

# Condensations of Crotonate Arsonium Ylide with Conjugated Carbonyl Compounds

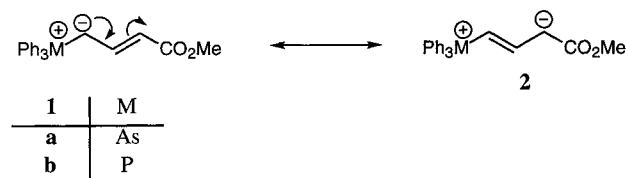
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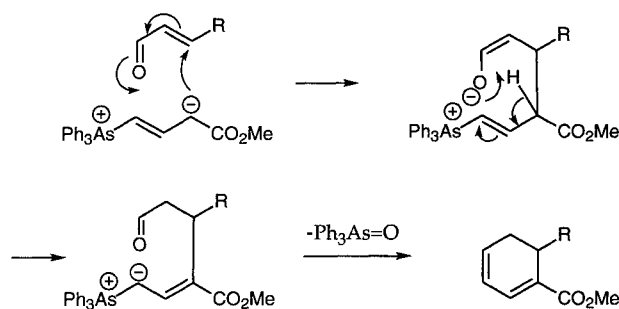
**Abstract:** Condensations of methyl 4-(triphenylarsoranylidene)-2-butenolate **1a** and conjugated carbonyl compounds give 1,3-cyclohexadiene-1-carboxylates and/or acyclic trienes in superior yields compared to the condensations with the phosphonium analogue **1b**. However, the reaction of **1a** and ethyl 2-cyano-5-methyl-2,4-hexadienoate **7** gave a mixture of two diastereomeric *trans*-bisvinylcyclopropanecarboxylates **9**.

Some time ago, Wittig condensations of ethyl 4-(triphenylarsoranylidene)-2-butenolate and aliphatic aldehydes and ketones have been reported.<sup>1</sup>



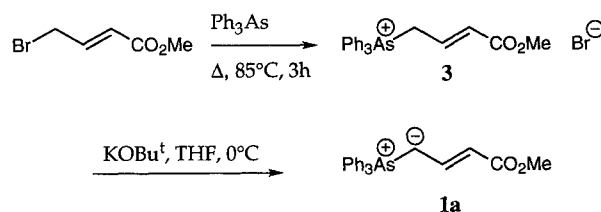
Scheme 1

This arsonium ylide is not well known.<sup>2,3</sup> Our interest in the arsonium ylide **1a** stems from the fact that the corresponding phosphonium ylide **1b** is well recognized to undergo first a Michael addition with conjugated carbonyl compounds followed by an intramolecular Wittig condensation producing 1,3-cyclohexadiene-1-carboxylates.<sup>4</sup> This type of Michael-Wittig condensation is now well established as a useful synthetic reaction.<sup>5,6,7,8,9</sup> Likewise it is expected that the reaction of the  $\gamma$ -ylide **2a** (Scheme 1) with conjugated carbonyl compounds, instead of a Wittig condensation, will first undergo a Michael addition with conjugated carbonyl compounds, followed by an intramolecular Wittig condensation to give 1,3-cyclohexadiene-1-carboxylates (Scheme 2). This so-called Michael-Wittig condensation of **1b** is very pronounced (yields of 20 - 60%).<sup>4</sup> It is therefore surprising that the arsonium ylide **1a** has not yet been investigated. In this paper we would like to draw the attention to the superior nature of this ylide **1a** over its phosphorus analogue **1b**.



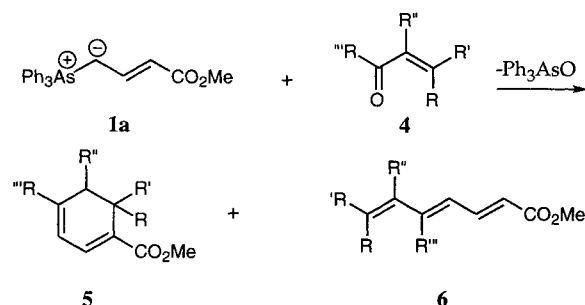
Scheme 2

The triphenylarsonium salt **3** was obtained in high yield and purity by heating methyl 4-bromo-2-butenolate and triphenylarsine at 85 °C for three hours (Scheme 3).<sup>10</sup>



