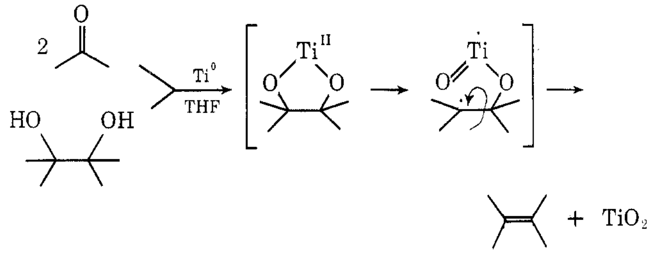
case. It is not necessary to preform the dianions since free diols reduce directly (presumably the dianions are formed in situ by reaction with Ti^0). Some of our results are given in Table II.

Several of the examples require special comment, and provide information which bears on the reaction mechanism. Both the meso and *dl* diols from 5-decene reduce in good yield, but neither reaction is stereospecific. Both the trans diequatorial diol **16** and the trans diaxial diol **18** reduce in good yield, although diol **20** is not reduced.

We wish to reserve a detailed discussion of our mechanistic studies for a full paper to be published later. We simply point out now, however, that all of our data are consistent with the suggestion that a five-membered ring intermediate is formed and then collapses in a nonconcerted manner.

Diaxial glycol **18** can form the required intermediate via a boat conformer, but glycol **20** cannot and is therefore unreactive.



In summary, we have developed new procedures for the reductive coupling of saturated ketones[8] and aldehydes to olefins and for the reduction of 1,2 diols to olefins. These reactions may well be of considerable use in synthesis.

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(8) We have not carried out a careful study of the reduction of aryl ketones with Ti^0, because the reaction can be carried out so easily with other titanium reagents (ref 1–3). In the cases we have studied, however (9-fluorenone, benzaldehyde), we observed considerable overreduction of the products to saturated hydrocarbons.

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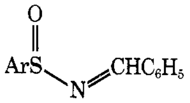
Trimethylsilyl 2-Nitrobenzenesulfenate (2-Nitrobenzenesulfenic Acid)

Summary: Trimethylsilyl 2-nitrobenzenesulfenate, prepared by heating *N*-benzylidene-2-nitrobenzenesulfinamide with trimethylsilyl chloride, is a convenient, high yield source of 2-nitrobenzenesulfenic acid and 2-nitrobenzenesulfenate ion when treated with alcohol and alkoxides, respectively.

Sir: Sulfenic acids are believed to be important intermediates in a variety of organic sulfur reactions including biological transformations.[1] However, their high reactivity and the lack of mild methods to prepare them has hindered a systematic study of their reactions and properties. Of the aromatic sulfenic acids, 2-nitrobenzenesulfenic acid (1) has been the most studied.[2] It is generally believed to be formed in the neutral or alkaline hydrolysis of sulfenyl halides,[2a,c] disulfides,[2h] and sulfenate esters.[2e–g] The major products isolated in these reactions are disulfide (ArSSAr), thiolsulfonate ($ArSO_2SAr$), and sulfinic acid ($ArSO_2H$).[2] Under certain conditions, orthanilic acid is also obtained.[2a,c,g] These products are all believed to involve initial formation of the sulfenic acid, **1**, with the disulfide and thiolsulfonate being formed by reaction of the solvent with the intermediate thiolsulfinate [ArS(O)SAr].[2–4] As a consequence of the methods used to generate **1**, neither the sulfenic acid nor the thiolsulfinate has ever been isolated.

ArSOX
1, X = H
2, X = $SiMe_3$



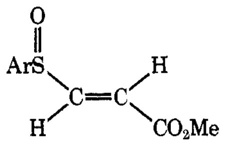
3

Ar = 2-nitrophenyl

Recently, we reported that the thermolysis of *N*-alkylidenearenesulfinamides is a useful method for generating arylsulfenic acids under mild nonaqueous conditions.[3] We wish to report the use of this method to prepare trimethylsilyl 2-nitrobenzenesulfenate (**2**) which when treated with alcohol provides a convenient high-yield source of **1**. The reactions of **1** prepared in this way are reported.

Compound **2** is a bright-orange liquid obtained in 75–80% yield by heating **3**[3,5] (mp 103–104°)[6] with trimethylsilyl chloride–hexamethyldisilazane (2:1)[1d] and is the first example of the trapping of an unstable sulfenic acid by these reagents. The similarity of the ir and NMR spectra of **2** with that of methyl 2-nitrobenzenesulfenate[7] is evidence for the proposed structure.[8]

When **2** was treated with 4 equiv of ethanol in the presence of methyl propynoate, **4** (mp 153–154°)[6] was obtained in 82% yield confirming that **2** is an unequivocal, high-yield source of **1**. The formation of **1** from **2** in ethanol–water–HCl and ethanol–water mixtures gave orthanilic acid (**5**, 54–66%) and **6** (mp 53–54°,[6] 15–20%) as major products. Disulfide and thiolsulfonate were minor products. These conditions are similar to those in which **1** is believed to be formed from sulfenyl halides.[2a,b]



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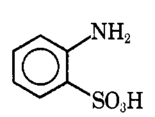

