Novel Reactions of Methyl 4-(Triphenylarsoranylidene)but-2-enoate and Substituted 2*H*-Pyran-5-carboxylates: the Preparation of Highly Functionalized *trans*-2,3-Divinylcyclopropanecarboxylates

J. Chem. Research (S), 1997, 130–131
J. Chem. Research (M), 1997, 0879–0866

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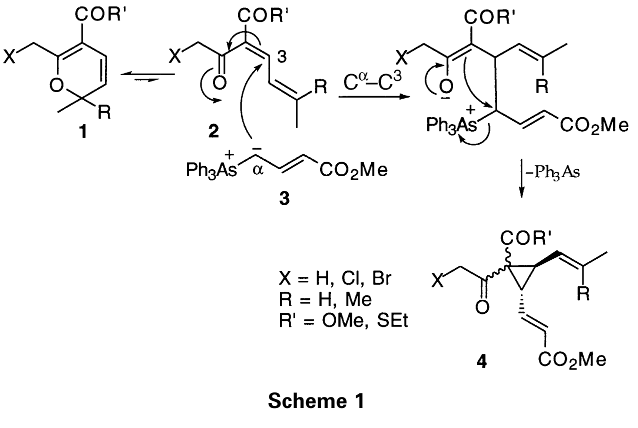
Crotonate arsonium ylide reacted with 2*H*-pyran-5-carboxylates to give divinylcyclopropanecarboxylates.

2*H*-Pyran-2-carboxylates **1**[3] have the unique character to undergo reversible electrocyclic ring opening to the keto-diene **2**,[5] making these compounds available for Michael attack (Scheme 1). In this paper we have investigated novel reactions of substituted 2*H*-pyran-5-carboxylates **1** and methyl 4-(triphenylarsoranylidene)but-2-enoate **3**.[7]

A C^{α}–C^{3} Michael attack of **3** to **2** followed by ring closure and expulsion of triphenylarsine gave mainly highly functionalized *trans*-2,3-divinylcyclopropanecarboxylates **4** (Scheme 1). Likewise, 2*H*-pyran-5-carboxylates **1b** and **1c** gave a mixture of diastereomeric *trans*-2,3-divinylcyclopropanecarboxylates **4b** and **4c**.

Table Products arising from reactions of 2*H*-pyran-5-carboxylates **1** with methyl 4-(triphenylarsoranylidene)-but-2-enoate **3**

2*H*-Pyran-5-carboxylate				Product yields (%)		
1	X	R	R′	**4**	**6**	**7**
a	H	Me	OMe	71	3	
b	Cl	Me	OMe	33	—	
c	H	Me	SEt	35	12	
d	H	H	OMe	47	2	9
e	Cl	H	OMe	24	—	8
f	Br	Me	OMe	2	—	

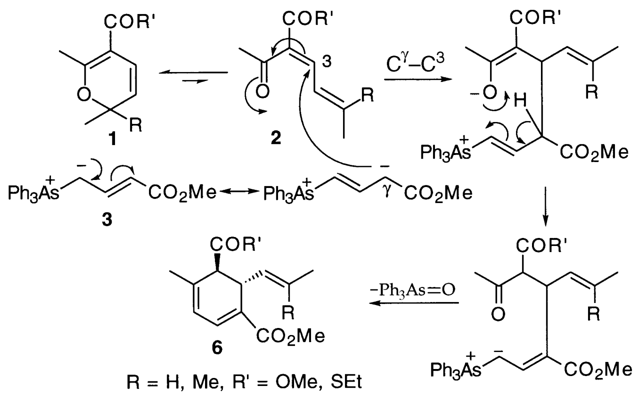


Scheme 1

Cyclopropanation from conjugated carbonyl compounds with arsonium ylides is known.[14] Vinylcyclopropanation from conjugated carbonyl compounds and arsonium ylides is less common.[16]

