as antioxidants and in volcanization processes.[4-6]

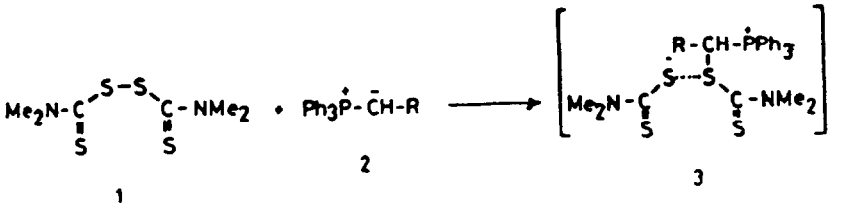
Disulfides, on the other hand, demonstrate interesting aspects of their chemical behaviour toward phosphorus reagents.[7-9] It has been previously reported that organic disulfides of general formula R-S-S-R (R= alkyl or aryl) react with trialkyl phosphites[7,8] and sodium dialkyl phosphonates[9-11] to give phosphorothioate esters (eq. 1 and 2). The favoured pathway for these reactions is ionic[8,10,12] and does not occur by a free

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

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

radical mechanism as has been proposed by Walling and Rabinowitz.[13] It, also, has been pointed out,[8,10] that the reaction takes place through the same valency expansion type by which trivalent phosphorus esters react with a large variety of chemical groupings susceptible to nucleophilic displacement (Arbuzov-type polar process). It seemed of interest to inquire whether another type of nucleophilic phosphorus reagent, ylide phosphoranes, can likewise cleave the disulfide-S-S linkage. similar attention, however, was not paid regarding the potentiality of these phosphonium ylides on organic disulfides, except in few cases.[14,15] Accordingly, the reaction of tetramethylthiuram disulfide (**1**) with Wittig reagents (**2a-d**) was investigated in some detail, and the products rationalized as proceeding via 1:1 intermediate which can be envisaged as having the anionic form **3**, in turn, relevant to their overall structures.

* Author to whom all correspondence should be addressed



2,3,a) R = $COOCH_3$ c) R = CN
b) R = $COOC_2H_5$ d) R = COC_6H_5

SCHEME 1

As early as 1972, the first investigation was undertaken to study the influence of Wittig reagent **2** (R = H) on organic disulfides, e.g., dibenzoyl disulfide.[14] The reaction led to the formation of the corresponding substituted ylide Ph_3 P=CRSC(O)Ph in ~ 50% yield together with unidentified products. Later on, in 1987[15] Galli reported that tetramethylthiuram disulfide (**1**) reacted with stabilized phosphorus ylide **2a** in benzene to give the corresponding substituted ylide **9a** as the sole reaction product in 92% yield (Scheme 2).

