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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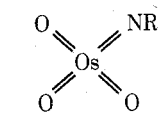
Received October 22, 1975

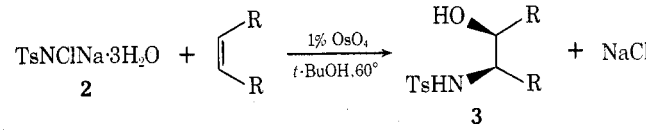
Osmium-Catalyzed Vicinal Oxyamination of Olefins by Chloramine-T

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



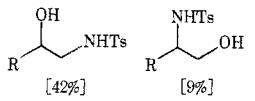
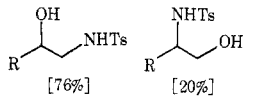
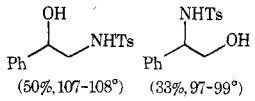
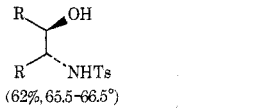
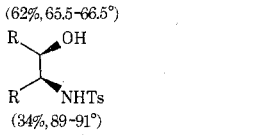
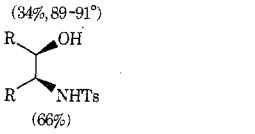
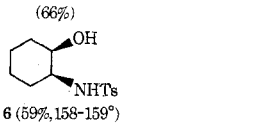
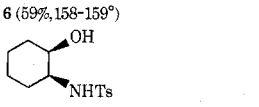
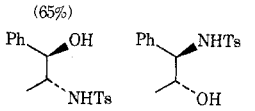
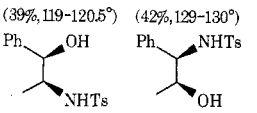
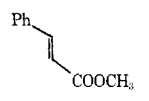
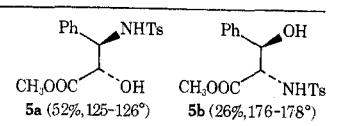
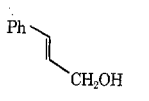
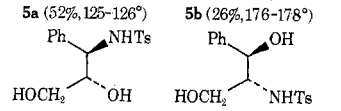
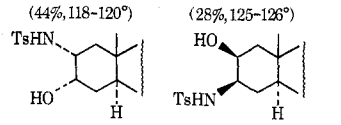
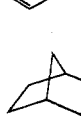
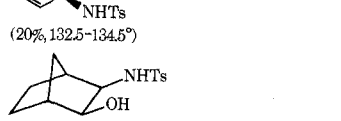
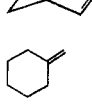
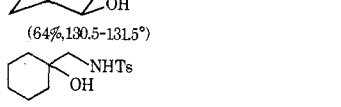
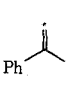
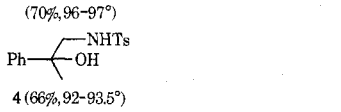
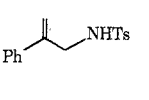
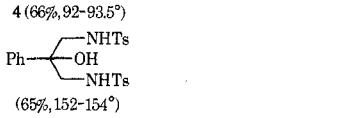
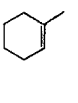
2 **3**

(**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-

Table I[a]

