

Vinyltriphenylphosphonium Salt Mediated One-pot Synthesis of Dialkyl 5-formyl-2H-pyran-2,3-dicarboxylate†

Ahmad Shaabani* and Faizeh Sadeghi Nejat

Chemistry Department, Shahid Beheshti University, PO Box 19395-4716, Tehran, Iran

Protonation of the highly reactive 1:1 intermediates produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates by triformylmethane leads to vinyltriphenylphosphonium salts which undergo an intramolecular Wittig reaction to produce dialkyl 5-formyl-2H-pyran-2,3-dicarboxylates in fairly high yields.

Organic chemists paid little attention to pyrans until 1950, but the number of papers has gradually increased in the past two decades. Many studies have been reported on the synthesis of the 2H-pyran ring structure from acyclic and cyclic precursors.¹⁻³ We wish to report a facile one-pot synthesis of dialkyl 5-formyl-3H-pyran-2,3-dicarboxylates (**4**) using an intramolecular Wittig reaction.⁴⁻⁸

Protonation of the highly reactive 1:1 intermediates produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates (**1**) by triformylmethane leads to vinyltriphenylphosphonium salts (**2**), followed by attack of enolate anion of triformylmethane on the vinyltriphenylphosphonium cation to form the phosphorane (**3**), which undergo an intramolecular Wittig reaction to produce dialkyl 5-formyl-2H-pyran-2,3-dicarboxylates in fairly high yields (Scheme 1).

The structures of compounds **4a-c** were deduced from elemental analysis, ¹H and ¹³C NMR and IR spectra. The mass spectra of these compounds displayed molecular ion peaks at *m/z* 226, 254 and 310, respectively.

The ¹H NMR spectrum of **4a** exhibited six single lines that are readily recognizable as arising from two methyl groups (δ 3.60, 3.86), O-CH (δ 4.50), two olefinic CH (δ 7.57, 7.66) and formyl O=C-H (δ 9.52) protons. The proton decoupled ¹³C NMR spectrum of **4a** displayed 10 distinct resonances, in agreement with the proposed structure.

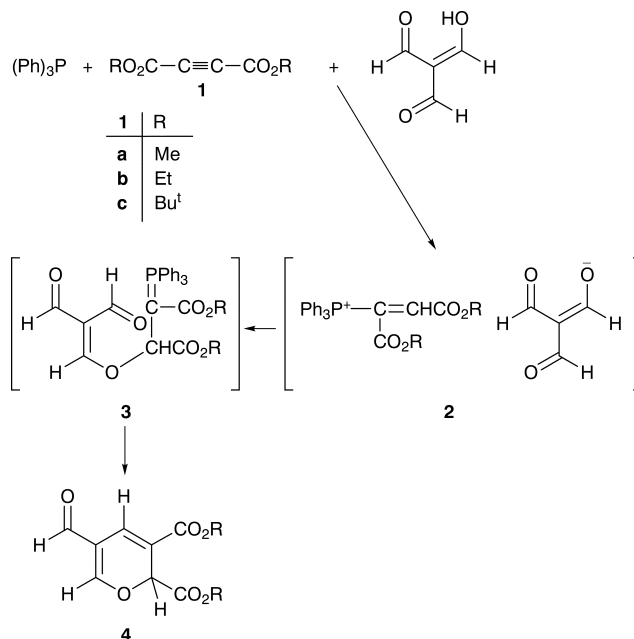
The ¹H and ¹³C NMR spectra of **4b** and **4c** are similar to those of **4a** except for the ester groups, which exhibit characteristic signals with appropriate chemical shifts.

In summary, the major synthetic advantages of this reaction are the mild reaction conditions, the high yield and experimental simplicity.

