freshly from the sodium salt) in 3 mL of ethylene glycol, preheated to 125 °C, was added 1.32 g (0.01 mol) of cinnamaldehyde. After 3 min more at 125 °C, 3 mL of isopropyl alcohol was added. Cooling, filtration and rinsing with isopropyl alcohol and isopropyl ether gave 2.9 g (90%) of material, mp 158–159 °C, identical with the product obtained via method A.

2-[2-*p*-(Toluenesulfonyl)ethyl]-1,3-dioxolane (4).[13] Freshly distilled acrolein, 5.6 g (0.10 mol), was added with stirring to 34 g (0.20 mol) of TosH in 30 mL of ethylene glycol. The temperature rose within 4 min to 68 °C. Stirring was continued for 18 h whereupon the viscous slurry was poured onto 100 mL of ice–water containing 10 mL of ammonium hydroxide solution. The solids were filtered off; rinsing with water, cold isopropyl alcohol, and ether gave 16.1 g (67%) of crystals melting at 79–80 °C. Recrystallization from isopropyl alcohol furnished the analytical sample: mp 80–80.5 °C; NMR ($CDCl_3$) δ 1.80–2.29 (m, 2, $TosCCH_2$), 2.44 (s, 3, $TosCH_3$), 2.98–3.41 (m, 2, CH_2Tos), 3.57–4.07 (m, 4, $(OCH_2)_2$), 4.87 (t, 1, CHO_2), 7.10–7.69 (m, 4, ArH).

Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29. Found: C, 56.34; H, 6.33.

Registry No. 3a, 71370-80-4; **3b**, 71370-81-5; **3c**, 71370-82-6; **3d**, 71370-83-7; **4**, 63305-66-8; **5**, 5395-20-0; **6a**, 14902-09-1; **6b**, 71370-84-8; **7a**, 71370-85-9; **7b**, 71370-86-0; **7c**, 71370-87-1; **7d**, 71370-88-2; **8**, 71370-89-3; NaTos, 824-79-3; benzyl chloride, 100-44-7; propargyl bromide, 106-96-7; ethylene glycol, 107-21-1; TosH, 536-57-2; 3-phenylpropenal, 104-55-2; 3-(*o*-nitrophenyl)propenal, 1466-88-2; 3-(2-furyl)propenal, 623-30-3; 3-(2-thienyl)propenal, 14756-03-7; diethyl 2-(cyclohexylamino)vinylphosphonate, 20061-84-1; thiophene-2-ca-

Supplementary Material Available: Analytical data for compounds **3b–d** and **7b–d** (1 page). Ordering information is given on any current masthead page.

Communications

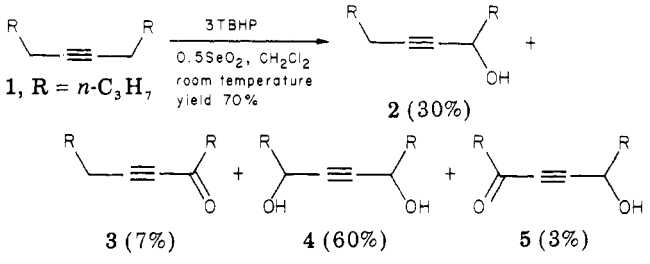
Oxidation of Acetylenes with *tert*-Butyl Hydroperoxide Catalyzed by Selenium Dioxide. α,α'-Dioxygenation of Internal Alkynes

Summary: Unlike olefins, acetylenes show a strong tendency to undergo α,α'-dioxygenation upon reaction with SeO_2. The oxidation of ten different acetylenes allowed assignment of the reactivity sequence: $CH_2 \simeq CH > CH_3$. Alkynes bearing one methylene and one methine substituent afforded the enynone as the major product.

Sir: We have reported that *tert*-butyl hydroperoxide (TBHP), in the presence of SeO_2 as a catalyst, is a very effective system for the allylic oxidation of olefins.[1] A single acetylene (1-decyne) was examined in that earlier study[1] and it was noted that, like the olefins, it was readily α-oxygenated.[2] More recently we had need for 5-decyn-4-ol (**2**) and set out to prepare it by oxidation of 5-decyne (**1**) with the SeO_2/TBHP procedure.[1] We were surprised to find that this internal acetylene showed a pronounced tendency for oxygenation on both sides of the acetylenic group (see Scheme I). Thus, in addition to the expected monooxygenated products **2** and **3**, substantial amounts of the α,α'-dioxygenated products **4** and **5** were also found. This pattern of oxidation (i.e. α,α'-attack) is very rare[3] with olefins and never accounts for the major products. Table I reveals that α,α'-oxidation is a general phenomenon with internal acetylenes.