Example	Olefin	Procedure, °C, hr	Products[b]
1	1-Decene	A, 60, 3	 [42%] [9%]
2	1-Decene	B, 25, 2	 [76%] [20%]
3	Styrene	B, 25, 15	 (50%, 107-108°) (33%, 97-99°)
4	(*E*)-5-Decene	A, 60, 36	 (62%, 65.5-66.5°)
5	(*Z*)-5-Decene	A, 60, 3	 (34%, 89-91°)
6	(*Z*)-5-Decene	B, 25, 22	 (66%)
7	Cyclohexene	A, 60, 12	 6 (59%, 158-159°)
8	Cyclohexene	B, 25, 6[c]	 (65%)
9		B, 60, 15	 (39%, 119-120.5°) (42%, 129-130°)
10		B, 60, 15	 (26%, 111-113°) (59%, 104-105°)
11		B, 60, 20	 5a (52%, 125-126°) 5b (26%, 176-178°)
12		B, 60, 20	 (44%, 118-120°) (28%, 125-126°)
13	Δ²-Cholestene	B, 60, 20	 (56%, 235-237°) (31%, 185-188°)
14		A, 60, 44	 (20%, 132.5-134.5°)
15		A, 60, 44	 (64%, 130.5-131.5°)
16		A, 60, 15	 (70%, 96-97°)
17		A, 60, 15	 4 (66%, 92-93.5°)
18		A, 60, 72	 (65%, 152-154°)
19		A, 60, 92	 (82%)

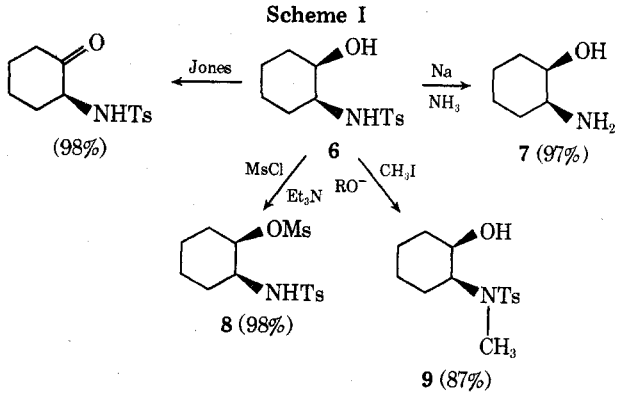
[a] All reactions were performed on a 5-mmol scale as described in detail under procedures A and B. All new compounds exhibited consonant analytical and spectral data. [b] Except in the case of 1-decene where yields (in brackets) were determined by GLC, all yields are for isolated, pure substances. When mixtures were formed, chromatography (on silica gel or basic alumina) was used to separate the regioisomers. When only one hydroxysulfonamide was formed, recrystallization of the crude reaction product was the preferred method of isolation. Melting points are given after the yields. [c] Under these conditions two analogues of Chloramine-T (para-hydrogen and parachloro) also gave with cyclohexene comparable yields of the hydroxysulfonamides related to 6.

up, silver chloride was removed by filtration, and (5) chromatography of the crude product (1.65 g of pale yellow solid) on silica gel gave 0.92 g (52%) of the hydroxy sulfonamide, **5a**, mp 125–126°, and 0.46 g (26%) of the isomer, **5b**, mp 176–178°.

As shown in Scheme I, we have briefly explored some transformations of the hydroxy sulfonamide **6**, derived from cyclohexene. The reduction of **6** to the cis amino alcohol **7** proceeds readily.[9] Because of the acidity of the sulfonamide hydrogen in **6**, the nitrogen can be selectively derivatized (**9**). By means of the mesylate (**8**) and the amino alcohol (**7**) either the oxygen or the nitrogen of these cis vicinal hydroxy amides can be transformed into a leaving group. This should in many cases allow for unique control over the course of molecular rearrangements.

The following olefins either failed to react or gave very low yields of hydroxy sulfonamide: cholesteryl acetate, tetramethylethylene, 1-phenylcyclohexene, cyclohexen-3-one, 1-acetoxycyclohexene, and dimethyl fumarate. In spite of these limitations this new catalytic reaction should prove useful in organic synthesis. It is interesting that in many cases it gives better yields and fewer by-products than the corresponding osmium-catalyzed processes for production of vicinal diols from olefins.[3,4]

Scheme I



Acknowledgment. We are grateful to the National Science Foundation (MP-57-21260) and Hoffmann-La Roche Inc. for support of this research.

