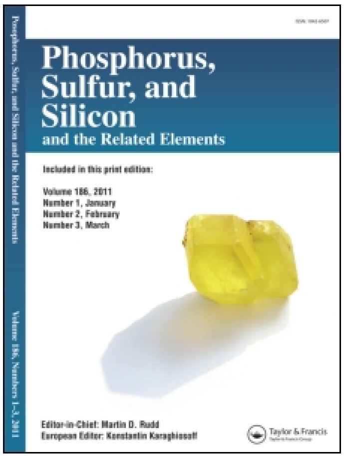


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE SYNTHESIS OF 2-ARYLIDENE OR 2-ALKYLIDENE-1,3-DITHIOLES BY USING BU$_3$P-CS$_2$ ADDUCT

Xiao-Dong Chen[a]; Yu-Xiu Liu[a]; Ru-Zhen Cao[a]; Mei Xue[a]; Lun-Zu Liu[a]
[a] National Key Laboratory of Elemento-Organic Chemistry, Institute of Elemento-Organic Chemistry, Nankai University, Tianjin, People's Republic of China

To cite this Article Chen, Xiao-Dong , Liu, Yu-Xiu , Cao, Ru-Zhen , Xue, Mei and Liu, Lun-Zu(1999) 'THE SYNTHESIS OF 2-ARYLIDENE OR 2-ALKYLIDENE-1,3-DITHIOLES BY USING BU$_3$P-CS$_2$ ADDUCT', Phosphorus, Sulfur, and Silicon and the Related Elements, 152: 1, 185 — 190

To link to this Article: DOI: 10.1080/10426509908031629

URL: http://dx.doi.org/10.1080/10426509908031629

Phosphorus, Sulfur and Silicon, 1999, Vol. 152, pp. 185-190
Reprints available directly from the publisher
Photocopying permitted by license only

THE SYNTHESIS OF 2-ARYLIDENE OR 2-ALKYLIDENE-1,3-DITHIOLES BY USING BU_3P-CS_2 ADDUCT

XIAO-DONG CHEN, YU-XIU LIU, RU-ZHEN CAO, MEI XUE and LUN-ZU LIU*

National Key Laboratory of Elemento-Organic Chemistry,
Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071,
People's Republic of China

(Received December 06, 1998; In final form February 21, 1999)

The cycloaddition of some alkynes with the tributylphosphine-carbondisulfide adduct provides the corresponding ylide, which in situ reacts with aldehydes by the Wittig reaction process to afford novel 2-arylidene or 2-alkylidene-1,3-dithioles in moderate yields.

Keywords: tributylphosphine-carbondisulfide adduct; cycloaddition; ylide; Wittig reaction; 1,3-dithioles

INTRODUCTION

Although an adduct formed between tributyl phosphine and carbon disulfide, in general, undergoes the cycloaddition reaction with electron deficient acetylenic compounds[1–6], its behavior toward that bearing either electron-releasing groups or heteroatom groups has not been reported.

