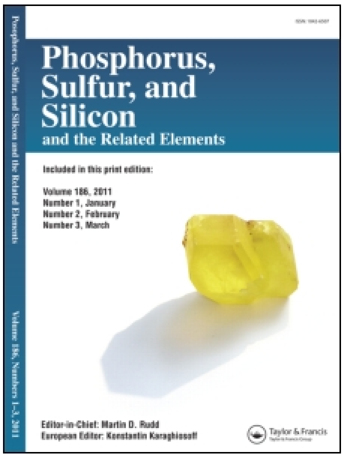

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Ylide Chemistry, Part II. Addition Reactions of Triphenyl-Phosphine(Carbonyl)Methylenes with 1,3-Dithia-2,4-Diphosphetane-2,4-Disulfides

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YLIDE CHEMISTRY, PART II.† ADDITION REACTIONS OF TRIPHENYLPHOSPHINE(CARBONYL)METHYLENES WITH 1,3-DITHIA-2,4-DIPHOSPHETANE-2,4-DISULFIDES

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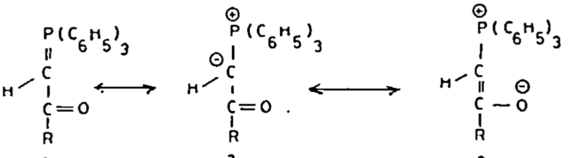
Triphenylphosphine(benzoyl)methylene **1a** reacts with 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide **7a** to give a mixture of 1,2,4-thiadiphosphetane derivative 10 and 1,3,2-oxathisphosphole derivative **11** or compound **12**, while compounds **7b–d** give only 1,2,4-thiadiphosphetane derivatives **15a–c**. Compounds **16a–d** are obtained from the reaction of compound **1b** with the corresponding **7a–d**. Mechanistic considerations on the formation of the products are discussed.

Key words: 1,3-Dithia-2,4-diphosphetanes, phosphine(carbonyl)methylenes, thiadiphosphetanes, oxathiaphosphole.

INTRODUCTION

The properties of the phosphine-methylenes[1] such as their stability, and their ability to react with aldehydes and ketones,[2] seem to be closely related to the distribution of the negative charge in the molecule of type (**1**↔**2**↔**3**).



1 2 3

a, R = C_6H_5
b, R = OC_2H_5

Phosphinemethylenes **4** react with carbon dioxide,[3] carbon disulfide,[4] and nitrile oxides[5,6] to give the products **5** and **6** respectively.

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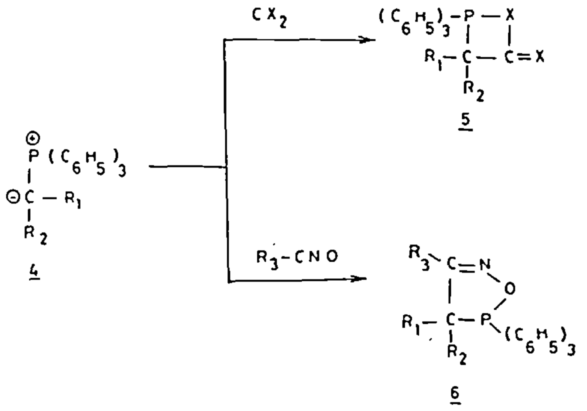
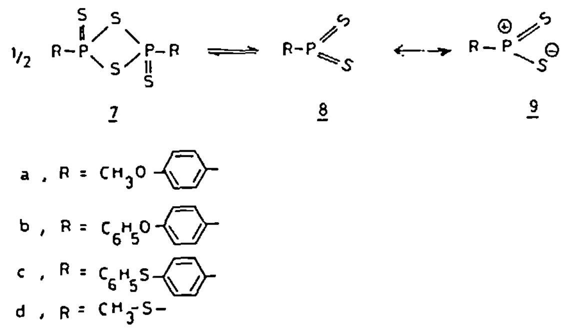
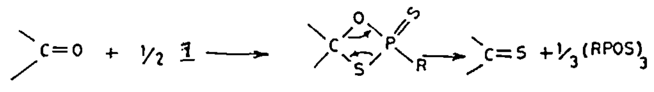
† Part I. See reference 13.
‡ This work is dedicated to the memory of the late Prof. Dr. S.-O. Lawesson.



