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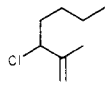
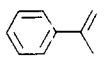
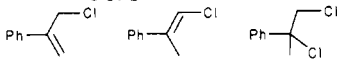
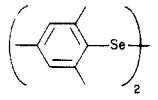
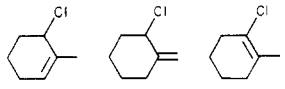
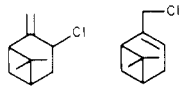
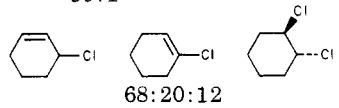
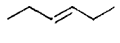
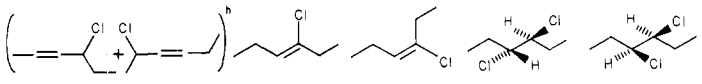
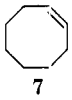
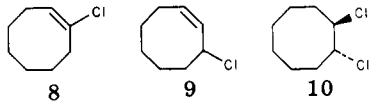
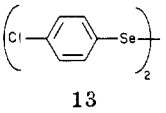
Selenium-Catalyzed Nonradical Chlorination of Olefins with *N*-Chlorosuccinimide

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-

0022-3263/79/1944-4204$01.00/0

Table I

entry	olefin	product/ratio[a,b]	% yield[b] (isolated)	aryl diselenide catalyst
1.	 1	 2 3 96:4	87[c] (78)	PhSeSePh 11
2.		 89:9:2	93[d] (89)[e]	 12
3.		 47:49:3	89[c]	11
4.	 4	 5 6 99:1	88[c] (83)[f]	11
5.		 68:20:12	93[g]	12
6.		 67:16:2:12:2	96[i]	11[j]
7.	 7	 8 9 10 94:4:5	97[k]	12
8.	7	8 9 10 69:27:5	94[k]	 13
9.	7	8 9 10 74:12:15	30[k,l]	11

[a] All the compounds were adequately characterized by analytical and spectral data and by comparison with authentic samples. [b] Ratio and yield were determined by GLC relative to internal standards of *n*-alkanes. The GLC analyses of the products were performed at 60–120 °C on 6 ft × 0.125 in. glass columns packed with 10% UCW-98 on Chromosorb W, 10% Carbowax 20M on Gas Chrom Q, and a 3 ft × 0.125 in. glass column packed with 3% OV-17 on Gas Chrom Q. The injector temperature was always set at the same temperature as that of the column and on-column injection was practiced. [c] The reaction mixture (1 mmol of olefin, 3 mol % of catalyst, 10 mol % of pyridine,[9] and 1.1 mmol of NCS in 2.5 mL of CH_2Cl_2) was stirred for 6 h at room temperature. [d] The reaction mixture (1 mmol of olefin, 3 mol % of catalyst, and 1.1 mmol of NCS in 2.5 mL of CH_2Cl_2) was stirred for 24 h at 30 °C. [e] 20-mmol scale preparation. The distilled chlorides contain only a trace amount of the dichloride. [f] 0.1 mol of β-pinene was chlorinated following the preparative method for olefin 1 except that the reaction was performed at 20 °C (water bath) for 6 h. The ratio of 5 and 6 was 96:4, bp 57–58 °C (0.5 mm). A 1-mol scale preparation at room temperature without pyridine gave a 92:8 mixture of 5 and 6 in 74% yield. [g] The reaction mixture (1 mmol of olefin, 3 mol % of catalyst, and 1.1 mmol of NCS in dichloroethane) was stirred for 48 h at 70 °C. [h] NMR showed 1:1 mixture of the isomers. The two isomers might be equilibrating during the reaction or during preparative GLC separation.[10] [i] Reaction was performed in dichloroethane for 24 h, with 6 mol % of diphenyl diselenide. [j] PhSeSePh is more reactive than dimesityl diselenide in this case. [k] The reaction mixture (1 mmol of olefin, 3 mol % of catalyst, and 1.1 mmol of NCS in dichloroethane) was stirred for 24 h at 30 °C. [l] 70% of the starting olefin remained.

fins. This work has led to the discovery of several useful catalytic procedures for both oxygenation[1] and oxyamination[2] of olefins. We have for some time been searching for ways to extend this class of reactions beyond oxygen and nitrogen to include a halogen, and the first moderately successful outcome of these explorations is reported here.

