

Syntheses of Cyclopropanes and Dihydrofurans from α -Chlorovinyl Sulphones

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Reactions of α -chlorovinyl sulphones (**1a** and **b**) with the monosodium salt of diethyl malonate gave cyclopropanes (**2a** and **b**) in good yield. In contrast, 4,5-dihydrofuran-3-carboxylates (**3a** and **b**) were obtained in the reaction of compounds (**1a** and **b**) with the monosodium salt of ethyl acetoacetate. The formation mechanisms of these compounds are discussed.

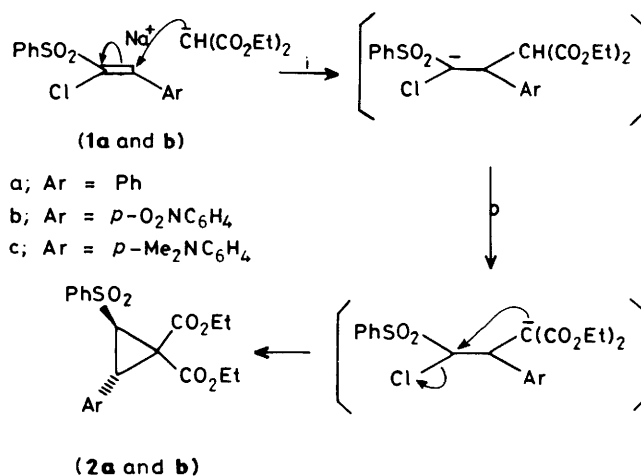
The utilisation of vinyl sulphones as dienophiles,¹ Michael acceptors,² and precursors of vinyl anions³ has been shown in the literature and, as a consequence of their importance, many methods have been devised for their preparation,⁴ but only a few reports of the syntheses and reactions of α -halogenovinyl sulphones are to be found.⁵ In our preliminary communication,⁶ we reported a synthesis of α -chlorovinyl sulphones from the Horner–Wittig reaction of diethyl chloro-(phenylsulphonyl)methylphosphonate with aromatic aldehydes. In this paper, we report some convenient syntheses of cyclopropanes and 4,5-dihydrofuran-3-carboxylates from α -chlorovinyl sulphones.

Results and Discussion

Reaction of sulphone (**1a**) with the sodium salt of diethyl malonate in tetrahydrofuran (THF) did not give a simple Michael adduct, but instead gave a cyclopropane derivative, (**2a**), in 93% yield. The product (**2a**) showed a strong ester carbonyl stretching band at 1740 cm^{-1} in its i.r. spectrum, and a singlet at δ_{H} 3.86, due to two protons of the cyclopropane ring, in its ^1H n.m.r. spectrum. The ^{13}C n.m.r. data were also in accord with this structure. Furthermore, an X-ray crystal structure analysis showed that the phenylsulphonyl and phenyl groups are *trans* to each other (Figure 1). On using the *p*-nitrophenyl compound (**1b**) instead of (**1a**), the corresponding cyclopropane (**2b**) was obtained in 96% yield, but no reaction occurred when the *p*-dimethylaminophenyl reagent (**1c**) was used as an electrophile. Based on these results, the cyclopropanes (**2a** and **b**) can be assumed to arise from the nucleophilic Michael attack of the anion of diethyl malonate, followed by (1,3)-migration of a proton, and cyclization together with elimination of chloride anion as illustrated in Scheme 1. In the case of the *p*-dimethylamino compound (**1c**), the *p*-dimethylamino substituent would increase the electron density of the Michael acceptor, so that attack of the nucleophile would be inhibited.

On the other hand, the reaction of compounds (**1a** and **b**) with ethyl acetoacetate in the presence of sodium hydride in refluxing dioxane gave 4,5-dihydrofuran-3-carboxylates (**3a** and **b**), not cyclopropanes. In the reaction of the *p*-dimethylamino compound (**1c**), only starting material was recovered. The structures of compounds (**3a** and **b**) were confirmed by spectral data and microanalysis as well as X-ray crystallographic analysis (Figure 2). The X-ray analysis showed that the geometry between the phenylsulphonyl and aryl groups was again *trans*.