1,3-Dithia-2,4-diphosphetane-2,4-disulfides **7a–c** exists in equilibrium with the monomeric species **8** or **9**.[7,8,9]



Carbonyl to thiocarbonyl transformations can easily and smoothly be performed by use of thionation reagents e.g. **7a–d**.[10,11,12] The mechanism is suggested to be a (2 + 2) cycloaddition as follows:-



The 4-membered intermediate has not been isolated, but due to the oxophilicity of phosphorane, ring opening occurs. Recently, we studied the reactions of pyridinium- and related *N*-ylides with compounds **7a–d** to give 1,4,2-thiazaphosphole derivatives.[13]

The present work reports on the addition reactions of triphenylphosphine-(carbonyl)methylenes with 1,3-dithia-2,4-diphosphetane-2,4-disulfides.

RESULTS AND DISCUSSION

Triphenylphosphine(benzoyl)methylene **1a** reacts with 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide **7a** in methylene chloride at 20°C to give a mixture of 2(4-methoxyphenyl)-3-benzoyl-4-triphenyl-3H-1,2,4-thiadiphosphetane-2-sulfide **10** and 2(4-methoxyphenyl)-4-triphenylphosphine-1,3,2-oxathiaphosphole-2-sulfide **11** or 2(4-methoxyphenyl)-4-phenyl-6-triphenyl-3,1,2,6-oxathiaphosphixine-2-sulfide **12**.

The structure of compound **10** is deduced from microanalysis, IR, ^{1}H NMR, MS, and ^{13}C NMR (Tables I–II).

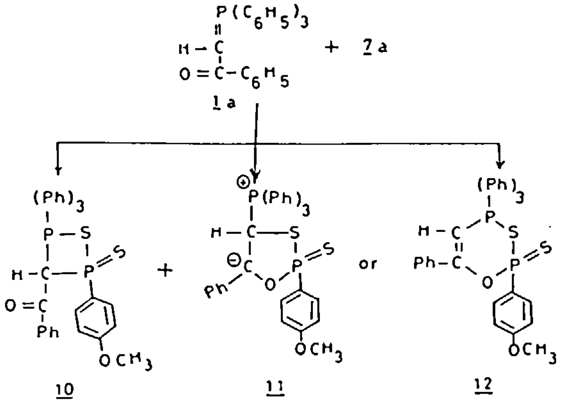


TABLE I

Experimental data and ^{1}H NMR spectra for the reaction of triphenylphosphine-(carbonyl)methylenes with **7a–d**

Product	M.p. °C	Yield %	^{1}H NMR[d,e] (ppm)
10[a,b]	69–70	30	3.7(3H, s, OCH_3), 4.9–5.2(1H, q, CH), 6.8–8.3(24H, br, aromatics).
11	191–192	65	—
15a[c]	99–100	80	4.9–5.1(1H, q, CH), 6.5–8.4(29H, br, aromatics).
b	90–91	77	4.8–5.1(1H, q, CH), 6.5–8.1(29H, br, aromatics).
c	83–84	55	2.5–2.7(3H, d), 4.9–5.1(1H, q, CH), 6.8–8.5(20H, br, aromatics).
16a	58–59	85	1.3(3H, t, CH_3), 3.85(3H, s, OCH_3), 4.2 (2H, q, OCH_2), 4.8(1H, q, CH), 6.9–8.5 (19H, br, aromatics).
b	59–60	79	1.2(3H, t, CH_3), 4.3(2H, q, OCH_2), 4.9–5.1 (1H, q, CH), 6.5–8.4(24H, br, aromatics).
c	60–61	70	1.2(3H, t, CH_3), 4.2(2H, q, OCH_2), 4.8–5.1(1H, q, CH), 6.4–8.4(24H, br, aromatics).
d	25–26	60	1.3(3H, t, CH_3), 2.4–2.5(3H, d, CH_3S), 4.2 (1H, q, OCH_2), 4.9–5.2(1H, q, CH), 6.5–8.3 (15H, br, aromatics).

