

Adailton J. Bortoluzzi,* Luciano
Fernandes and Marcus M. SáDepartamento de Química – UFSC, 88040-900
Florianópolis, SC, Brazil

Correspondence e-mail: adajb@qmc.ufsc.br

Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
 R factor = 0.039
 wR factor = 0.111
Data-to-parameter ratio = 14.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Methyl (Z)-2-(bromomethyl)-3-(3,4-methylene-
dioxylphenyl)prop-2-enoate

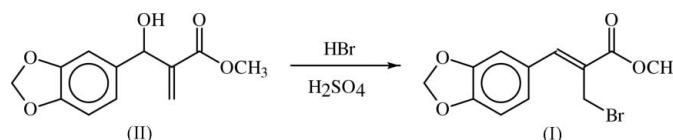
The title compound, $\text{C}_{12}\text{H}_{11}\text{BrO}_4$, is an allylic bromide, which is an interesting precursor in organic synthesis. The skeleton of the molecule is nearly planar, indicating delocalization. The crystal packing is governed by $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, with the molecules stacked along the [100] and [010] directions.

Received 26 May 2006

Accepted 12 July 2006

Comment

Multifunctional allylic bromides such as the title compound, (I), are versatile building blocks for the stereoselective construction of natural products and heterocycles of biological relevance (Drewes & Emslie, 1982; Hoffmann & Rabe, 1985; Cheskis *et al.*, 1990; Roush & Brown, 1993; Basavaiah & Hyma, 1996; Grassi *et al.*, 1997; Mateus *et al.*, 2001; Fernandes *et al.*, 2004). Preparation of allylic bromide (I) can be achieved in good yield and excellent stereoselectivity by treating the corresponding α -methylene- β -hydroxy ester (II) (a Baylis–Hillman adduct) (Basavaiah *et al.*, 2003; Ciganek, 1997; Sá, 2003; Hoffmann & Buchholz, 1991) with a combination of HBr and H_2SO_4 , as previously reported (Fernandes *et al.*, 2004). Careful crystallization from hexane–ethyl acetate (9:1) furnished colourless crystals (m.p. = 343–344 K), allowing structural elucidation by X-ray crystallographic techniques.



The benzo[1,3]dioxole unit is nearly planar, whereas the five-membered [1,3]dioxole ring is slightly envelope shaped, with atom C11 lying 0.129 (6) Å out of the mean plane of all five atoms. The propenoate group C7/C8/C9/O3/O4 is also nearly planar (r.m.s. deviation = 0.043 Å), with a C1–C7–C8–C9 torsion angle of 178.6 (4)°. The dihedral angle between the aromatic ring and the plane of the propenoate group [6.1 (2)°] and the torsion angle C2–C1–C7–C8 [168.3 (4)°] indicate that there is electron delocalization in the skeleton of (I). An intramolecular $\text{C}-\text{H}\cdots\text{O}$ interaction (Table 1) contributes to the planarity of the molecular skeleton. Bond lengths and angles are as expected.

The packing arrangement of (I) is mainly governed by $\text{C}-\text{H}\cdots\text{O}$ weak interactions (Table 1), with the molecules stacked along the [100] and [010] directions (Fig. 2).

Experimental

The title compound was synthesized according to the method of Fernandes *et al.* (2004).

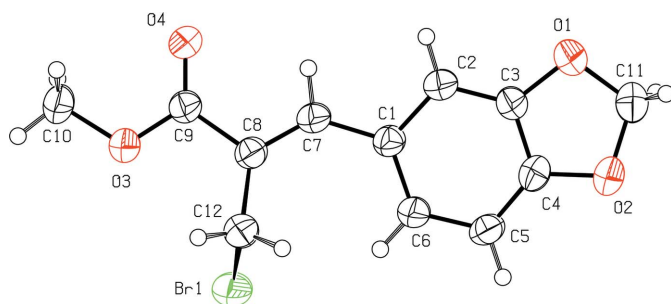


Figure 1
The molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level.

Crystal data

$C_{12}H_{11}BrO_4$ $V = 584.5 (3) \text{ \AA}^3$
 $M_r = 299.12$ $Z = 2$
 Triclinic, $P\bar{1}$ $D_x = 1.699 \text{ Mg m}^{-3}$
 $a = 6.725 (3) \text{ \AA}$ $\text{Mo K}\alpha$ radiation
 $b = 8.845 (2) \text{ \AA}$ $\mu = 3.52 \text{ mm}^{-1}$
 $c = 9.941 (1) \text{ \AA}$ $T = 293 (2) \text{ K}$
 $\alpha = 91.41 (2)^\circ$ Irregular block, colourless
 $\beta = 90.98 (2)^\circ$ $0.50 \times 0.47 \times 0.43 \text{ mm}$
 $\gamma = 98.49 (2)^\circ$

