

3-(1-Chlorovinyl)-2,4,6-trimethoxybenzaldehyde

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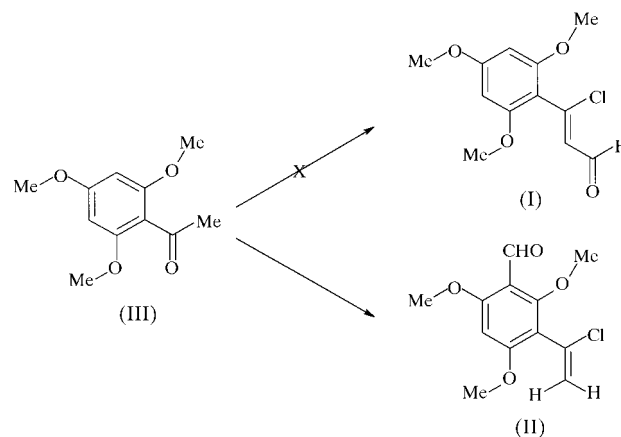
The title compound, C₁₂H₁₃ClO₄, was prepared from the Vilsmeier–Haack reaction on phloracetophenone. The chlorovinyl and one of the methoxy substituents are twisted through about 75° with respect to the aromatic plane, whilst the other substituents are almost coplanar with the ring. Intermolecular hydrogen bonding involving C–H···O interactions generates one-dimensional chains in the direction of the *a* axis.

Comment

The Vilsmeier–Haack reaction, using disubstituted formamide and phosphorous oxychloride, has been extensively employed for the formylation of active aromatic rings yielding arylaldehydes (Minkin & Dorofeenko, 1960), of acetophenones yielding β-chloro-β-arylacroleins (Rosenblum *et al.*, 1966) and of *ortho*-hydroxyacetophenones yielding chromon-3-carboxaldehydes (Nohara *et al.*, 1974). β-Chloro-β-arylacroleins have been a source for arylacetylenes, which are useful for the synthesis of 2-arylbenzofurans (Duffley & Stevenson, 1977). In continuation with our work on the synthesis of nor-neolignans (Parthasarathy & Mohakhud, 1995), we have investigated the formylation of phloracetophenone trimethyl ether, (III). Instead of the expected product, (I), we obtained a colourless crystalline compound, (II), whose ¹H NMR spectrum did not show the expected coupling (*J* = 7 Hz) between the formyl proton and the α-olefinic proton (Parthasarathy & Mohakhud, 1995). Furthermore, the alkaline degradation of (II) to the corresponding arylacetylene was very sluggish and required a higher temperature and a longer reaction period than reported earlier for compounds similar to (I). The resulting product from alkaline degradation of (II) was a yellow crystalline material, containing a carbonyl group, as indicated by IR and ¹³C NMR studies. The question of structural identity of (II) was resolved using single-crystal X-ray diffraction.

The molecular structure of (II) is illustrated in Fig. 1. The bond lengths and angles are largely unremarkable. The methoxy substituents at C4 and C6, together with the aldehyde group at C1, are almost coplanar with the aromatic ring

(the largest torsional deviation being less than 7°). In contrast, the torsion angles C8–O2–C2–C1 [73.4 (2)°] and C4–C3–C9–C11 [75.2 (2)°] (Table 1) illustrate the considerable twisting of the C2 methoxy and chlorovinyl substituents with respect to the aromatic ring.



The intermolecular forces responsible for the integrity of the crystal are of interest. The shortest separation between the centroids of aromatic rings is 4.12 Å and suggests that any intermolecular forces between these rings must be very weak. A detailed analysis of the shortest intermolecular atomic separations suggests that C–H···O hydrogen bonding is likely to provide the major intermolecular forces. The O1···C12(1 + *x*, *y*, *z*) separation of 2.998 (3) Å is about 0.22 Å

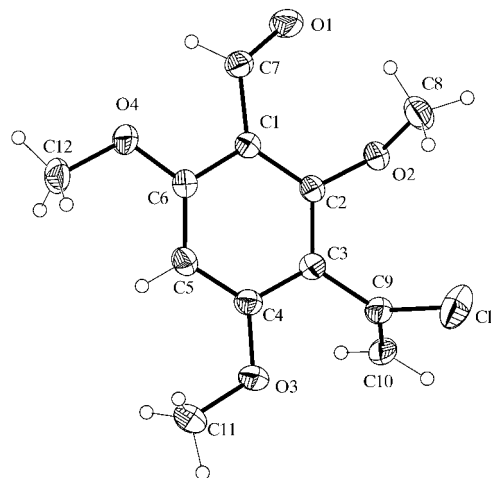


Figure 1

View of a molecule of (II) showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

less than the sum of the van der Waals radii of these two atoms (Bondi, 1964); this suggests a weak C12–H contact to O1 and is consistent with C12 adjoining the electron-withdrawing O4 atom which will impart a fractional positive charge on the C12 H atoms. Since the C12 methyl H atoms were refined as part of a rigid group, the derived C–H···O angle may not provide a reliable hydrogen-bonding parameter. The overall effect of these C–H···O interactions [*i.e.* O1 to C12(1 + *x*, *y*, *z*) and C12 to O1(*x* – 1, *y*, *z*)] is to generate one-dimensional chains in the direction of the *a* axis.

