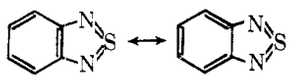
The ^{15}N chemical shifts of **1** and **2** are at about 45 ppm higher field than those of dimethylfurazan and benzofurazan in the same solvent (see Table I). Comparable upfield shifts for ^{15}N resonance of pyridines upon N-oxidation have also been observed.[8]

Furazans and furazan oxides are weak bases (the pK_a values of **2** and **4** are −8.3 and −8.4, respectively[9]) and are not protonated in trifluoroacetic acid ($pK_a = -2.5$[10]), but are expected to be extensively hydrogen bonded to this solvent. The relatively small solvent shifts (6–18 ppm) observed for **1–4** are in agreement with this conclusion. The influence of trifluoroacetic acid on the ^{15}N chemical shift of 2,1,3-benzothiadiazole (**5**) is only slightly larger than that observed for compounds **1–4.** On the other hand, substantial upfield shifts are observed for the ^{15}N resonance of 2,1,3-benzoselenadiazole (**6**) in trifluoroethanol and trifluoroacetic acid (18.5 and 61.7 ppm, respectively). The solvent shift of 61.7 ppm observed in trifluoroacetic acid seems to be too large to be accounted for by hydrogen bonding and therefore is attributed to protonation.

Replacement of the oxygen in benzofurazan by sulfur to give 2,1,3-benzothiadiazole (**5**) leads to a large upfield shift of about 85 ppm. Interestingly, the ^{15}N chemical shift of 2,1,3-benzoselenadiazole (6) appears only 43 ppm upfield from that of benzofurazan. The unexpectedly high-field position of the ^{15}N resonance of **5** indicates that the type of bonding between sulfur and nitrogen may well be different from that between oxygen and nitrogen (and selenium and nitrogen as well). Participation of 3d orbitals of sulfur to form sulfur diimide type resonance structures **5a** and **5b** is one possible explanation. Similar resonance is highly unlikely for benzofurazan, and the 4d orbitals of selenium may not be easily involved (because of the large difference in sizes of nitrogen and selenium orbitals) for this type of π bonding.

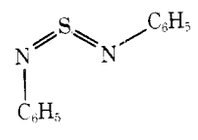
To help determine the importance of resonance structures **5a** and **5b** for 2,1,3-benzothiadiazole (**5**), we have obtained ^{15}N



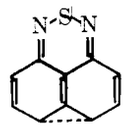
5a **5b**

NMR spectra of two sulfur diimides, namely naphtho[1,8-*cd*][1,2,6]thiadiazine-2-S^{IV} (**7**) and *N,N'*-diphenylsulfur diimide (**8**) (see Table I). The ^{15}N chemical shifts of **7** and **8** are at even higher fields than those of **4,** which lends support to the postulation of the sulfur diimide type resonance forms **5a** and **5b.**

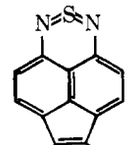
N,N'-Diphenylsulfur diimide (**8**) is known from dynamic NMR spectroscopy to have an unsymmetrical structure (**8a**), and the free-energy barrier ($\Delta G^{\ddagger}$) for its symmetrization is only about 11 kcal/mol.[11] Thus, at room temperature, the time-averaged ^{15}N spectrum of **8** should be observed and the single ^{15}N resonance is consistent with this conclusion. The ^{15}N chemical shift of diphenylsulfur diimide (**8**) is 30 ppm toward higher field than that of **7.** This relatively large difference may be due solely to the possibility of *Z,Z*, *Z,E*, and *E,E* configurations for **8,** but only *Z,Z* for **7.** However, it may be that resonance as exemplified by structure **7a** with a formal bond between the 4,5 carbons contributes to the hybrid and, if this is so, one might well expect a lower field ^{15}N shift for **7** than for **8.** Structure **7a** is consistent with the fact that **7** readily undergoes 1,11-cycloadditions with substances such as dimethyl acetylenedicarboxylate to give compounds of type **10.**[12]



8a



7a



10

Experimental Section

Compounds **1,**[13] **2,**[14] **3,**[15] **4,**[16] **5,**[17] **7,**[18] and **8**[19] were prepared as previously described. Compound **6** was obtained from Aldrich and used without further purification. Reagent grade acetone, dimethyl sulfoxide, trifluoroethanol, and trifluoroacetic acid were employed as solvents.

The natural-abundance ^{15}N spectra were obtained at a frequency of 18.25 MHz with a Bruker WH-180 pulse spectrometer that has been described in detail elsewhere.[20] With 25 mL of 2 M solutions in 25-mm o.d. spinning sample tubes, useful spectra could usually be obtained with accumulation times of 2–3 h, a 45° pulse angle, 4K data points, 3000-Hz spectrum width, and a pulse interval of 30 s. A 5-mm concentric tube containing a 1 M solution of 98% ^{15}N-enriched nitric acid in D_2O provided both the external reference standard and the field-frequency lock. The protons were decoupled at a power of 4 W by the gating technique.[21] The sample temperatures for normal spectra were about 30 °C. Chemical shifts are reported in parts per million from $H^{15}NO_3$ with a precision of about ±0.1 ppm.