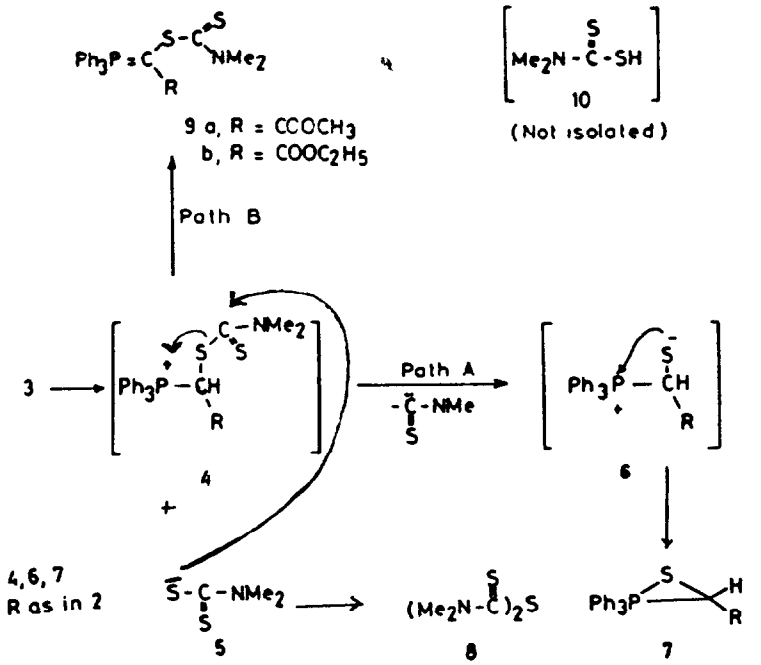
RESULTS AND DISCUSSION

A tetrahydrofuran solution of the disulfide (**1**) and one equiv. of methoxycarbonylmethylene-(**2a**) and/or ethoxycarbonylmethylenetriphenylphosphorane (**2**) was heated under reflux for 6 h. Concentration of the solution to a small volume, gave colourless crystals of the substituted ylides **9**. Resolving the filtrate on column chromatography afforded colourless crystals of the episulfides (**7a,b**) of the corresponding ylides, red yellow needles of tetramethylthiurammonosulfide (**8**) and traces of colourless crystals of triphenylphosphine sulfide (Scheme 2).

Thiaphosphiran heterocycles (**7**) were isolated as colourless crystals in ca 20% yield. The mass spectrum of **7b** displayed a molecular ion peak at m/z 380 (M^+, 22%), m/z 348 (M^+ -32, 100%) and m/z 262 (M^+ -118, 66%). ^{31}P NMR spectroscopy showed a sharp signals at δ -8.4 ppm which is in accord with that of the precedents for, the little known **7**.[16] ^{13}C NMR spectrum of **7b** showed a carbon signals at (δ)172.6 (C.C=O), 51.3 (OCH_2), 28.5 (P-CH-) and δ 15.8 ppm[16,17] Moreover, the IR spectrum of **7** revealed the absence of ethylenic absorption and the ^{1}H-NMR data were fully in accord with structure **7**. The identity of compounds **7** was further characterized by reduction with triphenylphosphine to reform their parent ylides (cf. experimental section).

Ylides **9** were obtained as main products in 62% yield. Structural assignment for **9** is based upon the following observations: (a) The ^{1}H-NMR spectra (200 MHz) of **9** reveal the lack of any signal due to the methine proton which presents in the PMR spectra of **2** at ca δ 5.5 ppm. However, the ^{1}H-NMR spectrum of **9b** showed two singlets at δ 3.12 and 3.28 ppm whose peak area integrated to 6 protons, and are assigned to the methyl groups (-N-Me_2).[18] The splitting of the spectral lines is probably due to the asymmetry of the molecule. The spectrum, also, disclosed the methoxy group of ester as a triplet at δ 1.3 (C-CH_3) and a quartet at 3.72 (OCH_2). The aromatic protons appeared as a complex pattern in the 7.17-8.0 ppm region. (b) In the IR spectrum (KBr, expressed in cm^{-1}) of **9b**, the strong absorption band observed at 1482 has been assigned to the thiuram moiety [-N-C(S)].[19,20] Moreover, it revealed absorptions at 1690 cm^{-1} for P-C (phenyl). (c) The ^{31}P-NMR measurements support the ylide structure. For example **9b** exhibits a sharp signal at δ 26.7 ppm (vs. H_3PO_4).[21] (d) The mass spectrum of **9b** shows M^+ at 467.

However, the other two compounds, tetramethylthiurammonosulfide (**8**) and triphenylphosphine sulfide were characterized by comparison with authentic samples (cf. experimental part).



SCHEME 2

On the basis of the isolated products, the conditions applied, and several leading mechanisms discussed in the literature for the reactions of disulfides (especially **1**) with nucleophilic reagents,[7-12, 22,23] the mechanism that accounts for the reaction of **1** with resonance stabilized phosphoranes (**2a,b**) is presented in Schemes 1 and 2. Thus, the initial nucleophilic attack by the carbanion centre in the ylide **2a** and/or **2b** on the weak -S-S-linkage in **1** leads to an elusive 1:1 intermediate species **3** which cleaves under thiuram-sulfide ion (**5**) elimination to afford another intermediate **4**, which in turn undergoes further displacement reactions. Thus, attack of **5** on **4** yields tetramethylthiurammonosulfide (**8**) and thiaphosphiran (**7**) via the intermediate (**6**) (path A) or abstraction of the acidic hydrogen from **4** by the dithiocarbamyl anion (**5**) itself, gives rise to the substituted ylide (**9**) and dimethyldithiocarbamic acid (**10**) (path B). The absence of dimethyldithiocarbamic acid (**10**) among the products can be reasonably interpreted by its decomposition during the reaction (eq. 3).[24]