A plausible pathway for the formation of compounds (**3a** and **b**) is shown in Scheme 2, *i.e.* an initial nucleophilic attack of ethyl acetoacetate to vinyl sulphone (**1a** or **b**) and subsequent



Scheme 1. Reagents and conditions: i, $\text{Na}^+\text{CH}(\text{CO}_2\text{Et})_2^-$, THF, reflux

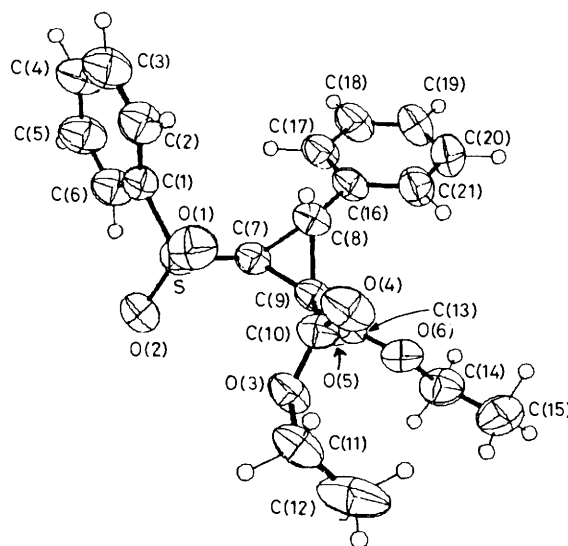


Figure 1. Perspective view of compound (**2a**) with hydrogen atoms drawn as circles with arbitrary radius

(1,3)-proton migration in intermediate (**4**) would occur to form a second intermediate (**5**) in the same manner as in the formation of compounds (**2a** and **b**), followed by a cyclization at the carbonyl oxygen with concomitant elimination of chloride ion.

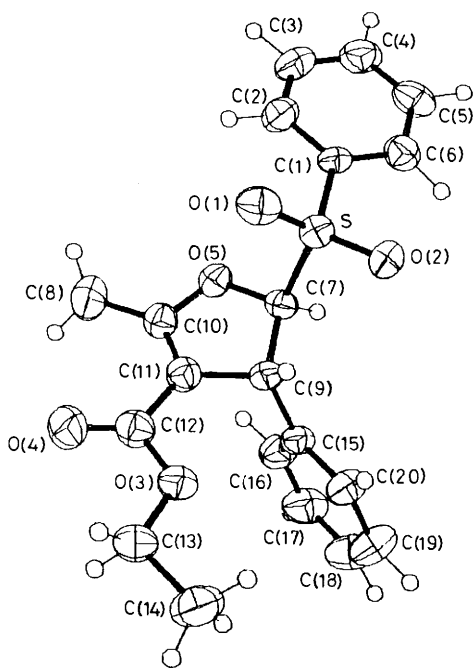
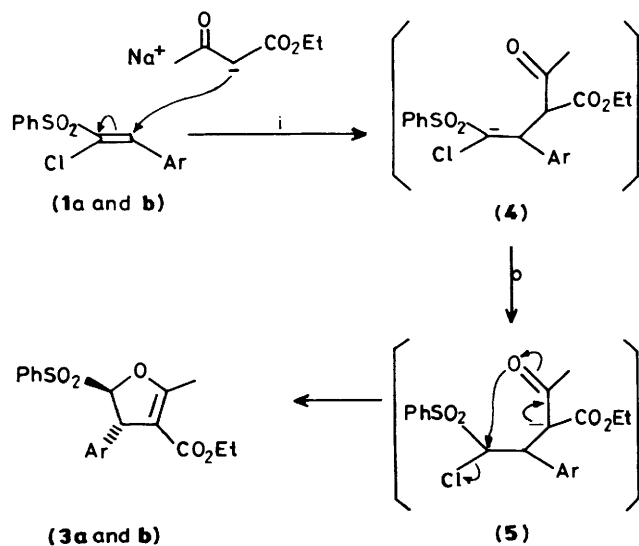


Figure 2. Perspective view of compound (3a) with hydrogen atoms drawn as circles with arbitrary radius



