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DIRECT SYNTHESIS OF α-ACYL METHYLENETRIPHENYLARSORANES FROM READILY AVAILABLE ARSONIUM SALTS

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Abstract: α-Acyl arsoranes can be synthesized by the acylation of readily available salts in the presence of triethylamine in moderate to good yields.

α-Acyl arsoranes have intensively been applied in the synthesis of unsaturated ketones.[1] Decomposition of α-acyl arsorane **3** under mild conditions provides a synthetic method for β-ketoester and β-diketones, especially for fluorinated β-ketonesters and β-diketones.[2] Difference from the conversion of α-acyl phosphoranes into allenes, [3] the reaction of α-acyl arsoranes **3** with $PCl_5/POCl_3$ followed by treatment with alkali can generate disubstituted acetylenes in good yields.[4] The resultant acetylenes are valuable synthetic intermediates and can be employed in a variety of reactions such as Michael reaction, [5] cycloaddition,[6] etc.

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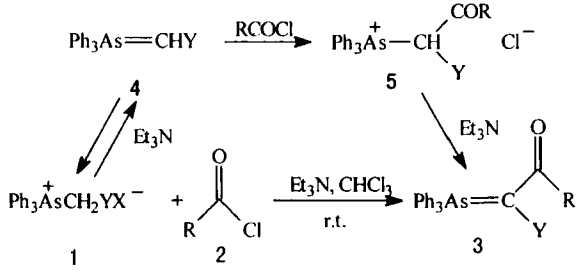
There are several reported methods for the synthesis of α-acyl arsoranes **3**. They can be synthesized by the condensation reaction of reactive methylene compounds with triphenylarsine oxide in the presence of Ac_2O or P_2O_5/Et_3N usually in low yields.[1d] Typically, α-acyl arsoranes **3** are prepared by a transylidation reaction.[7,1a] However, the transylidation reaction takes play to affords an equimolar mixture of the desired arsorane **3** and arsonium salt when treating the starting arsoranes **4** with acid chlorides or anhydrides, and are rather cumbersome, requiring two steps from the readily available arsonium salts **1**.

Considering that α-hydrogen of the arsonium salts **1** with an electron-withdrawing substituent group has some acidity, the presence of a suitable base in the reaction mixture can directly convert arsonium salts to arsorane **3,** and thus avoid transylidation. However, to our knowledge, no reports have appeared describing the direct conversion of arsonium salts **1** to arsoranes **3** in the presence of a base such as triethylamine.



Scheme 1

Our experimental results show that 1 equiv. arsonium salts **1** can be directly converted into α-acyl arsoranes **3** by the treatment with acid chlorides **2** in the presence of 2 equiv. triethylamine (**Scheme 1**). The arsoranes **3** are formed in

moderate to good yields when Y is an electron-withdrawing group such as alkoxyacyl, cyano or acyl; or in low yields when Y is phenylthio or phenylseleno. The results are compiled in **Table 1**. We believe that the equilibrium between arsonium salt **1** and arsorane **4**, which is established in the presence of triethylamine, favours arsorane **4** when Y is an electron-withdrawing group, or arsonium salt **1** when Y is phenylthio or phenylseleno. The reaction does not take place when Y is hydrogen. The acylation of arsorane **4** affords arsonium salt **5**, followed by the elimination of hydrogen chloride with another molecule of triethylamine to produce arsorane **3** (**Scheme 1**).

Compared to the synthesis of α-acyl arsoranes **3** by the transylidation reaction, this method has the advantage of starting from arsonium salts **1** rather than the stabilized arsoranes **4**, and so avoids the preparation of arsoranes **4**, which are usually not commercially available.

Experimental

Proton nuclear magnetic resonance (^{1}H NMR) spectra were determined in $CDCl_3$ with a JEOL PMX60SI (60MHz) using tetramethylsilane (TMS) as the internal standard. Infrared (IR) spectra were obtained as KBr disks on a PE 683 instrument. Mass spectra data were obtained with electron ionization (EI) on a HP5989A mass spectrometer.

Trichloromethane was dried with P_2O_5 and redistilled before use. Melting points were uncorrected. Carbonylmethoxymethyltriphenylarsine bromide, carbonyl- ethoxymethyltriphenylarsine bromide, benzoylmethyltriphenylasine

