***exo*-6-Tricyclo[6.2.1.0^{2,6}]undec-2-ene (5). (i) Bicyclo[3.2.1]octan-2-one Pyrrolidine Enamine (9).** A mixture comprising 47.0 g (0.38 mol) of bicyclo[3.2.1]octan-2-one,[17] 37.7 g (0.53 mol) of pyrrolidine, and 120 mL of benzene was heated under reflux for 10 h, while the water formed was continuously separated and removed from the reaction mixture. The reaction mixture was concentrated, and the residue was fractionally distilled to give 36.5 g (55% yield) of bicyclo[3.2.1]octan-2-one pyrrolidine enamine (**9**): bp 78–80 °C (0.2 mm); IR (neat) 3050, 2950, 2860, 1390, 1360, 1340, 1290, 1280 cm^{-1}.

Anal. Calcd for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.0; H, 10.9; N, 8.1.

(ii) 3-(2-Oxopropyl)bicyclo[3.2.1]octan-2-one (10). To a solution of 34.0 g (0.19 mol) of the enamine **9** in 100 mL of benzene at ambient temperature was added dropwise with stirring a solution of 25.0 g (0.18 mol) of α-bromoacetone in 70 mL of benzene, and the reaction was heated under reflux for 4 h. Water (40 mL) was then added to the reaction, and the resulting mixture was heated under reflux for 2 h. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer and ether extract were washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was fractionally distilled to give 14.5 g (42% yield) of 3-(2-oxopropyl)bicyclo[3.2.1]octan-2-one (**10**): bp 89–91 °C (0.4 mm).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.0; H, 9.2.

Fractionation of the sample on preparative VPC gave the equatorial (exo) isomer **10x** [IR (neat) 2950, 2880, 1720, 1360, 1260, 1190, 1170, 1090, 1050, 1000 cm^{-1}; mass spectrum, m/e (relative intensity) 180 (28, M$^+$), 162 (28), 137 (100), 134 (29), 123 (63), 81 (29), 79 (28), 77 (29), 67 (92)] and the axial (endo) isomer **10n** [IR (neat) 2950, 2880, 1710, 1360, 1320, 1260, 1160, 1120, 1030, 920 cm^{-1}; mass spectrum, m/e (relative intensity) 180 (39, M$^+$), 137 (100), 123 (67), 95 (22), 93 (30), 80 (24), 67 (74)].

(iii) *exo*-6-Tricyclo[6.2.1.0^{2,6}]undec-2-en-4-one (11). A sample (9.5 g, 53 mmol) of the diketone mixture **10** obtained above was mixed with 300 mL of a 20% potassium hydroxide solution and heated under reflux with stirring for 20 h. The reaction mixture was extracted with ether, and the ether solution was concentrated. The residue was purified by elution with ether through an alumina-packed column to give 6.3 g (73%) of *exo*-6-tricyclo[6.2.1.0^{2,6}]undec-2-en-4-one (**11**): IR (neat) 3060, 2950, 1710, 1690, 1280, 1250, 1180, 980, 960, 920, 840, 830, 810 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 23.52 (t), 29.98 (t), 36.06 (d), 38.46 (t), 39.05 (t), 40.02 (t and d), 47.11 (d), 130.14 (d, CH=C), 182.77 (s, CH=C), 208.82 (s, C=O); mass spectrum, m/e (relative intensity) 162 (100, M$^+$), 134 (50), 105 (42), 95 (36), 91 (40), 67 (60), 66 (85).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.6; H, 8.6.

