

Synthesis of α -Phenylthioacrylmethylene Triphenylarsoranes and their Wittig-type Reactions†

Gui-Sheng Deng, Zhi-Zhen Huang, Xiao-Chun Yu and Xian Huang*

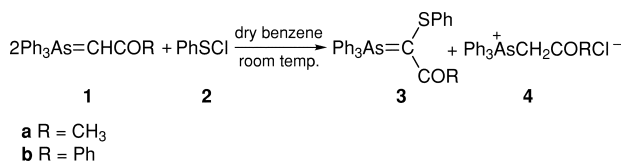
Department of Chemistry, Zhejiang University Xixi Campus, Hangzhou, 310028, P.R. China

J. Chem. Research (S),
1999, 144–145†

α -Phenylthio acrylmethylene triphenylarsoranes, the first stable α -thiyl arsonium ylides, are prepared by phenylsulfenylation–transylidation reaction of the corresponding acrylmethylene triphenylarsoranes with phenylsulfenyl chloride; Wittig reactions are carried out under mild reaction conditions on the arsonium ylides to provide α -phenylthio- α,β -unsaturated ketones.

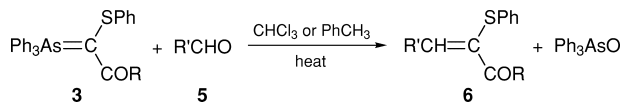
Wittig reagents with a heteroatom such as aryl or alkylthio on the α -position can play a special role in synthesis. These Wittig reagents behave as an equivalent of the acyl anion, and are very useful intermediates in organic synthesis. Thus, it is of interest to introduce a thiyl group into ylides. Although α -arylthio acrylmethylene phosphonium ylides have been synthesized by Saikachi and Nakamura,¹ they were rather unreactive and only reacted with very reactive aromatic aldehydes.² We synthesized the phosphonium ylides according to ref. 1 and found they reacted with difficulty with aromatic aldehydes, *e.g.* benzaldehyde. Therefore, their application in the synthesis of α -arylthio- α,β -unsaturated ketones is limited. Considering that arsonium ylides are relatively easy to prepare, and it being of particular interest that they are more reactive than analogous phosphonium or sulfonium ylides in Wittig reactions, we therefore synthesized α -phenylthioacrylmethylene triphenylarsoranes and studied their Wittig-type reactions. α -Phenylthio- α,β -unsaturated ketones are, as expected, produced upon Wittig reaction.

α -Phenylthioacrylmethylene triphenylarsoranes **3** were formed from acrylmethylene triphenylarsoranes **1** and benzenesulfonyl chloride **2** by a phenylsulfenylation–transylidation reaction. Two equivalents of acrylmethylene triphenylarsorane **1** were treated with 1 equivalent of benzenesulfonyl chloride **2** in dry benzene at room temperature to produce white crystalline α -phenylthio acrylmethylene triphenylarsoranes **3a** and **3b** (Scheme 1) in near quantitative yield and the arsonium salts **4a** and **4b** were recycled in 90 and 93% yields respectively. Compounds **3**, to our knowledge, represent the first stable α -thio arsonium ylides, showing moderate stability to heat, light and moisture. They can be stored for more than six months in a drying apparatus at room temperature. However, they turn yellow when heated up to their melting points.



Scheme 1

As expected, the reaction of compounds **3** with aromatic aldehydes **5** proceeded under mild conditions much more easily than for the corresponding phosphonium ylides to give the expected α -phenylthio- α,β -unsaturated ketones **6** in good yields (Scheme 2). However, arsonium ylides **3** do not react with aliphatic aldehydes; results are shown in Table 1.



Scheme 2

Chloroform was found to be superior to toluene as reaction solvent. The ratio of *Z* to *E* isomers was easily estimated by ¹H NMR spectroscopy, as the β -vinyl proton occurs at much lower field in the *Z*-isomer than in the *E*-isomer. ¹H NMR data of **6a**, **6b**, **6c** and **6f** were in agreement with those of refs. 3, 4, 5 and 6, respectively. The stereochemistry of this reaction and the location of the β -vinyl proton of the product are analogous to those observed in the Wittig-type reaction of α -selenoarsonium ylides.⁷ The results show that *Z*-isomers are the dominant products.

Experimental

Proton nuclear magnetic resonance (¹H NMR) spectra were determined using a Varian PMX60SI (60 MHz) or a AZ-300 MHz spectrometer using tetramethylsilane (TMS) or hexamethyldisilane (HMDS) as the internal standard. Infrared (IR) spectra were obtained as neat capillary cells (liquid products) or KBr disks (solid products) on a PE 683 instrument. Mass spectra data were obtained by electron ionization (EI) on a HP5989A mass spectrometer.

All reactions were carried out under nitrogen. All solvents were dried and redistilled before use. Melting points were uncorrected. Acrylmethylene triphenylarsorane, benzoylmethylene triphenylarsorane, and phenylsulfenyl chloride were prepared according to refs. 8, 9 and 10, respectively.