Data collection

Enraf–Nonius CAD-4 diffractometer 2166 independent reflections
 ω - 2θ scans 1691 reflections with $I > 2\sigma(I)$
 Absorption correction: ψ scan $R_{\text{int}} = 0.018$
 (North *et al.*, 1968) $\theta_{\text{max}} = 25.5^\circ$
 $T_{\text{min}} = 0.200$, $T_{\text{max}} = 0.225$ 3 standard reflections
 2567 measured reflections every 200 reflections
 intensity decay: 1%

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 0.5446P]$
 $R[F^2 > 2\sigma(F^2)] = 0.039$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.111$ $(\Delta/\sigma)_{\text{max}} = 0.001$
 $S = 1.05$ $\Delta\rho_{\text{max}} = 0.99 \text{ e \AA}^{-3}$
 2166 reflections $\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$
 155 parameters
 H-atom parameters constrained

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C7-H7\cdots O4$	0.93	2.33	2.756 (5)	108
$C2-H2\cdots O4^i$	0.93	2.44	3.318 (5)	158
$C11-H11A\cdots O4^{ii}$	0.97	2.50	3.300 (6)	140
$C10-H10B\cdots O1^{iii}$	0.96	2.52	3.334 (5)	143
$C12-H12A\cdots O2^{iv}$	0.97	2.58	3.458 (5)	150

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $x - 1, y + 1, z$; (iv) $-x + 2, -y + 1, -z + 2$.

H atoms were placed in calculated positions and refined as riding, with $C-H = 0.93-0.96 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ or $1.5U_{\text{eq}}(\text{methyl } C)$. The highest residual peak is located 1.10 \AA from the Br atom.

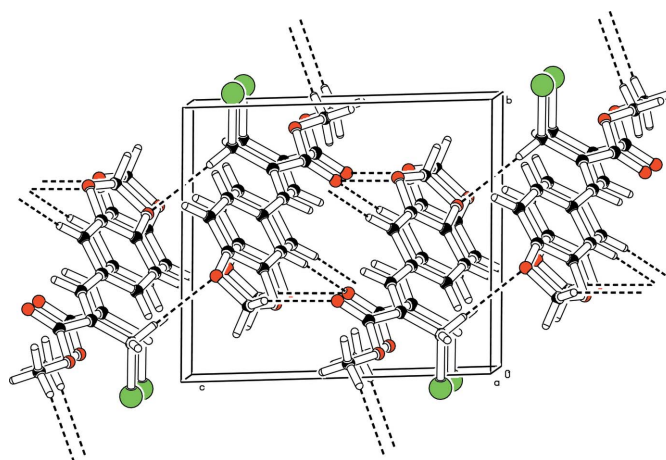


Figure 2
A view along the a axis of the partial packing of the title compound, showing the intermolecular hydrogen bonds (dashed lines).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *SET4* in *CAD-4 EXPRESS*; data reduction: *HELENA* (Spek, 1996); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

We are indebted to FAPESC, CAPES, CNPq and FINEP for financial support of this work.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
 Basavaiah, D. & Hyma, R. S. (1996). *Tetrahedron*, **52**, 1253–1258.
 Basavaiah, D., Rao, A. J. & Satyanarayana, T. (2003). *Chem. Rev.* **103**, 811–891.
 Cheskis, B. A., Moiseenkov, A. M., Shpiro, N. A., Stashina, G. A. & Zhulin, V. M. (1990). *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)*, **39**, 716–720.
 Ciganek, E. (1997). *Org. React.* **51**, 201–350.
 Drewes, S. E. & Emslie, N. D. (1982). *J. Chem. Soc. Perkin Trans. 1*, pp. 2079–2083.
 Enraf–Nonius (1994). *CAD-4 EXPRESS*, Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
 Fernandes, L., Bortoluzzi, A. J. & Sá, M. M. (2004). *Tetrahedron*, **60**, 9983–9989.
 Grassi, D., Lippuner, V., Aebi, M., Brunner, J. & Vasella, A. (1997). *J. Am. Chem. Soc.* **119**, 10992–10999.
 Hoffmann, H. M. R. & Buchholz, R. (1991). *Helv. Chim. Acta*, **74**, 1213–1221.
 Hoffmann, H. M. R. & Rabe, J. (1985). *J. Org. Chem.* **50**, 3849–3859.
 Mateus, C. R., Feltrin, M. P., Costa, A. M., Coelho, F. & Almeida, W. P. (2001). *Tetrahedron*, **57**, 6901–6908.
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 Roush, W. R. & Brown, B. B. (1993). *J. Org. Chem.* **58**, 2151–2161.
 Sá, M. M. (2003). *J. Braz. Chem. Soc.* **14**, 1005–1010.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Spek, A. L. (1996). *HELENA*. University of Utrecht, The Netherlands.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.