(14); $n^{25}D$ 1.5760. The yield based on methanesulfenyl chloride was 70%. Anal. Calcd for $C_8H_{11}NS$: C, 62.74; H, 7.19. Found: C, 62.92; H, 7.17.

***N*-Methylethane- and 1-Methylethanesulfenanilide.** The same procedure was followed as outlined for *N*-methylmethanesulfenanilide beginning with the appropriate disulfide. The yields were similar and analytical data are as follows respectively: $n^{25}D$ 1.5653; bp 70 °C (0.1 mm); NMR δ 7.18–6.5 (m, 5, aromatic), 3.2 (s, 3, NCH_3), 2.6 (q, 2, J = 8 Hz, $\mathbf{SCH_2}CH_3$), 1.1 (t, 3, J = 8 Hz, $SCH_2\mathbf{CH_3}$); MS *m/e* (rel intensity) 169 (3.9), 168 (9), 167 (54), 152 (5.4), 140 (3.9), 139 (18), 138 (45), 123 (11.8), 122 (11.8), 109 (27), 108 (4.5), 107 (45), 106 (100), 105 (18), 104 (30), 98 (57), 80 (34), 79 (34), 78 (100), 66 (16), 65 (18), 64 (9), 51 (50). Anal. Calcd for $C_9H_{13}NS$: C, 64.67; H, 7.78; N, 8.35. Found: C, 64.37; H, 7.64; N, 8.37.

***N*-Methyl-1-methylethanesulfenanilide:** $n^{25}D$ 1.5575; NMR δ 7.2–6.5 (m, 5, aromatic), 3.32 (s, 3, NCH_3), 3.28 (septuplet, 1, $\mathbf{SCH}(Me)_2$), 8.82 (d, 6, J = 8 Hz, $SCH(\mathbf{CH_3})_2$); MS *m/e* (rel intensity) 181 (100), 139 (15), 117 (5), 116 (5), 106 (10), 105 (11), 99 (13), 97 (90), 76 (15), 75 (20), 74 (80), 64 (33), 60 (20), 59 (15), 58 (55). Anal. Calcd for $C_{10}H_{15}NS$: C, 66.29; H, 8.28; N, 7.73. Found: C, 66.11; H, 8.14; N, 7.56.

***N*-Methyl-1,1-dimethylethanesulfenanilide.** The sulfenyl chloride was prepared by dissolving 10.7 g of *tert*-butyl disulfide in 50 mL of chloroform and chlorinolysis at room temperature with 2.26 mL of liquid chlorine. Titration and NMR indicated an 85% yield of *tert*-butylsulfenyl chloride based on the amount of chlorine. The condensation with 10.7 g of *N*-methylaniline and purification was done as described earlier. The product was distilled at 0.1 mmHg with the head temperature ranging from 80 to 90 °C. The analytical data are as follows: $n^{25}H$ 1.5505; NMR δ 7.18–6.5 (m, 5, aromatic), 3.35 (s, 5, NCH_3), 1.22 (s, 9. $SC(CH_3)_3$); MS *m/e* (rel intensity) 197 (0.7), 196 (1.4), 195 (14), 141 (7), 140 (10), 139 (100), 123 (7), 122 (10), 107 (93), 96 (28), 78 (21), 77 (21), 76 (93), 60 (36), 56 (86), 50 (32). Anal. Calcd for $C_{11}H_{17}NS$: C, 67.69; H, 8.71; N, 7.18. Found: C, 67.45; H, 8.60; N, 7.09.

Rearrangement of *N*-Methylmethanesulfenanilide. Rearrangement was accomplished with either pure or crude sulfenanilide by heating it at 150 °C in an oil bath. The extent of reaction was determined by monitoring the concentration of starting material by GLC. After all of the starting material had vanished, the reaction mixture was distilled under 0.1 mm of pressure and several fractions were collected, ranging from 45 to 90 °C. GLC analysis of the fractions indicated the presence of *N*-methylaniline and two other components. Separation of each component was accomplished by column chromatography. The column was packed with Florisil at a weight ratio of 30/1 and hexane was used as the eluent. Fractions with similar composition as determined by TLC were combined, concentrated under reduced pressure, and then distilled at 0.1 mmHg. The overall yield of rearranged products using *N*-methylaniline as the limiting reagent was 35%.

2-Methylthio-*N*-methylaniline: bp 70 °C (0.1 mm); NMR δ 7.48–6.3 (m, 4, aromatic), 4.7 (s, 1, NH), 7.3 (s, 3, NCH_3), 2.18 (s, 3, SCH_3); IR (neat) 3500 (NH), 750 cm^{-1} (ortho-disubstituted benzene). Anal. Calcd for $C_8H_{11}NS$: C, 62.74; H, 7.10. Found: C, 63.00; H, 7.35.

4-Methylthio-*N*-methlaniline: bp 78 °C (0.1 mm); NMR δ 7.38–6.08 (m, 4, ArH), 3.68 (s, 1, NH), 2.6 (s, 3, NCH_3), 2.25 (s, 3, SCH_3); IR (neat) 3500 cm^{-1} (NH), 820 cm^{-1} (para-disubstituted benzene). Anal. Calcd for $C_8H_{11}NS$: C, 62.74; H, 7.19. Found: C, 63.01; H, 7.17.