Scheme 2. Reagent: i, $\text{Na}^+ \text{CH}_3\text{COCHCO}_2\text{Et}$, dioxane

Experimental

Diethyl trans-2-Phenyl-3-phenylsulphonylcyclopropane-1,1-dicarboxylate (2a).—A solution of diethyl malonate (2.9 g, 18 mmol) in THF (50 ml) was added to a suspension of NaH (60% oil; 1.0 g, 25 mmol) in THF (50 ml) at room temperature under nitrogen, then a solution of the chloride (1a) (5.0 g, 18 mmol) in THF (30 ml) was added, and the mixture was refluxed for 3.5 h. After being cooled and subjected to aqueous work-up, the mixture was extracted with ether. The extract was washed with brine, dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure to give the cyclopropane (2a) (6.7 g, 93%), m.p. 86.5–87.5 °C; ν_{max} (KBr) 1740 cm^{-1} ; δ_{H} (CDCl_3) 0.93 (3 H, t, CH_3), 1.33 (3 H, t, CH_3), 3.86 (2 H, s, cyclopropane protons), 3.88 (2 H, q, CH_2), 4.32 (2 H, q, CH_2), and 6.83–8.16 (10 H, m,

Table 1. Fractional atomic co-ordinates of (2a) for non-hydrogen atoms with standard deviations in parentheses.

	x	y	z
S	0.495 0(1)	0.054 9(1)	0.266 9(1)
O(1)	0.488 6(4)	0.136 9(5)	0.124 2(4)
O(2)	0.428 0(3)	0.144 8(4)	0.351 4(4)
O(3)	0.664 5(3)	0.319 0(4)	0.165 3(3)
O(4)	0.737 9(4)	0.222 1(4)	0.001 8(3)
O(5)	0.867 0(4)	-0.066 0(4)	0.426 4(3)
O(6)	0.935 0(3)	0.087 0(4)	0.231 6(3)
C(1)	0.440 7(4)	-0.107 3(6)	0.316 0(5)
C(2)	0.428 8(5)	-0.152 7(7)	0.219 6(5)
C(3)	0.379 5(6)	-0.273 6(8)	0.259 0(6)
C(4)	0.348 1(6)	-0.347 2(7)	0.390 6(7)
C(5)	0.362 2(6)	-0.301 3(7)	0.485 4(6)
C(6)	0.410 0(5)	-0.181 0(7)	0.449 2(5)
C(7)	0.658 7(4)	-0.042 8(5)	0.305 0(5)
C(8)	0.759 1(5)	-0.103 6(5)	0.206 4(5)
C(9)	0.754 4(4)	0.040 5(5)	0.230 1(4)
C(10)	0.716 8(5)	0.203 5(6)	0.116 4(5)
C(11)	0.640 8(6)	0.485 7(6)	0.069 4(6)
C(12)	0.743 0(8)	0.534 5(8)	0.079 7(8)
C(13)	0.856 2(5)	0.013 0(5)	0.309 8(5)
C(14)	1.043 6(5)	0.072 6(7)	0.291 5(6)
C(15)	1.115 9(6)	0.165 5(9)	0.182 3(8)
C(16)	0.867 0(5)	-0.262 3(6)	0.252 6(5)
C(17)	0.844 3(5)	-0.397 0(6)	0.350 1(5)
C(18)	0.946 6(6)	-0.546 2(6)	0.391 2(6)
C(19)	1.070 1(5)	-0.560 4(6)	0.338 2(6)
C(20)	1.093 9(5)	-0.429 2(7)	0.242 8(6)
C(21)	0.992 2(5)	-0.279 2(6)	0.200 1(5)

Ph); m/z (75 eV) 403 ($M^+ + 1$); δ_{C} (CDCl_3) 13.8 (q), 13.9 (q), 33.9 (d), 44.7 (s), 48.5 (d), 62.5 (t), 62.8 (t), 128.0, 128.5, 128.6, 129.5, 131.8, 132.5, 134.1, 140.2, and 164.4 p.p.m. (s) (Found: C, 62.6; H, 5.9. $\text{C}_{21}\text{H}_{22}\text{O}_6\text{S}$ requires C, 62.7; H, 5.5%).

Similarly, diethyl trans-2-(p-nitrophenyl)-3-phenylsulphonylcyclopropane-1,1-dicarboxylate (2b) was obtained (6.4 g, 96%) from compound (1b) (5.0 g, 15 mmol), NaH (60% oil; 0.8 g, 20 mmol), and diethyl malonate (2.4 g, 15 mmol). Compound (2b) had m.p. 121.5–122.5 °C; ν_{max} 1720 cm^{-1} ; δ_{H} (CDCl_3) 1.00 (3 H, t, CH_3), 1.36 (3 H, t, CH_3), 3.93 (2 H, q, CH_2), 3.96 (2 H, s, cyclopropane protons), 4.36 (2 H, q, CH_2), and 7.06–8.20 (9 H, m, ArH); m/z (75 eV) 448 (M^+); δ_{C} (CDCl_3) 13.7, 33.0, 44.5, 48.3, 62.7, 62.9, 123.5, 127.8, 129.5, 134.3, 139.1, 139.5, 147.7, 163.6, and 163.8 p.p.m. (Found: C, 56.2; H, 4.7; N, 3.0. $\text{C}_{21}\text{H}_{21}\text{NO}_8\text{S}$ requires C, 56.4; H, 4.7; N, 3.1%).