Scheme 3

The arsonium ylide **1a** was prepared *in situ*. Thus adding *Kt*-*OBu* to a powdered suspension of white arsonium salt **3** in anhydrous THF at 0 °C gave the bright yellow ylide **1a**. It is very important to note that under these conditions no ylide **1a** salt **3** coupling reaction occurred.<sup>11</sup> This is a problematic side reaction during the preparation of **1b**.<sup>11,12</sup>



Scheme 4

Table 1<sup>13</sup>

	4	Product	Yield (%)		
			Tot- al	5	6
a		R=R'=R''=R'''=H	33	33	<1
b		R'=Me, R=R''=R'''=H	99 <sup>a</sup>	36	63
c		R'=R''=Me, R=R'''=H	89	~0	89
d		R=R'=R''=H, R'''=Me	64	~0	64 <sup>b</sup>
e		R=R'=Me, R''=R'''=H	87 <sup>c</sup>	0	87
f		R=R'=R''=H, R'''=Me	77	77 <sup>d</sup>	~0
g		R=R'=R''=Me, R'''=H	- <sup>e</sup>	-	-

a: 55% yield with **1b** (ref. 4) b: a mixture of (*E,E*)-, (*Z,E*)- and (*E,Z*) isomers; 60%  
5 with **1b** (ref 4). c: 39% yield (ref 14) d: 20% yield with **1b** (ref 4). e: no reaction.

The ylide **1a** was used at once. Thus 2-propenal (acrolein) **4a** in THF was added to the arsonium ylide **1a** at 0 °C and stirred for 30 minutes at 0 °C. The reaction was exothermic and the colour change to brown-orange within 10 minutes which indicated when the condensation was complete. The Michael-Wittig product, methyl 1,3-cyclohexadiene-1-carboxylate **5a**, was the only major product isolated in an unoptimised yield of 33% (Scheme 3, Table 1). Likewise, 2-butenal **4b** gave the Michael-Wittig product **5b** in 36% yield and the acyclic (*E,E,E*)- and (*E,Z,E*)-trienoates **6b** in a yield of 49% and 14% respectively; a total yield of condensation products of 99% was obtained. An investigation into the effect of different solvents and temperatures on the condensation of 2-butenal **4b** and **1a** was carried out. An increase in temperature favours the production of acyclic **6b** (and the all-*trans* isomer (*E,E,E*)-**6b** more than (*E,Z,E*)-**6b**); however, the overall yield was lower (Table 2). DMPU<sup>15</sup> seems to lower the total yield of products, but at 0 °C improves the formation of the Michael-Wittig product **5b**.

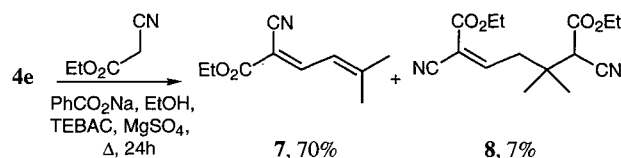
Table 2

entry	Solvent, temp	Yield (%)			
		Total	<b>5b</b>	<b>6b</b> ( <i>E,E,E</i> )	<b>6b</b> ( <i>E,Z,E</i> )
1	THF, rt	99	36	49	14
2	THF, 65 °C	86	27	47	12
3	THF: DMPU (1:2), 65 °C	65	36	25	4
4	DMPU, 0 °C	70	40	24	6
5	Phosphonium ylide, THF, 60 °C	36 <sup>a</sup> (55) <sup>4</sup>	36	0	0

a: This reaction was carried out in a similar manner as the arsonium ylide **1a** condensations.

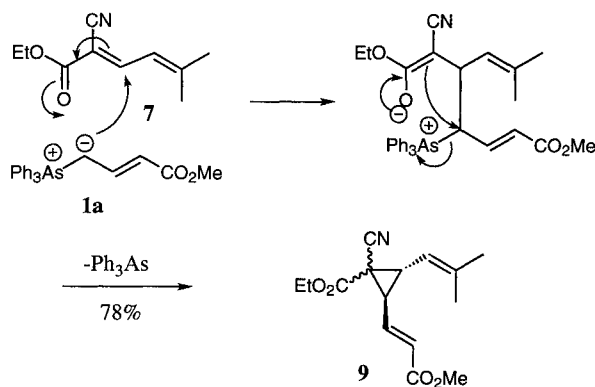
Unexpectedly, aldehyde **4c** showed no Michael-Wittig product, but instead **6c**. 3-Methyl-2-butenal **4e**, due to the steric hindrance of an extra  $\beta$ -methyl group, gave only acyclic ester **6e**. Methylvinylketone **4f** gave exclusively only the Michael-Wittig product **5f** because Michael-attack is so much favoured compared to direct carbonyl attack. We were unable to condense 4-methyl-3-penten-2-one **4g** and **1a** even in refluxing THF.

