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Novel Reactions of Arsonium Ylides and Substituted 2*H*-Pyran-5-Carboxylates, A New Preparation for Functionalised Vinylcyclopropanecarboxylates and Dihydrofurans.

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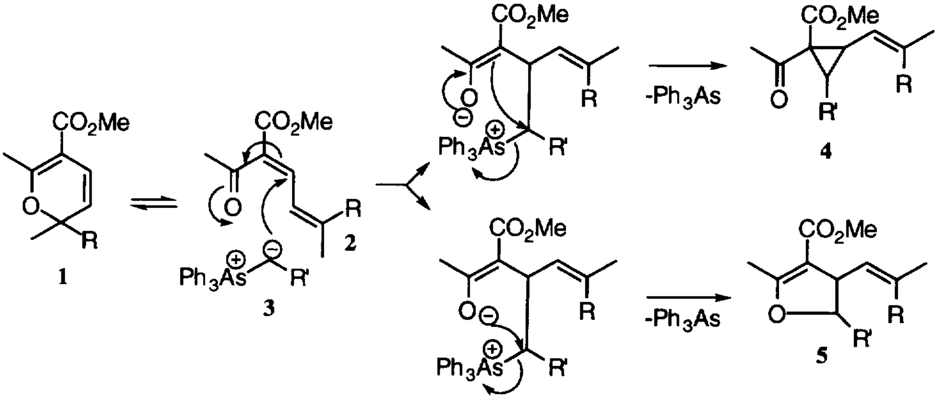
Abstract: Substituted alkyl 2-pyran-5-carboxylates have been condensed with arsonium ylides to form substituted vinylcyclopropanecarboxylates and in a number of cases also vinyldihydrofurans.

2*H*-pyran-5-carboxylates **1**[1,2] have the unique property to undergo reversible electrocyclic ring opening to **2**, making these compounds available for nucleophilic carbonyl attack and Michael attack. In this study we have found that a number of arsonium ylides **3** prepared *in situ* from their arsonium salts and potassium *tert*-butoxide react with 2*H*-pyran-5-carboxylates **1** in THF between 0 °C at room temperature to form highly functionalised *trans*-2-vinylcyclopropanecarboxylates **4**. In some cases, substituted vinyldihrofurans **5** (Scheme 1) also formed.

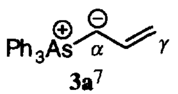
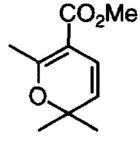
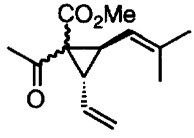
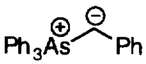
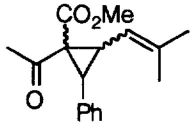
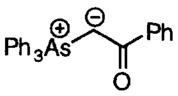
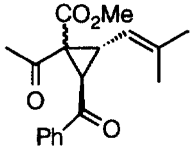
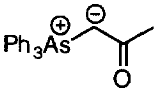
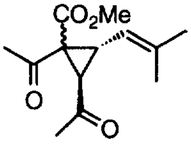
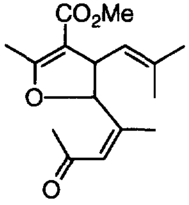
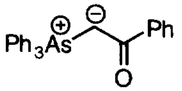
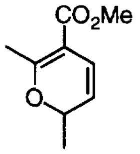
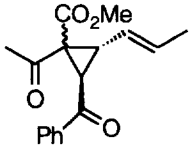
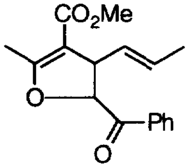
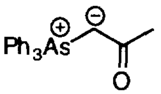
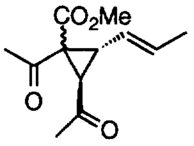
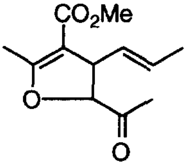
Scheme 1