Rearrangement of *N*-Methylethanesulfenanilide. The same procedure as was described earlier for *N*-methylmethanesulfenanilide was followed and the rearranged products were separated the same way. The combined yield of rearranged products was 30% based on *N*-methylaniline.

2-Ethylthio-*N*-methylaniline: bp 80 °C (0.1 mm); NMR δ 7.32–6.22 (m, 4, ArH), 4.92 (s, 1, NH), 2.78 (s, 3, NCH_3), 2.58 (q, 2, $\mathbf{SCH_2}CH_3$), 1.16 (t, 3, J = 8 Hz, $SCH_2\mathbf{CH_3}$); IR (neat) 3600 (n-H), 760 cm^{-1} (ortho-disubstituted benzene); MS *m/e* (rel intensity) 169 (5.2), 168 (13), 167 (100), 139 (4.3), 138 (30), 137 (53), 136 (8.6), 135 (22), 134 (13), 110 (6.5), 109 (6.5), 108 (22), 105 (22), 104 (8.6), 103 (8.6), 96 (86), 79 (4.3), 78 (8.6), 77 (22), 65 (17), 58 (17), 43 (22).

4-Ethylthio-*N*-methylaniline: bp 85 °C (0.1 mm); NMR δ 7.2–6.18 (m, 4, 4 ArH), 3.58 (s, 1, N_1H), 7.34 (s, 3, NCH_3), 2.62 (q, 2, J = 8 Hz, $\mathbf{SCH_2}CH_3$), 1.18 (t, 3, J = 8 Hz, $SCH_2\mathbf{CH_3}$); IR (neat) 3550 (NH), 815 (para-disubstituted benzene); MS *m/e* (rel intensity) 169 (3.8), 168 (7.1), 167 (50), 154 (11), 153 (22), 152 (22), 150 (22), 139 (22), 139 (14), 138 (100), 136 (18), 106 (14), 76 (14), 58 (14), 43 (64.5). Anal. Calcd for $C_9H_{13}NS$: C, 64.67; H, 7.78. Found: C, 65.20; H, 7.82.

Rearrangement of Ia in *N,N*-Dimethylaniline. A solution of 100 μL of *N*-methylmethanesulfenanilide and 200 μL of *N,N*-dimethylaniline in 1 mL of CD_3CN was placed in a small test tube closed with a cork stopper and kept at 60 °C. The reaction was followed by observing the intensity of the *N*-methyl protons of Ia in the NMR spectrum of the mixture. After complete disappearance of the starting sulfenanilide, the reaction mixture was analyzed by GC/MS and NMR. The GC/MS indicated the presence of two components with *m/e* 167 for the parent ions corresponding to the molecular weights of the two isomeric crossover products *o*- and *p*-methylthio-*N,N*-dimethylaniline. Coinjection of samples of *o*- and *p*-methylthio-*N,N*-dimethylaniline prepared by the reaction of methanesulfenyl chloride with *N,N*-dimethylaniline in chloroform onto a gas chromatograph with the product mixture obtained from the rearrangement reaction gave enhancement of the peaks that corresponded to the material with molecular weights of 167.

Acknowledgments. We gratefully acknowledge support of this work by the Committee on Faculty Research at The University of Mississippi and the assistance of Dr. S. Billets of the Research Institute of Pharmaceutical Sciences of The University of Mississippi in obtaining the mass spectra.

Registry No.—Ia, 65605-22-3; Ib, 63533-62-0; IC, 63533-63-1; Id, 65605-23-4; *N*-methylaniline, 100-61-8; dimethyl disulfide, 624-92-0; diethyl disulfide, 110-81-6; diisopropyl disulfide, 4253-89-8; methanesulfenyl chloride, 5813-48-9; ethanesulfenyl chloride, 1496-75-9; isopropanesulfenyl chloride, 19760-04-4; *tert*-butyl disulfide, 110-06-5; *tert*-butanesulfenyl chloride, 52322-55-1; 2-methylthio-*N*-methylanine, 13372-62-8; 4-methylthio-*N*-methylaniline, 58259-33-9; 2-ethylthio-*N*-methylanilene, 65605-24-5; 4-ethylthio-*N*-methylanilene, 65606-25-6.