Ethyl-2-Methyl-4-phenyl-5-phenylsulphonyl-4,5-dihydrofuran-3-carboxylate (3a).—A solution of ethyl acetoacetate (2.3 g, 18 mmol) in dioxane (30 ml) was added to a suspension of NaH (60% oil; 1.0 g, 25 mmol) in dioxane (40 ml) at room temperature under nitrogen. Then a solution of compound (1a) (5.0 g, 18 mmol) in dioxane (50 ml) was added dropwise, and the resultant mixture was refluxed for 14 h, followed by aqueous work-up and extraction with ether. The extract was washed with brine, dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure to give the dihydrofuran (3a) (6.7 g, quantitative). Compound (3a) had m.p. 142.5–143.5 °C; ν_{max} (KBr) 1690 and 1650 cm^{-1} ; δ_{H} (CDCl_3) 1.03 (3 H, t, CH_2CH_3), 2.24 (3 H, d, J 1.6 Hz, 2CH_3), 3.96 (2 H, q, CH_2), 4.90 (1 H, dq, J 4 Hz, 1.6 Hz, CHPh), 5.10 (1 H, d, J 4 Hz, CHSO_2Ph), and 7.00–8.10 (10 H, m, Ph); m/z (75 eV) 373 ($M^+ + 1$); δ_{C} (CDCl_3) 13.6 (q, CH_3), 13.9 (q, CH_3), 49.1 (d, CHPh), 59.7 (t, CH_2), 99.9 (d, CHSO_2Ph), 1.08 (s, C=), 127.1, 127.5, 128.8, 129.1, 129.4, 134.4, 135.7, and 140.5 (aromatic carbons), 163.6 (s, C=), and

Table 2. Fractional atomic co-ordinates of (3a) for non-hydrogen atoms with standard deviations in parentheses

	x	y	z
S	0.082 9(1)	0.168 8(2)	0.371 5(1)
O(1)	0.034 2(3)	-0.037 5(5)	0.301 8(4)
O(2)	0.024 6(3)	0.260 7(6)	0.473 4(3)
O(3)	0.268 2(3)	-0.092 8(5)	0.653 0(3)
O(4)	0.333 4(4)	-0.274 2(5)	0.484 7(4)
O(5)	0.300 5(3)	0.148 2(5)	0.346 6(3)
C(1)	0.092 4(4)	0.279 5(7)	0.260 7(4)
C(2)	0.114 4(5)	0.183 0(8)	0.139 9(5)
C(3)	0.120 2(6)	0.267 2(9)	0.053 2(5)
C(4)	0.100 2(5)	0.440 3(9)	0.086 2(6)
C(5)	0.077 7(5)	0.535 1(8)	0.206 6(6)
C(6)	0.074 3(5)	0.453 6(8)	0.297 0(5)
C(7)	0.238 8(4)	0.239 4(7)	0.442 7(4)
C(8)	0.379 6(6)	-0.112 7(9)	0.275 8(6)
C(9)	0.243 6(4)	0.162 6(7)	0.550 0(4)
C(10)	0.322 6(4)	0.003 9(7)	0.373 4(5)
C(11)	0.291 4(4)	0.001 1(7)	0.483 6(5)
C(12)	0.301 2(5)	-0.137 5(7)	0.536 6(5)
C(13)	0.266 0(5)	-0.225 7(8)	0.713 8(6)
C(14)	0.244 4(7)	-0.126 7(10)	0.848 1(6)
C(15)	0.325 8(4)	0.320 1(7)	0.670 7(4)
C(16)	0.446 2(5)	0.415 9(8)	0.667 6(5)
C(17)	0.520 7(5)	0.558 6(9)	0.778 0(6)
C(18)	0.475 5(6)	0.606 1(9)	0.891 9(6)
C(19)	0.355 8(6)	0.509 7(9)	0.895 3(5)
C(20)	0.281 6(5)	0.368 9(8)	0.784 0(5)

166.8 p.p.m. (s, C=O) (Found: C, 64.7; H, 5.5. C₂₀H₂₀O₅S requires C, 64.5; H, 5.4%).