Registry No.—(*Z,Z*)-**8,** 66085-13-0; (*Z,E*)-**8,** 66085-14-1; (*E,E*)-**8,** 66085-15-2.

References and Notes

(1) Supported by the Public Health Service, Research Grant No. GM-11072, from the Division of General Medical Sciences, and by the National Science Foundation.
(2) V. Markowski, G. R. Sullivan, and J. D. Roberts, *J. Am. Chem. Soc.*, **99,** 714 (1977); D. Gust and J. D. Roberts, *ibid.*, **99,** 3637 (1977).
(3) G. E. Hawkes, E. W. Randall, and W. E. Hull, *J. Chem. Soc., Perkin Trans. 2,* 1268 (1977).
(4) G. C. Levy, C. E. Holloway, R. C. Rosanske, J. M. Hewitt, and C. H. Bradley, *Org. Magn. Reson.*, **8,** 643 (1976).
(5) G. Englert, *Z. Electrochem.*, **65,** 854 (1961); M. Witanowski, L. Stefaniak, and H. Januszewski in "Nitrogen NMR", M. Witanowski and G. A. Webb, Ed., Plenum Press, New York, N.Y., 1973, p 231.
(6) F. B. Mallory and A. Cammarata, *J. Am. Chem. Soc.*, **88,** 61 (1966).
(7) K. I. Dahlqvist and S. Forsén, *J. Magn. Reson.*, **2,** 61 (1970); F. A. L. Anet and I. Yavari, *Org. Magn. Reson.*, **8,** 158 (1976).
(8) I. Yavari and J. D. Roberts, *Org. Magn. Reson.*, in press.
(9) A. J. Boulton and P. B. Ghosh, *Adv. Heterocycl. Chem.*, **10,** 1 (1969).
(10) F. Klages, K. Bott, and P. Hegenberg, *Angew. Chem., Int. Ed. Engl.*, **1,** 563 (1962).
(11) J. Kuper, P. I. Van Vliet, and K. Vrieze, *J. Organomet. Chem.*, **108,** 257 (1976).
(12) S. F. Gait, M. J. Rance, C. W. Rees, R. W. Stephenson, and R. C. Storr, *J. Chem. Soc., Perkin Trans. 1,* 556 (1975).
(13) J. H. Boyer and U. Toggweiller, *J. Am. Chem. Soc.*, **79,** 895 (1957).
(14) P. A. S. Smith and J. H. Boyer, "Organic Syntheses", Collect. Vol. 5, Wiley, New York, N.Y., 1963, p 74.
(15) L. S. Behr and J. T. Brent, ref 14, p 349.
(16) R. J. Gaughran, J. P. Picard, and J. V. R. Kaufman, *J. Am. Chem. Soc.*, **76,** 2233 (1954).
(17) A. O. Fitton and R. K. Smally, "Practical Heterocyclic Chemistry", Academic Press, New York, N.Y., 1968, p 63.
(18) H. Beecken, *Chem. Ber.*, **100,** 2164 (1967).
(19) G. Kresze and W. Wucherpfenning, *Angew. Chem., Int. Ed. Engl.*, **6,** 149 (1967).
(20) D. Gust, R. B. Moon, and J. D. Roberts, *Proc. Natl. Acad. Sci. U.S.A.*, **72,** 4696 (1975).
(21) Gated proton decoupling was employed to quench the NOE. In this technique, the proton decoupler is on only during data acquisition (1.3 s) following the observing pulse, and is off for a relatively long time (30 s) between the end of one data acquisition period and the start of the next.

Improvements in the Osmium-Catalyzed Oxyamination of Olefins by Chloramine-T

Eugenio Herranz and K. Barry Sharpless[33]

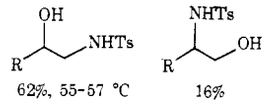
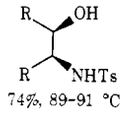
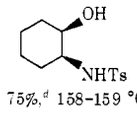
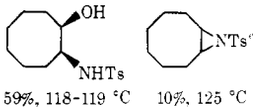
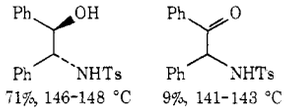
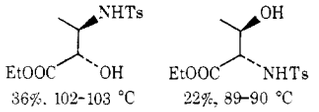
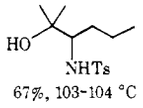
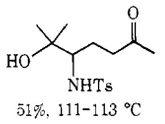
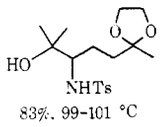
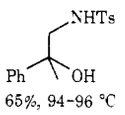
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received January 17, 1978

We have reported that Chloramine-T (**1**) reacts with olefins in the presence of an osmium catalyst to afford vicinal hydroxy *p*-toluenesulfonamides (**2**).[1] This catalytic procedure was a