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A Major Improvement in the Osmium Catalyzed Vicinal Hydroxylation of Olefins by *tert*-Butyl Hydroperoxide

Kageyasu Akashi, Robert E. Palermo, and K. Barry Sharpless*[1]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received November 8, 1977

We recently described a new osmium catalyzed procedure for the cis dihydroxylation of olefins.[2] Although generally superior to the existing[3] methods for this transformation, it involves rather alkaline conditions, and thus is successful only with molecules which are not sensitive to base. This limitation has now been removed with the discovery that Et_4NOH can be replaced by Et_4NOAc[4] if at the same time the solvent is changed from *tert*-butyl alcohol to acetone.[5]

As revealed in Table I, this new procedure works well for base-sensitive molecules. Esters are not hydrolyzed (entries 4–7), and ethyl crotonate gave only the *threo*-glycol (entries 4–6) with no sign of the epoxide which would arise if conjugate addition of *tert*-butyl hydroperoxide were a competing process. Furthermore, even for simple olefins such as 4-octene

0022-3263/78/1943-2063$01.00/0

Table I. Vicinal Diols from Olefins[a]

Olefin	Scale in mol	Equiv of[b] Et_4NOAc	% yield[c]
1. (*E*)-4-Octene	0.1	0.25	81
2. (*E*)-4-Octene	1.0	0.25	78
3. (*E*)-4-Octene	0.1	0.25[d]	74
4. Ethyl crotonate	0.1	0.25	71
5. Ethyl crotonate[e]	1.0	0.25	72
6. Ethyl crotonate[f]	0.1	0.25	58
7. Citronellol acetate	0.05	0.25	83
8. Cyclohexene	0.1	0.125	51
9. Cyclohexene[e]	0.1	0.125	52
10. Cyclohexene	0.1	0.125[d]	45
11. 2,3-Dimethyl-2-octene	0.1	0.25	0

[a] In all cases the amount of OsO_4 catalyst was 0.2% (1/500) of the amount of the olefin. [b] Equivalent here is based on the amount of olefin. [c] All yields are for distilled or recrystallized products. [d] In this case Et_4NOAc was generated in situ by stirring $Et_4NCl{\cdot}H_2O$ and anhydrous NaOAc together in acetone. [e] The oxidant here was 70% *tert*-butyl hydroperoxide. [f] In this preparation one-half the usual volume of acetone was used.

(entry 1) the yields were about 10% better than those realized with the Et_4NOH method.[2] Interestingly, the Et_4NOAc method fails with tetrasubstituted olefins (entry 11); it appears that the more vigorous hydrolytic conditions of the Et_4NOH method account for its success with this substitution type.

It is important to emphasize that both these methods (Et_4NOAc and Et_4NOH) still have shortcomings. For example, neither procedure succeeds with cholesterol, and it seems reasonable to anticipate negative results with most hindered tri- and tetrasubstituted olefins. As discussed previously,[2] we feel the problem lies in the inertness of hindered osmate esters to further reaction. Consistent with this hypothesis is the observation that olefins which fail to react in these systems are potent inhibitors of the catalytic process. Thus when the hydroxylation of a normally reactive olefin, such as cyclohexene, is attempted in the presence of cholesterol no reaction occurs. The cholesterol apparently traps the osmium by forming an extremely stable osmate ester. In order to further improve these catalytic hydroxylations we are seeking more effective ways for hydrolyzing such obstinate osmate esters.

These new catalytic procedures (Et_4NOH/TBHP[2] and Et_4NOAc/TBHP) for vicinal cis dihydroxylation of olefins are the most economical methods currently available for this transformation. The only other *effective* catalytic method for this conversion is that employing *N*-methylmorpholine *N*-oxide; this technique was recently reported by chemists at Upjohn.[6a] The *N*-oxide procedure is very impressive especially with disubstituted olefins. It is not yet known how generally applicable it is to trisubstituted olefins (one example was given).[6a] In our hands it failed to react with 2,3-dimethyl-2-octene; this tetrasubstituted olefin is readily converted to the corresponding diol using the Et_4NOH/TBHP procedure.[2] It seems likely that the Et_4NOAc/TBHP procedure and especially the Et_4NOH/TBHP procedure[2] will prove more reliable for tri- and tetrasubstituted olefins than the *N*-oxide method. Another important factor in comparing the TBHP and *N*-oxide methods is cost. A mole of TBHP (Aldrich) is 20 times less expensive than a mole of *N*-methylmorpholine *N*-oxide (E.K.). Since TBHP is available at much lower prices in bulk quantities (55-gal drums and tank cars), this price differential would be even larger for industrial scale applications. A recent patent describes the use of TBHP for the osmium catalyzed oxidation of allyl alcohol to glycerol.[6b]

In conclusion, these new TBHP-based methods are applicable to a wider range of olefin types than are the other catalytic methods.[3,6a] However, it must be pointed out that the most certain means for producing a *cis*-diol from an olefin is still reaction with a stoichiometric amount of osmium tetroxide in pyridine.

Experimental Section

The olefins are available commercially and were used without purification. Reagent grade acetone was employed as the solvent, except in the 1-mol scale oxidation of (*E*)-4-octene (entry 2, Table I) where wash grade acetone was utilized without significant deleterious effect (yield was only 3% lower). $Et_4NOAc{\cdot}4H_2O$ (Eastman Kodak), $Et_4NCl{\cdot}H_2O$ (Aldrich), and anhydrous NaOAc (Aldrich) were used as obtained.