Similarly, ethyl 2-methyl-4-(p-nitrophenyl)-5-phenylsulphonyl-4,5-dihydrofuran-3-carboxylate (3b) was obtained (1.1 g, 85%) from compound (1b) (1.0 g, 3.1 mmol), NaH (60% oil; 0.9 g, 23 mmol), and ethyl acetoacetate (0.4 g, 3.1 mmol), and had m.p. 189.5–190.5 °C; ν_{\max} (KBr) 1690 and 1658 cm⁻¹; δ_{H} (CDCl₃) 1.06 (3 H, t, CH₂CH₃), 2.90 (3 H, d, J 1.6 Hz, 2-CH₃), 3.96 (2 H, q, CH₂), 5.00 (2 H, m, 2 × CH), and 7.06–8.30 (9 H, m, ArH); m/z (75 eV) 417 (M⁺); δ_{C} (CDCl₃) 13.9, 14.0, 49.0, 60.2, 75.2, 99.1, 107.2, 121.7, 124.2, 128.4, 129.4, 129.5, 134.9, 135.5, 147.6, 148.0, 163.4, and 168.0 p.p.m. (Found: C, 57.4; H, 4.5; N, 3.2. C₂₀H₁₉NO₇S requires C, 57.6; H, 4.6; N, 3.4%).

Crystal Data.—Compound (2a); C₂₁H₂₂O₆S, $M = 402.5$, triclinic, space group $P\bar{1}$, $a = 11.402(8)$, $b = 9.870(6)$, $c = 11.198(7)$ Å, $\alpha = 64.65(4)$, $\beta = 76.95(4)$, $\gamma = 65.22(4)$; $V = 1032.4$ Å³, $Z = 2$, $D_c = 1.29$ g cm⁻³. Compound (3a); C₂₀H₂₀O₅S, $M = 372.4$, triclinic, space group $P\bar{1}$, $a = 11.783(7)$, $b = 7.939(5)$, $c = 11.441(6)$ Å, $\alpha = 111.65(4)$, $\beta = 91.56(4)$; $\gamma = 108.00(4)^\circ$, $V = 933.9$ Å³, $Z = 2$, $D_c = 1.32$ g cm⁻³.

Crystallographic Measurements.—The diffraction data for each crystal were measured at room temperature on a microcomputer-controlled four-circle diffractometer.⁷ The unit-cell constants were derived from a least-squares fit to the observed Bragg angles. The intensities were measured up to

* For details of the Supplementary Publications Scheme see Instructions for Authors (1985), *J. Chem. Soc., Perkin Trans. 1*, 1985, issue 1.

$2\theta = 120^\circ$ by a θ – 2θ scan technique using Ni-filtered Cu-K α radiation. Backgrounds were counted for 5 s on both sides of the scan range. The reflections whose intensities were greater than $2\sigma(I)$ were used for subsequent calculations. Periodically monitored reflections showed no significant change in intensity. The intensities were corrected for Lorentz and polarization factors.

Structure Determination.—Both structures were determined by the heavy-atom method. The positional and anisotropic temperature factors for non-hydrogen atoms were refined by the block-diagonal least-squares method.⁸ All hydrogen atoms were located in the difference Fourier synthesis, and included in the successive refinements with isotropic temperature factors. Extinction corrections were made for seven reflections for compound (2a) and six reflections for compound (3a). Unit weight was given to all reflections. The final R values were 0.071 for 2 586 significant reflections for compound (2a), and 0.074 for 2 512 significant reflections for compound (3a). The atomic scattering factors were taken from the International Tables for X-ray Crystallography.⁹ Perspective views of the molecules drawn by DCMS3¹⁰ are shown as Figures 1 and 2. Atomic co-ordinates are given in Tables 1 and 2.

Tables of bond lengths and angles, atomic parameters of hydrogen atoms, and anisotropic temperature factors for non-hydrogen atoms, are given in Supplementary Publication SUP 56346 (7 pp). * Structure factors are available from the editorial office on request.

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