$$Me_2NC(S)SH \longrightarrow Me_2NH + CS_2 \qquad (3)$$

Alternatively, formation of thiaphosphirans can be reasonably interpreted by the [1+2] cycloaddition of sulfur of the disulfide to the ylidic P-C bond, whereby the ring closure could well be concerted with formation of **8**. The latter mechanism is in accordance with that previously reported by Niecke et al.[16]

On the other hand, formation of triphenylphosphine sulfide (4%) in the above reaction, can be rationalized in terms of slow decomposition of ylide (**9**) releasing triphenylphosphine which undergoes desulfuration[25] of the disulfide (**1**), leading to triphenylphosphine sulfide and tetramethylthiurammonosulfide (**8**).

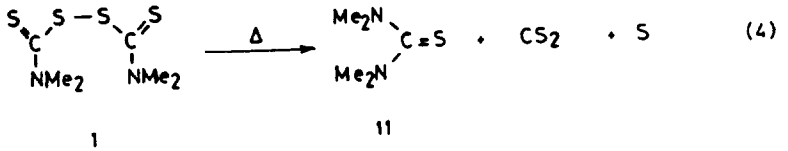
Next, the reaction of **1** with cyanomethylenetriphenylphosphorane (**2c**) was, expectedly, not quite so rapid as that with **2a** or **2b**. Treatment of the disulfide (**1**) with one equiv. of **2c** in refluxing toluene for 36 h gave a mixture of two main products **7c** and **12** which could be resolved by the usual technique. Triphenylphosphine sulphide (TPPS) and monosulfide (**8**) were also isolated and identified.

The first product (12.6%) was assigned thiaphosphiran (**7c**) since its elemental analyses and molecular weight determination agreed with molecular formula $C_{20}H_{16}NPS$, and its spectral properties are consistent with expectation. Moreover, **7c** yielded its parent ylide on reduction with triphenylphosphine.

The second product (33%) was devoid of sulfur as inferred from its elemental analyses. However, its composition is established by determination of the exact mass of **12** and by elemental analysis. Its IR spectrum lacked absorption bands in the region 1490-1460 recorded for the thiuram moiety [N-C(S)] in the starting material **1** and adducts **9**. Characteristic absorption bands are observed at 2238 (-CN) and 1620 ($\rangle C = C\langle$). The ^1H NMR spectrum of **12** showed two singlets at δ 2.24 and 2.26 ppm attributed to the methyl groups (12H) and a singlet at δ 5.97 ppm assigned for the methine proton.

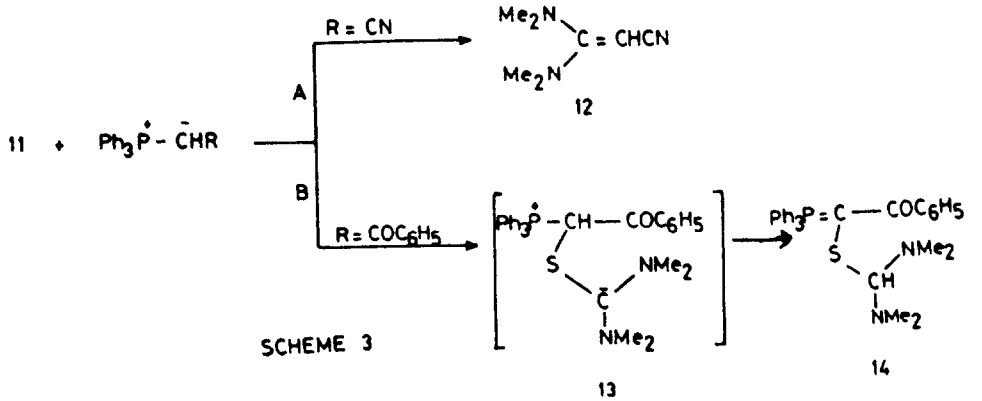
Following the trend of decreasing reactivity, **2d** was the least reactive of the four phosphorus ylides investigated. The reaction hardly proceeded in boiling toluene, being completed within 36 h with formation of **7d** (15%), the addition product **14** (18%) and other unidentified products. Tripheylphosphine sulfide and **8** were also isolated and identified. Thiaphosphiran **7d** was fully characterized by its spectroscopic and chemical data. For further corroboration of both structures **12** and **14**, tetramethylthiourea (**11**) was treated with **2c** and/or **2d**, in boiling toluene. The reaction products **12** and/or **14** were isolated, respectively, and identified (mp. and mixed mps. as well as comparative spectra).