(iv) *exo*-6-Tricyclo[6.2.1.0^{2,6}]undec-2-ene (5). A mixture comprising 3.0 g (18.5 mmol) of the tricycloundecenone **11**, 9.3 g of an 80% hydrazine hydrate solution, 8.3 g of potassium hydroxide, and 100 mL of diethylene glycol was heated under reflux for 3 h and then at 220 °C for 2 h when the water formed and the excess hydrazine were gradually distilled off. The reaction mixture was diluted with water and extracted with *n*-hexane. The hexane extract was washed with a saturated sodium chloride solution and dried over anhydrous sodium sulfate. Evaporation of the hexane and purification of the residue by preparative VPC gave 1.8 g (66%) of the tricycloundecene **5**: IR (neat) 3050, 1660, 1320, 1290, 1160, 1010, 930, 790 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–3.0 (complex m, 15 H), 5.2–5.4 (br s, 1 H, C=CH); ^{13}C NMR ($CDCl_3$) δ 24.28 (t), 27.45 (t), 29.28 (t), 31.59 (t), 35.61 (t), 36.59 (t), 39.33 (t), 40.49 (d), 51.61 (d), 123.89 (d, C=CH), 143.22 (s, C=CH); mass spectrum m/e (relative intensity) 148 (44, M$^+$), 119 (68), 91 (52), 81 (28), 80 (61), 79 (57), 67 (80), 66 (100).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.2; H, 10.6.

Dehydration–Rearrangement of *exo*-Norbornane-2-spiro-1′-cyclopentan-2′-ol (2) and Related Compounds. The spiro alcohol **2** (or the tricyclodecylcarbinol **7** or 4-homoisotwistan-3-ol, **8**) (1.66 g, 10 mmol) was treated with the catalyst (and the solvent, if any) under the reaction conditions specified in Table I.

When Amberlyst-15 was used as the catalyst (runs 4, 6, and 7), product isolation was conducted by filtration of the resin, which was then washed with the solvent *n*-hexane. The combined filtrate and washings were dried over anhydrous sodium sulfate and concentrated. When phosphoric acid was used as catalyst, separation of the organic layer from the reaction mixture and extraction of the aqueous layer with the same solvent as used in the reaction enabled product isolation (runs 1, 2, and 5). In contrast, products of iodine-catalyzed reactions were distilled from the reaction mixture under diminished pressure as soon as they were formed.

Registry No. **1**, 51269-23-9; **2**, 73210-19-2; **3**, 57496-70-5; **4**, 57526-52-0; **5**, 73245-81-5; **6**, 43000-53-9; **7**, 59728-11-9; **8**, 57234-55-6; **9**, 41455-22-5; **10n**, 73198-85-3; **10x**, 73198-86-4; **11**, 73245-82-6; bicyclo[3.2.1]octan-2-one, 5019-82-9; pyrrolidine, 123-75-1; α-bromoacetone, 598-31-2.

(17) Alder, K.; Reubke, R. *Chem. Ber.* **1958**, *91*, 1525.

Improved Procedure for the Oxyamination of Olefins with Trioxo(*tert*-butylimido)osmium(VIII)

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A few years ago, we reported on the vicinal oxyamination of olefins by stoichiometric quantities of *t*-BuNOsO$_3$ (**1**).[2] Although this reaction has been largely supplanted by the osmium-catalyzed vicinal oxyamination reaction,[3] we would like to report some additional observations which serve to improve the original stoichiometric reaction in some cases. In the original reports,[2] it was noted that consistently higher yields of amino alcohol and higher ratios of amino alcohol to diol could be attained with the use of a coordinating solvent such as pyridine. Even so, a number of olefins (e.g., citronellol methyl ether) could not be cleanly converted to amino alcohols by this procedure, and tetrasubstituted olefins (e.g., 2,3-dimethyl-2-butene) yielded only the corresponding diols. We now report that some of these olefins give a much-improved ratio of amino alcohol to diol on reaction of the olefin with **1** in a noncoordinating solvent in the presence of certain tertiary alkyl bridgehead amines.

Although the mechanism of reaction of **1** with olefins is not known, the effect of pyridine on this reaction is almost certainly a result of coordination of pyridine to the metal center at some point along the reaction pathway. However, IR spectroscopy reveals no evidence for complexation of **1** with pyridine.[2b] Griffith and co-workers have noted that a number of tertiary alkyl bridgehead amines, such as quinuclidine (**2**), form adducts with OsO$_4$ which are much more stable than the corresponding pyridine adduct.[4] We now find that reaction of **1** with **2**,

(1) NSF Predoctoral Fellow, 1976–1979.

