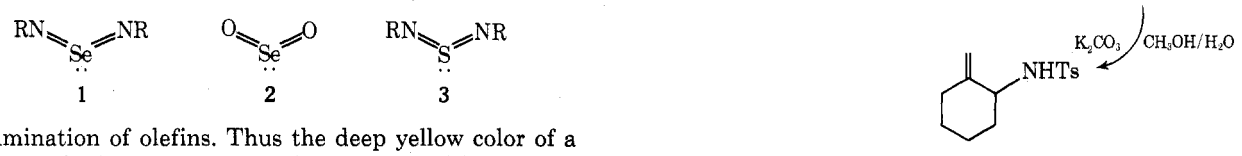
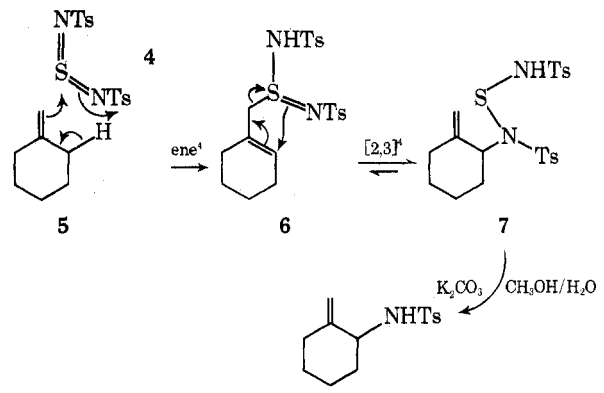
Allylic Amination of Olefins and Acetylenes by Imido Sulfur Compounds

Summary: The sulfur dimide species 4 (TsN=S=NTs) was found to be a powerful enophile in its reactions with simple olefins and acetylenes. Following hydrolysis of the initial ene products, allylic sulfonamides are produced in good yield.

Sir: We have reported that imido selenium compounds (**1**) effect allylic amination of olefins,[1] and thus mimic the well-known allylic oxygenation of olefins by selenium dioxide (**2**). We have now discovered that the analogous sulfur imido compounds (**3**)[2] are also excellent reagents for the allylic amination of olefins. Thus the deep yellow color of a solution of bis(*p*-toluenesulfonyl)sulfodimide (**4**) in methylene chloride was immediately[3] discharged when an equivalent of methylene cyclohexane (**5**) was added. TLC indicated a single product, and spectroscopic evidence (NMR and ir) suggested that it was principally disulfenamide **7**, perhaps containing some of the initial ene product **6** as a minor component.[5] As indicated in Table I, the reactions of sulfodiimide **4** were also explored with several other olefins and with one acetylene. In each case reaction occurred to produce intermediates analogous to **6** and **7**. These sulfenamide intermediates are easily cleaved to the corresponding allylic sulfonamides (e.g., **8**). As an alternative to the rather slow basic (K_2CO_3) hydrolysis described below, they can be rapidly cleaved by treatment with trimethyl phosphite in methanol at room temperature.



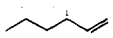
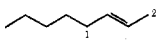
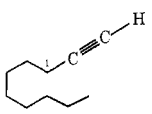
1 **2** **3**



8 (84%)

General Procedure. (Diimide **4**[6] reacts instantly with water; therefore rigorously anhydrous conditions are essential.) To a solution of 278 mg (2.9 mmol) of methylene cyclohexane (**5**) in 2.8 ml of dry CH_2Cl_2 (passed through alumina) was added a solution of 1.11 g (3 mmol) of diimide **4** in 12 ml of CH_2Cl_2 while stirring in an ice-bath under nitrogen. The yellow color of reagent **4** disappeared quickly. The resulting solution was stirred at room temperature for 14 hr and then concentrated to afford an oil. This crude sulfenamide (**7**) was hydrolyzed by stirring at room temperature for 14 hr with 20 ml of a solution consisting of 2.4 g of K_2CO_3, 12 ml of

Table I
Allylic Amination[a]

Example	Olefin or acetylene	Mole ratio of 4/substrate	% yield[b] (mp, °C) Site 1[c]	Site 2[c]
1		1.04	45	
2		1.04	56	3
3		1.12	70 (101–102)	
4		1.04	84 (120–121)	
5[d]		2.06	63[d] (201–202)	
6		1.04	63 (192–193)	
7		1.04	38 (77–78)	33 (68–69)
8		1.55	37 (65–66)	