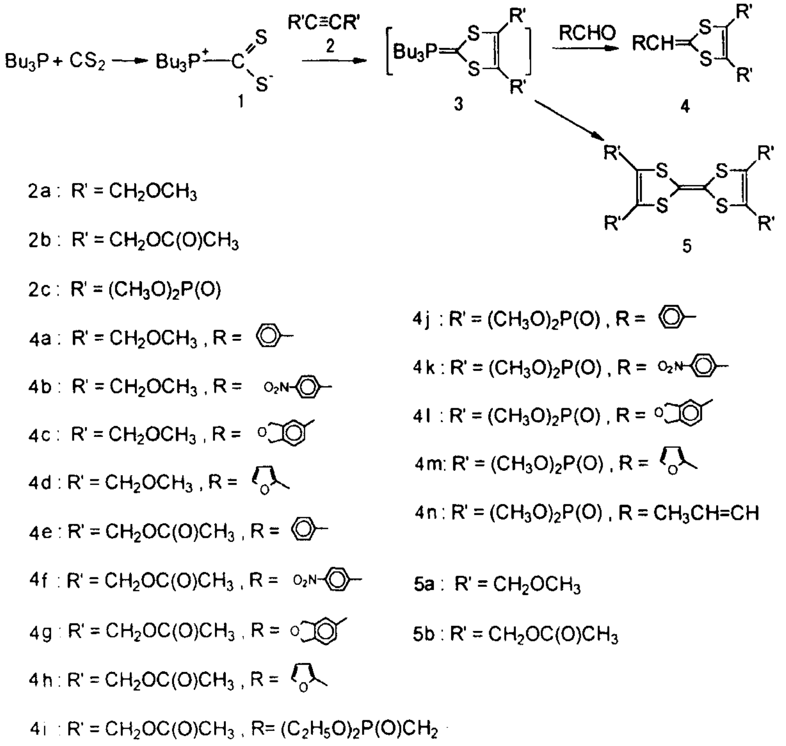
The present paper is concerned with the outstanding problems noted above. We are primarily interested in assessing the reactivity of the adduct with different acetylenic compounds. A secondary objective of this study is to extend the range of the adduct as a synthetic reagent in preparing dithioles.

---

* Correspondence Author.

RESULTS AND DISCUSSION

We selected 1,4-dimethoxy-2-butyne (**2a**), 1,4-diacetoxy-2-butyne (**2b**) and bis(dimethoxyphosphonyl)acetylene (**2c**) as dipolarophiles, and successfully performed a one pot reaction of the dipolarophiles with $Bu_3P\text{-}CS_2$ adduct and some aldehydes (Scheme 1).



SCHEME 1

Aldehyde and acetylene derivative are successively added to preformed $Bu_3P\text{-}CS_2$ solution. After several hours, compounds **4** are separated from the reaction mixture, and their structures are characterized by ^1H NMR and elemental analysis (Table I).

TABLE I ^{1}H NMR Spectral Data and Elemental Analysis of 2-Arylidene or 2-Alkylidene-1,3-Dithioles 4

No.	*sol.*[a]	*m.p (°C)*	*yield*[d] *(%)*	*^{1}H NMR*			*Elemental Analysis*[e]		
				R	*RC$\underline{H}$=C*	*R′*	*C*	*H*	*N*
4a	PE:EA 4:1[b]		25.6	7.32–7. 11 (m, 5H)	6.45 (s, 1H)	4.21 (s, 4H) 3.36 (s, 6H)	59.93 (60.00)	5.68 (5.71)	-
4b	PE:EA 6:1[c]	93-94	48.8	8.17 (d, 2H, m-C_6H_4) 7.30 (d, 2H, o-C_6H_4)	6.55 (s, 1H)	4.25 (s, 4H) 3.38 (s, 6H)	52.64 (51.69)	4.66 (4.62)	4.20 (4.31)
4c	PE:EA 4:1[b]		26.7	6.76 (m, 3H, C_6H_3) 5.93 (s, 2H, OCH_2O)	6.40 (s, 1H)	4.21 (s, 4H) 3.36 (s, 6H)	55.46 (55.56)	4.67 (4.94)	-
4d	PE:EA 4:1[b]		31.8	7.35 (s, 1H, 5-C_6H_3O) 6.5–6.3 (m, 2H, 3,4-C_4H_3O)	6.40 (s, 1H)	4.20 (s, 4H) 4.34 (s, 6H)	52.76 (53.33)	4.90 (5.19)	-
4e	PE:EA 4:1[b]		30.8	7.33–7.22 (m, 5H)	6.45 (s, 1H)	4.87 (s, 4H) 2.07 (s, 6H)	56.87 (57.14)	5.08 (4.71)	-
4f	PE:EA 2:1[c]	127-128	68.0	8.16 (d, 2H, m-C_6H_4) 7.28 (d, 2H, o-C_6H_4)	6.53 (s, 1H)	4.94 (s, 4H) 2.10 (s, 6H)	50.10 (50.39)	4.08 (3.94)	3.75 (3.67)
4g	PE:EA 4:1[b]		26.2	6.76–6.70 (m, 3H, C_6H_3) 5.93 (s, 2H, OCH_2O)	6.35 (s, 1H)	4.86 (s, 4H) 2.07 (s, 6H)	53.45 (53.68)	4.43 (4.21)	-
4h	PE:EA 4:1[b]		34.5	7.35 (s, 1H, 5-C_4H_3O) 6.39–6.07 (m, 2H, 3,4-C_4H_3O)	6.31 (s, 1H)	4.85 (s, 4H) 2.05 (s, 6H)	51.81 (51.53)	4.61 (4.29)	-
4i	PE:EA 4:1[b]		43.1	4.08 (m, 4H, CH_3CH_2O-) 1.29 (m, 6H, CH_3CH_2O-) 2.53 (dd, 2H)	5.2 (m, 1H)	4.80 (s, 4H) 2.05 (s, 6H)	43.43 (43.90)	5.72 (5.61)	-
4j	acetone[b]		42.8	7.33–7.16 (m, 5H)	6.40 (s, 1H)	3.86 (d, 6H $^3J_{HP}$=10.8Hz)	40.92 (41.18)	4.36 (4.41)	-

