Catalytic Dimerization of Allyl Phenyl Sulfone in the Presence of a Proazaphosphatrane Catalyst

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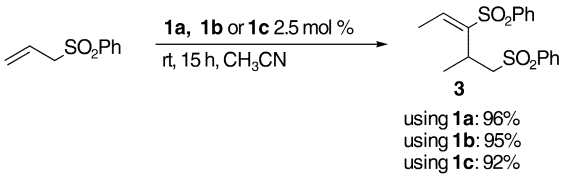
Abstract: In the presence of a proazaphosphatrane catalyst $P(RNCH_2CH_2)_3N$, allyl phenyl sulfone readily dimerizes to give the product shown, for which only incomplete and inconclusive data exist in the literature. The dimer was shown from ^1H NMR spectral considerations to have the *E* configuration.

Keywords: dimerization; Michael addition; organic catalysis; proazaphosphatrane catalyst; sulfone



Scheme 1. Dimerization of allyl phenyl sulfone with proazaphosphatranes.

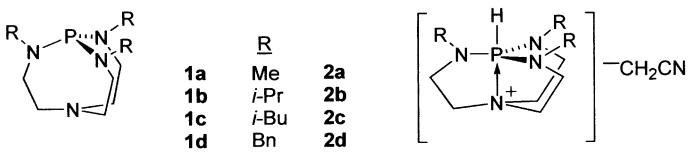
Vinyl sulfones are valuable starting materials in organic synthesis owing to activation of the alkene functionality by the sulfonyl group.[1] These compounds are very good acceptors in Michael additions[2] and they easily undergo cycloaddition[3] and elimination reactions.[4] Stereospecific alkene synthesis *via* vinyl sulfones is also made facile by the ease with which the sulfone group can be reductively removed.[5] Chromene derivatives can be pharmacologically active, and recently vinyl sulfones have been utilized in the synthesis of 3-substituted chromenes under Baylis–Hillman conditions.[6]

Many stereoselective syntheses of vinyl sulfones have been developed,[7–10] among which the base-catalyzed conjugation of readily available allyl sulfones is an attractive example. Although this isomerization is not thermodynamically favored in more than a few cases,[11] it is possible to control the synthesis of vinyl sulfones kinetically and stereoselectively, as, for instance, *via* the formation of allylsilane intermediates that can undergo protodesilylation.[12]

Strong non-ionic bases are valuable for catalyzing a wide variety of organic transformations.[13] The non-ionic phosphazene base P_2-Et has been used to conjugate carbocyclic vinyl sulfones to their allyl analogues considerably more efficiently than with DBU or KO-*t*-Bu.[14] Here we report, that acyclic allyl phenyl sulfone, however, dimerizes in the presence of the strong non-ionic bases **1a**, **1b**, or **1c** (2,8,9-trialkyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecanes) to give **3** stereospecifically in high yields at room temperature (Scheme 1).The reaction in Scheme 1 occurs under mild conditions to give **3** in excellent yields. It may be noted that **3** was claimed to be formed as a single (though unspecified) isomer in only 8% yield by electrolytically reducing 1-phenylsulfonylpropene in DMF *via* an anion radical mechanism.[15] Only 60 MHz ^1H NMR and low resolution mass spectral data were provided. In order to attain a yield of 56% of this single unspecified isomer, it was necessary to carry out the reduction indirectly at a higher potential with the use of an organic mediator. Also of relevance here is that the dimerization of vinyl phenyl sulfone at room temperature gave only a 20% yield of **4a** (an analogue of **3**) using DBU.[6] It may also be noted that methyl acrylate has recently been shown to dimerize to **4b** in 85% yield in the presence of **1c** as a catalyst.[16]

Compound **5**, also an analogue of **3**, was reported to have been synthesized regioselectively in 50% yield as shown in Scheme 2.[17] However, the stereochemical configuration of **5** was only tentatively assigned and no characterization details were given. Also related to this result is the observation that intermediate **8**, formed in the reaction of RR′CHCHO with acetonitrile in the presence of **1a**, deprotonates to give a resonance-stabilized anion that undergoes Michael addition to another molecule of **8** to give dimer **9**.[18]

Our assignment of the stereochemistry of **3** is based on a comparison of its ^1H NMR chemical shifts for the CH_3 C=C (1.89 ppm) protons and particularly for its HC=C



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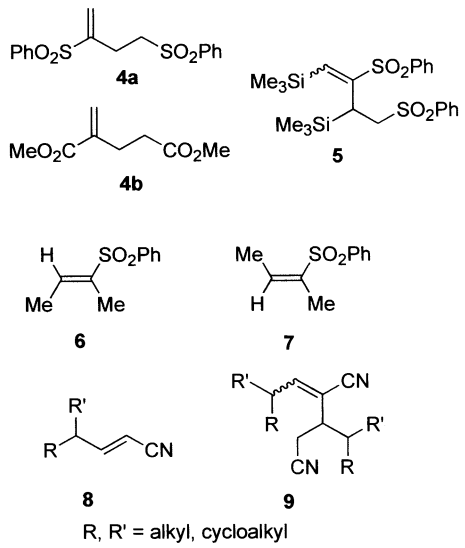
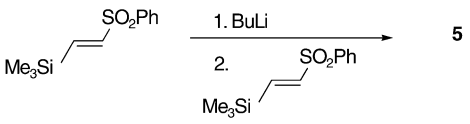