Experimental

POCl₃ (0.3 ml) was added dropwise at 273 K to a shaken flask containing dry *N,N*-dimethylformamide (DMF) (0.3 ml). Phloroacetophenone trimethylether [(III), 0.4 g] in dry DMF (10 ml) was added to the reaction mixture and the contents were heated on an oil bath at 343–353 K for 6 h. The reaction mixture was then cooled to 273 K and a saturated solution of sodium acetate (25 ml) was added slowly with shaking (as the reaction is exothermic). Instantaneous precipitation occurred, the solid was filtered, washed with water and dried to give a brown solid (0.33 g) which was then recrystallized from benzene/petrol to give colourless plates, melting at 388 K. IR (KBr) ν_{\max} : 2944, 1676, 1641, 1589, 1140, 1103 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ (p.p.m.) 3.89 (3H, s), 3.94 (6H, s), 5.38 (1H, s), 5.76 (1H, s), 6.26 (1H, s), 10.32 (1H, s); ¹³C NMR (75.4 MHz, CDCl₃): δ (p.p.m.) 56.1 (*q*), 63.2 (*q*), 90.7 (*d*), 112.2 (*s*), 117.5 (*s*), 119.7 (*t*), 130.7 (*s*), 162.1 (*s*), 163.1 (*s*), 164.1 (*s*), 187.4 (*d*); ESMS (*m/z*, relative intensity): 257/259 (*M*⁺ + 1, 35/13), 243 (30.5), 227 (2), 222 (11), 221 (100), 206 (2), 193 (3), 178 (1), 165 (6), 161 (2.5), 122 (1.5), 105 (1).

Crystal data

C ₁₂ H ₁₃ ClO ₄	<i>Z</i> = 2
<i>M_r</i> = 256.67	<i>D_x</i> = 1.424 Mg m ⁻³
Triclinic, <i>P</i> 1	Mo <i>K</i> α radiation
<i>a</i> = 8.0516 (12) Å	Cell parameters from 2942 reflections
<i>b</i> = 8.1214 (12) Å	θ = 2.06–28.46°
<i>c</i> = 9.9064 (15) Å	μ = 0.319 mm ⁻¹
α = 88.427 (4)°	<i>T</i> = 180 (2) K
β = 86.171 (4)°	Block, colourless
γ = 67.868 (3)°	0.48 × 0.28 × 0.26 mm
<i>V</i> = 598.71 (15) Å ³	

Data collection

Siemens SMART CCD area-detector diffractometer	2267 reflections with <i>I</i> > 2 σ (<i>I</i>)
ω scans	<i>R</i> _{int} = 0.029
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 1996)	θ_{\max} = 27.00°
<i>T</i> _{min} = 0.862, <i>T</i> _{max} = 0.922	<i>h</i> = -7 → 10
3564 measured reflections	<i>k</i> = -9 → 10
2478 independent reflections	<i>l</i> = -12 → 11
	Intensity decay: none

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0703P)^2 + 0.3956P]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.137$	$(\Delta/\sigma)_{\max} < 0.001$
<i>S</i> = 1.102	$\Delta\rho_{\max} = 0.47 \text{ e } \text{Å}^{-3}$
2478 reflections	$\Delta\rho_{\min} = -0.71 \text{ e } \text{Å}^{-3}$
157 parameters	
H-atom parameters constrained	

Table 1

Selected torsion angles (°).

C8–O2–C2–C1	73.4 (2)	C2–C1–C7–O1	-5.8 (3)
C11–O3–C4–C5	0.6 (3)	C2–C3–C9–Cl1	75.2 (2)
C12–O4–C6–C5	-6.6 (3)		

Table 2

Short-contact geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
Cl2–H12B...O1 ⁱ	0.98	2.48	2.998 (3)	113

Symmetry code: (i) *x* – 1, *y*, *z*.

H atoms were added at calculated positions and refined using a riding model. H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameters of their parent atoms and C–H distances were restrained to 0.95 Å for those bonded to C5, C7 and C10, and 0.98 Å for the remainder.

Data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1428). Services for accessing these data are described at the back of the journal.

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