From a synthetic point of view, the most useful halogenations of olefins are those producing allylic halides, and direct allylic halogenations[3] of olefins are almost always accomplished by free-radical chain processes. The nearly[4] unique capacity of selenium(IV) species (X=Se=X, X = O or NR) to effect allylic oxygenation[1e,5] and amination[6]

(1) (a) Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6136. (b) Michaelson, R. C.; Palermo, R. E.; Sharpless, K. B. *Ibid.* **1977**, *99*, 1990. (c) Sharpless, K. B.; Akashi, K. *Ibid.* **1976**, *98*, 1986. (d) Akashi, K.; Palermo, R. E.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2063. (e) Umbreit, M. A.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 5526. (f) Hori, T.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1689.

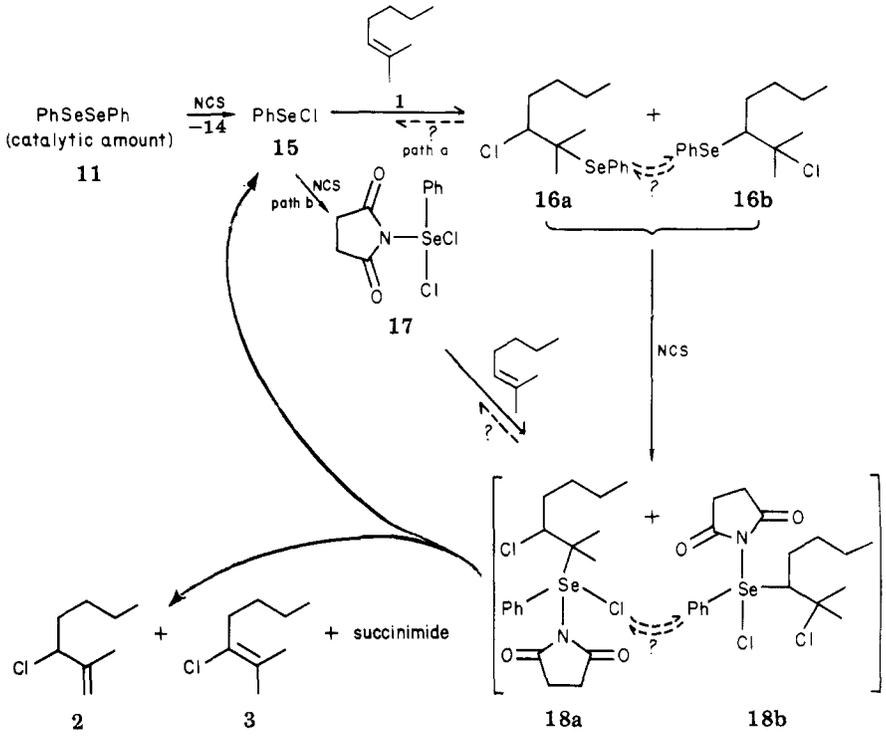
(2) Sharpless, K. B.; Chong, A. O.; Oshima, K. *J. Org. Chem.* **1976**, *41*, 177. Herranz, E.; Biller, S. A.; Sharpless, K. B. *J. Am. Chem. Soc.* **1978**, *100*, 3596. Herranz, E.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2544.

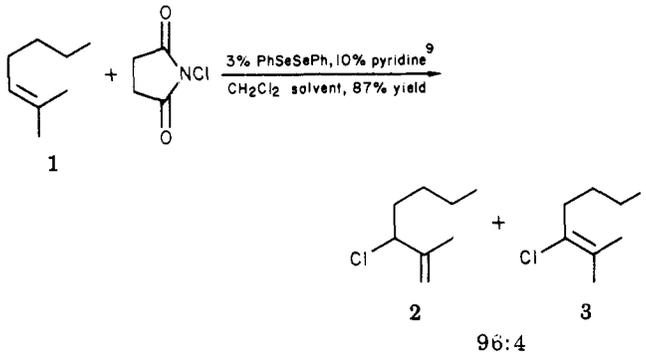
(3) For reviews see De La Mare, P. B. D. "Electrophilic Halogenation"; Cambridge University Press: Cambridge, Mass., 1976; Chapter 6. Anbar, M.; Ginsburg, D. *Chem. Rev.* **1954**, *54*, 925. Huyser, E. S. "The Chemistry of the Carbon–Halogen Bond"; Patai, S., Ed.; Wiley: New York, 1973; Part I, Chapter 8.