[a] With the noted differences in stoichiometry in cases 3, 5, and 8, all reactions were carried out on 2.9 mmol of substrate as described in detail for methylene cyclohexane (**5**). The acetylene (case 8) was slow to react; so the usual 14-hr reaction period was extended to 3 days. The allylic sulfonamide products were characterized by comparison with authentic materials.[1] [b] Yields were determined by isolation, which, in the case of the solid products, involved recrystallization. [c] Site of amination as indicated on the substrate. [d] In this case the bis amide was produced; the sites of amination are indicated by the arrows.

CH_3OH, and 8 ml of H_2O. Then 100 ml of ether was added and the organic phase was washed with 20 ml of a solution made up of two parts 1 *N* aqueous NaOH and one part saturated aqueous NaCl.[7] The ether layer was further washed with water and brine and then dried ($MgSO_4$) and concentrated to give 674 mg of pale yellow crystals. Recrystallization from CCl_4–hexane afforded 648 mg (84%) of the pure allylic sulfonamide **8**, mp 120–121°.

Examination of Table I reveals that these sulfodiimide reagents (**3**) are likely to prove superior to the previously developed selenodiimide reagents (**1**).[1] Of special importance in the case of the sulfur reagent (**4**) is the ease with which the pure products can be isolated without chromatography. At present the Chloramine-T/Se^0 derived reagent (**1**, R = Ts)[1] is much easier to prepare than the sulfur diimide reagent **4**. However, we are trying to develop a convenient in situ method for the generation of **4**.

The present work provides a rare example wherein the discovery of a new reaction in sulfur chemistry was inspired by the prior discovery of the related process in selenium chemistry. It has almost always happened the other way around.

Acknowledgment. We are grateful to the National Institutes of Health (GM21686) for support of this research.

References and Notes

(1) K. B. Sharpless, T. Hori, L. K. Truesdale, and C. O. Dietrich, *J. Am. Chem. Soc.*, submitted for publication.
(2) For an excellent review on the preparation and the reactions of the imides of sulfur dioxide, see G. Kresze and W. Wucherpfennig, *Angew. Chem., Int. Ed. Engl.*, **6**, 149–167 (1964). The Diels–Alder addition of these imido sulfur species (**3**) to 1,3-dienes is well known, but, surprisingly, their facile ene reaction with simple olefins has not been described previously.
(3) In the case of less reactive substrates (e.g., case 1, 3, and 8 of Table I) the yellow color remained even after 14 hr. In these instances excess reagent and even longer reaction times might improve the yields.
(4) This proposed mechanism for formation of **7** is directly analogous to the accepted mechanism for the oxidation of olefins by selenium dioxide: (a) K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **94**, 7154 (1972); (b) D. Arigoni, A. Vasella, K. B. Sharpless, and H. P. Jensen, *ibid.*, **95**, 7917 (1973); H. P. Jensen and K. B. Sharpless, *J. Org. Chem.*, **40**, 264 (1975).
(5) Allyl sulfinic acids (i.e., oxygen analogues of **6**) are known to undergo retroene reaction (see ref 2) rather than [2,3] rearrangement. Allyl sulfoxides tend to exist as sulfoxides rather than the 2,3-shifted allyl sulfenate esters [see D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974), and references cited therein]. However, for evidence in support of **7** being the stable side of the [2,3] equilibrium between **6** and **7** in related cases where nitrogen has been substituted for oxygen, see R. S. Atkinson and S. B. Awad, *J. Chem. Soc. D*, 651 (1975), and references cited therein.
(6) Prepared from TsN=S=O as described by W. Wucherpfennig and G. Kresze, *Tetrahedron Lett.*, 1671 (1966). Dry bag techniques were used to avoid contact of **4** with moisture.
(7) The presence of the NaCl in this basic wash allows extraction of *p*-toluenesulfonamide but prevents extraction of the product, which can be a problem in the case of the smaller olefins (e.g., cases 1 and 3). We recommend that this modification of the alkaline wash also be adopted for the selenium-based aminations (see ref 1).