There are three commonly available grades of *tert*-butyl hydroperoxide (TBHP) and all are sold by Lucidol, a division of the Pennwalt Corporation. They differ in the amounts of *tert*-butyl alcohol (TBA), water, and di-*tert*-butyl peroxide (DTBP) present as impurities. There are two 70% grades: one (Lucidol-TBHP-70X) contains TBHP (~70%), water (~30%), and traces (<1%) of aldehydes and TBA; the other (Lucidol-TBHP-70) contains TBHP (~70%), DTBP (~19%), and ~11% of TBA and water. The third grade (Lucidol-TBHP-90) contains ~90%TBHP, ~6%TBA, ~4% H_2O, and <1%DTBP; this 90% grade is also available from Aldrich Chemical Co. We describe here procedures using both the 90% grade (density = 0.90, ~9.0 mmol of TBHP/mL) of TBHP and the 70% grade (density = 0.94, ~7.2 mmol of TBHP/mL) which is free of DTBP (i.e., Lucidol-TBHP-70X). Both work equally well in these oxidations. The only grade to be avoided in this and other catalytic applications of TBHP is that containing ~19% DTBP (i.e., Lucidol-TBHP-70). The presence of DTBP dramatically lowers the thermal stability of TBHP. Although care should always be exercised in handling compounds with O–O bonds, TBHP is one of the most stable commercially available peroxidic substances, and the 70% grade which contains 30% water is sold in 55-gal drums. Detailed information on the use and handling of organic peroxides is contained in various technical bulletins available from Lucidol.

The OsO_4 (Matthey Bishop, Inc.) catalyst solution was prepared as described by Daniels and Fischer with the exception that *tert*-butyl hydroperoxide was used in place of H_2O_2 as the stabilizer and reagent grade *tert*-butyl alcohol was used without further purification. Recipe: 1 g of OsO_4, 199 mL of reagent grade *tert*-butyl alcohol, and 1 mL of 90+% *tert*-butyl hydroperoxide; each milliliter contains 5 mg ($\sim 2 \times 10^{-5}$ mol) of OsO_4.[7]

Two general procedures (A and B) are described below. Although they are very similar, the differences are worth pointing out. Procedure B is intended for cases where water-soluble diols are produced, hence the modification in the workup where the aqueous phase is concentrated before the final extractions. Procedure B also differs from procedure A in that less Et_4NOAc is employed. Less Et_4NOAc is required to obtain good results with olefins (e.g., cyclohexene) which are not prone to over-oxidation than with olefins (e.g. 4-octene) which are. If one is uncertain about how the olefin at hand should be regarded in this context, the higher (25%) level of Et_4NOAc of procedure A should be utilized. Using more Et_4NOAc than the minimum necessary to obtain the optimium yield with a given olefin has no adverse effect. For reasons which are not obvious to us, Et_4NOAc is fairly expensive at present. This provided the incentive for developing a modification (entries 3 and 10, Table I) wherein Et_4NOAc is generated in situ by combining the inexpensive ingredients Et_4NCl and anhydrous NaOAc in acetone (we thank Dr. Irwin Klundt of Aldrich for suggesting this approach).

The reaction in acetone is less vigorous than that in the *tert*-butyl alcohol system,[2] and the amount of heat evolved upon addition of catalyst is dependent upon the olefin. With the volumes used here, the reaction mixtures warm only slightly if at all. The initial cooling serves to slow the reaction at first and this appears to have favorable effects on the yields and helps suppress over-oxidation. If the initial volume of acetone is halved, the pot temperature rises to ca. 40 °C unless cooled with a water bath. While the yield with this reduced solvent volume looked promising by GLC, isolated yields were inferior to those at lower concentrations.

Procedure A. *threo*-4,5-Dihydroxyoctane. A 1-L Erlenmeyer flask, equipped with magnetic stirrer, was charged with 200 mL of acetone, 11.2 g (100 mmol) of (*E*)-4-octene, 6.5 g (25 mmol) of $Et_4NOAc{\cdot}4H_2O$, and 18 mL (ca. 162 mmol) of 90+% *tert*-butyl hydroperoxide. After stirring at room temperature until the Et_4NOAc had dissolved, the resulting solution was cooled in an ice bath and 10 mL (i.e., 50 mg or 0.2 mmol of OsO_4) of the catalyst solution containing OsO_4 in *tert*-butyl alcohol was added in one portion. The solution immediately became brownish purple. After 1 h the ice bath was re-

moved and the reaction mixture was allowed to warm to room temperature, stoppered loosely, and stirred overnight. Ether (400 mL) was added and the resulting mixture was cooled by stirring in an ice bath. Then 50 mL of freshly prepared 10% $NaHSO_3$ solution was added in one portion.[11] The ice bath was removed and stirring was continued for 1 h, at which point the organic layer had become almost colorless. Solid NaCl was added until the aqueous layer was saturated and stirring of the two-phase mixture was continued for several minutes. The organic layer was separated and washed with 50 mL of brine. The combined aqueous layers were extracted twice with 100-mL portions of ether. The combined organic layers were dried (Na_2SO_4), and when concentrated afforded an oil which upon distillation gave 11.8 g (81%) of *threo*-4,5-dihydroxyoctane: bp 87–90 °C (3 mm) [lit.[10a] bp 109.8–110 °C (8 mm)].

