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# Stereoselective Synthesis of (3*E*,5*E*)-Dien-2-ones and (2*E*,4*E*)-Dienals via 2-Phenylsulfonyl 1,3-Dienes

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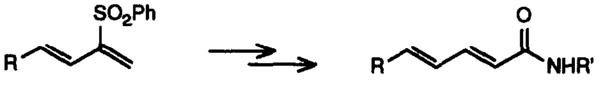
**Summary.** Michael addition of nitroalkanes to 2-phenylsulfonyl 1,3-dienes proceeded smoothly in the presence of DBU to give nitrosulfones (e.g. **2**) in high yield. Transformation of the nitro group of the adduct to a keto function (Nef type reaction) and subsequent elimination of benzenesulfinic acid afforded conjugated dienones and dienals with high stereoselectivity.

We have recently demonstrated the use of 2-phenylsulfonyl 1,3-dienes as versatile building blocks in organic synthesis.[1,2] One application involved the transformation of long-chain sulfonyldienes **1** to naturally occurring 2,4-dienamides via the use of a carboxy anion equivalent (eq. 1).



**1**

(eq. 1)

Conjugated dienones and dienals related to the dienamides in equation 1 are useful synthetic intermediates in natural product synthesis.[3,4] Furthermore they belong to an important class of compounds that occur in flavors of tobacco, tea, and agricultural products.[5-7] We now report a simple and highly stereoselective synthesis of conjugated dienones and dienals involving the addition of an acyl and formyl anion equivalent, respectively, to 2-phenylsulfonyl 1,3-dienes.

The synthetic sequence is outlined in Scheme I. The sulfonyldienes **1** are readily obtained via a one-pot selenosulfonation-elimination procedure[2,8] or a mercurysulfonation-elimination.[1a,9] For the long-chain dienes the selenosulfonation method was preferred.[2] Michael addition of a nitroalkane to the sulfonyldiene **1** in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) afforded the nitrosulfone **2**. The use of nitroethane gave good to high yields of adduct **2**, whereas nitromethane gave a lower yield due to formation of a side product resulting from reaction of nitromethane with two molecules of sulfonyldiene.[10] The latter side

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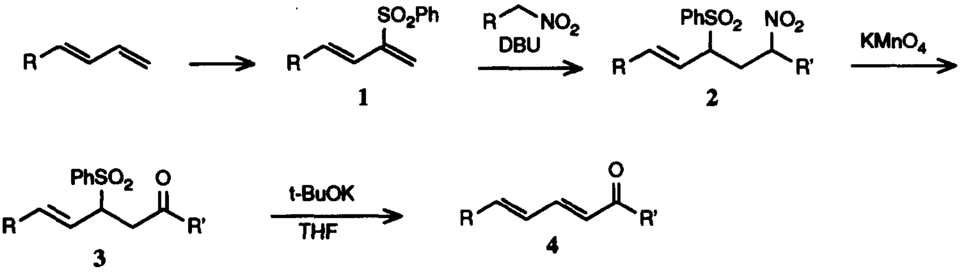
Scheme I



reaction was minimized by slow addition of the sulfonyldiene to the reaction mixture. The Nef type transformation of the nitrosulfone **2** to a ketone or aldehyde (**3**) was achieved by potassium permanganate oxidation of the salt of **2**.[11] Subsequent elimination of benzenesulfinic acid was accomplished by treatment of **3** with potassium *tert*-butoxide in tetrahydrofuran (THF). This reaction was highly stereoselective (>95% E-α,β-double bond) in accordance with the analogous elimination of benzenesulfinic acid from 3-(phenylsulfonyl)-4-alkenoic acid derivatives.[2] The overall yields for the two-step transformation of nitrosulfone **2** to dienone (dienal) **4** together with the yields of the Michael addition of nitroalkanes to **1** are given in Table I.