(4) Certain sulfur(IV) diimides have also been found to effect allylic amination: Schönberger, N.; Kresze, G. *Justus Liebigs Ann. Chem.* **1975**, 1725. Sharpless, K. B.; Hori, T. *J. Org. Chem.* **1976**, *41*, 176.

(5) (a) For mechanism, see Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 7154. Arigoni, D.; Vasella, A.; Sharpless, K. B.; Jensen, H. P. *Ibid.* **1973**, *95*, 7917. Jensen, H. P.; Sharpless, K. B. *J. Org. Chem.* **1975**, *40*, 264. (b) For a general review, see Rabjohn, N. *Org. React.* **1976**, *24*, 261.

Scheme I. Possible Catalytic Cycle Yielding Rearranged Allylic Chlorides and Vinyl Chlorides





of olefins by nonradical pathways led us to investigate the reactivity of certain halogenated selenium(IV) substances (e.g., O=$SeCl_2$, TsN=$SeCl_2$,[7] PhCON=$SeCl_2$,[7] and $SeCl_4$) toward olefins. Allylic chlorides were produced with all of these substances,[8] but none of these selenium species proved as effective (especially in catalytic applications) as the more recently discovered process which employs *N*-chlorosuccinimide (NCS) in the presence of catalytic amounts of arylselenenyl chlorides (ArSeCl) or aryl diselenides (ArSeSeAr).

As shown above the principal product derived from 2-methyl-2-heptene (**1**) is the rearranged allylic chloride **2**. Although the vinyl chloride **3** is a minor product in the case of this trisubstituted olefin (**1**), examination of the results for other olefins shown in Table I reveals that the ratio of rearranged allylic chloride to vinyl chloride in the product mixtures varies considerably. This ratio is sensitive not only to the structure of the olefin but also to the nature of the aryl diselenide catalyst used (e.g., see entries 7, 8, and 9 in Table I).

The chlorination of β-pinene (**4**) produced almost exclusively the unrearranged allylic chloride **5**.[11] This is a clear exception to the course of reaction observed for the other olefins (Table I) which give rearranged allylic chlorides along with vinyl chlorides. That allylic chloride **5** does not arise by rearrangement of **6** is demonstrated by the observation that **5** rearranges cleanly to the allylic isomer **6** upon passage through a GLC injector at 250 °C. The explanation as to why β-pinene follows a different reaction path than the other olefins has been traced to the operation of two different catalytic reaction cycles. The unique outcome when β-pinene is the substrate is a story in its own right and is presented elsewhere.[12] The possible catalytic cycle which we favor for formation of the rearranged and vinyl chlorides is shown for olefin **1** in Scheme I.

Some of the key experiments which lend support to the mechanism shown in Scheme I are presented in Scheme II.[13] Space permits only the briefest discussion. *N*-(phenylseleno)succinimide (**14**) is a new compound, and its unusual reaction with β-pinene is the subject of the accompanying report.[12] With the exception of β-pinene, selenoimide **14** does not react with the olefins[15] in Table I. The other selenium species generated by NCS cleavage (eq 1, Scheme II) of PhSeSePh is PhSeCl (**15**), and it seems

(6) Sharpless, K. B.; Hori, T.; Truesdale, L. K.; Dietrich, C. O. *J. Am. Chem. Soc.* **1976**, *98*, 269.

(7) Tosylimidoselenium dichloride and benzimidoselenium dichloride were generated in situ by mixing 1 equiv of the corresponding amide and 1 equiv of selenium tetrachloride in methylene chloride in the presence of 2 equiv of triethylamine at 0 °C; the reaction mixture was then allowed to warm to room temperature.

(8) Hori, T.; Sharpless, K. B., unpublished results.

(9) Addition of 10 mol % of pyridine suppressed the formation of isomeric allylic chlorides. For example, a few percent of **6** was usually produced when pyridine was not present during the chlorination of β-pinene (**4**), and the formation of 1-chloro-2-methyl-2-heptene was completely suppressed by the presence of 10 mol % of pyridine during the chlorination of 2-methyl-2-heptene (**1**).