It has been reported[3,4] that cyclopropanation of conjugated carbonyl compounds and arsonium ylides occurs, producing cyclopropanes. The preparation of vinylcyclopropanes using arsonium ylides and conjugated carbonyl compounds is less common.[5,6] To our knowledge, this is the first time that 2*H*-pyran compounds have been used to form *trans*-2-vinylcyclopropanecarboxylates. For example, a suspension of finely powdered (2-propenyl)triphenylarsonium bromide[7] in anhydrous THF was treated with potassium *tert*-butoxide at 0 °C to form the orange brown arsonium ylide **3a**. Addition of methyl 2,2,6-trimethyl-2*H*-pyran-5-carboxylate **2a** (**1a**, R=Me) gave a diastereomeric mixture, *trans*-*bis*vinylcyclopropan-2-carboxylates **4a**, in an unoptimised yield of 15%. CAUTION, triphenylarsine could be eluted with 100% petroleum ether followed by elution of cyclopropanecarboxylates **4** with ether:petroleum ether (1:9).

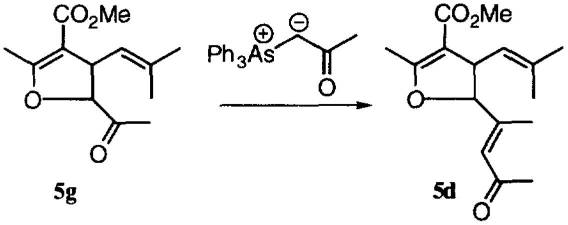
Spontaneous electrocyclic rearrangement of **4a** to methyl 1-acetyl-4,4-dimethyl-2,6-cycloheptadiene-carboxylate did not occur (heating **4a** in a $CDCl_3$ solution for 3 days at 60 °C also produced no rearrangement). Michael attack of the γ-ylide **3a** on **2a** followed by an intramolecular Wittig reaction[8] could produce methyl 2-methyl-6-(2-methyl-1-propenyl)-2,4-cyclohexadienecarboxylate; however, no detectable

Table 1

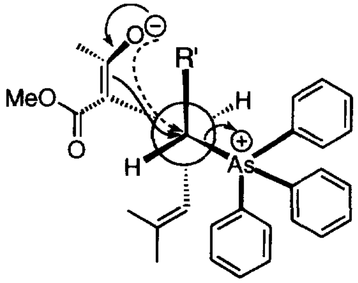
run	Arsonium ylide 3	2H-pyran 1	Yield of Products (%)	
			Cyclopropane 4	Dihydrofuran 5
1	 **3a**[7]	 **1a**	 **4a** (15%)	-
2	 **3b**[9]	**1a**	 **4b** (30%)	-
3	 **3c**[10]	**1a**	 **4c** (64%)	trace
4	 **3d**[11]	**1a**	 **4d** (56%)	 **5d** (29%)
5	 **3c**	 **1b**	 **4e** (31%)	 **5e** (13%)
6	 **3d**	**1b**	 **4f** (46%)	 **5f** (16%)

amount could be isolated. The arsonium ylides **3b**[9], **3c**[10] and **3d**[11] were prepared *in situ* from the corresponding arsonium salts as described for **3a**. Thus, **3b** reacted with 2H-pyran **1a** and gave 2-vinylcyclopropancarboxylates **4b** (3 diastereomers in a ratio of 1:1:1). Likewise, **4c** (two *trans*-diastereomers), **4d** (two *trans*-diastereomers) **4e** (2 *trans* diastereomers) and **4f** (2 *trans*-diastereomers) were isolated. The arsonium ylides **3c** and **3d** also gave 4-vinyl-2,3-dihydrofuran-4-carboxylates **5d, 5e** and **5f** (Scheme 1 and Table 1[12]), **5d** being the result of a further Wittig condensation of **3d** and **5g**. (Scheme 2).

Scheme 2



Scheme 3



In the majority of cases we have investigated, *trans*-cyclopropanation occured due to *trans* elimination of the bulky triphenylarsine in the conformation depicted in Scheme 3. The production of dihydrofurans from arsonium ylide and conjugated carbonyl compounds is rather rare.[13] At this stage we have found that higher reaction temperatures seem to increase the yield of dihydrofuran **5**. 2,3-Dihydrofurans are of interest for synthesis of natural compounds.[14] We are currently investigating the use of different bases and solvents for the optimal formation of dihydrofurans **5**.[15,16,17,18,19]