1-Mol Scale. The same procedure was also carried out on (*E*)-4-octene on a 1.0-mol scale and afforded 113.9 g (78%) of the distilled *threo*-diol (entry 5, Table I). In this case the amount of all the ingredients was simply increased by a factor of 10 over that employed in the 0.1-mol scale oxidation described in detail above.

Generation of Et_4NOAc in Situ. The Et_4NOAc was generated by combining 4.60 g (25 mmol) of $Et_4NCl{\cdot}H_2O$ and 4.10 g (50 mmol, 2 equiv based on $Et_4NCl{\cdot}H_2O$) of NaOAc in 200 mL of acetone and stirring for ca. 1 h (this use of NaOAc and $Et_4NCl{\cdot}H_2O$ in a molar ratio of 2:1 was found to afford better yields of diol than a 1:1 molar ratio). In the case of (*E*)-4-octene (entry 3, Table I), a somewhat lower yield (74%) was realized with this variation. We have established that chloride ion has a deleterious effect on these catalytic oxidations[8] and the incomplete precipitation of chloride ion (as NaCl) is probably responsible for the slightly poorer yield with this modification. It would be worthwhile to seek a means for causing more complete precipitation of the chloride ion. If chloride ion remains a problem it should be possible to find less expensive routes to tetraalkylammonium acetates ($Et_4NOAc{\cdot}4H_2O$ is presently selling for ca. 80¢/g). In any case, even in its present form this inexpensive method of generating Et_4NOAc should prove useful, especially for large-scale applications.

Procedure A. *threo*-2,3-Dihydroxyethyl Butyrate. Ethyl crotonate (11.4 g, 100 mmol) was transformed (as described in detail for (*E*)-4-octene) into 10.4 g (71%) of the *threo*-diol, bp 102–104 °C (6 mm)[lit.[3h] bp 123–125 °C (18 mm)]. The complete absence of the *erythro*-diol was established by its synthesis and subsequent spectral and chromatographic comparison with the threo reaction product.

Procedure A. 70% TBHP Modification: 1-Mol Scale Oxidation of Ethyl Crotonate. In a 6-L Erlenmeyer flask, equipped with magnetic stirrer, freshly distilled ethyl crotonate (114.14 g, 1 mol), 63.35 g (250 mmol) of $Et_4NOAc{\cdot}4H_2O$, and 240 mL (ca. 1.7 mol) of 70% *tert*-butyl hydroperoxide (Lucidol-70X) were combined in 2 L of acetone and stirred until the salt had dissolved.[9] The solution was cooled in an ice bath and 100 mL of the catalyst stock solution (2 mmol OsO_4) was added in one portion. After stirring for 1 h, the ice bath was removed, the flask was lightly stoppered, and the contents was left to stand overnight at room temperature. The resulting golden solution was divided into two 1250-mL portions and each portion was worked up identically. Two liters of ether was added to each and the mixture cooled by stirring in an ice bath; 250 mL of freshly prepared 10% $NaHSO_3$ solution was added in one portion to each half.[11] The ice bath was then removed from each and stirring continued for 1 h. Sufficient salt was added to saturate the aqueous layer and stirring was continued for several minutes. The phases were partitioned in a 4-L separatory funnel and the organic phase of each half was washed with 250 mL of brine. The aqueous layers of each portion were then extracted with two 500-mL portions of ether. The combined organic layers were dried overnight (Na_2SO_4) and concentrated to afford a residue that still contained considerable amounts of water. This material was diluted with 1500 mL of CH_2Cl_2 and an aqueous layer of ca. 75 mL separated. The two phases were partitioned and the aqueous phase was saturated with solid NaCl. This was then extracted with three 50-mL portions of CH_2Cl_2. The combined organic layers were dried again (Na_2SO_4) and concentrated to afford a clear oil which upon distillation gave 106.3 g (72%) of pure *threo*-2,3-dihydroxyethyl butyrate: bp 106–108 °C (7 mm).

Procedure A. Doubled Concentration. In a 500-mL Erlenmeyer flask, 11.86 g of 96% ethyl crotonate (100 mmol), 6.5 g (25 mmol) of $Et_4NOAc{\cdot}4H_2O$, and 24 mL (ca. 170 mmol) of 70% *tert*-butyl hydroperoxide were combined in 100 mL of acetone. This was chilled by stirring in an ice bath, and 10 mL of OsO_4 stock solution was added in one portion. After 1 h the ice bath was removed and the contents allowed to warm to room temperature. When the pot temperature exceeded 25 °C, it was immersed in a bath of 20 °C tap water, lightly stoppered, and allowed to stand in the bath overnight. The resulting golden solution was diluted with 200 mL of ether and chilled by stirring in an ice bath. Then 25 mL of freshly prepared 20% $NaHSO_3$ solution was added in one portion,[11] the ice bath was removed, and the contents of the flask was stirred for 1 h. The aqueous layer was saturated with NaCl and the two phases were partitioned. The organic layer was washed with 25 mL of brine. The combined aqueous layers were washed with two 50-mL portions of ether. The combined organic layers were dried overnight (Na_2SO_4) and concentrated, and the residue was taken up in 350 mL of CH_2Cl_2 which was then dried again (Na_2SO_4). Concentration of this solution gave a clear oil which upon distillation afforded 8.62 g (58%) of *threo*-2,3-dihydroxyethyl butyrate: bp 102 °C (6 mm).