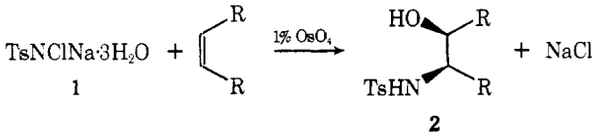
0022-3263/78/1943-2544$01.00/0

Table I[a]

Example	Olefin	Registry no.	Procedure (hours)	Products,[b] yield, mp	Registry no.
1	1-Decene[c]	872-05-9	A (12)	 62%, 55-57 °C; 16%	58107-38-3, 58107-39-4
2	(*Z*)-5-Decene	7433-78-5	A (36)	 74%, 89-91 °C	58162-20-2
3	Cyclohexene	110-83-8	A (12)	 75%,[d] 158-159 °C	58107-40-7
4	Cyclooctene	931-88-4	A (72)	 59%, 118-119 °C; 10%, 125 °C	65996-40-9, 65996-41-0
5	(*E*)-Stilbene	103-30-0	A (12)	 71%, 146-148 °C; 9%, 141-143 °C	65996-42-1, 65996-43-2
6	(*E*)-Ethyl crotonate	623-70-1	A (12)	 36%, 102-103 °C; 22%, 89-90 °C	65996-44-3, 66036-34-8
7	2-Methyl-2-hexene[f]	2738-19-4	B (24)	 67%, 103-104 °C	66027-68-7
8	2-Methyl-2-hepten-6-one[g]	110-93-0	B (2)	 51%, 111-113 °C	65996-45-4
9	2-Methyl-2-hepten-6-ethylene ketal[h]	3695-38-3	B (24)	 83%, 99-101 °C	65996-46-5
10	α-Methylstyrene[i]	98-83-9	B (16)	 65%, 94-96 °C	58107-54-3

[a] Unless noted otherwise, all of the reactions were performed on a 1-mmol scale as described in detail under procedures A and B. All new compounds exhibited appropriate spectral and analytical data. [b] All yields are for isolated pure substances and are based on initial moles of olefin. When mixtures were formed, chromatography on silica gel was employed to separate the regioisomers. When only one hydroxysulfonamide was formed, recrystallization of the crude product was the preferred method of isolation. [c] When Chloramine-T was generated in situ by the reaction of *p*-toluenesulfonamide with Chlorox, similar yields of the oxyamination products were obtained. [d] Comparable yields were also obtained on 0.1-, 0.5-, and 1-mol scale oxyaminations of cyclohexene. [e] A control experiment revealed that the formation of the aziridine was not dependent on the presence of the osmium catalyst. [f] Addition of dicyclohexyl-18-crown-6 or tetraethylammonium acetate (0.05 mmol) accelerated the reaction (presumably by increasing the concentration of the TsNCl anion in solution), but the final yields were not affected by these additives. [g] Due to the presence of the ketone in this substrate, the usual borohydride reduction step in the workup (procedure B) was omitted. [h] Prepared from the ketone under standard conditions (ethylene glycol, TsOH, benzene; reflux). [i] This reaction was run on a 1.0-mol scale with relatively less solvent (1000 mL of *tert*-butyl alcohol; therefore, five times more concentrated).

significant improvement over the stoichiometric oxyamination reaction,[2] but it exhibited an unusual dependence on silver(I) ion. For monosubstituted and sym-disubstituted olefins the addition of silver nitrate generally resulted in faster reactions



2

and better yields of oxyaminated products,[3a] while for unsym-disubstituted and trisubstituted olefins the presence of silver ion generally had a deleterious effect on the desired oxyamination reaction.[3b] This situation led us to recommend two different (one with added $AgNO_3$ and one without) procedures for these two different classes of olefins. We report here a new procedure, employing phase-transfer catalysis (PTC), which is ideal for the oxyamination of monosubstituted and sym-disubstituted olefins. This PTC method is intended to replace the silver nitrate method ("procedure B"

in our original publication[1]). It is not only more economical (no silver salts) but also seems to afford better yields[4] and may have a somewhat greater scope[5] than the earlier method.

The PTC method (procedure A of Table I) employs benzyltriethylammonium chloride as the phase-transfer catalyst. The recipe calls for 5% of the PTC catalyst, and this is the optimum amount; the use of more or less catalyst gives less satisfactory results. Both benzene–water and chloroform–water systems were tried and found to be equally effective.

As with the earlier silver method,[1] the PTC method gives poor results with trisubstituted and unsym-disubstituted olefins.[6] The oxyamination product may still form, but it will usually be accompanied by a number of byproducts. Fortunately, this class of olefins is successfully oxyaminated by a simple alternative procedure. One performs the reaction by dissolving the olefin in *tert*-butyl alcohol, adding Chloramine-T and the osmium catalyst, and then stirring the resulting suspension while heating in an oil bath maintained at 55–60 °C. This is designated as procedure B in this work and is almost identical with "procedure A" in our earlier[1] publication. The only important difference is in the workup procedure employed.