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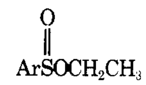


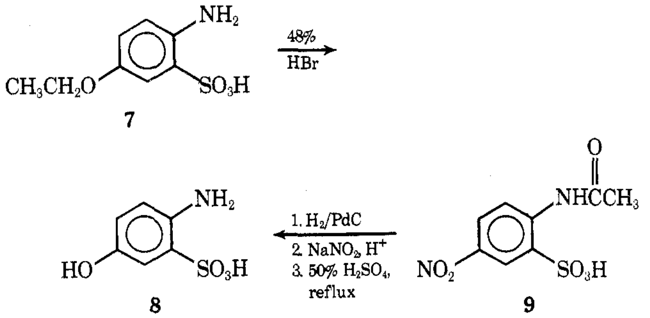
$ArS(=O)OCH_2CH_3$

6

The sequence of steps leading from **1** to **5** is unknown, although the ability of an *o*-nitro group to exchange its oxygens with an adjacent sulfur is well known.[9] Hogg and Stewart have recently suggested that thiolate and sulfenate ions may be reducing agents in the rearrangement of **1** to **5**.[2g] Under our conditions, however, this seems unlikely since disulfide was a minor product and sulfinic–sulfonic acids were not detected.

Ethyl 2-nitrobenzenesulfinate (**6**), previously undetected in the reactions of **1** in alcohols, is probably formed by nucleophilic attack of the solvent on the sulfinyl sulfur of the intermediate thiolsulfinate.[3] The isolation of **6** is further evidence in support of thiolsulfinate intermediates in the reactions of sulfenic acids.

When **2** was refluxed in absolute ethanol a 50% yield of 2-amino-5-ethoxybenzenesulfonic acid (**7**) was obtained.[6,10] This unusual product was identified by conversion with 48% HBr to the phenol **8**; an authentic sample of **8** was prepared from **9** as shown. The presence of both the nitro and sulfenic acid functional groups are apparently required for the formation of **7** and may involve some intermediate on the reaction path between **1** and **5**. In addition to **7**, **6** (15%) was also obtained.



Compound **2**, is also a convenient source of sulfenate anion (ArSO$^-$). Treatment of **2** with ethanol–water–sodium hydroxide gave a blue solution (λ_{max} 588 nm). The blue color, which has been attributed to the 2-nitrobenzenesulfenate ion,[2f] rapidly faded and, after neutralization of the reaction mixture, gave disulfide (10–16%) and sulfinic acid (33–40%) as principal products. Disulfide is the major product obtained when the sulfenate anion is generated from ethyl 2-nitrobenzenesulfenate (**2**, X = Et).[2f] Treatment of **2** in THF–water–sodium methoxide with methyl iodide gave the sulfoxide [ArS(O)Me, 19%], sulfone [ArS(O$_2$)Me, 20%], and disulfide (30%). The disulfide and sulfone may be formed in a variety of ways from the thiolsulfonate and intermediate thiolsulfinate.[2,3] The sulfoxide undoubtedly results from the direct reaction of iodide with the sulfenate ion.

The lack of stability of the sulfenate ion in protic solvents most likely results from formation of the sulfenic acid which reacts further.[2f,g] In support of this argument is the stability of the sulfenate ion in aprotic media in which the blue color persisted for more than 6 h. The sulfenate ion was prepared by treatment of **2** with potassium *tert*-butoxide in benzene containing 18-crown-6. Sulfoxide (45–50%), sulfone (5%), and disulfide (30–35%) were obtained when the reaction mixture was treated with methyl iodide. It is interesting to note that the 2-nitrobenzenesulfenate anion is considerably more stable than **1**. This is in sharp contrast with the azetidinesulfenic acid which has been isolated[1d] and its conjugate base which is reported to be very unstable.[11]

We are currently exploring other reactions of **1** and the sulfenate ion prepared by this method. The synthesis of other sulfenic acids by this procedure is also under investigation.

Acknowledgment. We thank Ms. Rita Vasta for obtaining the uv spectra of **2**. This investigation was supported in part by Public Health Service Research Grant No. CA-14341 from the National Cancer Institute.

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(8) Compound **2** has the following properties: bp 106–108° (0.05 mm); ir (thin film) 1300 (S–O), 850 (Si–C); NMR (CDCl$_3$) δ 0.3 (s, 9, CH$_3$), 7.7 (m, 3), 8.3 (d, 1); MS *m/e* 243 (M), 73 (B, SiMe$_3$); uv (cyclohexane) λ_{max} nm 242 (ϵ 4400). *Caution:* an explosion of unknown origin occurred when a large quantity (i.e., >30 g) of **2** was distilled. No problem has been encountered in distilling <7-g quantities of **2**.

(9) For a review of the pertinent literature, see F. A. Davis and R. P. Johnston II, *J. Org. Chem.*, **37**, 854 (1972).

(10) Compound **7** has the following properties: mp 275–276° (d); NMR (DMSO-d_6); δ 1.25 (t, 3, Me), 4.03 (q, 2, CH$_2$), 7.11 (m, 3) and 7.80 (broad, 3, NH$_2$, SO$_3$H).

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