Typical Procedure. Synthesis of α -Phenylthio Acrylmethylene Triphenylarsine **3a.**—A solution of phenylsulfenyl chloride **2** (5.65 mmol) in 8 cm³ dry benzene was added dropwise to a stirred solution of acrylmethylene triphenylarsorane **1a** (11.3 mmol) in 80 cm³ dry benzene at room temperature during 40 min. The reaction mixture was then stirred for two hours. After the suspension was filtered off, the residue was recycled to obtain 1.85 g arsonium salt **4a** in 90% yield. The filtrate was evaporated under reduced pressure to obtain 2.61 g α -phenylthio acrylmethylene triphenylarsorane **3a** in 98% yield as white crystals, which were recrystallized from EtOH, mp 184–185 °C, δ_{H} (60 MHz, CDCl₃, TMS), 7.43–7.11 (m, 20 H) and 2.28 (s, 3 H); *m/z* 470 (M, 4.98%), M + 1, M + 2, 320, 306, 227, 152 (100), 121, 105, 77, 51, 43. IR $\nu_{\text{max}}/\text{cm}^{-1}$, 1590 s, 1520 vs, 1480 s, 735 vs, 685 vs (Found: C, 68.96; H, 5.03. Calc. for C₂₇H₂₃AsOS: C, 68.93; H, 4.93%).

The arsonium salt **4b** was recycled in 93% yield, and compound **3b** was obtained as white crystals in 91% yield using the above procedure, mp 176–177 °C, ¹H NMR (60 MHz, CDCl₃, TMS), δ_{H} 7.90–7.74 (m, 2 H), 7.60–6.98 (m, 23 H); *m/z* 532 (M, 4.5%), 305, 227, 152 (100), 105, 77, 51. IR $\nu_{\text{max}}/\text{cm}^{-1}$ 1590 s, 1440 s, 750 s, 680 s (Found: C, 72.44; H, 4.74. Calc. for C₃₂H₂₅AsOS: C, 72.17; H, 4.73%).

Typical Procedure. Synthesis of 4-Phenyl-3-phenylthiobut-3-en-2-one (6b**).**—A mixture of α -phenylthio acrylmethylene triphenylarsorane **3a** (0.38 g, 0.8 mmol) and benzaldehyde **5b** (0.06 g, 0.7 mmol) in 5 cm³ toluene was stirred at 90 °C in an oil-bath for 6 days under nitrogen atmosphere. After completion of the reaction, the mixture was concentrated, and the product separated by flash chromatography on a preparative TLC (light petroleum–diethyl ether, 10:1) to afford **6b** in 75% yield. Oil. δ_{H} (60 MHz, CCl₄, HMDS) 7.18–6.91 (m, 10 H), 7.64 (s, *Z*-C=CH); 6.76 (s, *E*-C=CH)

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Wittig-type reaction of α -phenylthioacylmethylene triphenylarsoranes

Product	R	R'	Solvent	T/°C	Reaction time	Isolated yield (%)	Ratio (Z/E)
6a	Me	<i>p</i> -O ₂ NC ₆ H ₄	C ₆ H ₅ Me	90	15 h	85	2.5:1
6b	Me	Ph	C ₆ H ₅ Me	90	6 d	75	6:1
6c	Me	<i>p</i> -BrC ₆ H ₄	CHCl ₃	50	6 d	80	4:1
6d	Me	<i>p</i> -MeC ₆ H ₄	CHCl ₃	50	6 d	71	8:1
6e	Ph	<i>p</i> -O ₂ NC ₆ H ₄	C ₆ H ₅ Me	90	35 h	68	2.5:1
6f	Ph	<i>p</i> -MeOC ₆ H ₄	CHCl ₃	50	8 d	55	2.5:1

(Z + E = 1 H); 2.12 (s, Z-CH₃), 1.98 (s, E-CH₃) (Z + E = 3 H). IR $\nu_{\max}/\text{cm}^{-1}$ 1700 vs, 1590 s, 1225 m, 1180 s, 735 s, 685 s.

4-(4-Nitrophenyl)-3-phenylthiobut-3-en-2-one (**6a**).—Mp 56–60 °C (diethyl ether) δ_{H} (60 MHz, CCl₄, HMDS) 8.13–7.98 (d, *J* = 9 Hz, 2 H), 7.78–7.63 (d, *J* = 9 Hz, 2 H), 7.29–7.16 (m, 5 H), 7.56 (s, Z-C=CH), 6.65 (s, E-C=CH) (*E* + *Z* = 1 H), 2.11 (Z-CH₃, s), 2.04 (E-CH₃, s) (*E* + *Z* = 3 H). IR $\nu_{\max}/\text{cm}^{-1}$ 1700 s, 1590 w, 1520 vs, 1345 vs, 740 s, 680 w.