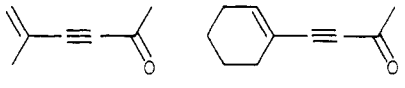
The results in Table I allow formulation of a set of selectivity rules for oxidation of unsymmetrical acetylenes analogous to the rules of Guillemonat.[4] The reactivity sequence for alkynes is $CH_2 \simeq CH > CH_3$.[5] Methine is

Scheme I



essentially identical in reactivity to methylene, but both are much more reactive than methyl.

In those cases (entries 4 and 5, Table I) where the acetylene bears one methylene and one methine substituent, the enynone (e.g. **6** and **7**) becomes an important product.



6 **7**

Formation of the olefinic linkage in enynones **6** and **7** presumably results from dehydration at the diol and/or the ketol stage. Consistent with this speculation is the observation that the diol (isolated from case 5a, Table I) is transformed to enynone **7** when resubjected to the conditions of the reaction.

Diol **4** derived from 5-decyne was shown to be an approximately 1:1 mixture of the meso and *d,l* isomers.[6] By contrast, the diol derived from cyclododecyne appears to be a single isomer.[7] In considering this stereochemical point, it is worth pointing out an interesting difference between SeO_2 oxidations of olefins and acetylenes. In the case of olefins the allylic seleninic acid intermediate **8** can in principle give rise to allylic alcohol by a 2,3-shift to either

(1) Umbreit, M. A.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 5526. For a review on this and other metal-catalyzed oxidations with TBHP see Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, No. 4, in press.

(2) Reports of acetylene oxidations under the usual stoichiometric SeO_2 oxidation conditions are rare. Rabjohn's recent review cites only six examples (see Rabjohn, N. *Org. React.* **1976**, *24*, 261).

(3) We have encountered minor (almost trace), α,α'-dihydroxylation products of olefins in these SeO_2/TBHP systems (Umbreit, M. A. Ph.D. Dissertation, Massachusetts Institute of Technology, 1977).

(4) Guillemonat, A. *Ann. Chim. (Paris)* **1939**, *11*, 143.

(5) This contrasts with Guillemonat's rules for olefins which give the reactivity sequence as $CH_2 > CH_3 > CH$. However in the case of olefins the reactivity of methine groups varies so that examples are known where they are more reactive than methyl groups (see Büchi, G.; Wüest, H. *J. Org. Chem.* **1969**, *34*, 857).

(6) Diol **4** was converted (pyridine/Ac_2O) to the diacetate. The NMR spectrum of this compound was recorded in the presence of increasing amounts of the chiral shift reagent tris[3-heptafluoropropylhydroxymethylene-*d*-camphorato]europium(III). In the presence of 20% of the reagent, the singlet belonging to the acetate methyl at δ 2.00 becomes two doublets (at δ 3.46 and 3.55) of equal area. For a similar example see Gaudemer, A. In "Stereochemistry, Fundamentals and Methods"; Kagan, H. B., Ed.; Georg Thieme: Stuttgart, 1977; Vol. I, p 75.

(7) In the same type of experiment described in footnote 6 the NMR signal due to the methyl groups of the diacetate (mp 64–65 °C) split into two singlets in the presence of the chiral shift reagent.

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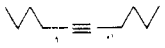
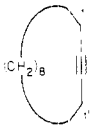
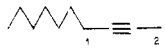
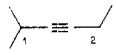
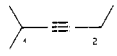
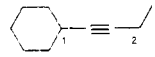
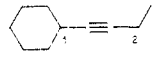
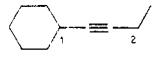
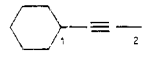
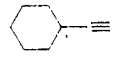
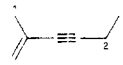
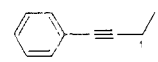
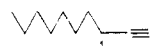
Table I. α-Oxygenation of Acetylenes[a]

case	acetylene[b]	equiv of TBHP	reaction time, h	% yield[c] (% recovered acetylene)	products[d] (rel ratio) alcohol[e]	ketone[e]	diol[f]	ketol	enynone
1		3	29	70 (5)	30	7	60	3	
2		2	15	55 (10)			100		
3		2	48	58 (15)	70	9	20	≃1[g]	
4a		3	6	15 (70)	100[h]				
4b		3	48	70 (20)			77		23
5a		3	30	78 (0)	8[h]	6[i]	68		18
5b		3	72	78 (0)			52		48
5c		3	80[j]	70 (0)			26		74
6		2	30	48 (20)	77		23		
7		2	96	88 (11)	100				
8		2	28	55 (20)	100				
9		2	48	70 (9)	76	24			
10		2	25	48 (~40)[h]	91	9			