However, the unexpected behaviour of **2c** and **2d** toward the disulfide (**1**) leading to the olefin (**12**) and the addition product (**14**), respectively, may be considered to proceed via formation of **11** (eq. 4):



(4)

1 11



12 13 14

SCHEME 3

Decomposition of **1** to tetraalkylthiourea along with carbon disulfide and sulfur is well documented.[26,27] Subsequent thiocarbonyl olefination by one mole of Wittig reagent (**2c**) affords **12** (Scheme 3, path A).

On the other hand, the mechanism that accounts for the generation of the addition product (**14**) is presented in Scheme3, path B. This mechanism parallels the reaction course of similar phosphorus ylides with thiourea, previously reported by Zbiral.[28]

CONCLUSION

As a consequence following from the data reported above for the reactions of tetramethylthiuram disulfide (**1**) with Wittig reagents, two main pathways of homolytic cleavage of the disulfide and nucleophilic displacement on sulfur are observed. The first (**1 + 2a, b**) is thought to involve a direct and simple displacement on sulfur (-S-S-linkage) as shown in Schemes 1 and 2. Another anomalous pathway (**1+2c, d**) occurs, sluggishly, whereby, decomposition of the disulfide **1** metathetically to thiourea **11** can compete effectively, furnishing the Wittig reaction of the break-down product (Scheme 3).

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were run at a Perking Elmer Infracord Spectrometer Model 197 (Grating) in KBr. The ^{1}H-NMR spectra are recorded with a Bruker Spectrometer Model WH-90 and 200 MHz and the chemical shifts are recorded in δ ppm relative to TMS. The ^{31}P-NMR spectra were carried out on Varian CFT 20 (vs. external 85% H_3PO_4). The mass spectra were run at (70 ev): MS-50 of Kratos (AEI) Spectrometer provided with data system. Elemental analyses were carried out at the "Microanalysis Laboratory, National Research Centre, Cairo".

Reaction of Tetramethylthiuram Disulfide (1) with Phosphorus Ylides (2a,b). General Procedure. To a solution of the disulfide (**1**)[29] (2.40g, 0.01 mol) in dry tetrahydrofuran (20 ml) was added a solution of ylide **2a**[30] or **2b**[30] (0.011 mol) in the same solvent (30 ml). The reaction mixture was refluxed for 6-8 h (TLC). The mixture was then concentrated at 40°C under reduced pressure. After cooling, colourless crystals were separated, recrystallized from the suitable solvent to give **9a** or **9b**.

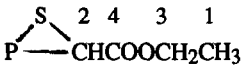
Compound **9a**, colourless crystals (2.98g, 65.8%) mp 233-235°C (ethyl acetate). Anal. Calcd. for $C_{24}H_{24}NO_2PS_2$ (453.547): C,63.55; H,5.33; N,3.09; P,6.83; S,14.14. Found: C,63.50; H,5.31; N,3.02; P,6.78; S,14.09. IR(KBr) cm^{-1}: 1665 (C=O, ester); 1680 and 1510 (C=P) and 1434 cm^{-1} (P-C, phenyl). ^{1}H-NMR (DMSO) δ, ppm 3.12 and 3.28 [2s, 6H-N(CH_3)$_2$], 3.45 (s, 3H, -OH_3) and 7.52 (m, 15H, Ar-H). ^{31}P-NMR(DMSO) δ = 28.8 ppm. MS: m/z = 453 (22%).