4-(4-Bromophenyl)-3-phenylthio-3-buten-2-one (**6c**).—Oil. δ_{H} (60 MHz, CCl₄, HMDS) 7.57–7.11 (m, 9 H), 7.65 (s, Z-C=CH), 6.73 (s, E-C=CH) (*Z* + *E* = 1 H), 2.15 (Z-CH₃, s), 2.02 (E-CH₃, s) (*Z* + *E* = 3 H). *m/z* 333 (M, 7.16%), *M* + 2, 218, 210, 185, 154, 109 (100), 77, 69, 65, 51, 43. IR $\nu_{\max}/\text{cm}^{-1}$ 1700 vs, 1590 s, 1390 s, 740 vs, 690 s, 570 w (Found: C, 57.91; H, 4.19; Br, 23.98. Calc. for C₁₆H₁₃BrOS: C, 57.69; H, 3.93; Br, 24.15%).

4-(4-Methylphenyl)-3-phenylthiobut-3-en-2-one (**6d**).—Oil. δ_{H} (60 MHz, CCl₄, HMDS) 7.59–6.97 (m, aromatic H and *E*-olefinic H, 9.11 H), 7.75 (s, Z-C=CH, 0.89 H), 2.27 (s, 2.67 H); 2.15–2.12 (d, 3.33 H). *m/z* 268 (M, 100%), *M* + 1, *M* + 2, *M* + 3, *M* + 4, 253, 225, 218, 210, 178, 159, 147, 109, 91, 77, 69, 65, 51, 43. IR $\nu_{\max}/\text{cm}^{-1}$ 1685 vs, 1590 s, 740 s, 690 m (Found: C, 75.85; H, 6.18. Calc. for C₁₇H₁₆OS: C, 76.08; H, 6.01%).

1-Phenyl-3-(4-nitrophenyl)-2-phenylthioprop-2-en-1-one (**6e**).⁵—Mp 118–122 °C (diethyl ether) [lit.⁶ 123–124 °C (1,4-dioxane–ethanol)]. δ_{H} (300 MHz, CDCl₃, TMS), 8.06 (d, *J* = 9 Hz, 2 H), 7.66 (d, *J* = 9 Hz, 2 H), 7.93–7.15 (m, 10 H), 8.02 (s, Z-C=CH), 6.85 (s, E-C=CH) (*E* + *Z* = 1 H). IR $\nu_{\max}/\text{cm}^{-1}$ 1670 s, 1600 m, 1525 s, 1350 vs, 745 m, 685 s.

1-Phenyl-3-(4-methoxyphenyl)-2-phenylthioprop-2-en-1-one (**6f**).⁶—Mp 93–96 °C (diethyl ether) [lit.⁶ 97–98 °C (methanol)]. δ_{H} (300 MHz, CDCl₃, TMS), 8.01 (d, 2 H, *J* = 8.5 Hz), 6.93 (d, 2 H, *J* = 8.5 Hz), 7.81–7.22 (m, 10 H), 7.99 (s, Z-C=CH), 6.79 (s,

E-C=CH) (*Z* + *E* = 1 H), 3.85 (s, Z-CH₃), 3.77 (s, E-CH₃) (*E* + *Z* = 3 H). IR $\nu_{\max}/\text{cm}^{-1}$ 1670 s, 1610 vs, 1520 s, 1260 s, 1220 s, 725 w, 690 w.

Project 29502006 was supported by the National Nature Science Foundation of China.

Received, 6th October 1998; Accepted, 18th November 1998
Paper E/8/07764I

References

- 1 H. Saikachi and S. Nakamura, *Yakugaku Zasshi*, 1968, **88**, 715.
- 2 H. Saikachi and S. Nakamura, *Yakugaku Zasshi*, 1969, **89**, 1446.
- 3 *Chem. Abstr.* 66: P115462 g; A. A. Schleppnik, *US Pat.*, 3, 305, 588 (Cl. 260-590), Feb. 21, 1967.
- 4 V. Rosnati and A. Saba, *Gazz. Chim. Ital.*, 1981, **111**, 249.
- 5 D. Dimon, O. Lafont, C. Combet Farxoux, M. Miocque, C. Delabos, J. Garnerl and P. Gayral, *Ann. Pharm. Fr.*, 1984, **43**, 271.
- 6 V. Baliah and C. Natarajan, *Indian J. Chem.*, 1970, **8**, 694.
- 7 Z.-Z. Huang, X. Huang and Y.-Z. Huang, *J. Chem. Soc., Perkin Trans. 1*, 1995, 95.
- 8 P. S. Kendurkar and R. S. Tewari, *J. Organomet. Chem.*, 1975, **102**, 141.
- 9 D. Wei-Yu *et al.*, *Chem. J. Chin. Univ.*, 1965, 540.
- 10 (a) W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, 1968, **90**, 2075; (b) M. Fieser and L. F. Fieser, *Reagents for Organic Synthesis*, John and Son Inc., 1975, vol. 5, 523.