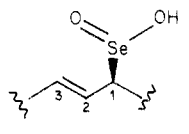
[a] In all the cases except case 9, the reactions were performed at room temperature using dichloromethane as solvent. In case 9 reflux in dichloroethane was necessary. When the reaction was done on a 10-20-mmol scale we found that the best method of purification was by column chromotography of the crude oil on silica gel followed, when preparing analytical samples, either by Kugelrohr distillation or by preparative GLC on an 8 ft × 0.25 in. stainless steel column packed with 20% SE-30 on 45-60 mesh Chromosorb W. In case 2 the diol was obtained crystalline (mp 122-123 °C). [b] All the alkynes except cyclododecyne were obtained from Farchan and used without further purification. The cyclododecyne was prepared according to the procedure of Lalezari, I.; Shaffie, A.; Yalpani, J. *J. Heterocycl. Chem.* **1972**, 1411. [c] Reactions were performed by stirring 0.4 mmol of alkyne, 0.2 mmol of SeO_2, and the necessary amount of TBHP in 4 mL of solvent. Yields were determined by GLC using an internal standard (linear alkane). Analyses were made at frequent intervals and maximum yields were recorded. [d] All products were characterized spectrally and by combustion analysis or by comparison with authentic samples or with literature spectra. [e] Unless otherwise noted the alcohol and the ketone are at site 1. [f] The diol is at sites 1 and 1' or at sites 1 and 2. [g] There was no sign of the corresponding aldol isomer. [h] The monohydroxy fraction was shown by NMR and GLC analysis to be a 1:1 mixture of the two alcohols at site 1 and site 2, respectively. [i] The ketone is, of course, at site 2 in this case. [j] In case 5c, the tightly capped flask of the reaction mixture from case 5b was, after the first 72 h of reaction, heated at 80 °C for 8 h. [k] In this case the maximum yield was not determined; longer reaction times should be explored.

Table II. Relative Rates for Reaction of SeO_2/TBHP with Olefins and Acetylenes[a]

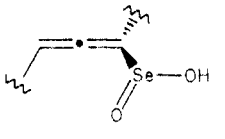
	k_{alkyne}/k_{alkene}
5-decyne/(*E*)-5-decene	2.15
5-decyne/(*Z*)-5-decene	1.24
2-decyne/(*E*)-2-decene	1.12
1-decyne/1-decene	0.61

[a] According to a procedure we described earlier (Patrick, D. W.; Truesdale, L. K.; Biller, S. A.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2628), the relative rates of reaction of the different alkynes and alkenes were determined by competing the alkyne against the alkene in presence of 0.5 equiv of SeO_2 and 2 equiv of TBHP. The disappearance of the starting materials was monitored by GLC relative to a suitable internal standard, and the reaction was analyzed at roughly 50% total starting material conversion.

face of the olefinic bond; this is a consequence of free rotation about the C-1 to C-2 bond in 8. However, in the case of acetylenes the putative allenic seleninic acid intermediate **9**, arising from an ene reaction of SeO_2 with the acetylene, has a fixed geometry and only one 2,3-transition state is feasible. This leads to the interesting conclusion that, with acetylenes, the stereochemistry of the oxidation product should be determined only by the stereochemistry of the initial ene reaction, which produces the allenic seleninic acid **9**.



8



9

Since only the allylic alcohol is obtained upon oxidation of the conjugated enyne **10** (entry 8, Table I) one might be tempted to conclude that olefins are more reactive than acetylenes. However, the relative rate data in Table II indicate that the alkynes are slightly more reactive than their corresponding olefins (the terminal olefin/acetylene pair being an exception). The unreactivity of the methy-

lene group (site 2) in the enyne of case 8 may be related to our observation that the conjugated diacetylene 4,6-decadiyne is inert to oxidation with the SeO_2/TBHP system (even at reflux in dichloroethane).