No.	*sol.*[a]	*m.p (°C)*	*yield*[d] *(%)*	^1H *NMR*			*Elemental Analysis*[e]		
				R	*RC$\underline{H}$=C*	*R′*	*C*	*H*	*N*
4k	acetone: PE 2:1[c]	140-141	69.0	8.18 (d, 2H, m-C_6H_4) 7.28 (d, 2H, o-C_6H_4)	6.45 (s, 1H)	3.87 (d, 6H $^3J_{HP}$=11.2Hz)	37.10 (37.09)	3.78 (3.75)	3.21 (3.09)
4l	acetone[b]		27.9	6.80–6.65 (m, 3H, C_6H_3) 5.94 (s, 2H, OCH_2O)	6.31 (s, 1H)	3.84 (d, 6H $^3J_{HP}$= 11.0Hz)	40.15 (39.82)	4.00 (3.98)	-
4m	acetone[b]		33.4	7.37 (s, 1H, 5-C_4H_3O) 6.36–6.08 (m, 2H, 3,4-C_4H_3O)	6.25 (s, 1H)	3.83 (d, 6H $^3J_{HP}$=10.8Hz)	35.92 (36.18)	4.06 (4.02)	-
4n	acetone[b]		31.1	5.90–5.50 (m, 2H, CH=CH 1.72 (d, 3H, CH_2)	5.60 (s, 1H)	3.80 (d, 6H $^3J_{HP}$=11.4Hz)	35.40 (35.48)	5.08 (4.84)	

a PE is petroleum ether. EA is ethyl acetate. b Column chromatography eluent. c Recrystallization solvent. d Calcd on Bu_3P weight. e Calcd in parentheses.

The formation of **4** might occur via the ylide **3**, which then reacts further with aldehyde in the manner expected in the Wittig reaction. It was found that the reaction (Scheme I) would go to completion until red color of the Bu_3P-CS_2 adduct disappeared. It showed that the rate-determining reaction was a nucleophilic attack of **1** on **2** to give the ylide **3**. Although the reaction could apply to various acetylenes, requisite reaction conditions and reaction rate vary with acetylenes. On the basis of disappearance of the red colored Bu_3P-CS_2 adduct as evidence of reaction completion, the reaction of **1** with electronegatively substituted acetylene **2c** has rapidly completed at –5°C within 3 hours. However, electropositively substituted acetylene **2a** reacted slowly at 35°C within 24 hours. Since **2b** is equal order of magnitude with **2a** in electronegativity, **2b** reacted at room temperature within 24 hours. The differences demonstrate that the nature of R′ in **2** played an important role in assessing the reaction rate. Moreover we also found that the ylide formed from adduct **1** and **2a**, **2b** reacted with aldehydes to give **5a**, **5b** respectively via selfcondensation in addition to the products **4**. The ylide formed from adduct **1** and **2c** reacted with aldehydes to give corresponding **4** without corresponding **5** being isolated. It appears that the stable ylide **3**, that is R′ being an electron withdrawing group, hardly undergoes selfcondensation. By comparison, the unstable ylide **3**, that is R′ being an electron-releasing group, readily undergoes self-condensation to give **5**. These interesting observations deserve further scrutiny.