(2) (a) Sharpless, K. B.; Patrick, D. W.; Truesdale, L. K.; Biller, S. A. *J. Am. Chem. Soc.* **1975**, *97*, 2305. (b) Patrick, D. W.; Truesdale, L. K.; Biller, S. A.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2628.

(3) (a) Sharpless, K. B.; Chong, A. O.; Oshima, K. *J. Org. Chem.* **1976**, *41*, 177. (b) Herranz, E.; Sharpless, K. B. *Ibid.* **1978**, *43*, 2544. (c) Herranz, E.; Biller, S. A.; Sharpless, K. B. *J. Am. Chem. Soc.* **1978**, *100*, 3596. (d) Herranz, E.; Sharpless, K. B. *J. Org. Chem.*, in press.

(4) (a) Cleare, M. J.; Hydes, P. C.; Griffith, W. P.; Wright, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 941. (b) More recently, we have prepared chiral vicinal diols by oxidation of olefins with OsO$_4$ in the presence of chiral quinuclidines (Hentges, S. G.; Sharpless, K. B., submitted for publication).

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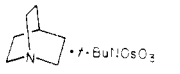
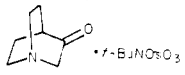
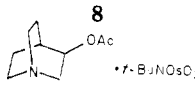
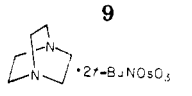
Table I. Spectral Data for 7-11

complex[a]	mp, °C	IR[b] ν(Os=N), cm^{-1}	IR[b] ν(Os=O), cm^{-1}
 7	89-99 dec	1207	882, 868
 8	118-120	1220	884, 874, 860
 9	99-109 dec	1208	886, 877, 869
 10	130 dec	1213	884, 871
$(CH_2)_6N_4 \cdot 2t\text{-BuNOsO}_3$ 11	174-175 dec	1219	890, 876

[a] Satisfactory elemental analyses (C, H, and N) were obtained for each complex. [b] KBr pellet.

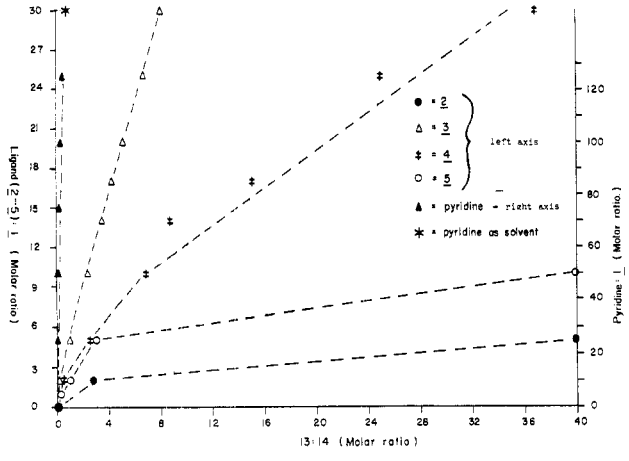
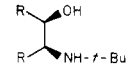
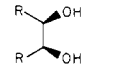


Figure 1.

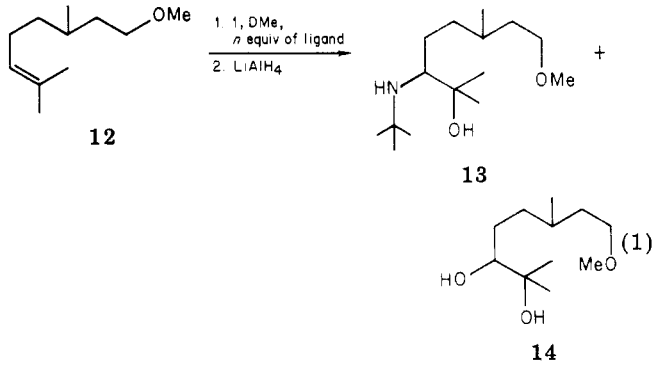
3-quinuclidinone (3), 3-quinuclidinyl acetate (4), 1,4-diazabicyclo[2.2.2]octane (5), or hexamethylenetetramine (6) gives rise to the stable crystalline 1:1 or 2:1 adducts 7-11. Relevant IR data for 7-11 are presented in Table I. In all cases, solutions of these complexes exhibit IR bands, in the oxo-stretch region (Os=O), which indicate that the solutions contain equilibrium mixtures of the complexes and uncomplexed 1.