Shortly after the original publication[1] *appeared, a rather serious drawback to the recommended isolation procedure was encountered.* In order to remove the *p*-toluenesulfonamide byproduct (by conversion to TsNClNa), the methylene chloride extract was washed with a dilute aqueous sodium hypochlorite solution. We and others[7] have since found that some vicinal hydroxy-*p*-toluenesulfonamide products are unstable to this washing procedure. *We therefore recommend that this hypochlorite wash be avoided.* An alternative method for removing the sulfonamide byproduct is employed here. It involves washing with a saturated sodium chloride[8] solution containing 1% sodium hydroxide.

Another difference in the workup applies only to procedure B. In this case sodium borohydride is used to reduce the osmate esters. This has proved superior to the bisulfite reductant used previously.[1] In situations where borohydride would react with another functionality present in the molecule (e.g., example 8 in Table I), one can either try bisulfite or omit the reduction step altogether. In the latter case the small (ca. 1%) amount of reddish-yellow osmate ester is removed by chromatography or crystallization.

The results in Table I are largely self-explanatory, but a few things deserve comment. Cyclooctene (example 4) yields not only the expected vicinal hydroxysulfonamide but also the corresponding aziridine. Interest in this side product was diminished by the observation that its formation is not dependent on the presence of the osmium catalyst.

This osmium-catalyzed oxyamination process seems to be less troubled by the type of over-oxidation problems (i.e., ketol formation and oxidative cleavage of the C–C bond) which accompany the analogous osmium-catalyzed vicinal dihydroxylation of olefins.[9] The *p*-toluenesulfonamide moiety, itself very resistant to oxidation,[10] seems to confer enhanced stability toward oxidants upon the adjacent hydroxyl group. However, in those cases where the product contains a secondary hydroxyl function, traces[11] of the α-ketosulfonamides resulting from further oxidation can usually be observed by GLC analysis.

We[12] have also observed that these α-ketosulfonamides are further oxidized under the reaction conditions in a process which consumes several moles of Chloramine-T.[13] The nature of all of the products formed in this process has not yet been determined,[13] but *p*-toluenesulfonamide is produced. This pathway probably accounts for most of the *p*-toluenesulfonamide byproduct produced in these catalytic oxyaminations. Consistent with this statement is the observation that only traces of *p*-toluenesulfonamide arise in those oxyaminations where the β-hydroxysulfonamide produced has a tertiary hydroxyl group.

An earlier report[14] on the osmium-catalyzed oxidative cleavage of carbonyl compounds with Chloramine-T, and our own observations with α-ketosulfonamides, suggested that ketonic functionality might be incompatible with these oxyaminations. The keto olefin in example 8 reveals that this is not the case. However, this ketone function does seem to interfere to some extent since the yield of oxyaminated product increases by 30% when it is protected as the ethylene ketal (example 9). This latter experiment also demonstrates that ketals are stable to the reaction conditions.

The chloramine derivatives ($ArSO_2NClNa$) of a variety of other arylsulfonamides (Ar = phenyl, *o*-tolyl, *p*-chlorophenyl, *p*-nitrophenyl, and *o*-carboalkoxyphenyl) have been used successfully in these catalytic oxyaminations.[15] Since only Chloramine-T (Ar = *p*-tolyl) and Chloramine-B (Ar = phenyl) are commercially available, we have developed a convenient procedure for generating the chloramines in situ for use in the modification involving phase-transfer catalysis. One simply stirs a suspension of the arylsulfonamide with an appropriate amount of Chlorox until a homogeneous solution is obtained. When this solution is used in the PTC method, the yields of oxyaminated products are comparable with those obtained with isolated chloramine salts.

Although the examples in Table I were performed on a 1-mmol scale, both procedures A and B have been easily carried out on a 1-mol scale. For convenience, these larger scale reactions were performed with relatively less solvent (up to five times more concentrated); high yields were still realized, and excessive heat evolution, which is a common problem for large scale oxidations, was not encountered.

In conclusion, although the improvements described here should significantly increase the utility of these catalytic oxyaminations, the reaction still has important limitations. For example, neither procedure (A or B) succeeds with tetramethylethylene,[16] cholesterol,[16] diethyl fumarate,[17] or 2-cyclohexen-1-one,[17] and it seems reasonable to anticipate negative results with most hindered tri- and tetrasubstituted olefins.[18] Finally, no matter how effective this version of the oxyamination process becomes, it is circumscribed by the obvious fact that the nitrogen is introduced bearing a sulfonamide protecting group. In some cases the sulfonamide moiety may be acceptable or even desirable, but in others the difficulties[19] associated with removing sulfonamide protecting groups will restrict the usefulness of these oxyaminations. Fortunately, for the latter cases, we have recently developed another modification of the osmium-catalyzed oxyaminations.[20] This new method employs *N*-chloro-*N*-argento-*tert*-butyl or benzyl carbamates and therefore produces oxyamination products which bear *t*-Boc or Boc protecting groups on the nitrogen.

