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SULFONYLMERCURATION OF CONJUGATED DIENES. A FACILE ROUTE TO ALLYL- AND DIENYL-SULFONES

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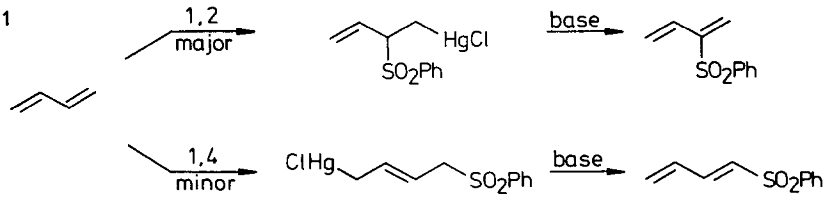
Summary: Phenylsulfonylmercuration of 1,3-dienes gives mercury adducts, which on treatment with base afford phenylsulfonyldienes. In most cases the reaction proceeds regioselectively to give 2-(phenylsulfonyl)-1,3-dienes. These are useful synthetic intermediates and can be readily transformed to a variety of functionalized allylsulfones by Michael-type addition.

Addition of nucleophiles and mercury(II) to an alkene (i.e. oxymercuration, solvomercuration etc.) is a well documented methodology in organic synthesis.[1,2] However, the related additions to conjugated dienes have attracted only a limited interest.[3] In connection with our work on metal-catalyzed functionalizations of conjugated dienes[4,5] we investigated the possibility of a mercury-promoted approach.

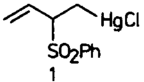
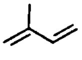
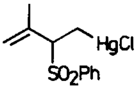
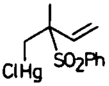
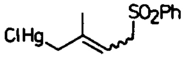
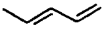
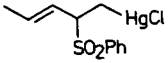
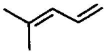
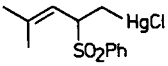
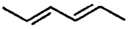
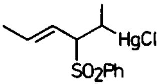
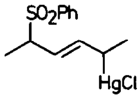
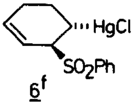
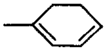
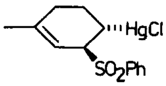
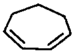
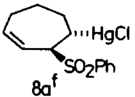
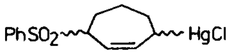
Sulfonyl-1,3-dienes are useful synthetic intermediates and recently we[5] and others[6] have reported methods for their preparation. In this communication we report a novel route to sulfonyl-1,3-dienes involving phenylsulfonylmercuration[2b] of 1,3-dienes (Scheme 1).

Scheme 1



The phenylsulfonylmercurations were carried out in water at room temperature using a preformed mercury benzenesulfinate complex.[7] In a typical procedure mercury(II) chloride (13.6 g, 50 mmol) was stirred with sodium benzenesulfinate (12.25 g, 62.5 mmol) in water (160 mL) - Me_2SO (40 mL) at 20 °C for 2 h. 1,3-cyclohexadiene (4.4 g, 55 mmol) was added to the resulting suspension and the mixture was stirred for 2 h at 20 °C, resulting in a white precipitate. The reaction mixture was cooled (ice bath) and the solid material was collected by filtration, washed with water, and dried (desiccator, 0.5 torr) to give 22.1 g (97%) of essentially pure 3-(phenylsulfonyl)-4-(chloromercuri)cyclohexene (6) as a white powder.

Table I. Phenylsulfonylmercuration of Conjugated Dienes.[a]

Entry	Diene	Reaction conditions[b]	Mercury adduct	Yield (%)[c]
1		A, 5 h	 1	56[d]
2		A, 18 h	 2a  2b  2c (E/Z=2/1) (52 : 35 : 13)	85
3		B, 5 h	 3	98[d]
4		B, 3h	 4	96[d]
5		A, 24 h	 5a[e]  5b[e] (83 : 17)	62
6		B, 2 h	 6[f]	97[d]
7		A, 1 h	 7	82[d]
8		A, 18 h	 8a[f]  8b[g] (56 : 44)	56

a. The reactions were performed at 20 °C in either water or water-Me$_2$SO (80:20) using NaSO$_2$Ph and HgCl$_2$. b. A. Water, B: Water-Me$_2$SO (80:20). c. Isolated yield. d. >95% 1,2-adduct. e. Only the E-isomer was observed. f. *trans*-stereochemistry indicated by ^{1}H NMR g. Mixture of *cis*- and *trans*-isomer.

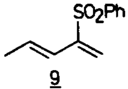
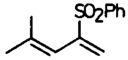
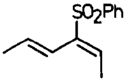
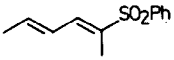
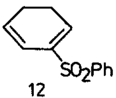
An analytical sample was obtained by recrystallization from ethyl acetate; mp 129 °C (dec.).

