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Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.044
 wR factor = 0.125
Data-to-parameter ratio = 12.7

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

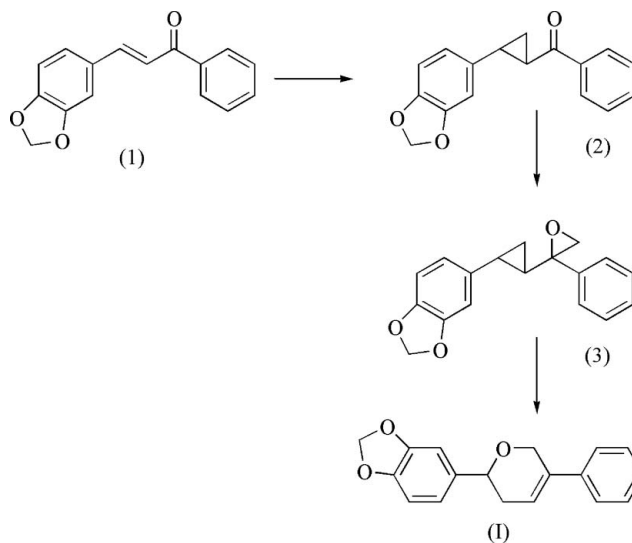
(*RS*)-2-(3,4-Methylenedioxyphenyl)-5-phenyl- 3,6-dihydro-2*H*-pyran

The title compound, $\text{C}_{18}\text{H}_{16}\text{O}_3$, crystallizes with one molecule in the asymmetric unit. The conformation of the dihydropyran ring features puckering of the O atom by 0.612 (2) Å from the least-squares plane defined by the five C atoms [maximum deviation 0.1025 (12) Å].

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Comment

The cyclopropanation of chalcones has been widely reported and generates cyclopropyl ketones that have been used as synthetic intermediates and probes for reaction mechanisms (Murphy & Wattanasin, 1981; Tanko & Drumright, 1990). As part of an undergraduate laboratory project, such reactivity of (*E*)-3-(3,4-methylenedioxyphenyl)-1-phenylprop-2-eneone, (1) (Yang *et al.*, 2006; Yathirajan *et al.*, 2006), was examined using the sulfur ylide generated from trimethylsulfoxonium iodide (Corey & Chaykovsky, 1965). However, if the reaction time was extended, a compound other than the cyclopropane, (2), was formed, as has been reported previously (Donnelly *et al.*, 1974). The sulfur ylide is also effective in epoxidizing ketone functional groups and, while this competing reaction is slow compared with cyclopropanation, the initially formed cyclopropyl ketone can react further. This cyclopropyl epoxide, (3), is not stable, and passage through a plug of silica gel results in an acid-catalysed rearrangement to yield the title compound, (I). While (I) has been synthesized previously, only the melting point was reported (see *Experimental*). Here, we report its X-ray crystal structure.



reaction work-up following cyclopropanation of the alkene and epoxidation of the ketone. Selected geometric parameters, describing the ring conformations and the planarity of the non-cyclic conjugated functionalities, are listed in Table 1.

Compound (I) represents the first structurally characterized 2,5-diaryl-substituted 3,6-dihydropyran. The heterocyclic ring conformation features the O atom displaced by 0.612 (2) Å from the otherwise essentially coplanar atoms of the six-membered ring [maximum deviation of 0.1025 (12) Å for atom C4 from the least-squares plane defined by the five C atoms] and is unique amongst the known solely 2,5-disubstituted derivatives. These examples have universally featured saturated C atoms directly bound to the 5-position and a variety of *Csp*²-based substituents in the 2-position. Their conformations appear to favour puckering of the C atom in the 2-position and, to a lesser extent, the O atom on opposite sides of the ring (Puliti *et al.*, 1990; De Rosa *et al.*, 1995; Cheung & Snapper, 2002; Cheung *et al.*, 2004), except for the case of one example where these same two atoms are substantially displaced on the same side of the ring, owing to the macrocyclic ring constraints of the substituents (Alvarez & Delgado, 1988).