Procedure A. 1-Acetoxy-6,7-dihydroxy-3,7-dimethyloctane. Citronellol acetate (7.8 g, 50 mmol) was converted to 9.6 g (83%) of the corresponding vicinal diol: bp 141–144 °C (3 mm) [lit.[10b] bp 90–95 °C (0.5 mm)].

Procedure A. Fails with 2,3-Dimethyl-2-octene. Attempted oxidation of 2,3-dimethyl-2-octene (14.0 g, 100 mmol) led to no reaction and the starting olefin was recovered.

Procedure B. *cis*-1,2-Dihydroxycyclohexane. The procedure works well on cyclohexene, with crude yields of crystalline diol approaching 80%. The limitation lies in further purification of this crude material, and recrystallization usually gives less than satisfactory results. Evaporation of mother liquors gives a syrupy residue that cannot be further recrystallized, but is nonetheless predominantly diol as verified by GLC.

Procedure B with cyclohexene (8.20 g, 100 mmol) is the same as A with the following exceptions: (1) Only 3.3 g (12.5 mmol) of $Et_4NOAc{\cdot}4H_2O$ was used (this is half the amount used in procedure A). (2) Before washing the NaCl saturated aqueous layer with ether it was concentrated almost to dryness on a rotary evaporator, then (as in procedure A) it was extracted twice with 100-mL portions of ether. The combined organic layers were dried (Na_2SO_4) and concentrated to give 8.54 g (74%) of white solid: mp 73–83 °C. Recrystallization from ether afforded 5.94 g (51%) of *cis*-1,2-dihydroxycyclohexane, mp 96.5–97 °C [lit.[10c] mp 98 °C]. Evaporation of the mother liquors gave approximately 3 g of yellow oil that was almost exclusively diol by GLC. Procedure B gives identical results when the larger amount of base, 6.5 g of $Et_4NOAc{\cdot}4H_2O$ (25 mmol), is used.

In another experiment, cyclohexene (8.20 g, 100 mmol) was oxidized by the above procedure to afford 8.68 g (75%) of crude solid. This was bulb-to-bulb distilled at reduced pressure to give 6.96 g (60%) of white solid, mp 85–86.5 °C. A single crystallization from chloroform/hexanes afforded 5.56 g (48%) of pure *cis*-1,2-dihydroxycyclohexane, mp 97.5–98 °C.

Procedure B. 70% TBHP Modification. The procedure is identical with that above except that 24 mL of Lucidol-70X TBHP was used as the oxidant. Cyclohexene (8.20 g, 100 mmol) was converted to 6.01 g (52%) of *cis*-1,2-dihydroxycyclohexane, mp 96–96.5 °C.

Procedure B. Generation of Et_4NOAc in Situ. $Et_4NCl{\cdot}H_2O$ (2.30 g, 12.5 mmol) and 2.05 g (25 mmol, 2 equiv based on $Et_4NCl{\cdot}H_2O$) of anhydrous NaOAc were combined in 200 mL of acetone and stirred for 1 h. A white solid remains suspended. Cyclohexene, oxidant, and catalyst stock were added as described above. When the reaction was complete, the golden solution was filtered before beginning the workup as previously described. Cyclohexene (8.20 g, 100 mmol) was converted to 8.49 g (73%) of crude diol. A single recrystallization (EtOAc) afforded 5.15 g (45%) of the cis diol, mp 95–96.5 °C.

Acknowledgment. We thank the National Science Foundation (CHE74-21260), Chevron Research Co., and Asahi Chemical Industry Corporation for financial support. We are grateful to Dr. Chester S. Sheppard of Lucidol for helpful discussions.

Registry No.—TBHP, 75-91-2; OsO_4, 20816-12-0; Et_4NOAc, 1185-59-7; *threo*-4,5-dihydroxyoctane, 59173-74-9; (*E*)-4-octene, 14850-23-8; *threo*-2,3-dihydroxyethyl butyrate, 6982-23-6; ethyl crotonate, 10544-63-5; 1-acetoxy-6,7-dihydroxy-3,7-dimethyloctane, 26759-58-0; citronellol acetate, 150-84-5; *cis*-1,2-dihydroxycyclohexane, 1792-81-0; cyclohexene, 110-83-8.