Compound **9b**, colourless crystals (2.9g, 61.6%), mp 218°C (chloroform). Anal. Calcd. for $C_{25}H_{26}NO_2PS_2$ (467.573): C,64.21; H,5.60; N,2.99; P,6.62; S,13.71. Found: C,63.88; H,5.53; N,2.95; P,6.74; S,13.66. IR (KBr)cm^{-1}: 1690 (C=O, ester), 1675, 1505 (C=P), 1482 (N-C(S)S-) and 980 (P-C, phenyl). ^{1}H-NMR (DMSO) δ 1.3 (t, 3H, C-CH_3, J_{HH}=7.08) and 7.55 ppm (m, 15H, Ar-H). ^{31}P-NMR (DMSO) δ = 26.7 ppm. MS: m/z = 467 (30%).

The mother liquors were 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. The fraction with 100% petroleum ether eluted red-yellow needls, mp 104°C (0.68g, 33%) of tetramethylthiurammonosulfide (mp, mixed mps, and comparative IR spectra).[26] The fraction (up to 3:2 v/v) yielded colourless crystals, recrystallized from the suitable solvent to give **7a** or **7b**.

Copound **7a**, colourless crystals (0.67g, 18.3%) mp 142°C (cyclohexane). Anal. Calcd. for $C_{21}H_{19}O_2PS$ (366.403): C, 68.83; H, 5.22; P, 8.45; S, 8.75. Found : C, 68.77; H, 5.09; P, 8.69; S, 8.68. IR (KBr) cm^{-1}: 1672 (>C=O, ester), 985 (P-C Phenyl). ^{1}H-NMR ($CDCl_3$)δ3.55 (s.3H,OCH_3), 4.8 (d, 1H,-CH, $^2J_{HP}$=15.5 Hz), and 7.41-7.82 ppm (m, 15H, Ar-H). MS: m/z = 366 (M^+, 30%). ^{31}P-NMR ($CDCl_3$) δ -6.2 ppm.

Compound **7b**, colourless crystals (0.8g, 21.5%) mp 132°C (acetone). Anal. Calcd. for $C_{22}H_{21}O_2PS$ (380.429): C, 69.45; H, 5.56; P, 8.14; S ,8.42. Found: C,69.41; H,5.52; P,8.02; S, 8.36. IR (KBr) cm^{-1}: 1655 (C=O, ester), 980 (C-P, phenyl). ^{1}H-NMR ($CDCl_3$) δ 1.27 (t, 3H, -C-CH_3, J_{HH} = 7Hz); 3.88 (q, 2H, CH_2); 4.6 (d, 1H, -CH, J_{HP} = 15.5 Hz), and 7.42-7.86 ppm (m, 15H, Ar-H). ^{31}P-NMR ($CDCl_3$) δ -8.4 ppm. MS: m/z = 380 (M+, 22%). ^{13}C-NMR ($CDCl_3$), δ 15.8 (C_1), 28.5 (C_2), 51.3 (C_3) and 172.6 ppm (C_4).



The fraction (up to 2:3 v/v) yielded colourless needles mp 162°C (4%), identified as triphenylphosphine sulfide (mp, mixed mps, and comparative IR Spectra).[31]

Reaction of Tetramethylthiuram Disulfide (1) with Phosphorus Ylides (2c,d). General Procedure: A mixture of **1** (2.40g, 0.01 mol) and ylide **2c**[32] or **2d**[33] (0.015 mol) in toluene (60 ml) was refluxed for 36 h (TLC). The reaction mixture was worked up as mentioned above. **12** and/or **14** were crystallized out from the reaction mixture and the mother liquors, then chromatographed on silica gel with pet. ether-chloroform (9:1, 6:4 and 4:6) to give the products **8**, **7c,d** and triphenylphosphine sulfide, in sequence.