Experimental

The synthesis of (I) was carried out as follows. Dimethyl sulfoxide (10 ml) was added dropwise to a mixture of sodium hydride (390 mg of 60% in mineral oil) and trimethylsulfoxonium iodide (2.0 g) under an atmosphere of nitrogen and stirred at 298 K for 20 min. The mixture was cooled to 283 K, compound (1) (1.0 g, 4.0 mmol; Ranu & Jana, 2005) was added in small portions over a period of 5 min, and then the mixture was heated at 323 K for 2 h before stirring overnight at 298 K. The mixture was poured into an ice-water slurry (100 ml) and extracted with ethyl acetate (3 × 20 ml), and the combined organic extracts were dried and evaporated to give an oil. The oily material was passed through a small plug of silica gel, eluted with 10% ethyl acetate/petroleum spirits. A solid precipitated from the eluent, and this was collected and recrystallized from ethyl acetate to yield the pyran, (I), as colourless crystals suitable for X-ray analysis [yield 60%; m.p. 425–427 K; literature value 430–431 K (Donnelly *et al.*, 1974)]. Spectroscopic data are available in the archived CIF.

Crystal data

C ₁₈ H ₁₆ O ₃	<i>V</i> = 685.7 (9) Å ³
<i>M_r</i> = 280.31	<i>Z</i> = 2
Triclinic, <i>P</i> $\bar{1}$	<i>D_x</i> = 1.358 Mg m ⁻³
<i>a</i> = 6.6380 (13) Å	Mo <i>K</i> α radiation
<i>b</i> = 7.911 (10) Å	<i>μ</i> = 0.09 mm ⁻¹
<i>c</i> = 13.498 (5) Å	<i>T</i> = 298 (2) K
<i>α</i> = 81.24 (5)°	Plate, colourless
<i>β</i> = 80.21 (2)°	0.55 × 0.45 × 0.10 mm
<i>γ</i> = 82.05 (4)°	

Data collection

Enraf–Nonius TURBOCAD-4 diffractometer	1932 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>ω</i> / <i>θ</i> scans	<i>R</i> _{int} = 0.019
Absorption correction: none	<i>θ</i> _{max} = 25.1°
2750 measured reflections	3 standard reflections
2413 independent reflections	frequency: 60 min
	intensity decay: 1%

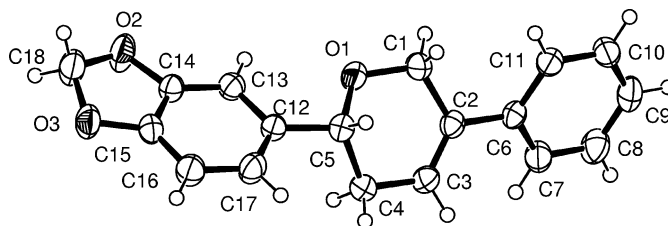


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size.

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0716P)^2 + 0.1555P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.125$	$(\Delta/\sigma)_{\max} < 0.001$
<i>S</i> = 1.06	$\Delta\rho_{\max} = 0.24 \text{ e \AA}^{-3}$
2413 reflections	$\Delta\rho_{\min} = -0.19 \text{ e \AA}^{-3}$
190 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

O1–C5	1.416 (2)	C2–C6	1.477 (2)
O1–C1	1.418 (2)	C3–C4	1.496 (2)
C1–C2	1.508 (2)	C4–C5	1.525 (2)
C2–C3	1.327 (2)		
C5–O1–C1	111.78 (14)	C2–C3–C4	123.14 (16)
O1–C1–C2	113.01 (14)	C3–C4–C5	110.94 (14)
C3–C2–C6	124.15 (15)	O1–C5–C12	108.62 (14)
C3–C2–C1	119.37 (15)	O1–C5–C4	110.16 (14)
C6–C2–C1	116.48 (14)	C12–C5–C4	113.69 (14)
C5–O1–C1–C2	52.1 (2)	C1–O1–C5–C4	–65.77 (19)
O1–C1–C2–C3	–18.6 (2)	C3–C4–C5–O1	44.0 (2)
C1–C2–C3–C4	–0.1 (3)	C3–C2–C6–C7	27.5 (3)
C2–C3–C4–C5	–12.5 (2)	C3–C2–C6–C11	–155.07 (17)

All H atoms were placed in calculated positions and refined using a riding model, with C–H distances constrained to 0.93 (aromatic CH), 0.97 (methylene CH₂) or 0.98 Å (methine CH), and with *U*_{iso}(H) = 1.2*U*_{eq}(carrier C).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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