



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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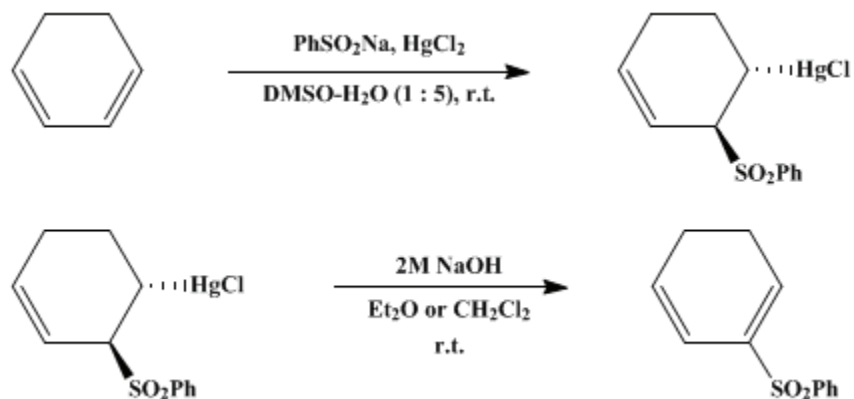
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Organic Syntheses, Coll. Vol. 8, p.540 (1993); Vol. 68, p.148 (1990).

2-(PHENYLSULFONYL)-1,3-CYCLOHEXADIENE

[Benzene, (1,5-cyclohexadien-1-ylsulfonyl)-]



Submitted by Jan-E. Bäckvall, Seppo K. Juntunen, and Ove S. Andell¹.

Checked by Willi-Kurt Gries and Larry E. Overman.

1. Procedure

A. *trans*-3-(Phenylsulfonyl)-4-(chloromercuri)cyclohexene. A 1-L, one-necked, round-bottomed flask equipped with a large magnetic stirring bar is charged with 32.6 g (120 mmol) of mercury(II) chloride (Note 1), 24.6 g (150 mmol) of sodium benzenesulfinate (Note 2), 80 mL of dimethyl sulfoxide, and 400 mL of water. The slurry is initially stirred at room temperature for 2 hr and then 10.6 g (132 mmol) of 1,3-cyclohexadiene (Note 3) is added dropwise under vigorous stirring at room temperature over a period of a few minutes. The reaction mixture is stirred for another 2 hr. The reaction flask is cooled with ice and the solid material collected by filtration using a Büchner funnel (Note 4), washed with 400 mL of water, and dried in a desiccator over calcium chloride at reduced pressure (oil pump), to give 53.0 g (97%) of essentially pure *trans*-3-(phenylsulfonyl)-4-(chloromercuri)cyclohexene (Note 5).

B. 2-(Phenylsulfonyl)-1,3-cyclohexadiene. A 1-L, one-necked, round-bottomed flask, equipped with a magnetic stirring bar, is charged with 53.0 g (116 mmol) of *trans*-3-(phenylsulfonyl)-4-(chloromercuri)cyclohexene and 600 mL of diethyl ether (Note 6) at room temperature. The slurry is stirred for 5 min (Note 7) and 175 mL (350 mmol) of a 2 M aqueous solution of sodium hydroxide is added under vigorous stirring (Note 8). The reaction mixture immediately turns black and the vigorous stirring is continued for 30 min (Note 9). The two layers are separated and the aqueous phase is extracted three times with 50-mL portions of diethyl ether. The combined organic layers are filtered through a short column containing 10 g of silica gel and the column is washed with 250 mL of diethyl ether. The ethereal solution is dried over anhydrous magnesium sulfate and filtered, and the solvent is removed at reduced pressure using a rotary evaporator to give 22.5–24.5 g (88–96%) of 2-(phenylsulfonyl)-1,3-cyclohexadiene as a colorless solid (Note 10).

2. Notes

1. Mercury(II) chloride was purchased from Merck & Company, Inc. and used as delivered. The checkers used material purchased from Mallinckrodt Inc.
2. Sodium benzenesulfinate (benzenesulfonic acid, sodium salt) was purchased from Aldrich Chemical Company, Inc. and used without further purification.
3. 1,3-Cyclohexadiene was obtained from Fluka Chemical Corporation and distilled before use. The distillation was performed at ambient temperature and reduced pressure (60–70 mm) and the diene was collected in a flask cooled with liquid nitrogen. The checkers used diene purchased from Aldrich

Chemical Company, Inc.

4. A funnel with a fine frit must be used.

5. The crude product melts at 119–123°C and is sufficiently pure for use in the next step. Recrystallization from [ethyl acetate](#) provides material melting at 128°C (dec). NMR spectral properties are as follows: ¹H NMR (250 MHz, CDCl₃) δ: 1.92–2.12 (m, 3 H), 2.36–2.51 (m, 1 H), 2.95–3.05 (m, 1 H, H-4), 4.24–4.34 (m, 1 H, H-3), 5.57–5.81 (m, 1 H, =CH), 6.04–6.16 (m, 1 H, =CH), 7.53–7.65 (m, 3 H, ArH), 7.82–7.87 (m, 2 H, ArH); ¹³C NMR (75 MHz/CDCl₃) δ: 26.5, 26.7, 44.1, 66.2, 119.6, 129.1, 129.3, 134.2, 135.4, 136.6.

6. The submitters report that [dichloromethane](#) can be used also as the solvent with similar results. This modification was not checked.

7. [trans-3-\(Phenylsulfonyl\)-4-\(chloromercuri\)cyclohexene](#) is only partly soluble in [diethyl ether](#) when the described proportions are used, whereas a clear solution is obtained when [dichloromethane](#) is used as solvent.