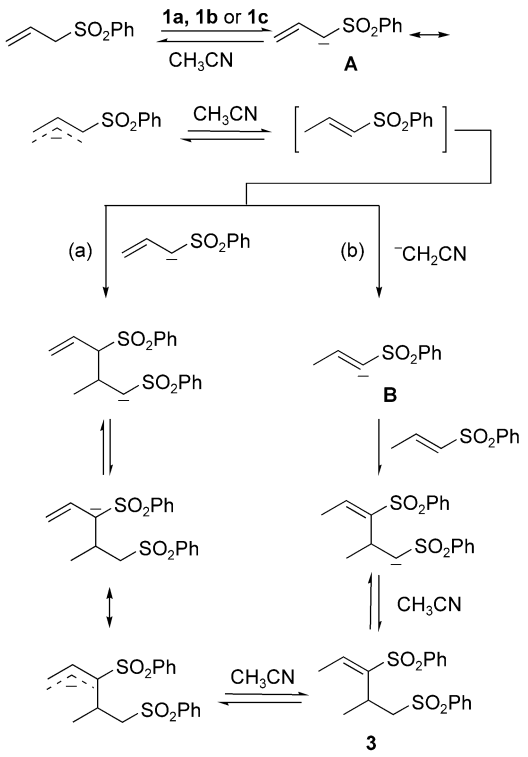
(6.94 ppm) protons, with those recorded earlier by others[19] for these protons in isomers **6** and **7**. Thus the chemical shifts for the $CH_3C{=}C$ and $HC{=}C$ protons in **6** (1.82 and 6.87 ppm, respectively) closely match those in **3**, while these chemical shifts appear at 2.13 and 6.07 ppm, respectively, in the proton spectrum of **7**. Here, the large downfield shift for the $HC{=}C$ protons from **7** to **6** can be taken as diagnostic of the *E* stereochemistry of **6**, and hence of **3**.

Our observation that no reaction occurred in the absence of acetonitrile under the conditions of Scheme 1 indicates that the proazaphosphatrane bases **1a**, **1b** and **1c** (*p*Ka *ca*. 33 in acetonitrile[13]) do not directly deprotonate allyl phenyl sulfone to a detectable extent. The mechanism we propose in Scheme 3 is based on the well documented capability of these proazaphosphatranes to deprotonate acetonitrile to the $^{-}CH_2CN$ anion, thus forming **2a**–**c**.[13] The vinyl sulfone intermediate in this scheme is speculated to occur in an equilibrium reaction *via* a deprotonation pathway involving $^{-}CH_2CN$ anions. This vinyl intermediate could then undergo Michael addition by **B** as depicted in path (b) or Michael addition by **A** to give **3** in path (a). We favor path (a), however, because both vinyl phenyl sulfone and phenyl *trans*-styryl sulfone remained unchanged when present as an additive in Scheme 1. Apparently, appreciable amounts of anion **B** were not generated by **1a**, **1b** or **1c** under our conditions.

In conclusion, the proazaphosphatranes **1a**–**1c** provide better than 90% isolated yields of dimerized allyl phenyl sulfone at room temperature in 15 hours. The dimerization reaction appears to proceed by a Michael-type addition pathway. Explorations of other activated olefins as substrates for oligomer formation are underway.



Scheme 2. Literature synthesis of **5** *via* lithiation.



Scheme 3. Possible mechanistic pathways for allyl sulfone dimerization.

Experimental Section

General Considerations

All reactions were carried out under a nitrogen or an argon atmosphere, as was the distillation of acetonitrile over calcium hydride. Substrates (Aldrich) were used as received.

General Procedure

Reactions were carried out in a 25-mL flask containing 5.0 mL of dry acetonitrile in which was dissolved 2.5 mol % of **1a**, **1b** or **1c**. To this was added 1.0 mmol of the substrate and the mixture was stirred at room temperature for 15 hours, after which it was concentrated under vacuum and subjected to column and thin layer chromatography on silica gel with 1:1 *n*-hexane/EtOAc as eluent. Conversions of allyl phenyl sulfone to **3** were 100% with these catalysts according to ^{1}H NMR spectroscopy and greater than 98% purity of the product was ascertained by the same technique. The yields of **3** from catalysis by **1a**, **1b** and **1c** were 96, 95 and 92%, respectively. ^{1}H NMR ($CDCl_3$): $\delta = 7.63$, 7.58, 7.57, 7.55 and 7.45 (2:2:1:3:2H, m each, 2×

Ph), 6.94 (1H, q, C=CH), 3.39 (1H, m, C_3CH), 3.30 (2H, q, CH_2), 1.89 (3H, d, C=CCH_3), 1.19 (3H, d, CHCH_3); ^{13}C NMR ($CDCl_3$): δ = 144.0, 140.2, 139.5, 139.3, 133.8, 133.2, 129.3, 129.1, 127.9, 127.8, 67.9, 60.2, 27.5, 25.5, 18.6, 14.5; HRMS: calcd. for M: 364.08030; found: 364.08110.

Acknowledgements

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