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REFERENCES AND NOTES

1. Krasnaya, Zh. A.; Prokof'ev, E.P.; Kucherov, V.F.; Zaripova, M. Sh. *Izv. Akad. Nauk. SSSR, Ser. Khim.*, **1973**, *10*, 2356; *Chem. Abstr.* **1974**, *80*, 47772v.
2. Krasnaya, Zh. A.; Prokof'ev, E.P.; Kucherov, V.F. *Izv. Akad. Nauk. SSSR, Ser. Khim.*, **1979**, *4*, 816 - 822; *Chem. Abstr.* **1979**, *91*, 38884h.
3. Huang, Y-Z.; Shen, Y-C.; Xin, Y-K.; Ma, J-J. *Sci. Sin. (Engl. Ed.)* **1980**, *23(11)*, 1396.
4. Huang, Y.; Xu, Y.; Li, Z. *Organic Prep. and Proced. Int.* **1982,** *14*, 373 - 380.
5. Shen, Y.; xiang, Y.*J. Chem. Research (S)* **1994**, 198.
6. Shen, Y.; Qi, M. *J. Chem. Research (S)* **1996**, 328.
7. Horner, L.; Ertel, I.; Ruprecht, H-D.; Belovsky, O. *Chem. Ber.* **1970** *103*, 1582 -1588.
8. Buchi, G.; Wuest, H. *Helv. Chim. Acta* **1971**, *54*, 1767.
9. Broos. R.; Anteunis, M. J. O. *Bull. Soc. Chim. Belg.* **1988**, *97*, 271.
10. Schiemenz, G. P. *J. Organometal. Chem.* **1973**, *52* 349 - 354.
11. Froyen, P. *Acta Chem. Scand.* **1971**, *25*, 2541.
12. Spectrometric data [NMR, $CDCl_3$, ^1H = 200 MHz; ^{13}C = 50 MHz]: **4a**: HRMS (EI) calcd for $C_{13}H_{18}O_3$ $(M^{+\cdot})$ *m/z* 222.1256, found 122.1258. ^1H NMR: δ = 1.688 (3H, s), 1.728 (3H, s), 2.244 (3H, s), 2.717 (1H, dd, J = 7.7, 8.1 Hz), 2.935 (1H, dd, J = 7.7 and 8.1 Hz), 3.770 (OMe), 4.848 (1H, dm, J = 8.1 Hz), 5.13-5.07 (1H, m), 5.33-5.29 (2H, m). ^{13}C NMR: δ = 18.43, 25.48, 29.89 ($3xCH_3$), 31.41 (CH), 38.47 (CH), 49.96 (C), 52.33 (OMe), 118.21 (CH_2=), 118.27 (CH=), 132.23 (CH=), 137.73 (C), 168.88, 199.78.

4b: HRMS (EI) calcd for $C_{17}H_{20}O_3$ $(M^{+\cdot})$ *m/z* 272.1412, found 172.1402. ^{1}H-NMR δ = 1.844 (3H, d, *J* = 1.2 Hz), 1.806 (3H, d, *J* = 1.1 Hz), 2.259 (3H, s), 3.52 - 3.29 (2H, m), 3.52 - 3.29 (3H, m), 5.003 (1H, dm, *J* = 4.7 Hz), 7.3 - 7.1 (5H, m).

4c: Calcd for $C_{18}H_{20}O_4$: C, 71.98 ; H, 6.71. Found : C, 72.21 ; H, 6.98. HRMS (CI) calcd for $C_{18}H_{21}O_4$ $(MH^{+\cdot})$ *m/z* 301.1440, found 301.1449. ^{1}H NMR: δ = 1.724 (3H, s), 1.812 (3H, d, J = 1.0 Hz), 2.286 (3H, s), 3.328 (1H, dd, J = 7.2 and 3.8 Hz), 3.767 (1H, d, J = 7.2 Hz), 3.708 (3H, s), 4.839 (1H, dm, J = 8.8 Hz), 7.60-7.41 (3H, m), 8.01-7.91 (2H, m). (minor isomer)^{1}H NMR: δ = 1.753 (3H, s), 1.794 (3H, s), 2.302 (3H, s), 3.273 (1H, dd, *J* = 7.0, 8.8 Hz), 3.712 (1H, d, *J* = 7.0 Hz), 3.806 (3H, s), 5.036 (1H, dm, *J* = 8.8 Hz), 7.630 - 7.424 (3H, m), 8.015 -7.966 (2H, m).^{13}C NMR: δ = 18.41, 25.45, 28.94 ($3xCH_3$), 33.72 (CH), 36.78 (CH), 51.33 (C), 52.57 (OMe), 116.58 (CH=), 128.10, 128.42, 133.28, 136.44, 139.39, 168.06, 194.03, 198.38. (minor isomer) δ = 18.37, 25.50, 29.62 ($3xCH_3$), 32.51 (CH), 39.11 (CH), 50.45 (C), 52.68 (OMe), 117.17 (CH=), 128.18, 128.49, 133.40, 136.40, 139.19, 167.61, 194.02, 198.65.