References and Notes

(1) (a) K. B. Sharpless, D. W. Patrick, L. K. Truesdale, and S. A. Biller, *J. Am. Chem. Soc.*, **97**, 2305 (1975); (b) K. B. Sharpless, D. W. Patrick, L. K. Truesdale, and S. A. Biller [a full paper on the alkyl imido reagents (**1a**) is in preparation].
(2) It is surprising that Chloramine-T has been so little used in organic synthesis. It is inexpensive and is formally a nitrogen analogue of sodium hypochlorite (NaOCl). Whereas NaOCl is formally a source of ":Ö:", TsNClNa is formally a source of "TsN̈". We have also found recently that anhydrous TsNClNa reacts with selenium metal to produce a potent reagent for allylic amination of olefins [K. B. Sharpless, T. Hori, L. K. Truesdale, and C. O. Dietrich, *J. Am. Chem. Soc.*, **98**, 269 (1976).
(3) K. A. Hoffmann, *Chem. Ber.*, **45**, 3329 (1912).
(4) N. A. Milas and S. Sussman, *J. Am. Chem. Soc.*, **58**, 1302 (1936).
(5) When $AgNO_3$ is added to a stirred suspension of TsNClNa in *tert*-butyl alcohol at room temperature a new more flocculent precipitate is formed: this solid is the silver salt of Chloramine-T (TsNClAg). TsNClAg was prepared by a known method [G. Wittig and D. Hellwinkel, *Chem. Ber.*, **97**, 789 (1964)] and was found to have the same properties in these reactions as the combination of $AgNO_3$ + TsNClNa.
(6) Commercial bleach was diluted 5 to 1. This treatment converts the *p*-toluenesulfonamide, sometimes a by-product of these oxidations, to Chloramine-T, which is preferentially extracted into the aqueous phase. Although the *p*-toluenesulfonamide can also be extracted with aqueous NaOH, this procedure often removes some of the desired product as well.
(7) These crude products contain surprisingly little diol (usually <2%); recall that on the order of 1% diol is necessarily formed since the catalyst is added as osmium tetroxide. We have found that the solid osmate(VI) ester of pinacol also serves as a catalyst and results in no initial diol formation. However, we prefer to use osmium tetroxide because of the convenience of adding a solution.
(8) These $AgNO_3$ modifications were either run at 60 or at 25° as noted in Table I.
(9) Sodium naphthalene in glyme is also effective for the reductive cleavage of sulfonamides [S. Ji, L. B. Gantler, A. Waring, A. Battisti, S. Bank, and W. D. Closson, *J. Am. Chem. Soc.*, **89**, 5311 (1967)]; this procedure also works well for allylic and benzylic sulfonamides and thus should succeed with most of the hydroxy amides in Table I.
(10) Camille and Henry Dreyfus Teacher-Scholar Grant recipient; Alfred P. Sloan Fellow, 1973–1975.
(11) Rohm and Haas Graduate Fellow, 1974–1975.

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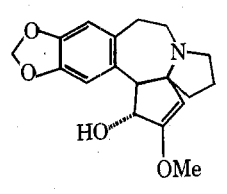
Received November 12, 1975

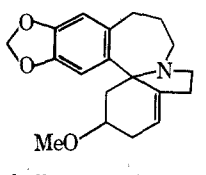
A Biogenetic-Type Approach to Homoerythrina Alkaloids[1]

Summary: A unified synthetic approach to homoerythrina alkaloids via the dibenz[*d,f*]azecine **11** has produced the schelhammera-type skeleton **12** and a new homoerysodienone skeleton **13.**