Preparation of ethyl 2-cyano-5-methylhexa-2,4-dienoate **7**<sup>16,17</sup> gave also some of the Michael adduct **8**.<sup>16</sup>



Scheme 5

Reaction of **1a** and **7** gave a diastereomeric mixture of *trans*-ethyl 1-cyano-3-(3-methoxycarbonyl-2-propenyl)-2-(2-methyl-1-propenyl)-cyclopropanecarboxylate **9**<sup>18</sup> in a good yield (Scheme 6). This is the first time that **1a** has been used in cyclopropanation<sup>19,20</sup> to form highly functionalised *bis*-vinylcyclopropanes.<sup>21,22</sup>



Scheme 6

In summary, we have described that the arsonium ylide **1a** is easier to prepare than the phosphonium ylide **1b**; apparently no ylide-salt coupling takes place. The condensations of the ylide **1a** is faster than with **1b** and can often be performed at 0 °C. The yields of condensations with **1a** are substantially higher than the yields obtained with **1b**. The major drawback is that the ylide **1a** is less prone to undergo the Michael-Wittig condensation. This is perhaps due to its greater nucleophilicity compared with the corresponding phosphonium ylide **1b**.

#### Acknowledgements

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#### References and Notes

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- 5a** HRMS calcd for C<sub>8</sub>H<sub>10</sub>O<sub>2</sub> *m/z* (EI) 138.0681, Found 138.0682;  $\nu_{\max}$  (film, cm<sup>-1</sup>) 1706 (vs), 1638 (w), 1575 (w); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 2.18 - 2.52 (4H, m), 3.760 (3H, s), 6.0-6.2 (2H, m), 7.001 (1H, dd, *J* = 5.1, 1.3 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 20.69, 22.79, 51.54, 123.89, 127.02, 133.20, 133.46, 167.87.
- 5b** HRMS calcd for C<sub>9</sub>H<sub>12</sub>O<sub>2</sub> *m/z* (EI) 152.0837, Found