Since the ligands 2-6 all bind to 1 much more tightly than does pyridine, we checked whether these ligands might also be more efficient than pyridine at inducing formation of amino alcohols in reactions of 1 with olefins. Citronellol methyl ether (12), which gives a 4:5 mixture of amino alcohol 13 and diol 14 on reaction with 1 in pyridine,[2] was used as the test olefin. Complex 1 was allowed to react with 12 in dimethoxyethane[5] in the presence of varying quantities of pyridine or 2-5,[7] and the yields of 13 and 14 were measured by quantitative GLC analysis after reductive hydrolysis with $LiAlH_4$ (eq 1). The

Table II

olefin[c]	products[c]	yields, % 2/DME[a]	yields, % pyridine[b]
12	13	83	38
	14	~3	45
		58	25
		~4	42

[a] Isolated yields of the amino alcohol/diol mixture. The ratio of amino alcohol to diol was determined by GLC analysis. [b] GLC yields from ref 2. [c] R = *n*-Bu.



results are tabulated in Figure 1. Clearly, 2-5 are much better than pyridine at inducing amino alcohol formation in this case, with 2 being the most efficient. Although we cannot give a mechanistic interpretation of these results, it appears that the amino alcohol-diol ratio is related to the nucleophilicity of the auxiliary ligand. In Table II are shown the results of the preparative-scale reactions of 12 and (*Z*)-5-decene with 1, using 5 molar equiv of 2. For comparison, the results with pyridine as solvent,[2] with no added ligand, are also shown. The effect of 2 on the reaction of 1 with the tetrasubstituted olefins 2,3-dimethyl-2-butene and 2,3-dimethyl-2-octene was also examined. Only the corresponding diols were observed as products when the reactions were run in dimethoxyethane with 5 molar equiv of 2 or in pyridine with no added ligands.[2b]

In summary, the stoichiometric oxyamination reaction is in some cases improved by the use of quinuclidine in dimethoxyethane in place of pyridine as the solvent.[8]

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 597 grating infrared spectrophotometer. GLC analyses were performed on a Perkin-Elmer 3920 gas chromatograph equipped with a Hewlett-Packard 3380A electronic integrating recorder. Microanalyses were performed by the Stanford University Microanalytical Laboratory.

Tetrahydrofuran and dimethoxyethane were distilled before use from a deep purple solution of sodium and benzophenone. Compounds 1 and 4 were prepared by literature procedures.[9]

(5) Methylene chloride was initially used as solvent; however, we soon discovered that 2-5 react with methylene chloride at room temperature. The products from reaction of 2 and 5 with methylene chloride are easily isolated as white crystalline solids and appear to be 1:1 quaternary ammonium salts. Similar salts have been reported previously.[6] Dimethoxyethane apparently does not function as a coordinating ligand in this reaction since the reaction of 1 with 12 gives the same amino alcohol-diol ratio in either methylene chloride or dimethoxyethane.

(6) Vincze, A.; Gefen, L. *Isr. J. Chem.* **1978**, *17*, 236.

(7) Hexamethylenetetramine (6) proved to be insufficiently soluble in dimethoxyethane to carry out these experiments.

(8) We have also found that use of dihydroquinine acetate (15) in place of quinuclidine allows for preparation of optically active vicinal amino alcohols (the extent of asymmetric induction in this reaction has not yet been determined). More complete results have been obtained with the OsO_4/15 system.[4b]

(9) (a) Chong, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420. (b) Grob, C. A.; Kaiser, A.; Renk, E. *Helv. Chim. Acta* **1957**, *40*, 2170.