Experimental

All melting points are uncorrected. Elemental analysis were performed using a Heraeus CHN-O rapid analyser. Mass spectra were recorded on a Finnigan-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were measured on a Shimadzu IR-470 spectrometer. The ¹H and ¹³C NMR spectra were recorded on a JEOL EX-90A spectrometer at 90 and 22.6 MHz, respectively. Triformylmethane was prepared according to published procedures.^{9,10}

Preparation of Dimethyl 5-Formyl-2H-pyran-2,3-dicarboxylate 4a.—To a magnetically stirred solution of triphenylphosphine (0.53 g, 2 mmol) and triformylmethane (0.20 g, 2 mmol) in CH₂Cl₂ (10 ml) was added, dropwise, a mixture of dimethyl acetylenedicarboxylate (245 μ l, 2 mmol) in CH₂Cl₂ (2 ml) at -10 °C over 10 min. The reaction mixture was then allowed to warm up to room temperature and stirred for 24 h. The solvent was removed under reduced pressure and the resultant viscous residue was purified by silica gel (Merck silica gel, 230-400 mesh) column chromatography using



Scheme 1

ethyl acetate-hexane (2:1) as eluent. The solvent was removed under reduced pressure and the product was obtained as white crystals (0.35 g, 77%). Mp 68-70 °C; $\nu_{\max}/\text{cm}^{-1}$ (KBr) 1726 (C=O), 1701 (C=O), 1670 (C=O); δ_{H} (CDCl₃, Me₄Si) 3.60, 3.86 (6 H, s, 2CH₃), 4.50 (1 H, s, HC-O), 7.57 (1 H, s, HC=C), 7.66 (1 H, s, O-HC=C), 9.52 (1 H, s, CHO); δ_{C} (CDCl₃, Me₄Si) 34.49 (C²), 52.16 and 52.81 (2OCH₃), 109.01, 118.50, 149.93, 157.79 (C³, C⁴, C⁵ and C⁶), 165.28 and 171.35 (2C=O), 188.82 (H-C=O); *m/z* 226 (M⁺, 4), 167 (M - CO₂Me, 100%). (Found: C, 53.2; H, 4.3. C₁₀H₁₀O₆ requires C, 53.1; H, 4.5%).

Preparation of Diethyl 5-Formyl-2H-pyran-2,3-dicarboxylate 4b.—Similar reaction conditions as above were employed but using diethyl acetylenedicarboxylate instead of dimethyl acetylenedicarboxylate yielded a yellow oil (0.36 g, 71%). $\nu_{\max}/\text{cm}^{-1}$ (KBr) 1729 (C=O), 1710 (C=O), 1680 (C=O); δ_{H} (CDCl₃, Me₄Si), 1.20 and 1.22 (3 H, s, 2CH₃), 4.10, 4.23 (4 H, m, 2CH₂), 4.40 (1 H, s, O-C-H), 7.42 (1 H, s, H-C=C), 7.60 (1 H, s, C=CH-O), 9.50 (1 H, s, CHO); δ_{C} (CDCl₃, Me₄Si), 14.05 and 14.17 (2CH₃), 34.86 (C²), 61.16 and 61.73 (2CH₂), 109.42, 118.74, 149.65 and 157.79 (C³, C⁴, C⁵ and C⁶), 170.86 and 178.11 (2C=O), 188.82 (H-C=O); *m/z* 254 (M⁺, 5), 181 (M - CO₂Et, 100%). (Found: C, 56.9; H, 5.7. C₁₂H₁₄O₆ requires C, 56.7; H, 5.6%).

Preparation of Di-tert-butyl 5-Formyl-2H-pyran-2,3-dicarboxylate 4c.—Similar reaction conditions as for **4a** but using di-tert-butyl acetylenedicarboxylate yielded white crystals (0.50 g, 80%). Mp 106-109 °C; $\nu_{\max}/\text{cm}^{-1}$ (KBr): 1725 (C=O), 1700 (C=O), 1672 (X=O); δ_{H} (CDCl₃, Me₄Si), 1.43 and 1.50 (18 H, s, 6 CH₃), 4.33 (1 H, s, O-C-H), 7.40 (1 H, s, H-C=C), 7.53 (1 H, s, C=CH-O), 9.50 (1 H, s, H-C=O); δ_{C} (CDCl₃, Me₄Si), 26.75 and 27 (6CH₃ of 2CMe₃), 34.9 (C²), 80.63 (2C of CMe₃), 109.90, 118.05, 147.73 and 156.45 (C³, C⁴, C⁵ and C⁶), 162.88, 168.79 (2C=O), 187.56 (H-C=O); *m/z* 310 (M⁺, 2), 209 (M - CO₂CMe₃, 12.5), 57 (Bu^t, 100%). (Found: C, 62.0; H, 7.4. C₁₆H₂₂O₆ requires C, 61.9; H, 7.1%).

*To receive any correspondence.

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