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Vinylphosphonium Salt Mediated Stereoselective Synthesis of Cyclobutene Derivatives . A Facile Route to Highly Electron-Deficient 1,3-Dienes

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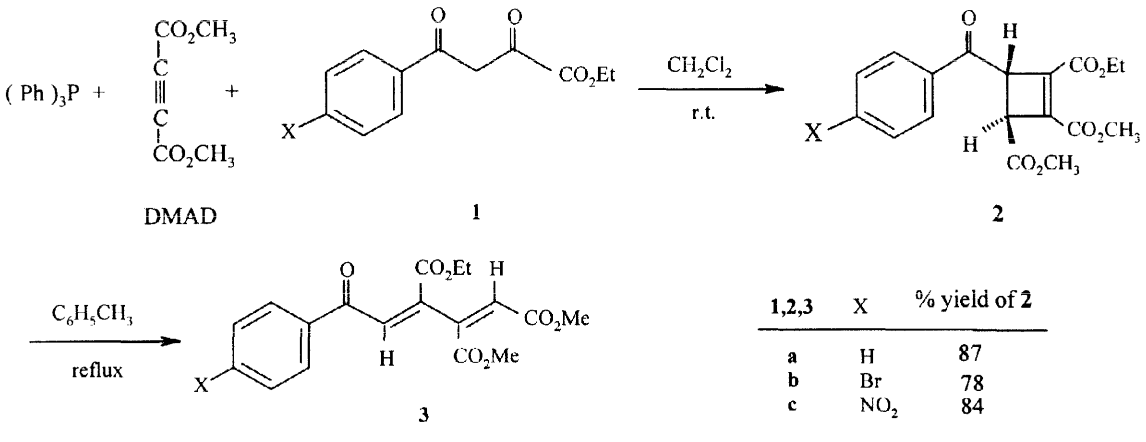
Abstract: Ethyl 4-aryl-2,4-dioxobutanoates undergo stereoselective intramolecular Wittig reaction with a vinyltriphenylphosphonium salt to yield cyclobutene derivatives, which undergo electrocyclic ring-opening reactions in boiling toluene to produce highly electron-deficient 1,3-dienes. © 1998 Elsevier Science Ltd. All rights reserved.

The intramolecular Wittig reaction has become one of the favourites among the numerous methods of cycloalkene syntheses.[1] Although the common 5-, 6-, and 7-membered ring cycloalkenes are produced fairly easily by intramolecular Wittig reaction, the formation of cyclopropenes and cyclobutenes have not received considerable attention.[2]

As part of our current studies on the development of new routes to carbocyclic and heterocyclic systems,[3] we thought that an easy approach to vinyltriphenylphosphonium salts could represent practical route to functionalized cyclobutenes *via* an intramolecular Wittig reaction. We now report a facile one-pot synthesis of trialkyl 3-aroyl-cyclobutene-1,2,4-tricarboxylates **2** in fairly high yields. Compounds **2a-c** undergo electrocyclic ring-opening reactions in boiling toluene to produce electron-deficient 1,3-dienes **3a-c** in quantitative yields.



DMAD 1 2

3

1,2,3	X	% yield of 2
a	H	87
b	Br	78
c	NO$_2$	84

Ethyl 4-aryl-2,4-dioxobutanoates **1**,[4] DMAD and triphenylphosphine undergo a smooth reaction in dichloromethane at room temperature to produce the cyclobutene derivatives **2** and triphenylphosphine oxide.[5] Compounds **2a-c** are stable crystalline products which are converted to the corresponding but-1,3-diene derivatives **3a-c** in nearly quantitative yields.[5] The cyclobutene derivative **2** may be regarded as a product of an intramolecular Wittig reaction. Such addition-cyclization products apparently result from initial addition of