Alcohol **2** (Scheme I) behaves as an intermediate should. When **2** is subjected to the usual reaction conditions ketone **3**, diol **4**, and ketol **5** are produced in the same relative amounts as found upon direct oxidation of 5-decyne. Under the normal reaction conditions ketone **3** is not oxidized to ketol **5**, but diol **4** is slowly transformed to **5**. The relative rates of oxidation of acetylene **1** and alcohol **2** were not determined but it is clear from the observed product distributions that the rates must be comparable.

In a typical procedure, 11.1 g (0.1 mol)[8] of SeO_2 was added to 200 mL of a 3 M solution of TBHP (0.6 mol) in dichloromethane.[9] The mixture was magnetically stirred in a 500-mL Erlenmeyer flask for 15 min at room temperature and 27.6 g (0.2 mol) of 5-decyne was added. The flask was loosely stoppered and the reaction mixture was stirred at room temperature for 30 h. Then 60 mL of 10% KOH was added to the reaction mixture (cooled in an ice bath), the phases were separated, and most of the CH_2Cl_2 was removed in vacuo at room temperature. The remainder was diluted with 100 mL of ether. The aqueous phase (pH $\simeq$ 5) was extracted with 100 mL of chloroform and the combined organic phases were washed with 40 mL of 5% KOH and with 20 mL of brine. To destroy excess TBHP, 37.8 g of sodium sulfite in 80 mL of water was added dropwise while cooling in an ice bath to keep the temperature below 40 °C. The reaction was then stirred at room temperature overnight. The aqueous phase was saved and the organic phase was washed with water (40 mL, two times). The combined aqueous phases were extracted with 100 mL of chloroform. The combined organic phases were washed with 50 mL of brine, dried ($MgSO_4$), and concentrated in vacuo to a pale-yellow oil. This oil was dissolved in 100 mL of absolute ethanol, and the resulting solution was cooled in an ice bath. Then 0.81 g (1.5 molar equiv based on the amount of ketone and ketol) of $NaBH_4$ in 20 mL of absolute ethanol was added dropwise (with stirring) over a period of 10–15 min.[10,11] The reaction was then left at autogeneous temperature for 30 min. The reaction was acidified (pH $\simeq$ 3–5) with 5% HCl, 100 mL of ether was added, and the organic phase was washed with water (50 mL, two times), dried ($MgSO_4$), and concentrated in vacuo to a yellow oil. Distillation gave a forerun of 2.64 g of 5-decyne, 7.1 g (23%) of 5-decyn-4-ol, bp 73–75 °C (1 mm),[11] and 11.3 g (33%) of 5-decyne-4,7-diol, bp 112–115 °C (1 mm).

The results in Table I suggest that this TBHP/SeO_2 procedure for α-oxygenation of acetylenes will prove useful in organic synthesis. In most cases a single oxygenation product predominates, and in those situations where more complex mixtures are produced they can be simplified by reduction (BH_4^-)[10a] or by oxidation (Jones).[10b] These TBHP/SeO_2 reactions are simple to perform, and no problems were encountered when running the process on a larger scale.[8]

Acknowledgment. We are grateful to the National Science Foundation (CHE77-14628), Hoffmann-LaRoche, and Eli Lilly for financial support. Bernard Chabaud thanks the Centre National de la Recherche Scientifique and NATO for their financial support. We are indebted to Oxirane and Witco Chemical Companies for gifts of TBHP.

Registry No. **1**, 1942-46-7; **2**, 1817-52-3; **3**, 13882-01-4; *dl*-**4**, 71393-74-3; *meso*-**4**, 71393-75-4; **5**, 25294-55-7; **6**, 53864-26-9; **7**, 13757-03-4; cyclododecyne, 1129-90-4; 2-cyclododecyne-1,4-diol, 71393-76-5; 2-decyne, 2384-70-5; 2-decyn-4-ol, 71393-77-6; 2-decyn-4-one, 34695-28-8; 3-decyne-1,4-diol, 71393-78-7; 1-hydroxy-2-decyn-4-one, 52804-65-6; 2-methyl-3-hexyne, 36566-80-0; 2-methyl-3-hexyn-2-ol, 5075-33-2; 5-methyl-3-hexyn-2-ol, 23293-50-7; 2-methyl-3-hexyne-2,5-diol, 5111-43-3; 1-butynylcyclohexane, 57497-06-0; 1-(1-butynyl)cyclohexanol, 15332-34-0; 1-cyclohexyl-1-butyn-3-ol, 65199-70-4; 1-cyclohexyl-1-butyn-3-one, 10564-83-7; 1-(3-hydroxy-1-butynyl)cyclohexanol, 5111-47-7; 1-propynylcyclohexane, 18736-95-3; 1-(1-propynyl)cyclohexanol, 697-37-0; 1-(3-hydroxy-1-propynyl)-cyclohexanol, 5686-96-4; ethynylcyclohexane, 931-48-6; 1-ethynylcyclohexanol, 78-27-3; 2-methyl-1-hexen-3-yne, 23056-94-2; 2-methylene-3-hexyn-1-ol, 71393-79-8; 1-butynylbenzene, 622-76-4; 4-phenyl-3-butyn-2-ol, 5876-76-6; 4-phenyl-3-butyn-2-one, 1817-57-8; 1-decyne, 764-93-2; 1-decyn-3-ol, 7431-23-4; 1-decyn-3-one, 51953-86-7.