(10) Huntress, E. H. "Organic Chlorine Compounds"; Wiley: New York, 1948; p 1063.

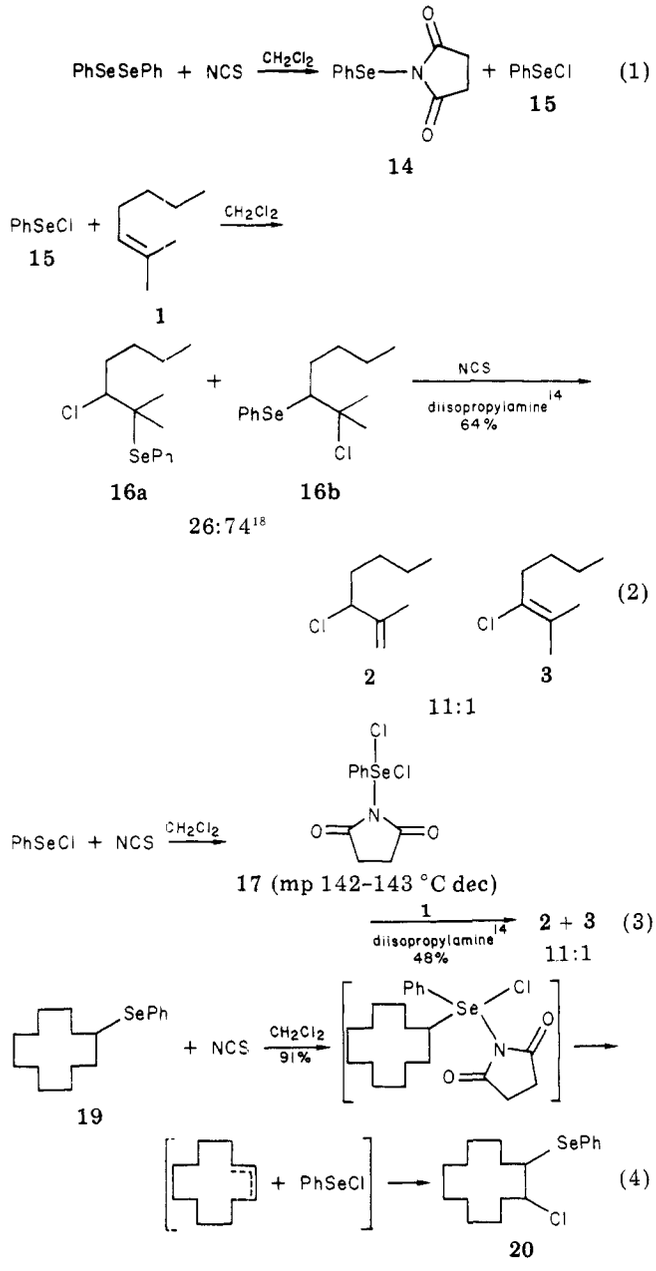
(11) In this case the regioselectivity is the same for allylic oxidation by SeO_2[1e] or allylic amination by TsN=Se=NTs.[6]

(12) Hori, T.; Sharpless, K. B. *J. Org. Chem.* following paper in this issue.

(13) These are but a few of many experiments which were aimed at clarifying the mechanism. Unfortunately, even now, some important details of the catalytic process remain obscure.

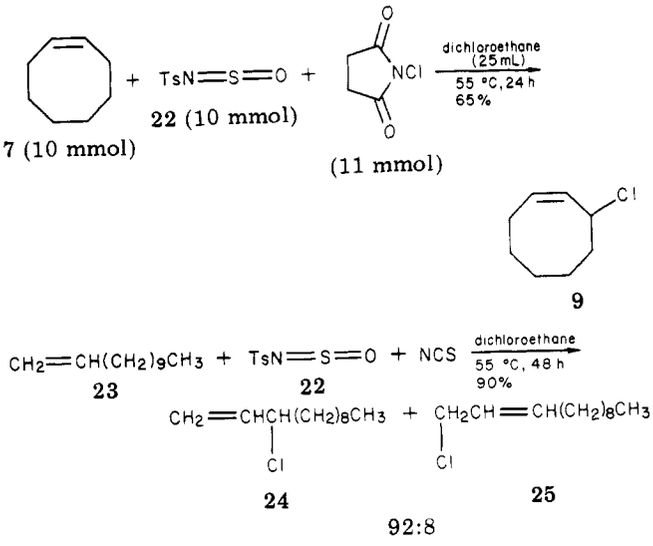
(14) The purpose of diisopropylamine is to trap PhSeCl as it is produced.