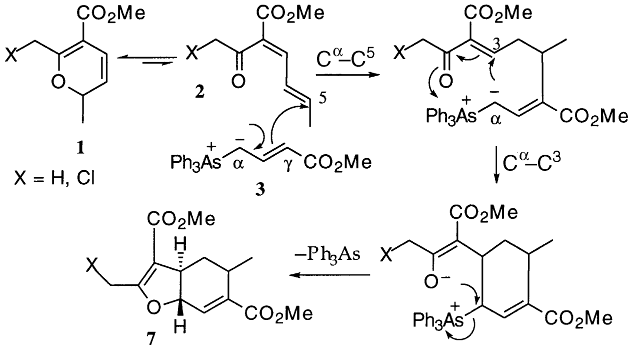
Both *trans*- and *cis*-2,3-divinylcyclopropanecarboxylates **4** show large vicinal coupling constants.[21] $J_{vic(trans)}$ was in the range 7.0–7.9 Hz, and $J_{vic(cis)}$ between 8.6 and 9.3 Hz.

Apart from a diastereomeric mixture of cyclopropanes **4c**, the reaction of **3** and **1c** gave cyclohexa-3,5-diene-1,3-dicarboxylate **6c**. A C^{γ}–C^{3}-Michael attack of the γ-ylide of **3** on **2c** followed by an intramolecular Wittig condensation gave **6c** (Scheme 2).[2,22]



Scheme 2

The 2*H*-pyrans **1d** and **1e** reacted with **3** and gave, apart from the expected mixture of diastereomeric *trans*-cyclopropanecarboxylates **4d** and **4e**, the *trans*-fused tetrahydrobenzofurans **7d** and **7e** respectively.



Scheme 3

This is the result of an initial C^{γ}–C^{5} Michael addition as illustrated (Scheme 3). Then an intramolecular C^{α}–C^{3} nucleophilic attack of the new intermediate arsonium ylide occurs. This is followed by an attack of the enolate oxygen on C^{α} with the simultaneous expulsion of triphenylarsine to give the tetrahydrobenzofuran **7**. The formation of dihydrofuran compounds is rare in arsonium ylide chemistry.[25]

Techniques used: ^{1}H NMR, ^{13}C NMR, CI HRMS, IR, UV

References: 25

Schemes: 6

Received, 14th November 1996; Accepted, 14th January 1997
Paper E/6/07733A

References cited in this synopsis

2 C. M. Moorhoff, Ph.D. Thesis, University of Stellenbosch, 1986.

3 Zh. A. Krasnaya, E. P. Prokof'ev, V. F. Kucherov and M. Sh. Zaripova, *Izv. Akad. Nauk. SSSR, Ser. Khim*., 1973, **10**, 2356 (*Chem. Abstr*., 1974, **80**, 47772v).

5 T. A. Gosink, *J. Org. Chem*., 1974, **39**, 1942.

7 Y.-Z. Huang, Y.-C. Shen, J. Zheng and S. Zhang, *Synthesis*, 1985, 57.

14 Y.-Z. Huang, Y.-C. Shen, Y.-K. Xin and J.-J. Ma, *Sci. Sin. (Engl. Ed.)*, 1980, **23**, 1396.

16 Y. Shen and Y. Xiang, *J. Chem. Res. (S)*, 1994, 198.

21 (*a*) Y. Tang, Z.-F. Chi, Y.-Z. Huang, L.-X. Dai and Y.-H. Yu, *Tetrahedron*, 1996, **52**, 8747.

22 For the phosphonium analogue, see: F. Bohlmann and C. Zdero, *Chem. Ber*., 1973, **106**, 3779.

25 V. G. Kharitonov, V. A. Nikanorov, S. V. Sergeev, M. V. Galakhov, S. O. Yakushin, V. V. Mikul'shina, V. I. Rozenberg and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, 1991, 319 (*Chem. Abstr*., 1992, **116**, 83474v).