(8) The same procedure (except the alkyne was added dropwise over 15 min while the stirred reaction mixture was maintained in a water bath at ambient temperature) was run on a 1-mol scale without difficulty. The yield was the same as in the 0.2-mol scale procedure described above.

(9) The 3 M solution of TBHP in dichloromethane was obtained by swirling 85 mL (0.61 mol) of commercial (Aldrich, WITCO, or Oxirane) TBHP (70% TBHP/30% H_2O, w/w, density = 0.935, ~7.2 mmol/mL) with 140 mL of dichloromethane in a separatory funnel. The milky mixture was allowed to stand until complete separation of the phases had occurred (30 min). The organic (lower) layer (ca. 200 mL containing 0.60 mol of TBHP) was separated from the aqueous layer (~21 mL) and used without further drying. In this procedure only ~1% of the TBHP (as determined by iodometric titration) was lost to the aqueous phase. Alternatively, one can use the 90% TBHP (w/w, density = 0.90, ~9.0 mmol/mL) supplied by Lucidol. In this case no phase separation occurs upon addition of the TBHP (66.67 mL, 0.60 mol) to the methylene chloride (~140 mL) and the resulting solution (~200 mL) can be used directly in the reaction. We used the 90% grade in our earlier work (see ref 1, footnote 9), but it is less available now since the DOT has ruled that it must be shipped by truck. Aldrich still offers 90% TBHP.

(10) (a) Reduction by $NaBH_4$ was one strategy used to simplify the product mixture from four compounds to two.[11] Another approach was found to be Jones oxidation. But in this case, because the diketone was thermally unstable (see Heilbron, I. M.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* **1946**, 39), the distillation of the crude oil, into a fraction of monooxygenated compounds and a fraction of dioxygenated compounds, had to be done before the oxidation. $NaBH_4$ reduction of the eynone did not give a significant amount of the 1,4-addition product (conjugate reduction is usually a serious problem in borohydride reductions of enones). A 98:2 mixture of 5-decyn-4-ol and (*E*)-5-decen-4-ol was formed upon reduction of a pure sample of 5-decyn-4-one. The presence of $CeCl_3$ during the reduction did not change this result (see Luche, J.-L.; Rodriguez-Hahn, L.; Crabbe, P. *J. Chem. Soc., Chem. Commun.* **1978**, 601, for the effect of $CeCl_3$ on the BH_4^- reduction of enones). (b) We have found that unlike allylic alcohols, α-acetylenic alcohols are cleanly oxidized to the ketones by Jones' reagent.

(11) It should be noted that this second step (i.e., $NaBH_4$ reduction of the over-oxidation products, ketone **3** and ketol **5**) was only employed in this 0.2-mol scale oxidation of 5-decyne. No reduction step was used in any of the cases reported in Table I.

(12) No detectable amount of the allylic alcohol was found in this fraction.

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Received April 27, 1979

Selenium-Catalyzed Nonradical Chlorination of Olefins with *N*-Chlorosuccinimide

Summary: Arylselenenyl chlorides (ArSeCl) or aryl diselenides (ArSeSeAr) were effective as catalysts for the chlorination of olefins with *N*-chlorosuccinimide. The principal product is a rearranged allylic chloride, and the vinyl chloride is usually a minor product. Another method for nonradical allylic chlorination of olefins involves reaction of the olefin with TsN—S—O and *N*-chlorosuccinimide and affords the unrearranged allylic chloride as the major product.

Sir: We have been engaged in developing selective, metal-catalyzed reactions for atom-transfer oxidations of ole-

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