Scheme II. Experiments Supporting Mechanism in Scheme I[13]



to be the actual catalyst at the initial stage of the catalytic cycle (eq 2 and 3, Scheme II). Equation 4 reveals that even simple alkyl phenyl selenides (e.g., **19**) undergo oxidation[16]–elimination[17] by NCS in methylene chloride. Whatever the mechanism[17] of this new oxidation–elimination sequence, it is obvious that this step is crucial to the success of the catalytic process. The most unusual fact to be gleaned from Scheme II is that PhSeCl addition to olefin **1** (eq 2) gives a 1:3 mixture[18] of regioisomers **16a** and **16b**, and yet NCS effected oxidation–elimination of this same mixture produces only the olefinic chlorides **2** and **3**, which, it would seem, can only arise from regioisomer **16a**. This phenomenon clearly requires equilibration at some point; the dotted arrows in Scheme I suggest equilibria which could be involved. We have found that PhSeCl reacts very rapidly with NCS to give the selenium(IV) derivative **17** (eq 3), and it is well known[26] that PhSeCl also reacts very rapidly with olefins to afford the 1,2-adducts (eq 2). Therefore, we cannot at this time distinguish between path a and path b in Scheme II; in fact, both paths could be operating.

Scheme III



The following procedure for the chlorination of 2-methyl-2-heptene is representative of the general method. A 200-mL round-bottom flask was charged with 2.24 g (20 mmol) of 2-methyl-2-heptene, 125 mg (0.6 mmol) of diphenyl diselenide,[19] 158 mg (167 μL, 2 mmol) of pyridine,[9] 50 mL of dry methylene chloride, and a magnetic stirrer. The resulting solution was stirred under a nitrogen atmosphere while cooling in an ice bath. *N*-chlorosuccinimide (2.94 g, 22 mmol) was added in one portion, and the resulting mixture was stirred for 6 h in the ice bath and then another 14 h at 5–10 °C. The reaction mixture was then concentrated to about one third its original volume, and 50 mL of pentane was added to precipitate most of the succinimide which was removed by filtration. The filtrate was washed in sequence with 15-mL portions of water, saturated $CuSO_4$ solution (to eliminate the pyridine), water, 10% Na_2CO_3 solution, water, and brine and was then dried (Na_2SO_4). Concentration afforded a pale yellow oil which was distilled to give 2.39 g (78%) of a 96:4 mixture of allylic chloride **2** and vinyl chloride **3**, bp 58–59 °C (15 mm).

A variety of diaryl diselenides was examined as catalysts for the chlorination of cyclooctene, which is a moderately reactive olefin in dichloroethane at 30 °C. Among them dimesityl diselenide (**12**), bis(2,4,6-triisopropylphenyl) diselenide,[20] and bis(4-chlorophenyl) diselenide (**13**) were

(15) Although **14** does not react with the olefins in Table I under anhydrous conditions, these olefins give β-hydroxyalkyl phenylselenides when exposed to **14** in the presence of water (Hori, T.; Sharpless, K. B., unpublished results).

(16) It is well known that NCS reacts with dialkyl sulfides to give sulfonium salts; see Vilsmaier, E.; Sprügel, W. *Justus Liebigs Ann. Chem.* **1971**, *747*, 151.

(17) Even though the reactions are performed under anhydrous conditions one cannot a priori exclude the possibility that the selenoxide is involved. For example, putative intermediates such as **18a** and **18b** could rearrange to the corresponding selenoxides with loss of 2-chloro-5-oxo-1-pyrroline.

(18) The ratio of **16a** to **16b** was determined by NMR in CH_2Cl_2 10 min after mixing the reactants. The ratio did not change even after 15 h at room temperature.