- 152.0841;  $\nu_{\max}$  (film,  $\text{cm}^{-1}$ ) 1708 (vs), 1617 (m), 1575 (m);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.989 (3H, d,  $J$  = 7.0 Hz), 2.179 (1H, dm), 2.544 (1H, ddm,  $J$  = 17.9, 9.3 Hz), 2.800 (1H, qm,  $J$  = 7.0 Hz), 3.760 (3H, s), 6.046–6.016 (2H, m), 6.968 (1H, dm,  $J$  = ~6.4, ~1.8 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 17.59, 25.20, 30.52, 51.44, 122.89, 131.48, 131.83, 132.18, 167.64.
- 6b** HRMS calcd for  $\text{C}_9\text{H}_{12}\text{O}_2$   $m/z$  (EI) 152.0837, Found 152.0841;  $\nu_{\max}$  (film,  $\text{cm}^{-1}$ ) 1712 (s), 1618 (s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.819 (3H, d,  $J$  = 6.6 Hz), 3.732 (3H, s), 5.841 (1H, d,  $J$  = 15.2 Hz), 5.929 (1H, dq,  $J$  = 14.9, 6.6 Hz), 6.151 (1H, ddd,  $J$  = 14.9, 10, 1.3 Hz), 6.269 (1H, dd,  $J$  = ~15, ~11 Hz), 6.524 (1H, dd,  $J$  = 15.0, 10 Hz), 7.288 (CH, dd,  $J$  = 15.2, 11.3 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 17.37, 51.24, 119.36, 127.36, 131.05, 134.97, 141.03, 144.88, 167.37.<sup>23</sup>
- 6c** HRMS calcd for  $\text{C}_{10}\text{H}_{14}\text{O}_2$   $m/z$  (EI) 166.0994, Found 166.0994;  $\nu_{\max}$  (film,  $\text{cm}^{-1}$ ) 1713 (s), 1611 (s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.767 (3H, s), 1.781 (3H, d,  $J$  = 7 Hz), 3.726 (3H, s), 5.783 (1H, q,  $J$  = 7 Hz), 5.863 (1H, d,  $J$  = 15.2 Hz), 6.217 (1H, dd,  $J$  = 15.2, 11.1 Hz), 6.567 (1H, d,  $J$  = 15.2 Hz), 7.338 (1H,  $J$  = 15.2, 11.1 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 11.55, 14.07, 51.07, 118.85, 123.14, 132.14, 134.38, 145.43, 145.69, 167.35.
- 6d** HRMS calcd for  $\text{C}_9\text{H}_{12}\text{O}_2$   $m/z$  (EI) 152.0837, Found 152.0842;  $\nu_{\max}$  (film,  $\text{cm}^{-1}$ ) 1714 (s), 1644 (m), 1626 (s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.899 (3H, s), 3.751 (3H, s), 5.186 (2H, sm), 5.931 (1H, d,  $J$  = 15.4 Hz), 6.302 (1H, ddd,  $J$  = 15.2, 11.1, 0.8 Hz), 6.647 (1H, d,  $J$  = 15.2 Hz), 7.350 (1H,  $J$  = 15.4, 11.1 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 18.13, 51.37, 120.61, 120.92, 126.39, 141.37, 143.23, 144.78, 167.31.
- 6e** HRMS calcd for  $\text{C}_{10}\text{H}_{14}\text{O}_2$   $m/z$  (EI) 166.0994, found 166.0995;  $\nu_{\max}$  (film,  $\text{cm}^{-1}$ ) 1717 (s), 1643 (m), 1613 (s);  $\lambda_{\max}$  = 209, 274 ( $\epsilon$  = 9700, 2200);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.839, 1.855 (6H, 2s), 3.744 (3H, s), 5.832 (1H, d,  $J$  = 15.2 Hz), 5.951 (1H, dm,  $J$  = 11.3 Hz), 6.206 (1H, dd,  $J$  = 14.7, 11.3 Hz), 6.790 (1H, dd,  $J$  = 14.7, 11.3 Hz), 7.362 (1H,  $J$  = 15.2, 11.3 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 18.50, 26.22, 51.14, 118.65, 124.99, 127.18, 137.39, 141.71, 145.35, 167.46; Anal. Calcd. for  $\text{C}_{10}\text{H}_{14}\text{O}_2$ : C, 72.26; H, 8.49. Found: C, 72.03; H, 8.78.
- 5f** HRMS calcd for  $\text{C}_9\text{H}_{12}\text{O}_2$   $m/z$  (EI) 152.0837, Found 152.0837;  $\nu_{\max}$  (film,  $\text{cm}^{-1}$ ) 1707 (s), 1646 (w), 1588 (s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.871 (3H, s), 2.195, 2.478 (4H, 2m), 3.741 (3H, s), 5.813 (1H, dq,  $J$  = 5.5, 1.5 Hz), 6.975 (1H, d,  $J$  = 5.5 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 21.44, 23.50, 28.65, 51.37, 119.17, 123.87, 134.29, 144.52, 167.96.