References and Notes

(1) Address correspondence to this author at the Department of Chemistry, Stanford University, Stanford, Calif. 94305.
(2) K. B. Sharpless and K. Akashi, *J. Am. Chem. Soc.*, **98**, 1986 (1976).
(3) (a) G. M. Robinson and R. Robinson, *J. Chem. Soc.*, **127**, 175 (1925); (b) J. E. Coleman, C. Ricciuti, and D. Swern, *J. Am. Chem. Soc.*, **78**, 5342 (1956); (c) K. A. Hofmann, *Ber. Dtsch. Chem. Ges.*, **45**, 3329 (1912); (d)

R. Criegee, *Justus Liebigs Ann. Chem.*, **522**, 75 (1936); (e) R. Criegee, B. Marchand, and H. Wannowius, *ibid.*, **550**, 99 (1942); (f) N. A. Milas and S. Sussman, *J. Am. Chem. Soc.*, **58**, 1302 (1936); (g) N. A. Milas and S. Sussman, *ibid.*, **59**, 2345 (1937); (h) N. A. Milas, S. Sussman, and H. S. Mason, *ibid.*, **61**, 1844 (1939); (i) N. A. Milas, J. H. Trepagnier, J. T. Nolan, and M. I. Iliopolus, *ibid.*, **81**, 4730 (1959); (j) R. B. Woodward and F. V. Brutcher, Jr., *ibid.*, **80**, 209 (1958); (k) R. Daniels and J. L. Fischer, *J. Org. Chem.*, **28**, 320 (1963).

(4) Et_4NF had a similar effect in acetone. However, neither Et_4NOAc nor Et_4NF had much effect on the reaction in *tert*-butyl alcohol (TBA), whereas the tetraethylammonium salts of chelating diacids such as *o*-phthalic, camphoric, and *cis*-1,2-cyclohexane dicarboxylic acid did substantially improve the reaction even in TBA. $C_6H_5PO_3(Et_4N)_2$ and $(Et_4N)_2CO_3$ also had good effects on the reaction in TBA.

(5) The use of acetone in place of *tert*-butyl alcohol as solvent dramatically increases the beneficial effect of weak bases, such as Et_4NOAc, on these reactions (see also ref 4).

(6) (a) V. Van Rheenen, R. C. Kelly and P. Y. Cha, *Tetrahedron Lett.*, 1973 (1976). (b) We are grateful to a referee for pointing out this patent which describes the use of TBHP in buffered (slightly alkaline) aqueous solution for the osmium catalyzed hydroxylation of allyl alcohol to glycerol [M. N. Sheng and W. A. Mameniskis, U.S. Patent 4 049 724 (1977)].

(7) A number of other osmium complexes were tried and proved to be equally active as catalysts. For example, in the oxidation of (*E*)-4-octene, $OsO_3(pyridine)_2$, $K_2O_2Os(OCH_3)_4$, and the imido complex OsO_3 (*N*-*tert*-butyl) all gave yields of diol comparable to that realized with OsO_4 as catalyst. These nonvolatile solids can simply be weighed out (0.2% based on olefin) and added to the reactions in place of the portion of OsO_4 stock solution.

(8) (a) K. Akashi and K. B. Sharpless, unpublished results; (b) K. B. Sharpless, A. O. Chong, and K. Oshima. *J. Org. Chem.*, **41**, 177 (1976).

(9) More hydrophobic olefins may oil out of the acetone solution due to the additional water in the 70% *tert*-butyl hydroperoxide. This only slows the initial rate and has no adverse effect on the reaction.

(10) (a) W. G. Young, L. Levanas, and Z. Jasaitis, *J. Am. Chem. Soc.*, **58**, 2275 (1936); (b) L. Lizzani and R. Luft, *Bull. Soc. Chim. Fr.*, **38**, 198 (1971); (c) M. B. Rothstein, *Ann. Chim.*, **14**, 461 (1930).

(11) In the present work we did not encounter any problems in using sodium bisulfite ($NaHSO_3$) as the reagent to reduce the excess *tert*-butyl hydroperoxide (TBHP). However, in other work[12] we have found that use of $NaHSO_3$ can have a deleterious effect on the isolated yields. The problem was especially serious when the product to be isolated contained either epoxide or allylic alcohol moieties. For more detailed discussion of this problem and for alternative means of dealing with the excess TBHP, see ref 12.

(12) (a) T. Hori and K. B. Sharpless, *J. Org. Chem.*, in press; (b) M. A. Umbreit and K. B. Sharpless, *J. Am. Chem. Soc.*, **99**, 5526 (1977); (c) R. C. Michaelson, L. E. Khoo, and K. B. Sharpless, manuscript in preparation.

A Synthesis of α-Azido Nitriles

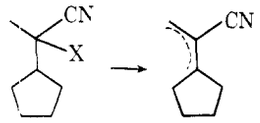
Anthony D. Barone, David L. Snitman, and David S. Watt*

Department of Chemistry, University of Colorado, Boulder, Colorado 80309

Received December 13, 1977

As part of our program to study the chemistry of nitriles bearing photoactive functionality in the α position,[1] we required a general synthesis of α-azidonitriles **4**. This intriguing synthon was first prepared by Moore[2] in the photochemical rearrangement of 2,3-diazido-1,4-quinones. Although the scope of this rearrangement process has not been determined, we were interested in devising other approaches which would utilize ketones **1** as starting materials.