[a] The reaction condition for the preparation of the products **10**, **11**, **15a–c** and **16a–d** is methylene chloride at 20°C for 5 hours.

[b] All products gave $M^{+\cdot}$ in MS.

[c] Compounds **15c** and **16d** 2.4–2.7(CH_3-S-P) $^3J_{PH} = 14$ Hz.

[d] In all the products 4.8–5.2(P—CH—P═S) $^1J_{PH} = 20$ Hz.

[e] The solvent used for ^{1}H NMR spectra is $CDCl_3$.

TABLE II

IR, ^{13}C NMR data; and elemental analysis for the products **10**, **11**, **15a–c**, and **16a–d**

Product	IR, cm^{-1}[a]	^{13}C C=O	^{13}C CH($J_{P\text{-}C}$) Hz	Formula mol. wt.	Analysis calc./found C	H	S
10	1690–1700	192.1	37.2 (54)	$C_{33}H_{28}O_2P_2S_2$ 582.6	68.02 68.0	4.84 5.0	11.01 11.0
11	—	—	—	$C_{33}H_{28}O_2P_2S_2$ 582.6	68.02 67.9	4.84 5.0	11.01 11.0
15a	1680–1700	192.3	37.3 (55)	$C_{32}H_{30}O_2P_2S_2$ 572.6	67.11 67.0	5.28 5.0	11.20 11.3
b	1690–1710	192.2	37.4 (56)	$C_{32}H_{30}OP_2S_3$ 588.7	65.28 65.0	5.14 4.9	16.34 16.0
c	1690–1710	192.2	37.5 (61)	$C_{27}H_{24}OP_2S_3$ 522.6	62.05 62.0	4.63 4.5	18.41 18.2
16a	1690–1700	164.4	32.3 (55)	$C_{29}H_{28}O_3P_2S_2$ 550.6	63.26 63.0	5.13 4.9	11.65 11.8
b	1680–1710	164.4	32.2 (56)	$C_{34}H_{30}O_3P_2S_2$ 612.7	66.65 66.9	4.94 5.0	10.47 11.0
c	1690–1710	164.3	32.5 (55)	$C_{34}H_{30}O_2P_2S_3$ 628.7	64.95 65.0	4.81 5.0	15.30 15.6
d[b]	1680–1700	164.1	32.7 (65)	$C_{23}H_{24}O_2P_2S_3$ 490.6	—	—	—

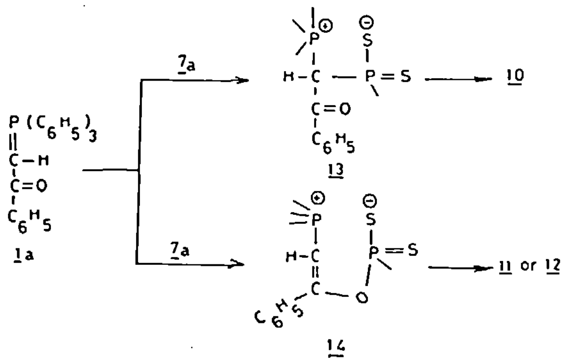
[a] The solvent used for IR was $CHCl_3$ for all products except for compound **11** (KBr).

[b] Compound **16d** is hygroscopic, so a satisfactory microanalysis could not be obtained.

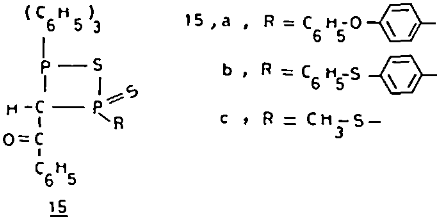
Compound **10** shows carbonyl absorption in the IR spectrum at 1700 cm^{-1} and in the ^{13}C spectrum at 192.1 ppm. The aliphatic carbon in ^{13}C (PCHP) is characterized by its large coupling to phosphorus of 54 Hz,[15] and in ^1H NMR spectrum for CHPS the coupling constant is 20 Hz.

In compound **11** the carbonyl absorption disappeared from the IR spectrum and it was not possible by chemical or spectroscopic means (difficult solubility) to ascertain if the structure is **11** or **12**.