Commercially available compounds were used without further purification.

General Procedure for GLC Monitored Reactions of 12 with 1 and Varying Quantities of Pyridine or 2–5. A mixture of **12** (42 μL, 34 mg, 0.2 mmol) and an appropriate amount of pyridine or **2–5** was dissolved in 2 mL of dimethoxyethane. To this stirred solution was added 62 mg of **1** (0.2 mmol), and stirring was continued overnight. Anhydrous ether (10 mL) and $LiAlH_4$ (50 mg, 1.3 mmol) were added, and stirring was continued 1 h. The reactions were quenched by sequential addition of 50 μL of H_2O, 50 μL of 15% NaOH, and 150 μL of H_2O. After addition of a weighed amount of *n*-docosane, as an internal standard, the yields of **13** and **14** were determined by GLC analysis, using previously determined response factors.

General Procedure for Reaction of 12 and (*Z*)-5-Decene with 1 and 2. A mixture of the olefin (3 mmol) and **2** (1.67 g, 15 mmol) was dissolved in 20 mL of dimethoxyethane. Complex **1** (1.16 g, 3.75 mmol)[10] was added with stirring, and the reactions were stirred 36 h. After dilution with 30 mL of anhydrous ether, $LiAlH_4$ (400 mg, 10.5 mmol) was carefully added, and stirring was continued 1 h. The reactions were quenched by sequential addition of 400 μL of H_2O, 400 μL of 15% NaOH, and 1.2 mL of H_2O. The solutions were filtered, and the filtrate was washed with three portions of H_2O and one portion of brine and dried over Na_2SO_4. Filtration and evaporation of solvent gave the crude product. Residual **2** was removed from the crude product under high vacuum. Bulb-to-bulb distillation then gave the pure products which were identified by comparison with authentic samples.[2]

General Procedure for Preparation of 7–11. Each complex was prepared by mixing the ligand with 1 or 2 molar equiv of **1** (depending on the stoichiometry of the product) in tetrahydrofuran (10 mL/mmol of **1**). Heptane (20 mL/mmol of **1**) was added, and the complexes were crystallized by slow evaporation of the solvent with a stream of nitrogen.

Acknowledgment. We are grateful to the National Science Foundation (Grant No. CHE77-14628) for financial support.

Registry No. **1**, 50381-48-1; **7**, 73384-36-8; **8**, 73384-37-9; **9**, 73395-64-9; **10**, 73384-38-0; **11**, 73384-39-1; **12**, 55915-70-3; **13**, 55915-77-0; **14**, 65760-61-4; (*Z*)-5-decene, 7433-78-5; (R*,S*)-6-[(1,1-dimethylethyl)amino]-5-decanol, 55915-74-7; (R*,S*)-5,6-decanediol, 3266-25-9.

(10) We have observed that **2** slowly reacts with **1** at room temperature and rapidly in refluxing dimethoxyethane to give an as yet unidentified purple osmium complex which probably is a complex of Os(VI). Because of this side reaction, we have used 1.25 molar equiv of **1** to ensure that all the olefin is consumed. A similar reaction was observed between OsO_4 and **2** and affords a green complex.

Convenient Stereoselective Syntheses of the Three Isomeric 2,6-Octadienes

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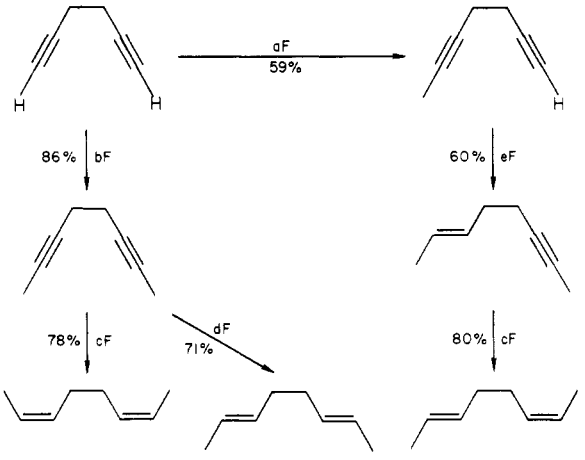
Received December 10, 1979