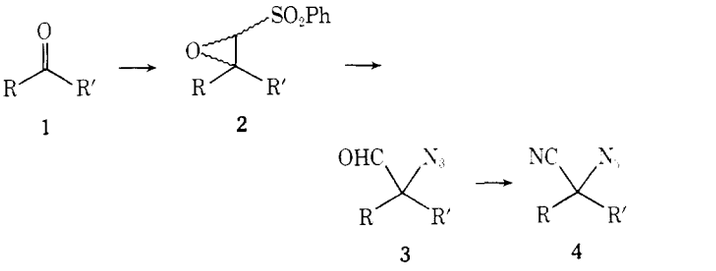
Our initial foray in this area focused on the substitution of α-iodo or α-mesyloxynitriles by azide ion. Although aware of the difficulties which beset such a reaction, we were prodded into exploring this reaction by a report[3] that tertiary α-bromo ketones underwent just such a substitution with azide ion in 82–88% yield. Our efforts to utilize **5** in such a reaction led exclusively to the expected α,β-unsaturated nitriles[4] **6**.



5a, X = I
b, X = OMs

6

An alternate route involving the ring opening of an epoxide ultimately proved successful in this connection. A modified Darzens condensation of ketones **1** with chloromethyl phenyl sulfone[5] provided the α,β-epoxy sulfones[6] **2**. Contrary to a report by Durst,[7] the ring opening of **2** with sodium azide in dimethylformamide provided the α-azidoaldehydes **3** in good yields. Conversion of **3** to the α-azidonitriles **4** was then accomplished by dehydration of the oximes derived from the aldehydes **3**. We have applied this sequence to the synthesis of α-azidonitriles **4** from aryl alkyl and dialkyl ketones **1** in



overall yields of 23 to 59% as shown in Table I. We have also explored the direct conversion of **3** to **4** using reagents such as hydroxylamine *O*-sulfonic acid but found that this latter procedure offered certain disadvantages. For example, the reaction of 20-azido-6β-methoxy-3α,5α-cyclopregnane-20-carboxyaldehyde (**3g**) with hydroxylamine *O*-sulfonic acid converted not only the aldehyde to the nitrile but also effected the ring opening of the isocyclopropyl ether to give 20-azido-3β-hydroxy-5-pregnene-20-carbonitrile. We are presently engaged in studying the photochemistry of α-azidoaldehydes **3** and α-azidonitriles **4**.

Experimental Section

Infrared spectra were determined on a Perkin-Elmer infracord spectrophotometer. The abbreviation TF denotes thin film. NMR spectra were determined on a Varian EM390 spectrometer. Mass spectra were determined on a Varian MAT CH5 mass spectrometer. Melting points were determined using a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Ga. Samples for elemental analysis were prepared by recrystallization or by chromatography on Merck silica gel F254 preparative layer plates followed by drying under high vacuum at 25 °C for 6–10 h.

The following is a typical experimental procedure.

1,1-Undecamethylene-2-(benzenesulfonyl)-1,2-epoxyethane (2c). The procedure of Tarares[6] was repeated using 1.05 g (5.5 mmol, 1.1 equiv) of chloromethyl phenyl sulfone[5] and 910 mg (5.0 mmol) of cyclododecanone to afford 1.69 g of solid which was recrystallized to furnish 1.15 g (68%) of the α,β-epoxy sulfone **2c**: mp 102–103 °C; IR (KBr) 7.55 and 8.69 μm; NMR ($CDCl_3$) δ 1.17–2.36 (m, 22, CH_2), 3.72 (s, 1, $CHSO_2Ph$), and 7.50–8.02 (m, 5, aromatic H); mass spectrum (70 eV) *m/e* (rel intensity) 250 (4), 196 (10), 185 (68), 177 (8, $M^+ - (PhSO_2 + H_2O)$), 94 (100), and 77 (31). The loss of *m/e* 159 was characteristic of all α,β-epoxy sulfones.

An analytical sample was prepared from two recrystallizations from dichloromethane–ether. Anal. Calcd for $C_{19}H_{28}O_3S$: C, 67.82; H, 8.39. Found: C, 67.83; H, 8.39.

1-Azidocyclododecane-1-carboxaldehyde (3c). To 890 mg (13.7 mmol, 4 equiv) of sodium azide in 10 mL of anhydrous dimethylformamide under a nitrogen atmosphere was added 1.15 g (3.4 mmol) of α,β-epoxy sulfone **2c** in 10 mL of dimethylformamide. The mixture was stirred for 18 h at 73 °C. This crude product was diluted with 60 mL of 30% dichloromethane–ether and washed with 50 mL of water. The aqueous layer was extracted with 60 mL of 30% dichloromethane–ether. The combined organic layers were washed with 50 mL of water and 50 mL of brine and dried over anhydrous $MgSO_4$. Evaporation of the solvent afforded 821 mg (100%) of **3c**: IR (TF) 4.76 and 5.80 μm; NMR ($CDCl_3$) δ 1.26–1.90 (m, 22, CH_2) and 9.48 (s, 1, CHO); mass spectrum (70 eV) *m/e* (rel intensity) 181 (50), 138 (29), 124 (44), 95 (44), 81 (39), and 69 (45).

Anal. Calcd for $C_{13}H_{23}N_3O$: C, 65.78; H, 9.77. Found: C, 65.99; H, 9.82.

1-Azidocyclododecane-1-carbonitrile (4c). To 530 mg (7.68 mmol, 3 equiv) of hydroxylamine hydrochloride and 307 mg (7.68

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