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- (17) **7** HRMS calcd for  $\text{C}_{10}\text{H}_{13}\text{NO}_2$   $m/z$  (EI) 179.0946. Found 179.0942;  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) 2223 (m), 1724 (s), 1623 (s), 1578 (s);  $\lambda_{\max}$  = 207, 301 ( $\epsilon$  = 2600, 22500);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.362 (3H, t,  $J$  = 7.1 Hz), 2.069 (6H, s), 4.318 (2H, q,  $J$  = 7.1 Hz), 6.483 (1H, dm,  $J$  = 12.3, 1.3 Hz), 8.134 (1H, d,  $J$  = 12.3 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 14.00, 19.89, 27.29 (3x $\text{CH}_3$ ), 61.95 ( $\text{CH}_2\text{O}$ ), 102.19 ( $\text{C}=\text{}$ ), 114.53 (CN), 122.07 ( $\text{CH}=\text{}$ ), 151.16 ( $\text{CH}=\text{}$ ), 158.59 ( $\text{C}=\text{}$ ), 162.69 ( $\text{C}=\text{O}$ ); Anal. Calcd. for  $\text{C}_{10}\text{H}_{13}\text{NO}_2$ : C, 67.02; H, 7.31; N, 7.82. Found: C, 67.00; H, 7.49; N, 7.89.
- 8** HRMS calcd for  $\text{C}_{15}\text{H}_{24}\text{N}_3\text{O}_4$   $m/z$  (CI,  $\text{M}+\text{NH}_4^+$ ) 310.1767, Found 310.1790;  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) 2233 (w), 1739 (vs), 1628 (m);  $\lambda_{\max}$  = 224 ( $\epsilon$  = 10400);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.279, 1.264 (6H, 2s), 1.355, 1.372 (6H, 2xt,  $J$  = 7.2 Hz), 2.777 (2H, d,  $J$  = 8.0 Hz), 3.514 (1H, s), 4.309, 4.343 (4H, 2xq,  $J$  = 7.2 Hz), 7.699 (1H, t,  $J$  = 8.0 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 13.64 (2x $\text{CH}_3$ ), 24.60, 25.13 (2x $\text{CH}_3$ ), 38.08 ( $\text{CH}_2$ ), 41.22 (CH), 47.66 (C), 62.32, 62.60 (2x $\text{CH}_2\text{O}$ ), 112.43 (CN), 112.97 (CN), 114.86 ( $\text{C}=\text{}$ ), 157.11 ( $\text{CH}=\text{}$ ), 160.26 ( $\text{C}=\text{O}$ ), 164.18 ( $\text{C}=\text{O}$ ); Anal. Calcd. for  $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_4$ : C, 61.63; H, 6.90; N, 9.58. Found: C, 61.34; H, 7.08; N, 9.51.
- (18) **9a** HRMS (CI) calcd for  $\text{C}_{15}\text{H}_{20}\text{NO}_4$  ( $\text{MH}^+$ )  $m/z$  278.1392, Found 278.1397;  $\nu_{\max}$  (film,  $\text{cm}^{-1}$ ): 2243 (m), 1730 (s), 1653 (m);  $\lambda_{\max}$  = 218 ( $\epsilon$  = 8900);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.340 (3H, t,  $J$  = 7.3 Hz) 1.786 (3H, s), 1.810 (3H, s), 2.970 (1H, dd,  $J$  = 8.3, 7.9 Hz), 2.581 (1H, dd,  $J$  = 9.8, 7.9 Hz), 3.733 (3H, s), 4.295 (2H, q,  $J$  = 7.3 Hz), 5.012 (1H, dm,  $J$  = 8.3 Hz), 6.159 (1H, d,  $J$  = 15.6 Hz), 6.888 (1H, dd,  $J$  = 15.6, 9.8 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 13.65, 18.55, 25.23 (3x $\text{CH}_3$ ), 27.98 (CH), 34.22 (CH), 39.65 (C), 51.32 (OMe), 62.77 ( $\text{CH}_2\text{O}$ ), 113.30 (CN), 117.05 ( $\text{CH}=\text{}$ ), 125.19 ( $\text{CH}=\text{}$ ), 138.72 ( $\text{C}=\text{}$ ), 139.67 ( $\text{CH}=\text{}$ ), 165.22 ( $\text{C}=\text{O}$ ), 164.33 ( $\text{C}=\text{O}$ ).  
(minor isomer): HRMS (CI) calcd for  $\text{C}_{15}\text{H}_{20}\text{NO}_4$  ( $\text{MH}^+$ )  $m/z$  278.1392, Found 278.1389;  $\nu_{\max}$  (film,  $\text{cm}^{-1}$ ): 2243 (m), 1729 (vs), 1655 (m);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.358 (3H, t,  $J$  = 7.2 Hz) 1.758 (3H, d,  $J$  = 1.0 Hz), 1.838 (3H, s), 2.807 (1H, dd,  $J$  = 9.8, 7.9 Hz), 2.868 (1H, dd,  $J$  = 8.0, 7.9 Hz), 3.766 (3H, s), 4.298 (2H, q,  $J$  = 7.2 Hz), 5.137 (1H, dm,  $J$  = 8.0 Hz), 6.190 (1H, d,  $J$  = 15.5 Hz), 6.745 (1H, dd,  $J$  = 15.5, 9.8 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 13.96, 18.85, 25.71 (3x $\text{CH}_3$ ), 28.20 (CH), 34.51 (CH), 35.71 (C), 51.70 (OMe), 63.22 ( $\text{CH}_2\text{O}$ ), 113.44 ( $\text{CH}=\text{}$ ), 114.55 (CN), 126.71 ( $\text{CH}=\text{}$ ), 138.92 ( $\text{C}=\text{}$ ), 142.51 ( $\text{CH}=\text{}$ ), 165.27 ( $\text{C}=\text{O}$ ), 166.56 ( $\text{C}=\text{O}$ ); Anal. Calcd. for  $\text{C}_{15}\text{H}_{19}\text{NO}_4$ : C, 64.97; H, 6.91; N, 5.05. Found: C, 65.01; H, 7.09; N, 5.16 (for mixture).
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