4d: Calcd for $C_{13}H_{18}O_4$: C, 65.53 ; H, 7.61. Found : C, 65.58 ; H, 7.86. HRMS (CI) calcd for $C_{13}H_{19}O_4$ $(MH^{+\cdot})$ *m/z* 239.1283, found 239.1291. ^{1}H NMR: δ = 1.694 (3H, d, *J* = 1.2 Hz), 1.786 (3H, d, *J* = 1.0 Hz), 2.219 (3H, s), 2.313 (3H, s), 3.076 (1H, dd, *J* = 7.3, 6.1 Hz), 3.129 (1H, d, *J* = 6.1 Hz), 3.795 (3H, s), 4.757 (1H, dm, *J* = 7.3 Hz). (minor isomer) δ = 1.730 (3H, d, *J* = 1.0 Hz), 1.790 (3H, d, *J* = 1.2 Hz), 2.336 (3H, s), 2.293 (3H, s), 3.010 (1H, dd, *J* = 6.7 and 5.7 Hz), 3.043 (1H, d, *J* = 6.7 Hz), 3.767 (3H, s), 4.940 (1H, dm, *J* = 5.7 Hz).^{13}C NMR: δ = 18.48, 25.55, 28.95, 31.39 ($4xCH_3$), 34.45 (CH), 39.51 (CH), 52.19 (C), 52.89 (OMe), 116.46 (CH=), 139.19, 168.24, 197.95, 203.22. (Minor isomer) δ = 18.46, 25.61, 29.71, 31.36 ($4xCH_3$), 32.97 (CH), 41.60 (CH), 50.74 (C), 52.77 (OMe), 117.16 (CH=), 138.94, 167.44, 199.11, 203.23.

5d: Calcd for $C_{16}H_{22}BrO_4$: C, 69.04 ; H, 7.97. Found : C, 69.43 ; H, 7.78. HRMS (CI) calcd for $C_{16}H_{23}O_4$ $(MH^{+\cdot})$ *m/z* 279.1596, found 279.1593. ^{1}H NMR: δ = 1.703 (3H, d, *J* = 1.3 Hz), 1.739 (3H, d, *J* = 1.1 Hz), 2.081 (3H, d, *J* = 1.2 Hz), 2.238 (3H, s), 2.285 (3H, d, *J* = 1.3 Hz), 3.832 (1H, m), 3.043 (1H, d, *J* = 6.7 Hz), 3.671 (3H, s), 4.561 (1H, d, *J* = 6.3 Hz), 5.102 (1H, dm, *J* = 10 Hz), 6.156 (1H, sm). ^{13}C NMR: δ = 14.11, 14,63, 17.91, 25.83, 31.98 ($5xCH_3$), 47.41 (CH), 50.74 (OMe), 90.26 (CH), 105.30 (C=), 121.03 (CH=), 125.61(CH=), 133.48 (C=), 152.80 (C=), 165.99, 167.36, 198.87.

4e: HRMS (EI) calcd for $C_{17}H_{18}O_4$ $(M^{+\cdot})$ *m/z* 286.1200, found 286.1205. ^{1}H NMR: δ = 1.698 (3H, dd, *J* = 6.5, 1.5 Hz), 2.308 (3H, s), 3.197 (1H, dd, *J* = 7.3, 8.9 Hz), 3.701 (3H, s,), 3.789 (1H, d, *J* = 7.3 Hz), 5.141 (1H, ddq, *J* = 15.3, 8.9, 1.6 Hz), 5.894 (1H, dqd, J=15.3, 6.5, 0.7 Hz), 7.62 - 7.42 (3H, m), 7.979 (2H, dm, J=9.0 Hz).^{13}C NMR: δ = 17.95, 29.22 ($2xCH_3$), 36.23 (CH), 37.02 (CH), 51.11 (C), 52.68 (OMe), 122.81, 128.29, 128.52, 131.80, 133.39, 136.49, 167.99, 193.89, 198.37.