(19) Since diaryl diselenides are both more available and more stable than the corrsponding arylselenenyl chlorides, we have generally used the diselenides as catalysts. However, this is somewhat wasteful because the selenoimide **14** is less (ca. one fifth in the case of olefin **1**) active than PhSeCl as a catalyst for the chlorination of most (β-pinene being an exception[12]) olefins. Therefore, we recommend use of PhSeCl as the catalyst for large-scale preparations.

(20) This diselenide (mp 96–98 °C) was prepared from 2,4,6-triisopropylphenyl bromide in the same manner as in the literature [Sharpless, K. B.; Young, M. W. *J. Org. Chem.* **1975**, *40*, 947] except that the reaction mixture was refluxed for 24 h after addition of the powered selenium.

found to be more reactive than diphenyl diselenide (**11**) and bis(4-*tert*-butylphenyl) diselenide and bis(4-methoxyphenyl) diselenide were found to be less reactive. For α-methylstyrene (entry 2) and cyclohexene (entry 5), dimesityl diselenide (**12**) was a better catalyst than diphenyl diselenide (**11**).

NCS is known to be a source of chlorine radicals in the presence of initiators such as light and benzoyl peroxide.[21] However, it seems unlikely that the present reaction involves free radicals since addition of the radical inhibitor 4,4′-thiobis(6-*tert*-butyl-*m*-cresol) to the reaction mixtures actually accelerated[22] (by as much as four times in the case of 2-methyl-2-heptene) the rate of the chlorination process.

During the present study we also found another method for nonradical allylic chlorination of olefins. We mention it briefly here because it complements the present method, which generally gives the rearranged allylic chloride and which fails with monosubstituted olefins. The process is outlined in Scheme III for cyclooctene (**7**) and 1-dodecene (**23**) and is formally related to our recently reported process for allylic deuteration and tritiation of olefins using the *N*-sulfinylsulfonamide **22**.[23] A likely reaction sequence would involve an initial ene reaction of the olefin and the *N*-sulfinylsulfonamide **22** followed by N-chlorination of the resulting *N*-tosylsulfinamide, and finally a halo analogue of a retro-ene reaction.

There are many chlorinating reagents for alkanes and alkenes, but only *tert*-butyl hypochlorite seems to provide a reliable method for allylic chlorination of olefins,[24] and this occurs by a radical chain process. Allylic bromination also involves free-radical chains and *N*-bromosuccinimide is the best known reagent for this transformation. Therefore, these new methods for allylic chlorination are unique in that they are the first nonradical processes for direct allylic halogenation of olefins which show promise for use in synthesis.[25] It seems reasonable to anticipate that these new catalytic allylic chlorinations will in some cases offer different selectivities than can be achieved with traditional radical chlorinations and brominations of olefins. For example, we have found that β-pinene gives almost exclusively the rearranged allylic chloride **6** (**6**/**5** = 98:2) in Walling's radical chlorination procedure[24] with *tert*-butyl hypochlorite.

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Registry No. 1, 627-97-4; **2**, 71518-90-6; **3**, 71518-91-7; **4**, 127-91-3; **5**, 71564-06-2; **6**, 30897-76-8; **7**, 931-88-4; **8**, 1890-22-8; **9**, 24618-80-2; **10**, 22828-42-8; **11**, 1666-13-3; **12**, 71518-92-8; **13**, 20541-49-5; **14**, 68395-72-2; **15**, 5707-04-0; **16a**, 71518-93-9; **16b**, 71549-31-0; **17**, 71518-94-0; **19**, 42066-65-9; **20**, 71518-95-1; **22**, 4104-47-6; **23**, 112-41-4; **24**, 42886-46-4; **25**, 42886-47-5; NCS, 128-09-6; bis(2,4,6-triisopropylphenyl) diselenide, 71518-96-2; bis(4-*tert*-butylphenyl) diselenide, 71518-97-3; bis(4-methoxyphenyl) diselenide, 38762-70-8; α-methylstyrene, 98-83-9; cyclohexene, 110-83-8; [1-(chloromethyl)ethenyl]benzene, 3360-52-9; (2-chloro-1-methylethenyl)benzene, 3360-55-2; (1,2-dichloro-1-methylethyl)benzene, 17221-23-7; 1-methylcyclohexene, 591-49-1; 6-chloro-1-methylcyclohexene, 17090-05-0; 1-chloro-2-methylenecyclohexane, 71518-98-4; 1-chloro-2-methylcyclohexene, 16642-49-2; 3-chlorocyclohexene, 2441-97-6; 1-chlorocyclohexene, 930-66-5; *trans*-1,2-dichlorocyclohexane, 822-86-6; 3-hexene, 592-47-2; 4-chloro-2-hexene, 6734-98-1; 2-chloro-3-hexene, 28046-62-0; (*Z*)-3-chloro-3-hexene, 17226-34-5; (*E*)-3-chloro-3-hexene, 17226-35-6; 3,4-dichlorohexane (isomer 1), 19117-19-2; 3,4-dichlorohexane (isomer 2), 71518-99-5.