Sir: Recently, attention has been focused on the total synthesis of cephalotaxine[2] **1**, since it is the alkaloidal portion of the antitumor esters[3] of *Cephalotaxus harringtonia.* The presence of schelhammera-type alkaloids[4] such as 3-epischelhammericine **2** in species of *Cephalotaxus*[5] has led us and others[5a] to the proposal that both the schelhammera-type and *Cephalotaxus* alkaloids are biogenetically related and may be classified as homoerythrina alkaloids. We have been interested in testing in the laboratory a unified approach to homoerythrina skeletons via the substituted phenethylisoquinoline **3** and the pivotal dibenz[*d,f*]azecine **5**, shown in Scheme I. It seemed reasonable that compound **5** could be a possible biogenetic precursor[6] to the *Cephalotaxus* (pathway c, Scheme I) and the *Schelhammera* alkaloids (pathway a, Scheme I) as well as the hitherto unknown homoerysodienone skeleton **8** (pathway b, Scheme I). In fact, the dibenz[*d,f*]azecine **5** is also a homolog of the alkaloid erybidine.[7] In this communication, we wish to report the synthesis of the dibenz[*d,f*]azecine **11** and its oxidative transformation into two homoerythrinadienones **12** and **13.**

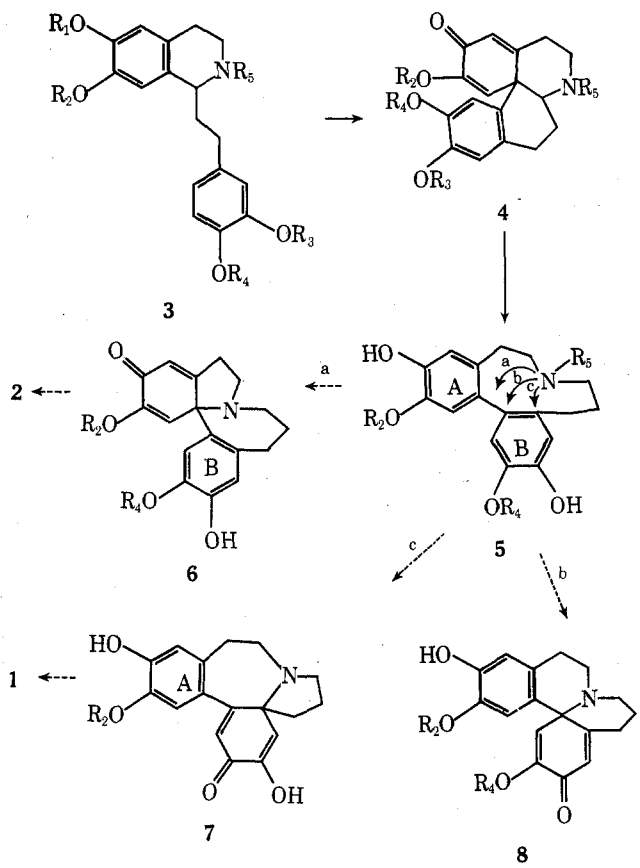


cephalotaxine **1**



schelhammercine **2**

Scheme I



The preparation of the prohomoerythrinadienone derivative **9** from the corresponding phenylethylisoquinoline precursor has been previously described by us.[8] The hydrolytic fragmentation process, which was affected with 1 *N* hydroxide at 0° in methanol, yielded the bisphenolic imine **10** (Scheme II) in quantitative yield. The stereoelectronics of the base-induced bond cleavage requires that the compound **10** initially possess the unusual trans-imine moiety.[9] The bisphenolic imine **10** was converted into its hydrochloride salt (dp 237–239°) with anhydrous hydrogen chloride in ethanol. This imminium chloride was reduced efficiently with sodium borohydride in ethanol to the crystalline bisphenolic amine **11** (R = H, mp 211.5–212.5°).[10] The overall yield from **9** to pure bisphenolic amine **11** was 76%. The preparation of the dibenz[*d,f*]azecine **11** constitutes an efficient synthesis[11] of the homoerybidine skeleton which very likely may occur as a natural product.

A variety of oxidative cyclizations were attempted on the free amine **11** (R = H) and its trifluoroacetamide **11** (R =