Compound **12**, yellow crystals (0.4g, 33%), mp 186-188°C (chloroform). Anal. Calcd. for $C_7H_{13}N_2$ (139.205): C, 60.39; H, 9.41; N, 30.18. Found: C, 60.32; H, 9.37; N, 30.09. IR (KBr) cm-^{1}: 2238 (-CN), 1620 (>C=C<). ^{1}H-NMR (DMSO) δ 3.24, 3.26 (2s, 12H-[$N(CH_3)_2]_2$), 5.97 ppm (=CHCN). MS: m/z = 139 (M^+, 42%).

Compound **14**, yellow crystals (0.8g, 28.5%) mp 242°C (chloroform). Anal. Calcd. for $C_{31}H_{36}N_2OP$ (483.625) C, 76.98; H, 7.50; N, 5.79; P, 6.41. Found: C, 76.88; H, 7.47; N, 5.72; P, 6.36. IR (KBr) cm^{-1}: 1540 (C=O). ^{1}H-NMR (DMSO) δ 3.45 (m, 12H[$N(CH_3)_2]_2$), 4.2 ppm (s, CH). ^{31}P-NMR (DMSO) δ 22.6 ppm. MS: m/z = 483 (M^+, 12%).

Compound **7c**, colourless crystals (0.42g, 12.6%) mp 112°C (cyclohexane). Anal. Calcd. for $C_{20}H_{16}NPS$ (333.377): C, 72.05; H, 4.84; N, 4.20; P, 9.29; S, 9.62. Found: C, 71.87; H, 4.81; N, 4.17; P,

9.26; S, 9.58. IR (KBr) cm^{-1} 2238 (-CN), and 994 (P-C, phenyl). ^{1}H-NMR ($CDCl_3$) δ 5.2 (d, 1H, -CH, J_{HP}=20.5 Hz) and 7.68 ppm (m, 15H, Ar-H). MS: m/z = 333 (12%).

Compound **7d**, colourless crystals (0.65g, 15.6%) mp. 98-100°C (acetone). Anal. Calcd. for $C_{26}H_{21}OPS$ (412.469): C, 75.70; H, 5.13; P, 7.51; S, 7.77. found: C, 75.07; H, 5.08; P, 7.37; S, 7.73. IR (KBr) cm^{-1}: 1529 (>C=O), 980 (P-C, phenyl). ^{1}H-NMR ($CDCl_3$) δ 5.35 (d, 1H, -CH, J_{HP} = 22.5 Hz) and 7.3 -8.04 ppm (m, 20H, Ar-H). MS: m/z = 413 (M^+ + 1, 8%).

Compound **8** and triphenylphosphine sulfide were also isolated and confirmed (mp, mixed mps, and comparative IR spectra).[26, 27]

Reduction of Thiaphosphirans 7a-d with Triphenylphosphine. General Procedure: Compound **7a** (0.36g, 0.001 mol) in acetonitrile (20 ml) was treated with a solution of triphenylphosphine (0.26g; 0.001 mol) in the same solvent (20 ml) and the mixture was refluxed for 8-12 h (TLC). The acetonitrile solution was concentrated under reduced pressure to half its original volume. The substance that deposited (0.27g, 80%) was filtered off, washed with petroleum ether (b.p., 40-60°C) and crystallized from benzene to give **2a** as colourless crystals mp 168°C.[30] Triphenylphosphine sulfide also, was isolated from the mother liquor and identified.[31]

Similarly, **2b-d** were isolated in 80-85% yield by the action of triphenylphosphine on the episulfide **7b-d**, respectively.

Reaction of Tetramethylthiourea (11) with Ylides 2c, d. A mixture of **11** (1.3g, 0.01 mol) and **2c** or **2d** (0.01 mol) in toluene (60 ml) was refluxed for 50 h. The reaction mixture was worked up as mentioned above whereby, **12** (11%, chloroform) and/or **14** (13%, chloroform) were obtained. However, **12** and **14** were identified by mp, mixed mps and comparative IR spectra. On the other hand, triphenylphosphine sulfide and other unidentified products were isolated from the filtrates.

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