Experimental Section

Materials. The olefins were obtained from either Chemical Samples Co. or Aldrich and used without purification. Reagent grade chloroform and *tert*-butyl alcohol were employed as solvents. Chloramine-T trihydrate[34] and benzyltriethylammonium chloride were used as obtained from Aldrich. Osmium tetroxide was purchased from Matthey Bishop, Inc.

Preparation of Osmium Tetroxide Catalyst Solution. Over the past few years we have tried a number of ways of preparing osmium tetroxide stock catalyst solutions. Solvents such as hexane, chloroform, carbon tetrachloride, and *tert*-butyl alcohol have all been used. In all of these solvents an insoluble precipitate (thought to be OsO_2) forms with time. If, however, one adds a small amount of *tert*-butyl hydroperoxide,[21] great stability is imparted to these organic solutions of OsO_4. We now use such stabilized *tert*-butyl alcohol solutions of OsO_4 for all[1,9] of our osmium-catalyzed processes.

Osmium tetroxide is commonly supplied in 1-g (3.94 mmol) amounts in sealed glass ampules. Working in a well-ventilated hood,

one of these ampules is scored in the middle and broken open, and the two halves are dropped into a clean brown bottle containing 199 mL of reagent grade *tert*-butyl alcohol and 1 mL of 90+% *tert*-butyl hydroperoxide (Aldrich). The bottle is capped (use caps with either polyethylene or Teflon liners) and then swirled for a while to ensure dissolution of the OsO_4. Each milliliter of this stock solution contains 5 mg (2.0 mmol) of OsO_4. These solutions are stored in the hood at room temperature and seem to be very stable.[22]

Procedure A (Phase-Transfer Method). A 25-mL one-neck round-bottom flask, equipped with a magnetic stirrer and a reflux condenser, is charged with 1 mmol of olefin, 5 mL of chloroform, 0.50 mL (0.01 mmol) of osmium tetroxide catalyst solution, 352 mg (1.25 mmol) of Chloramine-T trihydrate, 11.4 mg (0.05 mmol) of benzyltriethylammonium chloride, and 5 mL of distilled water. The flask is then placed in an oil bath maintained at 55–60 °C.[23] The mixture is stirred, and the progress of the reaction is monitored by following the disappearance of olefin by TLC or GLC.[24] When the reaction is completed, 104 mg (1 mmol) of sodium bisulfite is added and the mixture is refluxed for 3–6 h.[25] This step reduces[26] the trace (ca. 1%) of osmate ester present. After reduction, the two phases are separated, the flask and separatory funnel are washed with ca. 10 mL of chloroform, and the combined organic phase is washed with saturated brine containing 1% sodium hydroxide until the $TsNH_2$ has been extracted (usually once or twice) and then with saturated brine and dried ($MgSO_4$) to give a clear yellow[27] solution. Concentration affords the crude β-hydroxy-*p*-toluenesulfonamide which is purified by crystallization or chromatography.

Procedure A has also been performed without difficulty on a 1-mol scale. For convenience, these large scale reactions are run five times more concentrated (with respect to both the $CHCl_3$ and H_2O phases and the OsO_4 catalyst solution) than the 1-mmol scale reactions described in detail above. Thus, 82.2 g (1 mol) of cyclohexene afforded 205 g (76%) of the pure oxyaminated product. For these larger scale more concentrated reactions, it is sometimes necessary to modify the workup to deal with precipitation of the more highly crystalline oxyamination products.[28]

Procedure B (*tert*-Butyl Alcohol Method). A 10-mL one-neck round-bottom flask, equipped with a magnetic stirrer and a reflux condenser, is charged with 1 mmol of olefin, 5 mL of *tert*-butyl alcohol, 0.50 mL (0.01 mmol) of osmium tetroxide catalyst solution, and 352 mg (1.25 mmol) of Chloramine-T trihydrate. The flask is placed in an oil bath maintained at 55–60 °C, and the resulting suspension (Chloramine-T is only slightly soluble under these conditions) is stirred until, as judged by TLC or GLC, all of the olefin has been consumed.[29] Then 11.1 mg (0.03 mmol) of sodium borohydride is added, and the mixture is stirred for 1 h at room temperature.[30] The reaction mixture is concentrated (rotary evaporator) to remove most of the *tert*-butyl alcohol solvent, and the residue is taken up in 20 mL of methylene chloride. The resulting solution is washed with saturated brine containing 1% sodium hydroxide until the $TsNH_2$ has been extracted (usually once or twice) and once with saturated brine and dried ($MgSO_4$) to give a clear yellow[27] solution. Concentration affords the crude β-hydroxy-*p*-toluenesulfonamide which is purified by crystallization or chromatography.