8. The submitters report that if [dichloromethane](#) is used as solvent, 250 mL (500 mmol) of aqueous 2 M [sodium hydroxide](#) is added at this point.

9. The submitters report that if [dichloromethane](#) is used as solvent, the reaction mixture is stirred for 1.5 hr.


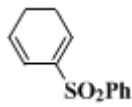
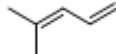
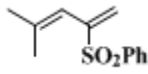
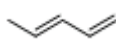
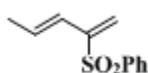
10. The crude product melts at 60–63°C. The spectral properties of [2-\(phenylsulfonyl\)-1,3-cyclohexadiene](#) are as follows: IR (KBr) cm⁻¹: 3060, 2982, 2923, 2880, 2830, 1585, 1450, 1305, 1150, 1090, 710, 690; ¹H NMR (250 MHz/CDCl₃) δ: 2.11–2.21 (m, 2 H), 2.35–2.45 (m, 2 H), 5.90–5.97 (m, 1 H, H-4), 6.07 (ddd, 1 H, *J* = 9.9, 3.6, 1.8, H-3), 6.91–6.95 (m, 1 H, H-1), 7.47–7.62 (m, 3 H, ArH), 7.84–7.88 (m, 2 H, ArH); ¹³C NMR (75 MHz/CDCl₃) δ: 20.7, 22.3, 118.4, 127.7, 129.1, 130.0, 133.2, 134.8, 138.6, 139.8.

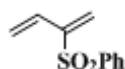
3. Discussion

This procedure^{2,3, 4} illustrates a highly selective and facile method for introducing a phenylsulfonyl group into the 2-position of 1,3-diene systems by using commercially available starting materials. The method can be applied to cyclic as well as acyclic systems giving 2-(phenylsulfonyl)-1,3-dienes. In an alternative synthesis^{5, 6} via condensation of [allyl sulfone](#) with aldehyde and subsequent acylation–elimination, the 2-(phenylsulfonyl)-1,3-dienes obtained are limited to acyclic systems.

The procedure described has been applied² to [4-methyl-1,3-pentadiene](#), [1,3-pentadiene](#) and [1,3-butadiene](#) (Table I). Caution must be taken in the handling of the [sulfonyldiene](#) products from the two latter dienes. They must be handled and stored in solution since they readily undergo Diels–Alder dimerization when concentrated. For the preparation of [2-\(phenylsulfonyl\)-1,3-pentadiene](#), final removal of solvent is never effected, giving a 10–50 mM solution of product in the preferred solvent. The solution can be stored at –20°C for several days (<5% dimerization), but the product was usually used within a few hours.

TABLE I
2-(PHENYLSULFONYL) 1,3-DIENES FROM 1,3-DIENES

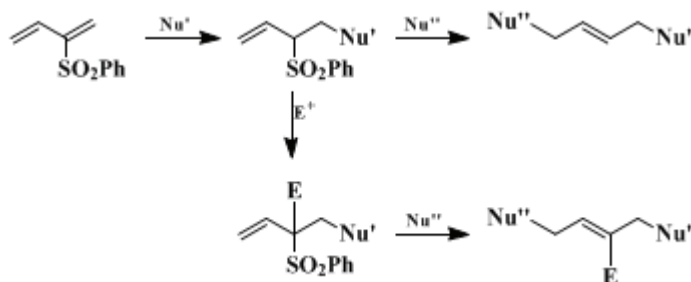
Olefin	Sulfonyl Diene	Yield(%)
		93 ^a
		67 ^a
		93 ^a



^aFrom ² and ^{3,4}.

^bA modified procedure, compared to that in ², was used. Acetone was used solvent in the first step and the reaction time was longer.

Phenylsulfonyl-1,3-dienes are versatile synthetic intermediates. They can participate in cycloaddition reactions and Michael-type additions^{3,4,7,8}, leading to adducts which can be further functionalized.^{3,4,7,8} In the latter case the resulting allylic sulfone can be functionalized by electrophiles, nucleophiles, or both:



Electron-deficient 1,3-dienes are potentially interesting Diels–Alder dienes. In our study with different kinds of olefins, we observed that 2-(phenylsulfonyl)-1,3-dienes show a duality in their Diels–Alder cycloaddition reactions, giving [4+2] adducts with both electron-deficient and electron-rich olefins.^{3,4} This dual reactivity of the 2-(phenylsulfonyl)-1,3-dienes in [4+2] cycloaddition increases the role they can play in organic synthesis.

References and Notes

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Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

2-(phenylsulfonyl)-1,3-dienes

Phenylsulfonyl-1,3-dienes

calcium chloride (10043-52-4)

ethyl acetate (141-78-6)

diethyl ether (60-29-7)

sodium hydroxide (1310-73-2)

nitrogen (7727-37-9)

acetone (67-64-1)

mercury(II) chloride (7487-94-7)

dichloromethane (75-09-2)

magnesium sulfate (7487-88-9)

1,3-Butadiene (106-99-0)

sulfonyldiene,
Sulfonyl Diene

4-methyl-1,3-pentadiene (926-56-7)

1,3-pentadiene (504-60-9)

dimethyl sulfoxide (67-68-5)

1,3-Cyclohexadiene (592-57-4)

sodium benzenesulfinate,
benzenesulfinic acid, sodium salt (873-55-2)

2-(Phenylsulfonyl)-1,3-cyclohexadiene,
Benzene, (1,5-cyclohexadien-1-ylsulfonyl)- (102860-22-0)

allyl sulfone

2-(phenylsulfonyl)-1,3-pentadiene

trans-3-(Phenylsulfonyl)-4-(chloromercuri)cyclohexene