Table 1. Synthesis of α-acyl arsoranes **3**

Entry[a]	Y	X	R	mp (°C)[b]	Isolated yield (%)
3a	CO_2CH_3	Br	CH_3	135-136	66
3b	$CO_2C_2H_5$	Br	CH_3	173-175[c]	65
3c	CO_2CH_3	Br	Ph	155-158[d]	68
3d	$CO_2C_2H_5$	Br	Ph	119-121[e]	70
3e	CO_2CH_3	Br	$CH_3(CH_2)_4$	134-136	64
3f	$CO_2C_2H_5$	Br	$CH_3(CH_2)_4$	89-92	67
3g	CN	I	CH_3	201-202	80
3h	CN	I	$CH_3(CH_2)_4$	124-126	85
3i	$COCH_3$	Br	CH_3	156-158[f]	59
3j	$COCH_3$	Br	$CH_3(CH_2)_4$	152-154	60
3k	$COCH_3$	Br	Ph	165-168[g]	45
3l	COPh	Br	CH_3	165-168[g]	55
3m	PhS	I	CH_3	184-185	6
3n	PhSe	I	CH_3	180(decomp.)[h]	8
3o	H	I	CH_3		0

[a] All new compounds were confirmed by ^{1}H NMR, IR, MS and elemental analysis. [b] Solid from CH_2Cl_2. [c]lit.[1d] m.p. 174-176°. [d]lit.[2] m.p. 160-161°. [e]lit.[1d] m.p. 118-121°, lit.[8] m.p. 118-125°. [f]lit.[1d] m.p. 152-154°. [g]lit.[1d] m.p. 165-167°, lit.[9] m.p. 174°. [h]lit.[10] m.p. 180° (decomp.).

bromide, phenylthiomethyltriphenylarsine iodide and triphenylmethylarsonium iodide were prepared according to refs. 11, 11, 12, 13, 14, respectively. Triphenylcyano- methylene arsonium iodide was synthesized by the reaction of chloroacetonitrile, triphenylarsine and potassium iodide in acetonitrile in 6h under reflux. Acetylmethyltriphenylarsine bromide was synthesized by reaction of bromoacetone and triphenylarsine in benzene in 2h under reflux. Phenylseleno-methylenetriphenylarsonium iodide was prepared by the reaction of chloromethyl phenyl selenide, triphenylarsine and potassium iodide in acetonitrile in 6h under reflux.

General procedure for the preparation of α-acyl arsorane **3a**. – A solution of arsonium salt **1** (1 mmol) in 1 ml of anhydrous $CHCl_3$ was cooled in ice-water, followed by the addition of triethylamine (2.2 mmol, 0.31 ml). After being stirred for 0.5 h, a solution of acid chloride (1 mmol) in 2 ml of anhydrous $CHCl_3$ was added dropwise to the above mixture and allowed to stir for 0.5 h at 0 °C, and 24 h at room temperature. The reaction mixture was concentrated under reduced pressure, followed by washing with water and recrystallization from methanol-water to afford a white solid **3a**. Alternatively, the reaction mixture, concentrated under reduced pressure, was separated by the preparative thin layer chromatography on silica gel (eluent: 8:2 ethyl acetate/petroleum ether (30-60°C)). Compound **3a**. ^{1}H NMR ($CDCl_3$) δ 7.60-7.38 (m, 15 H), 3.13 (s, 3 H), 2.46 (s, 3 H). IR (KBr)/ν_{max} cm^{-1} 1670, 1570, 1445, 1350, 1260, 1090, 750, 690. *m/z* 420 (M,

37%), 389, 347, 306, 229, 227, 265, 152 (100), 105, 77 (Found: C, 65.67; H, 5.10. Calc. for $C_{23}H_{21}AsO_3$: C, 65.72; H, 5.04%).

Compound **3b**. ^1H NMR ($CDCl_3$) δ 7.54-7.23 (m, 15 H), 4.02 (q, J = 7 Hz, 2 H), 1.97 (s, 3 H), 1.21 (t, J = 7 Hz, 3 H). IR (KBr)/ν_{max} cm^{-1} 1663, 1540, 1394, 1342, 1242, 1200, 728, 690. *m/z* 434 (M, 44%), 419, 391, 347, 306, 227, 165, 152 (100), 105, 77(Found: C, 66.12; H,5.48. Calc. for $C_{24}H_{23}AsO_3$: C, 66.38; H, 5.33%).

Compound **3c**. ^1H NMR ($CDCl_3$) δ 7.57-7.13 (m, 20 H), 3.03 (q, J = 7 Hz, 3 H), IR (KBr)/ν_{max} cm^{-1} 1673, 1530, 1450, 1375, 1305, 1085, 740, 690. m/z 482(M, 35%), 451, 423, 152(100), 105, 77 (Found: C, 69.46; H, 5.13. Calc. for $C_{28}H_{23}AsO_3$: C, 69.71; H, 4.80%).

Compound **3d**. ^1H NMR ($CDCl_3$) δ 7.67-7.22 (m, 20 H), 3.61 (q, J = 7 Hz, 2 H), 0.57 (t, J = 7 Hz, 3 H). IR (KBr)/ν_{max} cm^{-1} 1680, 1530, 1370, 1287, 1080, 745, 690. *m/z* 496 (M, 100%), 451, 347, 306, 229, 165, 152, 105, 77 (Found: C, 69.87; H, 5.36. Calc. for $C_{29}H_{25}AsO_3$: C, 70.16; H, 5.08%).

