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

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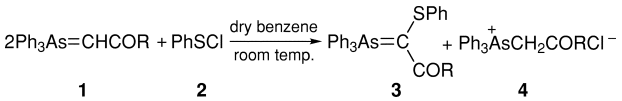
α-Phenylthio acylmethylene triphenylarsoranes, the first stable α-thiyl arsonium ylides, are prepared by phenylsulfenylation–transylidation reaction of the corresponding acylmethylene triphenylarsoranes with phenylsulfenyl chloride; Wittig reactions are carried out under mild reaction conditions on the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

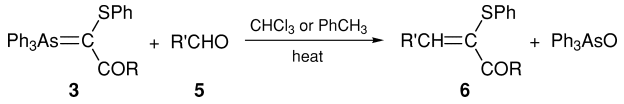
Wittig reagents with a heteroatom such as aryl or alkylthio on the α-position can play a special role in synthesis. These Wittig reagents behave as an equivalent of the acyl anion, and are very useful intermediates in organic synthesis. Thus, it is of interest to introduce a thiyl group into ylides. Although α-arylthio acylmethylene 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-phenylthioacylmethylene triphenylarsoranes and studied their Wittig-type reactions. α-Phenylthio-α,β-unsaturated ketones are, as expected, produced upon Wittig reaction.

α-Phenylthioacylmethylene triphenylarsoranes **3** were formed from acylmethylene triphenylarsoranes **1** and benzenesulfenyl chloride **2** by a phenylsulfenylation–transylidation reaction. Two equivalents of acylmethylene triphenylarsorane **1** were treated with 1 equivalent of benzenesulfenyl chloride **2** in dry benzene at room temperature to produce white crystalline α-phenylthio acylmethylene 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 ^{1}H NMR spectroscopy, as the β-vinyl proton occurs at much lower field in the *Z*-isomer than in the *E*-isomer. ^{1}H NMR data of **6a**, **6b**, **6e** 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 (^{1}H 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. Acetylmethylene triphenylarsorane, benzoylmethylene triphenylarsorane, and phenylsulfenyl chloride were prepared according to refs. 8, 9 and 10, respectively.

Typical Procedure. Synthesis of α-Phenylthio Acetylmethylene Triphenylarsine **3a**.—A solution of phenylsulfenyl chloride **2** (5.65 mmol) in 8 cm^3 dry benzene was added dropwise to a stirred solution of acetylmethylene triphenylarsorane **1a** (11.3 mmol) in 80 cm^3 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 acetylmethylene triphenylarsorane **3a** in 98% yield as white crystals, which were recrystallized from EtOH, mp 184–185 °C, δ_H (60 MHz, $CDCl_3$, 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 ν_{max}/cm^{-1}, 1590 s, 1520 vs, 1480 s, 735 vs, 685 vs (Found: C, 68.96; H, 5.03. Calc. for $C_{27}H_{23}AsOS$: 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, ^{1}H NMR (60 MHz, $CDCl_3$, 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 ν_{max}/cm^{-1} 1590 s, 1480 vs, 1440 s, 750 s, 680 s (Found: C, 72.44; H, 4.74. Calc. for $C_{32}H_{25}AsOS$: C, 72.17; H, 4.73%).

Typical Procedure. Synthesis of 4-*Phenyl*-3-*phenylthiobut*-3-*en*-2-*one* (**6b**)[4].—A mixture of α-phenylthio acetylmethylene triphenylarsorane **3a** (0.38 g, 0.8 mmol) and benzaldehyde **5b** (0.06 g, 0.7 mmol) in 5 cm^3 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, CCl_4, HMDS) 7.18–6.91 (m, 10 H), 7.64 (s, *Z*-C=CH); 6.76 (s, *E*-C=CH)

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Table 1 Wittig-type reaction of α-phenylthioacylmethylene triphenylarsoranes

Product	R	R′	Solvent	*T*/°C	Reaction time	Isolated yield (%)	Ratio (*Z*/*E*)
6a	Me	*p*-$O_2NC_6H_4$	C_6H_5Me	90	15 h	85	2.5:1
6b	Me	Ph	C_6H_5Me	90	6 d	75	6:1
6c	Me	*p*-BrC_6H_4	$CHCl_3$	50	6 d	80	4:1
6d	Me	*p*-MeC_6H_4	$CHCl_3$	50	6 d	71	8:1
6e	Ph	*p*-$O_2NC_6H_4$	C_6H_5Me	90	35 h	68	2.5:1
6f	Ph	*p*-$MeOC_6H_4$	$CHCl_3$	50	8 d	55	2.5:1

($Z + E = 1$ H); 2.12 (s, *Z*-CH_3), 1.98 (s, *E*-CH_3) ($Z + E = 3$ H). IR ν_{max}/cm^{-1} 1700 vs, 1590 s, 1225 m, 1180 s, 735 s, 685 s.

4-(4-*Nitrophenyl*)-3-*phenylthiobut*-3-*en*-2-*one* (**6a**)[3].—Mp 56–60 °C (diethyl ether) δ_H (60 MHz, CCl_4, 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*-CH_3, s), 2.04 (*E*-CH_3, s) ($E + Z = 3$ H). IR ν_{max}/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 HMz, CCl_4, 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*-CH_3, s), 2.02 (*E*-CH_3, 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 ν_{max}/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 $C_{16}H_{13}BrOS$: C, 57.69; H, 3.93; Br, 24.15%).

4-(4-*Methylphenyl*)-3-*phenylthiobut*-3-*en*-2-*one* (**6d**).—Oil. δ_H (60 MHz, CCl_4, 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 ν_{max}/cm^{-1} 1685 vs, 1590 s, 740 s, 690 m (Found: C, 75.85; H, 6.18. Calc. for $C_{17}H_{16}OS$: 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, $CDCl_3$, 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 ν_{max}/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, $CDCl_3$, 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*-CH_3), 3.77 (s, *E*-CH_3) ($E + Z = 3$ H). IR ν_{max}/cm^{-1} 1670 s, 1610 vs, 1520 s, 1260 s, 1220 s, 725 w, 690 w.

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