Procedure B has also been performed on a 1-mol scale at five times the concentration described above for the 1-mmol experiments. No problems associated with the scale-up were encountered. Thus, 118.2 g (1 mol) of α-methylstyrene gave 198 g (65%) of the pure oxyamination product.[31]

A Simple Method for In Situ Generation of the Chloramine Salts (from the Arylsulfonamides) for Direct Use in Procedure A. In a 25-mL one-neck round-bottom flask, equipped with a magnetic stirrer, are combined 1.25 mmol of the arylsulfonamide, 3.4 mL of distilled water, and 1.65 mL (ca. 1.25 mmol) of Chlorox.[32] The resulting suspension is stirred for 10 min (or until a homogeneous solution is produced) at room temperature. The flask is then fitted with a reflux condenser, and after adding 5 mL of chloroform, 1 mmol of the olefin, 0.01 mmol of OsO_4 catalyst, and 0.05 mmol of benzyltriethylammonium chloride, one proceeds as described in procedure A above.

Acknowledgment. We are grateful to the National Science Foundation (CHE74-21260), Hoffmann-LaRoche, and Eli Lilly for financial support. The oxyamination of olefins under phase-transfer conditions was first observed in our laboratory by Anthony O. Chong (Ph.D. Thesis, M.I.T., 1976), and we are indebted to him for this discovery.

Registry No.—1, 127-65-1; OsO_4, 20816-12-0.

References and Notes

(1) K. B. Sharpless, A. O. Chong, and K. Oshima, *J. Org. Chem.*, **41**, 177 (1976).
(2) (a) K. B. Sharpless, D. W. Patrick, L. K. Truesdale, and S. A. Biller, *J. Am. Chem. Soc.*, **97**, 2305 (1975); (b) D. W. Patrick, L. K. Truesdale, S. A. Biller, and K. B. Sharpless, *J. Org. Chem.*, in press.
(3) (a) The favorable effect of silver ion on these reactions appears to be due to two effects. Its most obvious role is to scavenge chloride ion. We have previously demonstrated that the presence of chloride ion retards the rate of these catalytic oxyaminations.[1] More recently we have found that the presence of excess silver ion has a general accelerating effect on the catalytic process (see also ref 20). (b) The unfavorable effect of silver ion in the case of these more highly substituted olefins may be rationalized as follows. The silver salt of Chloramine-T (TsNClAg), as demonstrated by control experiments, reacts with olefins in the absence of osmium catalyst to give various aminated products (e.g., allylic sulfonamides). The rate of this uncatalyzed reaction increases as the degree of olefin substitution increases, whereas the rate of the osmium-catalyzed oxyamination process decreases as the degree of olefin substitution increases (see ref 16).
(4) For example, compare the yields for cyclohexene and (*Z*)-5-decene in Table I with those reported previously.[1]
(5) This statement must be regarded as tentative since it is based on only one example (5, Table I). Stilbene did not react in the earlier systems.[1]
(6) Olefins are more prone toward direct (i.e., not involving osmium catalysis) reaction with those chloramine salts having silver or quaternary ammonium species as counterions.
(7) I. Dyong, Q. Lam-Chi, G. Schulte, B. Fraser-Reid, and J. L. Primeau, *Angew. Chem., Int. Ed. Engl.*, **16**, 553 (1977).
(8) Some β-hydroxysulfonamide products show a tendency to be extracted into aqueous base. This problem is prevented by the presence of the brine.
(9) (a) K. B. Sharpless and K. Akashi, *J. Am. Chem. Soc.*, **98**, 1986 (1976); (b) K. Akashi, R. E. Palermo, and K. B. Sharpless, *J. Org. Chem.*, **43**, 2063 (1978).
(10) Numerous attempts to oxidize (dehydrogenate to the imino structure) the allylic *p*-toluenesulfonamide derivative of cyclohexene all met with failure: S. A. Biller and K. B. Sharpless, unpublished results.
(11) Usually only 1–2%, but in the case of stilbene (example 5, Table I) 9%, of the α-ketosulfonamide was actually isolated.
(12) E. Herranz and K. B. Sharpless, unpublished results.
(13) Preliminary results indicate that the rate of further oxidation of the α-ketosulfonamides may vary considerably depending on the specific case. Thus, the fact that only traces of these products are present in most of the cases studied (Table I) may be due to their rapid further transformation. This possibility and the nature of the further transformation products derived from the α-ketosulfonamides are presently under investigation.
(14) S. P. Mushran, R. Saneki, and M. C. Agrawal, *Z. Naturforsch. B*, **27**, 1161 (1972).
(15) Oxyamination was not achieved with two arylsulfonamides bearing electron-donating substituents on the aromatic ring (Ar = 4-methoxyphenyl and 2,5-dimethoxyphenyl). However, failure may have been due to the instability of the chloramine derivatives in these cases.
(16) No reaction occurs, and the Chloramine-T is not consumed (see ref 18).
(17) Both the Chloramine-T and part of the olefin are consumed, but the oxyamination product has not been detected in the reaction mixtures. It seems likely that it forms but is unstable to the reaction conditions. Both of these olefins do form isolable oxyamination products under the milder (room temperature) conditions of a more recent oxyamination procedure.[20]
(18) See ref 9b for a discussion of the problems which are thought to prevent osmium-catalyzed oxidations of hindered olefins.
(19) Arylsulfonamide protecting groups are notoriously difficult to hydrolyze under both acidic and basic conditions.
(20) E. Herranz, S. A. Biller, and K. B. Sharpless, *J. Am. Chem. Soc.*, in press.
(21) In the past, hydrogen peroxide has been used to stabilize osmium tetroxide solutions; see, for example, R. Daniels and J. L. Fischer, *J. Org. Chem.*, **28**, 320 (1963). In our opinion *tert*-butyl hydroperoxide is superior to H_2O_2 for this purpose. It is more stable than H_2O_2 and has the added advantage of being very soluble in organic solvents.
(22) We have been using these solutions too fast to know much about their longevity. They are stable at room temperature for at least 4 months, and long-range stability tests are now under way.
(23) The reactions do not reflux, but the condensation of solvent droplets is observed.
(24) If olefin remains after a long reaction time, the aqueous layer should be tested (starch–iodide paper) for the presence of Chloramine-T. If this test is negative, more Chloramine-T may be added. This will result in consumption of the remaining olefin, but not necessarily a greater yield of the desired oxyamination product. The problem in these cases is thought to be due to over-oxidation or instability of the hydroxysulfonamide product. In extreme cases (see, for example, ref 17), none of the desired oxyamination product is observed.
(25) The rate of reduction of the osmate esters varies considerably. It is rapid for monosubstituted olefins but is much slower in the case of disubstituted olefins such as (*Z*)-5-decene. The reduction process can be monitored by TLC since the osmate esters give rise to a faint reddish-yellow spot which always moves faster than the free β-hydroxysulfonamides.
(26) The nature of the reduced osmium species is unknown. When the reduction is complete, most of the osmium is present as black particles suspended in both the aqueous and organic phases. The last of these particles is removed during the filtration to remove the $MgSO_4$ used to dry the organic phase.
(27) The nature of the substance which imparts this yellow color is unknown. Atomic absorption analysis reveals an osmium content of only 2.4%.