Compound **3e**. ^1H NMR ($CDCl_3$) δ 7.58-7.24 (m, 15 H), 3.09 (s, 3H), 2.87 (t, J = 7 Hz, 2 H), 1.59-0.72 (m, 9 H). IR (KBr)/ν_{max} cm^{-1} 1675, 1550, 1440, 1395, 1325, 1185, 1085, 745, 690. *m/z* 476 (M, 6%), 433, 405 (100), 377, 343, 306, 229, 152, 105, 77 (Found: C, 67.93; H, 6.20. Calc. for $C_{27}H_{29}AsO_3$: C, 68.07; H, 6.13%).

Compound **3f**. ^1H NMR ($CDCl_3$) δ 7.46-7.25 (m, 15 H), 3.63 (q, J = 7 Hz, 2 H), 2.84 (t, J = 7 Hz, 2 H), 1.77-0.50 (m, 12 H). IR (KBr)/ν_{max} cm^{-1} 1670, 1560, 1450, 1380, 1285, 1250, 1070, 740, 690. *m/z* 490 (M, 42%), 445, 419, 391, 347, 306, 229, 165, 152 (100), 105, 77 (Found: C, 68.51; H, 6.40. Calc. for $C_{28}H_{31}AsO_3$: C, 68.57; H, 6.37%).

Compound **3g**. ^{1}H NMR ($CDCl_3$) δ 7.54-7.34 (m, 15 H), 2.27 (s, 3 H). IR (KBr)/ν_{max} cm^{-1} 2175, 1570, 1500, 1340, 1190, 1090, 760, 695. *m/z* 387 (M, 93%), 372, 227, 152 (100), 77 (Found: C, 68.28; H, 4.75; N, 3.59. Calc. for $C_{22}H_{18}AsNO$: C, 68.22; H, 4.68; N, 3.62%).

Compound **3h**. ^{1}H NMR ($CDCl_3$) δ 7.60-7.40 (m, 15 H), 2.59 (t, J = 7 Hz, 2 H), 1.76-0.76 (m, 9 H). IR (KBr)/ν_{max} cm^{-1} 2165, 1580, 1445, 1385, 1170, 740, 690. *m/z* 443 (M, 12%), 387, 372, 347, 306, 229, 165, 152 (100), 91 (Found: C, 70.47; H, 5.80; N, 3.11. Calc. for $C_{26}H_{26}AsNO$: C, 70.43; H, 5.91; N, 3.16%).

Compound **3i**. ^{1}H NMR ($CDCl_3$) δ 7.46-7.11 (m, 15 H), 3.29 (s, 6 H). IR (KBr)/ν_{max} cm^{-1} 1600, 1540, 1380, 1300, 1085, 940, 735, 685 (Found: C, 68.04; H, 5.11. Calcl for $C_{23}H_{21}AsO_2$: C, 68.32; H, 5.24%).

Compound **3j**. ^{1}H NMR ($CDCl_3$) δ 7.44-7.16 (m, 15 H), 2.60 (t, J = 7 Hz, 2 H), 2.28 (s, 3H), 1.68-0.74 (m, 9 H). IR (KBr)/ν_{max} cm^{-1} 1645, 1595, 1540, 1450, 1390, 1090, 945, 745, 690. *m/z* 461 (M., 89%), 417, 389, 347, 306(100), 229, 152, 105, 77 (Found: C, 70.39; H, 6.37. Calc. for $C_{27}H_{29}AsO_2$: C, 70.43; H, 6.35%).

Compounds **3k** and **3l**. ^{1}H NMR ($CDCl_3$) δ 7.70-7.21 (m, 20 H), 1.80 (s, 3 H). IR (KBr)/ν_{max} cm^{-1} 1535, 1450, 1355, 740 (Found: C, 72.42; H, 4.68; Cals. for $C_{28}H_{23}AsO_2$: C, 72.10; H, 4.97%).

Compound **3m**. ^{1}H NMR ($CDCl_3$) δ 7.43-7.11 (m, 20 H), 2.28 (s, 3 H). IR (KBr)/ν_{max} cm^{-1} 1590, 1520, 1480, 735, 685. *m/z* 470 (M, 5%), 320, 306, 227, 152 (100), 121, 105, 77 (Found: C, 68.87; H, 4.90. Calc. for $C_{27}H_{23}AsOS$: C, 68.93; H, 4.93%).

Compound **3n**. ^{1}H NMR ($CDCl_3$) δ 7.86-7.05 (m, 20 H), 2.34 (s, 3 H). IR (KBr)/ν_{max} cm^{-1} 1575, 1500, 740, 690 (Found: C, 61.65; H, 4.72; Calc. for $C_{26}H_{23}AsOSe$: C, 61.80; H, 4.59%).

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