(21) Buu-Hoi, N. P.; Demerseman, P. *J. Org. Chem.* **1953**, *18*, 649. Hebelynck, M. F.; Martin, R. H. *Experientia* **1949**, *5*, 69.

(22) The reason for this acceleration is not known. The same radical inhibitor also slightly accelerated the reaction with cyclooctene.

(23) Hori, T.; Singer, S. P.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1456.

(24) Walling, C.; Thaler, W. *J. Am. Chem. Soc.* **1961**, *83*, 3877.

(25) Chlorination of olefins with molecular chlorine can yield allylic chlorides through an ionic pathway: Poutsma, M. L. *J. Am. Chem. Soc.* **1965**, *87*, 4285. Although interesting from the mechanistic point of view, this procedure is far from a general method for the preparation of allylic chlorides because it uses the olefins themselves as the solvents.

(26) For a review see Schmid, G. H.; Garratt, D. G. "The Chemistry of Double Bonded Functional Group"; Patai, S., Ed.; Wiley: New York, 1977; Part 2, p 855.

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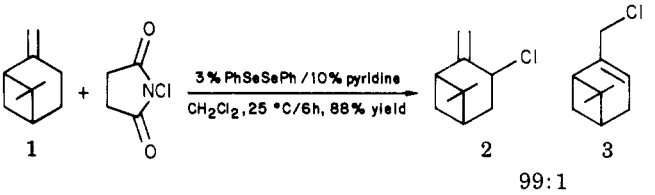
Conversion of Allylic Phenylselenides to the Rearranged Allylic Chlorides by *N*-Chlorosuccinimide. Mechanism of Selenium-Catalyzed Allylic Chlorination of β-Pinene

Summary: Reaction of diphenyl diselenide with NCS affords phenylselenenyl chloride (**4**) and *N*-phenylselenosuccinimide (**5**). The latter proved to be an active catalyst for the allylic chlorination of β-pinene by *N*-chlorosuccinimide (NCS). While studying the mechanism of this catalytic chlorination, it was found that allylic phenylselenides are transformed by NCS to the rearranged allylic chlorides in high yield. A convenient method for the preparation of *N*-(phenylseleno)succinimide was developed. It was demonstrated that an allylic phenylselenide affords the rearranged allylic sulfonamide upon treatment with anhydrous Chloramine-T.

Sir: In the accompanying report[1] on the arylselenenyl chloride (ArSeCl) catalyzed nonradical chlorination of olefins by *N*-chlorosuccinimide (NCS), we noted that the behavior of β-pinene (**1**) was anomalous. Whereas most olefins gave the rearranged allylic chlorides and the vinyl chlorides, β-pinene afforded almost exclusively the thermodynamically less stable[2] unrearranged allylic chloride **2**.



1 **2** **3**

99:1

The possible catalytic cycle we proposed (see Scheme I in ref 1) for the chlorination reaction accounted for the outcome with most olefins. However, by no stretch of the imagination could the results with β-pinene be made to fit the catalytic cycle proposed in that mechanism. We set out to determine why β-pinene behaved differently from other olefins, and discovered the interesting oxidative rearrangement of allylic phenylselenides, which is the main subject of this report.

We had noted earlier[3] that NCS cleaves diphenyl di-

(1) Hori, T.; Sharpless, K. B. *J. Org. Chem.* preceding paper in this issue.

(2) Allylic chloride **2** rearranges completely to the isomer **3** upon passage through a GLC injector at 250 °C.

(3) Hori, T.; Sharpless, K. B., unpublished results.

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