In connection with a mechanistic study,[1] we required multigram quantities of (*Z,Z*)-, (*E,E*)-, and (*E,Z*)-2,6-octadienes. These simple dienes are well-known in the literature and have been shown to be useful mechanistic probes.[2] In this sense they are the 1,5-diene analogues

Scheme I[a]



[a] (a) 1.8 molar equiv of NaH, THF/1% HMPA (v/v), 4 molar equiv of CH_3I, 72 h. (b) 3.6 molar equiv of NaH and as for a above. (c) P-2 Ni catalyst, ethylenediamine, H_2. (d) Na/liquid NH_3. (e) i, $NaNH_2$, liquid NH_3; ii, addition of Na^0; iii, addition of CH_3I.

of (*E*)- and (*Z*)-2-butene. The *Z,Z* isomer has been conveniently obtained in an isomerically pure state by catalytic hydrogenation of 2,6-octadiyne.[2b] The *E,E* isomer has been obtained by the nickel carbonyl promoted coupling of 1-chloro-2-butene and careful fractional distillation for removal of regioisomers.[2b] To date, the *EZ* isomer has only been obtained by preparative GC separation from the mixture of regio- and stereoisomers obtained from magnesium-promoted coupling of 1-chloro-2-butene.[2a]

Since we required relatively large quantities of all three dienes, we chose to devise a rational synthetic approach that would afford isomerically pure dienes without separation of regio- or stereoisomers. In this paper we report our approach, outlined in Scheme I, that utilizes the symmetrical diyne 1,5-hexadiyne[3] (**1**) as a common precursor of (*Z,Z*)-, (*E,E*)-, and (*E,Z*)-2,6-octadienes (**5**, **6**, and **7**, respectively) and allows their stereoselective preparation in a total of six synthetic steps.

Synthesis of the symmetrical dienes **5** and **6** is readily accomplished via the symmetrical diyne 2,6-octadiyne (**3**). Diyne **3**, in turn, is prepared by dialkylation of 1,5-hexadiyne (**1**). Thus, treatment of 1,5-hexadiyne (**1**) with *n*-BuLi in THF with 10% (v/v) HMPA followed by addition of methyl iodide to the resulting suspension readily affords 2,6-octadiyne (**3**) in 75% yield. Alternatively, the alkylation may be conveniently accomplished by a method developed in our laboratory where a reaction mixture containing the diyne, methyl iodide, and sodium hydride in the THF/HMPA (1% v/v) is stirred for 72 h at room temperature. Workup and simple distillation afford 2,6-octadiyne (**3**) in 86% yield. Though we have not optimized on the quantity of HMPA required for the reaction, deletion of this component decidedly lowers the reaction rate. We feel that this rate is determined by the rate of direct deprotonation of acetylene by solid sodium hydride and speculate that the HMPA acts by surface activation.

Hydrogenation of 2,6-octadiyne utilizing Lindlar catalyst as previously reported[2b] or P-2 nickel poisoned with ethylenediamine as catalyst[4] affords (*Z,Z*)-2,6-octadiene (**5**) in good yield. In our hands the product isolated by simple distillation contains ~5% of (*Z*)-2-octene, identified

(1) Walba, D. M.; Wand, M. D.; Wilkes, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4396–7.

(2) (a) Doering, W. v. E.; Roth, W. R. *Tetrahedron* **1962**, *18*, 67 74. (b) Ulery, H. E.; Richards, J. H. *J. Am. Chem. Soc.* **1964**, *86*, 3113–7 and references therein.

(3) Raphael, A. A.; Sondheimer, F. *J. Chem. Soc.* **1950**, 120–2.

(4) Brown, C. A.; Ahuja, V. K. *J. Chem. Soc., Chem. Commun.* **1973**, 553–4.

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