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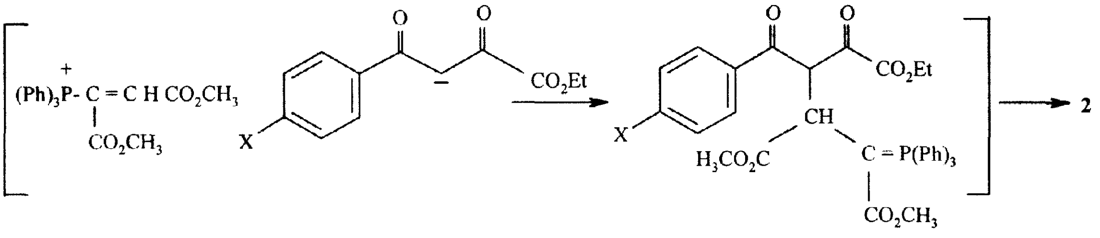
triphenylphosphine to the acetylenic ester and concomitant protonation of the 1:1 adduct, followed by attack of the anion of **1** to vinyltriphenylphosphonium cation to form a phosphorane **4**, which is converted to strained carbocyclic ring system **2**.



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Structure **2** was assigned to the isolated products on the basis of their elemental analyses and IR, ^{1}H NMR, ^{13}C NMR and mass spectral data.[6] The ^{1}H NMR spectra of compounds **2a-c** displayed signals for vicinal methine protons at $\delta = 3.9$ and 4.8, which appear as doublets with $^3J_{HH}$ value of 1.2 Hz. The torsion angle in cyclobutene derivatives are known. Typically, J_{cis} varies between 3 and 5 Hz and J_{trans} between 0.5 and 1.5 Hz.[7] Observation of $J_{HH} = 1.2$ Hz for the vicinal protons in **2** indicates a trans arrangement for these protons. The ^{13}C NMR spectrum of each of the isolated products **2a-c** exhibited sixteen resonances in agreement with the cyclobutene structure. The ^{1}H and ^{13}C NMR spectra of **3a-c** are similar to those of **2a-c**, except for the methine group, which displayed characteristic resonances of olefinic CH moieties at $\delta = 6.3$-7.1.

References and Notes

1. Becker, K. B. *Tetrahedron*, **1980**, *36*, 1717; Vollhardt, K. P. C. *Synthesis*, **1975**, 765.
2. Patai, S. (ed.), "The Chemistry of Alkenes", **1964**, Wiley, New York.
3. Yavari, I. and Baharfar, R. *Tetrahedron Lett.*, **1997**, *38*, 4259; *J. Chem. Res.(S)*, **1997**, 146.
4. Compounds **1a-c** were prepared from diethyl oxalate and the corresponding acetophenones by known methods (Shick, H. and Eichhorn, I. *Synthsis*, **1989**, 477) and identified by ^{1}H and ^{13}C NMR spectroscopy.
5. The typical process for the preparation of dimethyl (*Z*,*Z*)-4-benzoyl-3-ethoxycarbonyl-but-1,3-diene-1,2-dicarboxylate **3a**: to a magnetically stirred solution of ethyl 4-phenyl-2,4-dioxo-butanoate (0.22g, 1mmol) and triphenylphosphine (0.26g, 1mmol) in CH_2Cl_2 (8ml) was added dropwise a mixture of DMAD (0.142g, 1mmol) in CH_2Cl_2 (4ml) at -5 °C over 10 min.. The mixture was allowed to warm to room temperature and stirred for 24 hr. The solvent was removed under reduced pressure and the residue was purified by silica gel (Merck silica gel 60, 230-400 mesh) column chromatography using hexane-ethyl acetate as eluent. The solvent was removed under reduced pressure to afford dimethyl 4-benzoyl-1-ethoxycarbonylcyclobut-1-ene-2,3-dicarboxylate (**2a**) as yellow powder, 0.30g, 87%, m.p. 61-64 °C. Selected data for **2b**: yellow powder, 0.32g, 76%, m.p. 83-85°C; **2c**: light yellow oil, 0.32g, 84%. A solution of **2a** in toluene was refluxed for 6 hr to afford quantitatively **3a**: light brown powder, 0.30g, m. p. 68-70°C; **3b**: dark yellow powder, 0.32g, m.p. 88-90°C; **3c**: light brown oil, 0.32g.
6. Analytical and spectroscopic data for compounds **2** and **3** are in agreement with the proposed structures.
7. Gunther, H. "NMR Spectroscopy", 2nd ed., **1995**, Wiley, New York, chapter 4.