Elimination of mercury[2] to give the sulfonyldiene was accomplished by stirring 6 (4.58 g, 10 mmol) and Na_2CO_3 (4.24 g, 40 mmol) in Me_2SO (80 mL) - water (15 mL) followed by addition of 2 M aqueous NaOH (5 mL). After stirring at 20 °C for 15 min, 0.5 M aqueous $NaHCO_3$ (100 mL) was added. Filtration and extraction afforded 1.89 g (86%) of 2-(phenylsulfonyl)-1,3-cyclohexadiene.

The results from phenylsulfonylmercuration of some representative conjugated dienes are given in Table I. In most cases the selectivity for 1,2-addition is high (entries 1, 3, 4, 6 and 7). However, 1,3-cycloheptadiene gave a less regioselective reaction (entry 8), and isoprene and E,E-2,4-hexadiene afforded 1,2-/1,4 adducts in a ratio of 87:13 and 83:17 respectively (entries 2 and 5). The high selectivity for 1,2-addition (>95%) to 1,3-pentadiene (entry 3) is contrary to the corresponding oxymercuration of the same diene which has been reported to occur mainly 1,4.[3a,4] A reasonable explanation for these observations is that sulfonylmercuration occurs under kinetic control, whereas oxymercuration occurs under thermodynamic control.[4]

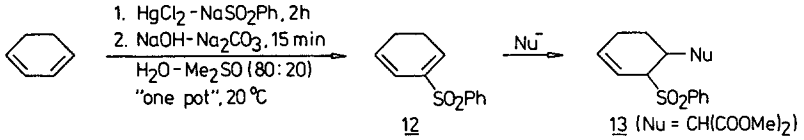
Elimination of mercury[2] from the sulfonylmercuration adducts is facile and can be performed with several bases (Table II). The choice of base and reaction conditions depend on the substrate and the stability of the product. For example, transformation of 3 and 4 to the sulfonyldienes 9 and 10 required great care and had to be carried out in aqueous Me_2SO using $NaOH-Na_2CO_3$ as base. The elimination of mercury from 5 and 6 to yield 11 and 12 was less sensitive to the reaction conditions.

Table II. Phenylsulfonyl-1,3-dienes from phenylsulfonylmercuration adducts.[a]

Entry	Mercury compound	Base	Reaction time	Product	yield (%)[b]
1	3	$NaOH-Na_2CO_3$[c]	5 min	 9	85
2	4	$NaOH-Na_2CO_3$[c]	15 min	 10	70
3	5a + 5b (83 : 17)	Na_2CO_3[d]	4 h	  11a 11b (83 : 17)	57
4	6	Na_2CO_3[d]	4.5 h	 12	89
		$NaOH-Na_2CO_3$[c]	15 min		86
		Et_3N[e]	24 h		76

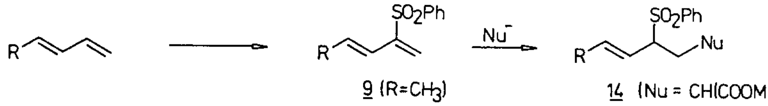
a. The reactions were performed at 20 °C. b. Isolated yields. c. In Me_2SO-water (80:20). d. In dioxane-water (50:50). e. In dioxane.

Since both the addition and elimination steps can be performed in water - Me_2SO, isolation of the mercury adduct is not necessary before the elimination. We have demonstrated this on 1,3-cyclohexadiene which was transformed into sulfonyldiene 12 in 84% yield in a one-pot procedure.



12

13 (Nu = $CH(COOMe)_2$)



9 (R=CH_3)

14 (Nu = $CH(COOMe)_2$, R=CH_3)

The 2-(phenylsulfonyl)-1,3-dienes, prepared by the present method, are versatile synthetic intermediates. They can be used in cycloaddition reactions,[9] and importantly, Michael-type addition of nucleophiles leads to allylic sulfones. A specific example was demonstrated by the addition of dimethyl malonate to 12 and 9 to give allylic sulfones 13 and 14 in 85 and 75% yield respectively. The allylic sulfones thus obtained are important synthetic intermediates,[6,10,11] that allow further functionalization by both electrophiles and nucleophiles. The regioselectivity of these further functionalizations will be investigated.

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7. This complex was not characterized, but mixing a homogeneous solution of mercury(II) chloride with a homogeneous solution of $PhSO_2Na$ resulted in a white precipitate.

8. On a very short reaction time oxymercuration of 1,3-pentadiene gives mainly 1,2-adduct.[3b,3e]

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