Although soluble in organic solvents, it remains at the origin on TLC plates and is therefore easily separated from the desired products. The yellow color also remains in solution if the products are purified by crystallization instead of chromatography.

(28) The product derived from cyclohexene is especially crystalline and begins to crystallize if the chloroform phase is allowed to cool (this problem does not arise in the more dilute general procedure described above). A detailed procedure for oxyamination of cyclohexene on large scales is being readied for submission to "Organic Syntheses".

(29) As in procedure A (see ref 24), olefin may remain even after all of the Chloramine-T has been consumed (i.e., negative starch–iodide test). This is the case in example 8 of Table I. We suspect that part of the Chloramine-T is spent in side reactions with the ketone function. This hypothesis is supported by the observation that the olefin is completely consumed when the ketone is protected as the ethylene ketal (example 9, Table I).

(30) This replaces the aqueous bisulfite reduction procedure used earlier. We found that although the bisulfite method would slowly reduce osmate esters from unsym-disubstituted olefins, the osmate esters derived from trisubstituted olefins were inert to this treatment. As mentioned earlier (ref 25), the reddish-yellow osmate esters can be detected by TLC. Treatment with $NaBH_4$ reduces even these more hindered osmate esters rapidly at room temperature. As with the bisulfite reduction used in procedure A (ref 26), the nature of the reduced osmium species is unknown. The last of the black, osmium-containing particles is removed when the $MgSO_4$ is separated from the organic phase by filtration.

(31) The procedure for oxyamination of α-methylstyrene on large scales is being readied for submission to "Organic Syntheses".

(32) Chlorox brand commercial household bleach was employed. The bottle states that it contains 5.25% of sodium hypochlorite. The approximate density of the solution is 1.076; thus, 1 mL contains ca. 0.759 mmol of NaOCl. Slight variations in the strength of these bleach solutions have been observed: M. J. Mintz and C. Walling, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 184.

(33) Address correspondence to this author at the Department of Chemistry, Stanford University, Stanford, Calif. 94305.

(34) Since an explosion has recently been reported [*Chem. Eng. News*, **55** (49), 56 (1977)] while handling anhydrous Chloramine-T, it is important to emphasize the difference in stability between anhydrous Chloramine-T and the corresponding trihydrate, which is required in the present work. Commercially available Chloramine-T trihydrate is a very stable substance, and no special precautions are necessary in handling it.