The ease of reaction of ylide **3** with aldehydes mainly depended on reactivity of aldehyde. Aryl aldehyde is more reactive than aliphatic aldehyde The reaction of ylide **3** with aliphatic aldehyde was attempted. With the exception of that bearing electron withdrawing group, such as phosphonyl ethyl aldehyde and croton aldehyde, aliphatic aldehydes do not react with ylide **3**. In the case of aryl aldehyde electronegatively substituted benzaldehydes are more reactive than unsubstituted.

A related study of the reactivity of Bu_3P-CS_2 adduct will be the subject of a separate publication.

EXPERIMENTAL SECTION

Proton NMR spectra were recorded on a BRUKER AC-P200 spectrometer. Elemental analyses were run on a Yana MT-3 instrument. All reactions were carried out under an atmosphere of dry nitrogen. 1,4-dimethoxy-2-butyne[7], 1,4-diacetoxy-2-butyne[8] and bis(dimethoxyphosphonyl)acetylene[9] were prepared according to published procedures.

General Procedure for the synthesis of compounds 4

To a solution of Bu_3P (95%, 1.06g, 5mmol), anhydrous THF(2ml) and anhydrous ether (10ml) was added carbon disulfide (0.76g, 10mmol) at 0°C for 10 min.. Immediately the solution was cooled to −15°C, aldehyde (5mmol) and acetylene derivative (5mmol) were successively added. The reaction mixture was stirred at -15°C for 1 hr, then slowly warmed to room temperature and stirred for several hours. When the red color of the $Bu_3P\text{-}CS_2$ adduct disappears, the reaction has completed. If product **4** is solid, it can be precipitated from the reaction mixture then filtered and purified by recrystallization. If the product **4** is liquid, it can be separated by column chromatography.

By the same procedure as described above, the ylide formed from adduct **1** and **2a** reacted with propyl aledhyde to be separated poor yields of bidithiole **5a**. Similarly, **5b** was separated. ^{1}H NMR 5a: 3.33(CH_3, s, 12H), 4.09(CH_2, s, 8H) 5b: 2.06(CH_3, s, 12H), 4.67(CH_2, s, 8H).

Acknowledgements
This research has been supported by National Natural Science Foundation of China(29672019)

References

[1] H.D. Hartzler, *J. Am. Chem. Soc*, **93**, 4961–4962 (1971).
[2] C.U. Pittman, Jr. and M. Narita, *J. Chem. Soc. Chem. Commun*, 960 (1975).
[3] M. Sato, N.C. Gonnella, and M.P. Cava, *J. Org. Chem.*, **44(6)**, 930–934 (1979).
[4] R.A. Aitken, G. Ferguson and S.V. Raut, *J. Chem. Soc. Chem. Commun*, 812–814 (1991).
[5] E.C. Taylor and R. Dotzer, *J. Org. Chem.*, **56**, 1816–1822 (1991).
[6] R.A. Aitken and S.V. Raut, *Tetrahedron*, **48**, 8023–8029 (1992).
[7] L. Berandsma, *Preparative Acetylenic Chemistry*, (Elsevier, Ansterdam, 1971). pp.173, 144.
[8] A.W. Johnson, *J. Chem. Soc.*, **149**, 1009–1014 (1946).
[9] D. Seyferth and J.D.H. Paetsch, *J. Org. Chem.*, **34**, 1483 (1969).