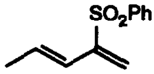
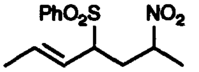
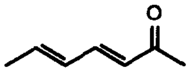
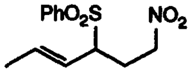
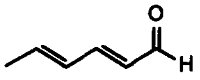
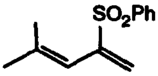
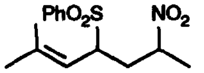
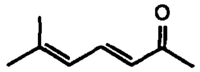
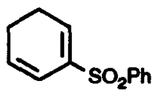
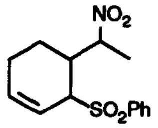
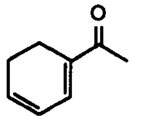
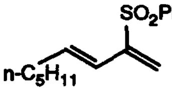
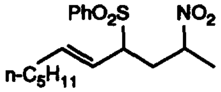
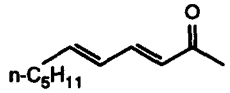
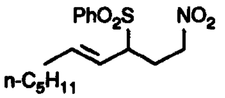
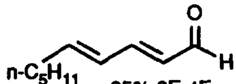
The reaction sequence in Scheme I was also applied to other 2-phenylsulfonyl 1,3-dienes (Table I). Thus, 4-methyl-2-(phenylsulfonyl)-1,3-pentadiene (entry 3) and 2-(phenylsulfonyl)-1,3-cyclohexadiene (entry 4) were transformed to the corresponding dienones in good overall yields. The Nef type reaction of the cyclic nitrosulfone (entry 4) had to be done with 30% $H_2O_2$, since attempts to employ the $KMnO_4$ procedure failed completely in this case.

Several of the products in Table I are naturally occurring compounds. Thus, (3*E*,5*E*)-hepta-3,5-dien-2-one (entry 1) and 6-methyl-(3*E*)-hepta-3,5-dien-2-one (entry 3) are aroma components of tea.[6] (3*E*,5*E*)-undeca-3,5-dien-2-one (entry 5) is an odor compound of meal flavor volatile[7] and (3*E*,5*E*)-deca-3,5-dien-1-al (entry 6) occurs in leaves of *Carphephorus* and is a tobacco aroma component.[5a]

Several methods for the preparation of conjugated dienones or dienals have been developed[4,12,13] and some recent procedures include the metal-catalyzed isomerization of α,β-ynones[4b,13] and condensation of carbonyl compounds with imines of 4-phosphoryl-2-butenals.[4a] Many of the previous methods give moderate yields and a varying degree of stereoselectivity. The present method for the synthesis of conjugated dienones and dienals from 2-phenylsulfonyl 1,3-dienes is highly stereoselective and demonstrates the synthetic utility of these sulfonyldienes. Furthermore, the procedure is quite general and can be applied to both acyclic and cyclic derivatives.

**General procedure for the preparation of nitro adducts. A. Addition of nitroethane.** To a solution of the 2-phenylsulfonyl 1,3-diene (10 mmol) in nitroethane (10 ml) was added DBU (0.5 mmol). The reaction mixture was stirred at room temperature for 45 minutes. Ether and water were then added to the reaction mixture and the layers were separated. The aqueous phase was extracted three times with ether and the combined organic phases were washed with 2M HCl, $H_2O$ (twice), and brine and dried ($MgSO_4$). Evaporation

**Table I.** Synthesis of Conjugated Dienones and Dienals

| entry | sulfonyl diene | nitrosulfone[a] | yield[b] % | method[c] | product | yield[b,d] % |
|---|---|---|---|---|---|---|
| 1 |  |  | 92 | A |  <br>> 95% 3E,5E | 62 |
| 2 | |  | 81 | A |  <br>> 95% 2E,4E | 38 |
| 3 |  |  | 89 | A |  <br>> 95% E | 74 |
| 4 |  |  | 79 | B |  | 31 |
| 5 |  |  | 60 | A |  <br>> 95% 3E,5E | 55 |
| 6 | |  | 43 | A |  <br>> 95% 2E,4E | 49 |

a. The nitrosulfones of entries 1,3,4, and 5 were mixtures of diastereomers ( ~1/1). b. Isolated yield. c. Method A: (i) t-BuOK, t-BuOH, $KMnO_4$, (ii) t-BuOK, THF, 30 min, 20 °C; method B: (i) 30% $H_2O_2$, 10h, 20 °C, (ii) t-BuOK, THF, 30 min, 20 °C. d. Overall yield for the two step transformation of nitrosulfone to dienone (dienal). The yields (%) of these steps for entries 1 - 6 were: (step 1, step 2) = (81,76), (56,67), (92,80), (35,89), (79,69), (77,64)

of the solvent on a rotary evaporator afforded very pure nitroadduct; it can be purified by flash chromatography (EtOAc: Hexane, 20:80 or 30:70).

**B. Addition of nitromethane.** The sulfonyldiene was added slowly to the reaction mixture, and in this case an equimolar amount of DBU to the diene was employed. Also more solvent was used (10 ml of nitromethane per mmol of substrate).

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