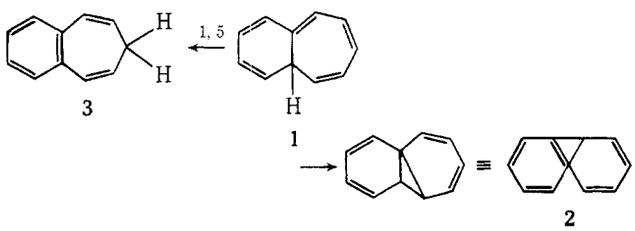
Attempted Synthesis of 2,4,8,10-Tricyclo[5.4.0.0^{1,6}]undecatetraene: Bisnorcaradiene

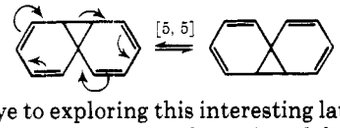
Richard H. Parker and W. M. Jones*

Department of Chemistry, University of Florida, Gainesville, Florida 32611

Received November 7, 1977

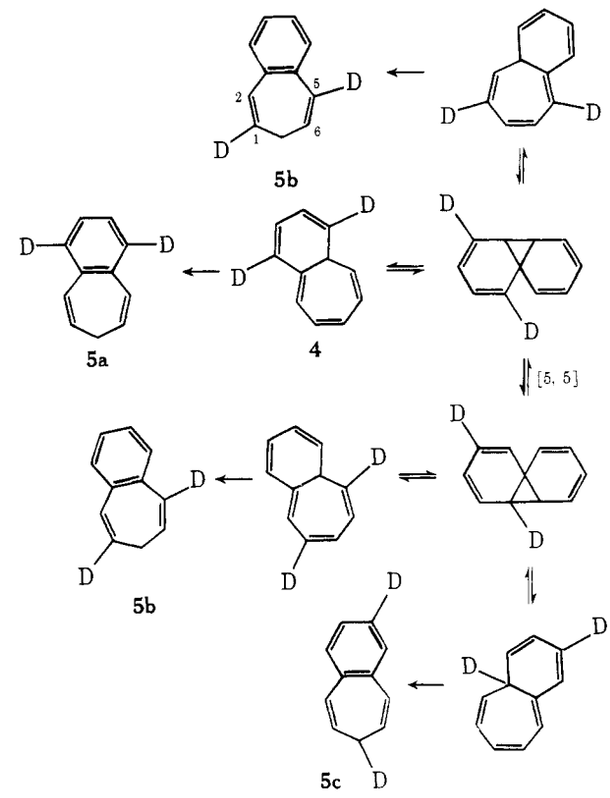
In addition to 1,5-sigmatropic rearrangement of hydrogen, 1,3,5,8,10-bicyclo[5.4.0]undecapentaenes are believed to undergo electrocyclic ring closure to 2,4,8,10-tricyclo[5.4.0.0^{1,6}]undecatetraenes **2** which have been euphemistically named "bisnorcaradienes." The latter have been suggested to explain substituent scrambling in a number of thermal and photochemical reactions[1] and have aroused further interest because they have the potential to undergo symmetry allowed, degenerate, concerted antara,antara[5,5]-sigmatropic rearrangements,[1b] reactions that are intriguingly reminiscent of semibullvalene rearrangements.[2]



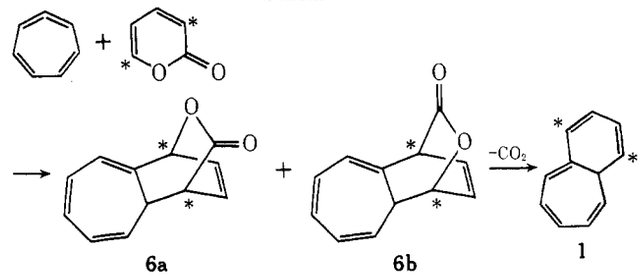


With an eye to exploring this interesting latter possibility, we undertook to generate a deuterium labeled 1,3,5,8,10-bicyclo[5.4.0]undecapentaene **4** which could reveal this degenerate rearrangement. Our plan of attack is outlined in Scheme I where it can be seen that a semibullvalene type of rearrangement would lead to a unique scrambling (**5c**) in the final product.

Scheme I



Scheme II



Our synthetic approach to the labeled bicyclopentaenes is outlined in Scheme II. The essence of the synthesis is a Diels–Alder addition of cycloheptatetraene to 2-pyrone (or, indistinguishably, addition of cycloheptatrienylidene followed by rearrangement) to give one or both of the polycyclic lactones **6a** and/or **6b** which could decarboxylate to the desired polyene.

Cycloheptatrienylidene–cycloheptatetraene has been generated by both base induced dehydrochlorination of a mixture of chlorocycloheptatrienes[3] and photolysis or pyrolysis of the sodium salt of tropone tosylhydrazone.[4] The sensitivity of 2-pyrone to strong base excluded the dehydrochlorination reaction as a viable alternative. The salt of tropone tosylhydrazone was therefore pyrolyzed (110 °C) and photolyzed (to −78 °C) in the presence of 2-pyrone. In no case was there any evidence of the bicyclopentaene **1** but in the pyrolysis reaction there was cleanly (NMR) obtained (30%) isolated 3,4-benzocycloheptatriene. The photolysis was not as clean (in some cases showing the isomeric 1,2-benzocycloheptatriene) but again, even at temperatures as low as −78 °C, there was no evidence for **1**. Again, the predominant product was the benzocycloheptatriene **3**.

Taking formation of **3** as presumptive evidence for **1**, we then undertook to explore the various degenerate rearrange-

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