5e: ^{1}H NMR: δ = 1.749 (3H,d, *J* = 4.7 Hz), 2.343 (3H, s), 3.648 (3H, s), 3.83-3.68 (1H, m), 5.555 (d, *J* = 7 Hz), 5.63 - 5.59 (2H, sm), 7.62 - 7.45 (3H, m), 7.96-7.91 (2H, sm). ^{13}C NMR: δ = 14.13, 17.80 ($2xCH_3$), 49.01 (CH), 50.74 (OMe), 86.90 (CH), 104.84 (C=), 127.84 (CH=), 128.67, 128.72, 130.20, 133.32, 133.74, 165.44 (C=), 168.38, 193.64.

4f: HRMS (EI) calcd for $C_{12}H_{16}O_4$ $(M^{+\cdot})$ *m/z* 224.1049, found 224.1048. ^{1}H NMR: δ = 1.672 (3H, dd, *J* = 6.5, 1.6 Hz), 2.242 (3H, s), 2.307 (3H, s), 2.960 (1H, dd, *J* = 8.9 and 6.9 Hz), 3.156 (1H, d, *J* = 6.9Hz), 3.787 (3H, s), 5.063 (1H, ddq, *J* = 15.3, 8.9, 1.6 Hz), 5.836 (1H, dqd, *J* = 15.3, 6.5 and 0.6 Hz). ^{13}C NMR: δ = 17.95, 29.09, 31.39 ($3xCH_3$), 37.69 (CH), 38.95 (CH), 51.80 (C), 52.88 (OMe), 122.68 (CH=), 131.67 (CH=), 168.05, 197.83, 202.89.

5f: HRMS (EI) calcd for $C_{12}H_{16}O_4$ $(M^{+\cdot})$ *m/z* 224.1049, found 224.1040. ^{1}H NMR: δ = 1.687 (3H, dd, *J* = 6.5, 0.6 Hz, CH_3-8), 2.199 (3H, s, CH_3-1), 2.287 (3H, d, *J* = 1.3 Hz), ~3.5 (1H, m), 3.682 (3H, s), 4.595 (1H, d, *J* = 5.2 Hz), 5.625 (1H, dq, *J* = 15.2, 6.3 Hz), (1H, ddq, *J* = 15.2, 7.2 and 1.0 Hz,).^{13}C NMR: δ = 14.12, 17.68, 25.63 ($3xCH_3$), 48.61 (CH), 50.72 (OMe), 89.98 (CH), 105.26 (C=), 127.21 (CH=), 130.79 (CH=), 165.39, 167.56, 205.68.

13. Kharitonov, V. G.; Nikanorov, V. A.; Sergeev, S. V.; Galakhov, M. V.; Yakushin, S. O.; Mikul'shina, V. V.; Rozenberg, V. I.; Reutov, O. A. *Dokl. Akad. Nauk SSSR* **1991**,*319(1)*, 177 - 80 [*Chem. Abstr.* **1992**, *116*, 83474 v].
14. Rao, Y. S. Chem. Rev. **1976**, *76*, 625.
15. Arnold, Z.; Kral, V.; Kryshtal, G. V.; Yanovskaya, L. A. *Synthesis* **1984**, 974 -976.
16. Farina, F.; Maestro, M. C.; Martin, M. V.; Soria, M. L. *Tetrahedron* **1987**, *43*, 4007 - 4014.
17. Saegusa, T.; Yonezawa, K.; Murase, I.; Konoike, T.; Tomita, S.; Ito, Y. *J. Org. Chem.* **1973**, *38*,, 2319- 2328.
18. Jaxa-Chamiec, A. A.; Sammes, P. G.; Kennewell, P. D. *J. Chem. Soc. Perkin Trans. I* **1980**, 170 - 175.
19. Kato, T.; Chiba, T.; Sato, H.; Ito, T. *Heterocycles* **1977**, *8*, 417 - 420.

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