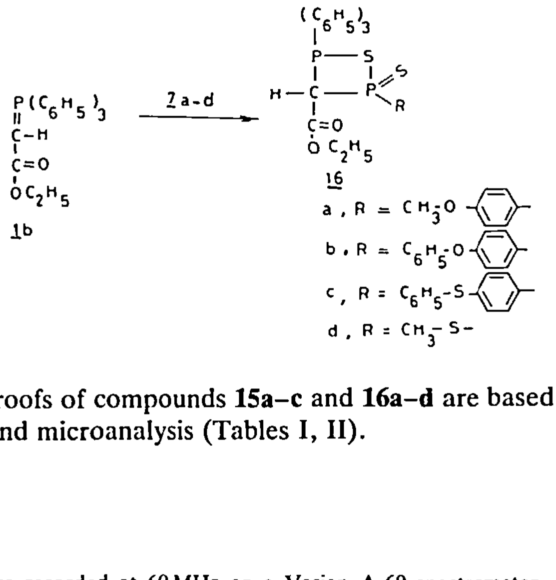
As to the formation of compounds **10** and **11** or **12**, it is suggested that either nucleophilic attack of the methine carbon of compounds **1a, b** occurs on the phosphorus of **7a** to give the intermediate 13, which collapses to give **10** (a 2 + 2 cycloaddition), occurs or that nucleophilic attack of the carbonyl oxygen of compound **1** occurs on the phosphorus of **7a** to give the intermediate 14, which gives the product **11** or **12** by 1,3 or 1,4 addition, respectively.



Triphenylphosphine(benzoyl)methylene **1a** reacts with other 1,3-dithia-2,4-diphosphetane-2,4-disulfides **7b–d** at 20°C to give only the corresponding 1,2,4-thiadiphosphetane derivatives **15a–c** via the intermediate 13.



Similarly, triphenylphosphine(ethoxycarbonyl)methylene **1b** reacts with 1,3-dithia-2,4-diphosphetane-2,4-disulfides **7a–d** to give the corresponding 1,2,4-thiadiphosphetane derivatives **16a–d**.



The structural proofs of compounds **15a–c** and **16a–d** are based on IR, ^1H NMR, MS, ^{13}C NMR and microanalysis (Tables I, II).

EXPERIMENTAL

^1H NMR spectra are recorded at 60 MHz on a Varian A-60 spectrometer. ^{13}C NMR spectra are recorded at 20 MHz on a Varian CFT-20 spectrometer. TMS is used as internal standered, and chemical shifts are expressed in δ values. IR spectra are recorded on a Beckman IR-18 spectrometer. MS spectra are recorded on a micromass 7070f spectrometer operating at 70 ev using direct inlet. Elementary analyses were carried out by NRC, Egypt. Melting points are not corrected.

Starting Materials. Triphenylphosphine derivatives **1a,b**[1,14] and 1,3-dithia-2,4-diphosphetane derivatives **7a–d**[16,17] were prepared as mentioned before.

Reaction of triphenylphosphine(benzoyl)methylene 1a with 7a. The starting triphenylphosphine(benzoyl)methylene (3.8 g, **1a**, 0.01 mol) and 2.02 g, (0.005 mol) of **7a** in 10 ml anhydrous methylene chloride at 20°C for 5 hours. The solid formed was removed by filtration, then crystallized from xylene to give compound **11** or **12**, and the filtrate was concentrated and the residue was crystallized from CH_2Cl_2-pet. ether to give compound 10.

General procedure for the preparation of compounds 15a–c. Compound **1a** (3.8 g, 0.0 mol) was added to 0.015 mole of compounds **7a–c** in 10 ml anhydrous methylene chloride at 20°C during 5 hours with stirring. The reaction mixture was concentrated and the residue was purified by crystallization from CH_2Cl_2-pet. ether to give the products **15a–c** (Tables I, II).

General procedure for the preparation of compounds ***16a–d.*** Compound **1b** (3.5 g, 0.01 mole) was added to 0.015 mole of compounds **7a–d** in 10 ml anhydrous methylene chloride at 20°C during 5 hours with stirring. The solvent was concentrated and the residue was purified by crystallization from CH_2Cl_2-pet. ether to give the products **16a–d**. (Tables I, II).

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