Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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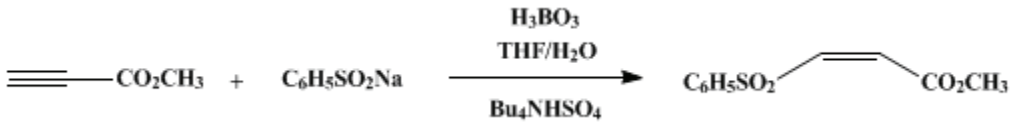
METHYL (*Z*)-3-(PHENYLSULFONYL)PROP-2-ENOATE

[2-Propenoic acid, 3-(phenylsulfonyl)-, methyl ester, (*Z*)-]



Submitted by G. C. Hirst[1] and P. J. Parsons.
Checked by Annette Prelle and Ekkehard Winterfeldt.

1. Procedure

Caution! Methyl propiolate is a lachrymator and must be handled in a fume hood.

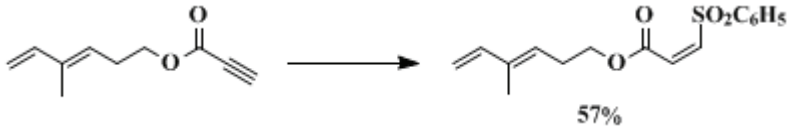
A two-phase mixture of methyl propiolate (5.0 g, 59.5 mmol), boric acid (5.5 g, 89 mmol), sodium benzenesulfinate (9.75 g, 59.5 mmol), and tetra-*n*-butylammonium hydrogen sulfate (3.0 g, 8.75 mmol) (Note 1) in tetrahydrofuran : water (200 mL, 1 : 1) is stirred vigorously at room temperature for 48 hr (Note 2). The solution is acidified to pH 4 (2 *N* hydrochloric acid) and extracted into diethyl ether (4 × 50 mL) (Note 3). The organic layer is dried ($MgSO_4$) and concentrated under reduced pressure to afford 13.75 g of yellow oil (Note 4), which is subjected to flash-column chromatography (1.5 : 1 hexanes : diethyl ether) to afford initially methyl (*E*)-3-(phenylsulfonyl)prop-2-enoate (400 mg, 2.9%) and then the desired *Z*-isomer (10.89 g, 81%) as a pale-yellow solid, pure by spectra study (Note 5).

2. Notes

1. All reagents were purchased from Aldrich Chemical Company, Inc. and were used without further purification.
2. A magnetic stirrer is usually adequate. An overhead stirrer was used for the larger scale reported here.
3. Slightly increased yields are observed if most of the organic material is removed under reduced pressure prior to extraction into ether.
4. Purity determines the structure of the product; the crude product is often a yellow solid at this point.
5. The isolated yield has ranged between 71 and 88%. The product has the following spectral and physical characteristics: mp 50.5–51.5°C (ether); IR (CH_2Cl_2) cm^{-1}: 3040 (m), 1732 (s), 1630 (m), 1440 (s), 1340 (s), 1310 (s), 1145 (s); ^1H NMR ($CDCl_3$, 360 MHz) δ: 3.92 (s, 3 H, CO_2CH_3), 6.52 (d, 1 H, J = 11.5), 6.57 (d, 1 H, J = 11.5), 7.55–8.05 (m, 5 H, Ar); ^{13}C NMR ($CDCl_3$, 90.56 MHz) δ: 52.43 (q), 127.93 (d), 129.23 (d), 131.5 (d), 133.95 (d), 135.50 (d), 139.42 (s), 164.22 (s); *m/z*: found, M^+ 226.02890; $C_{10}H_{10}O_4S$ requires M^+, 226.02998; 226 (M^+, 5), 195 (16), 161 (10), 131 (12), 77 (80), 51 (100).

3. Discussion

This procedure describes the short, one-pot, high-yield preparation of methyl (*Z*)-3-(phenylsulfonyl) prop-2-enoate. This route is shorter than a previously reported preparation.[2] We have been able to apply this technique to the preparation of a highly functionalized sulfonyl acrylate, although the generality of this reaction has not been studied (Eq. 1).[3]



Vinyl sulfones in general serve as excellent dienophiles in Diels–Alder reactions,[4] and we[5] and

others[2,4] have found the resultant cyclohexene to contain very useful functionality for further manipulation. Hence the vinyl sulfone moiety can serve as a synthon for ethylene,[6] terminal olefins,[7] acetylene,[8] and vinylsilanes[9] in [4+2]-cycloadditions as well as valuable synthetic intermediates in general.[10]

References and Notes

1. Present address: Department of Medicinal Chemistry, Glaxo Group Research Ltd., Park Road, WARE, Hertfordshire, SG16 ODP, U.K. This work was carried out at the University of Southampton, Southampton, U.K. Support from the SERC is gratefully acknowledged.
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

hexanes

acetylene (74-86-2)

hydrochloric acid (7647-01-0)

ether,
diethyl ether (60-29-7)

ethylene (9002-88-4)

boric acid (10043-35-3)

$MgSO_4$ (7487-88-9)

Tetrahydrofuran (109-99-9)

methyl propiolate (922-67-8)

tetra-n-butylammonium hydrogen sulfate (32503-27-8)

sodium benzenesulfinate (873-55-2)

Methyl (Z)-3-(phenylsulfonyl)prop-2-enoate,
2-Propenoic acid, 3-(phenylsulfonyl)-, methyl ester, (Z)- (91077-67-7)

methyl (E)-3-(phenylsulfonyl)prop-2-enoate