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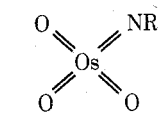
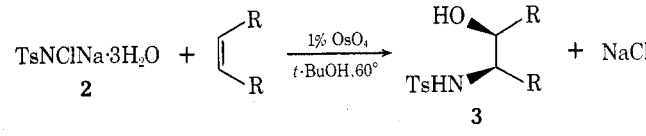
Osmium-Catalyzed Vicinal Oxyamination of Olefins by Chloramine-T

Summary: An osmium-catalyzed procedure which effects cis addition of the hydroxyl (OH) and arylsulfonamide ($ArSO_2NH$) moieties across an olefinic linkage is described; sixteen different olefin substrates were examined.

Sir: We have reported that *tert*-alkyl imido osmium compounds, such as **1a**, effect stereospecific vicinal oxyamination of olefins.[1] However, this new synthetic transformation suffers from two important limitations. It requires a stoichiometric amount of osmium reagent (**1a**) and it is difficult to remove the *tert*-alkyl group from the products. We have discovered a new procedure which solves both of these problems. The trihydrate of Chloramine-T[2] reacts with olefins in the presence of a catalytic amount of osmium tetroxide to produce vicinal hydroxy *p*-toluenesulfonamides



1a, R = *tert*-alkyl
b, R = Ts



2 **3**

(**3**). This is an aza analogue of the catalytic procedures developed by Hoffman[3] and Milas[4] for vicinal dihydroxylation of olefins. The sulfonyl imido osmium compound **1b** is presumed to be the effective reagent, and it must be continuously regenerated under these conditions. We soon discovered that the process is inhibited by the chloride ion which is released as the reaction proceeds. In the case of 1-decene this inhibition is dramatically overcome by the addition of an equivalent of silver nitrate[5] (compare examples 1 and 2 in Table I). Silver nitrate has a beneficial effect in the case of about half of the olefins listed in Table I. However, we were surprised to find that silver ion can also have a deleterious effect; this effect is so severe in some cases (e.g., 4, 15, 16, 17, and 19 of Table I) that only a trace of the usual hydroxy amide is formed in the presence of silver nitrate. Thus we have developed two general procedures: one without $AgNO_3$ (procedure A) and one with $AgNO_3$ (procedure B). An explanation for the variable effects of silver and chloride ions on these reactions is clearly beyond our current understanding. For almost all of the olefins in Table I both procedures (A and B) were tried; when only one procedure is given it means that it was superior to the other for that substrate.

Procedure A. To 0.59 g (5.0 mmol) of α-methylstyrene in 50 ml of reagent grade *tert*-butyl alcohol was added 1.76 g (6.25 mmol) of Chloramine-T trihydrate (EK) and 0.625 ml (0.05 mmol) of a 0.079 *M* solution of osmium tetroxide in olefin-free hexane. The flask was fitted with a reflux condenser and placed in an oil bath maintained at 60°. The resulting suspension was stirred magnetically until all olefin had disappeared (~15 hr). Then 20 ml of 2.5% aqueous sodium bisulfite was added and the mixture was refluxed for 1.5 hr. The *tert*-butyl alcohol was removed in vacuo, and the residue was taken up in 100 ml of methylene chloride and washed once with 150 ml of water. The suspended osmium-containing impurities were removed from the organic phase by stirring with magnesium sulfate followed by filtration. The solution was then washed once with 50 ml of 1% aqueous sodium hypochlorite solution[6] and then 100 ml of water. The organic phase was dried ($MgSO_4$) and concentrated to give 1.39 g of pale yellow oil[7] which solidified on standing. Recrystallization from ether gave a first crop of 0.87 g of colorless crystals, mp 92–93.5°, and a second crop of 0.14 g of crystals, mp 87–92.5°, for a total yield of 1.01 g (66%) of the hydroxy sulfonamide, **4**. When this same procedure was carried out on a ½-mol scale, 108 g (71%) of hydroxy sulfonamide **4** was produced; for convenience less *tert*-butyl alcohol was used so that the reaction was three times as concentrated as described above.

Procedure B. The procedure is the same as that described above for α-methylstyrene with the following exceptions: (1) the substrate was 0.81 g (5.0 mmol) of methyl cinnamate, (2) in addition to the other reagents 1.06 g (6.25 mmol) of silver nitrate was added, (3) the heterogeneous reaction mixture was stirred at 60°[8] until all olefin was consumed (~20 hr), (4) prior to the usual work-