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.

Acknowledgment. We are grateful to the National Science Foundation (CHE74-21260), Hoffmann-LaRoche, and Eli Lilly for financial support.

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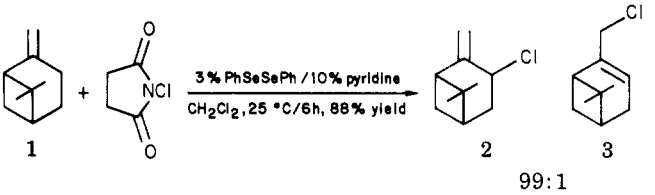
Conversion of Allylic Phenylselenides to the Rearranged Allylic Chlorides by *N*-Chlorosuccinimide. Mechanism of Selenium-Catalyzed Allylic Chlorination of β-Pinene

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-

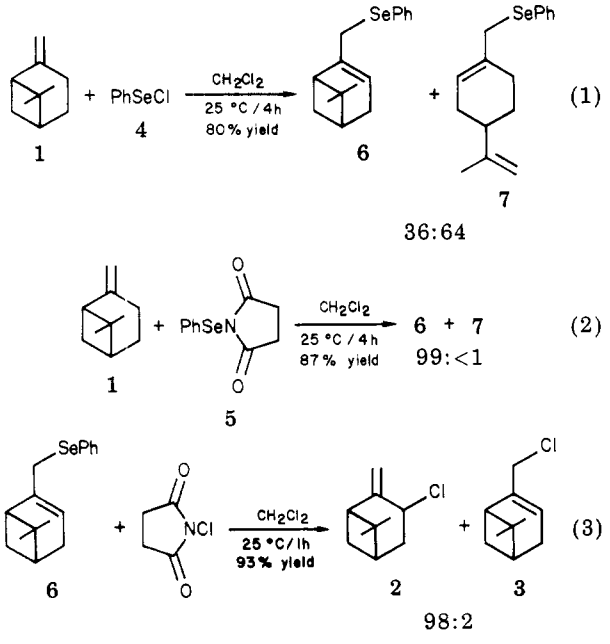
(1) Hori, T.; Sharpless, K. B. *J. Org. Chem.* preceding paper in this issue.

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

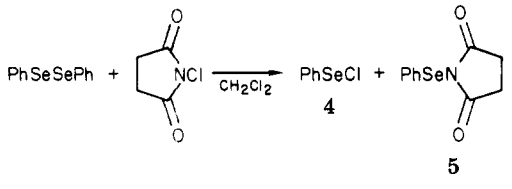
(3) Hori, T.; Sharpless, K. B., unpublished results.

0022-3263/79/1944-4208$01.00/0

Scheme I



selenide to give equal amounts of phenylselenenyl chloride (**4**) and the new substance, *N*-phenylselenosuccinimide (**5**).



The isolation of the succinimide derivative **5** proved difficult in the presence of selenenyl chloride **4**. This problem was overcome by addition of cyclohexene or norbornene to trap PhSeCl as the olefin adduct, followed by addition of hexane to precipitate **5** as crystals.[4]

As outlined in Scheme I β-pinene (**1**) was exposed, in separate experiments, to both PhSeCl (reaction 1) and *N*-(phenylseleno)succinimide (reaction 2). As can be seen in reaction 1, PhSeCl produces some of the rearranged allylic selenide **6**,[5] but the major product **7**[6] has the limonene skeleton arising from fragmentation of the four-membered ring in **1**. Both **6** and **7** are unusual products since most reactions of PhSeCl with olefins[7] involve addition processes and not substitutions. However, the facile reaction of **5** with β-pinene (reaction 2) to give only the rearranged allylic phenylselenide **6** was even more interesting, and phenylselenide **6** appeared to be a good candidate for the key intermediate in the catalytic chlorination sequence. Strong support for its probable role as an intermediate was obtained by exposure of selenide **6** to NCS under the usual conditions of the catalytic chlorination (reaction 3); the rearranged allylic chloride **2** was obtained in excellent yield. Taken together, reactions 2 and 3 in Scheme I constitute a closed catalytic cycle for the allylic chlorination of β-pinene by NCS as shown in Scheme II. Note that the outcome of reaction 1 in Scheme I virtually eliminates the need to consider PhSeCl as a possible participant in the catalytic cycle responsible for the allylic chlorination of β-pinene.[8] Thus, (phenylseleno)succinimide (**5**) appears to be the catalyst in the catalytic cycle for the chlorination of β-pinene, while PhSeCl is probably, as reported earlier,[1] the catalyst in an entirely different catalytic cycle for the chlorination of most other olefins.

Scheme II

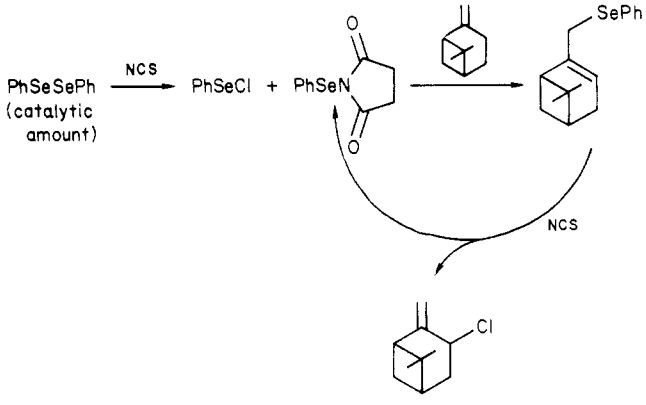
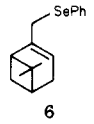
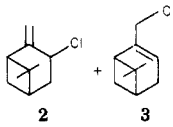
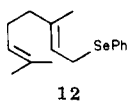
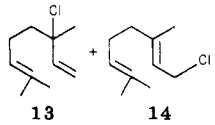


Table I[a]

allylic phenylselenide	product	% yield[b]
 6	 2 + 3	93
$PhSeCH_2CH{=}CH(CH_2)_8CH_3$ 8	$CH_2{=}CHCH(CH_2)_8CH_3$ | Cl 10	98[c]
$CH_2{=}CHCH(CH_2)_8CH_3$ | SePh 9	$ClCH_2CH{=}CH(CH_2)_8CH_3$ 11	95[d]
 12	 13 + 14 95:5	85

[a] All the compounds were adequately characterized by analytical and spectral data or by comparison with authentic samples. [b] Determined by GLC (relative to internal standards of *n*-alkanes). [c] The starting allylic phenylselenide contained 4% of isomer **9** and the product contains 5% of isomer **11**, which almost certainly derives from the 4% of isomer **9** present in the starting material. [d] The starting allylic phenylselenide contained 30% of isomer **8** and the product contains 31% of isomer **10**; allylic chloride **11** is a mixture of *E* and *Z* isomers.

The transformation of allylic phenylselenides to the corresponding rearranged allylic chlorides by treatment with NCS in CH_2Cl_2 seems to be a general process (Table I). In the four cases represented in the table, the reaction appears to occur with very high, if not complete,[9] trans-

(4) See ref 12 for a better preparative procedure.

(5) An oil isolated by chromatography on silica gel: NMR (60 MHz, CCl_4) δ 0.78 (3 H, s, CH_3), 1.28 (3 H, s, CH_3), 3.38 (2 H, m, CH_2SePh), and 5.22 (1 H, br s, $W_{1/2}$ = 6 Hz, CH=C).

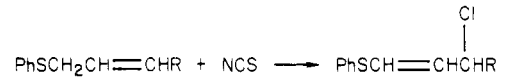
(6) An oil, isolated by chromatography on silica gel: NMR (60 MHz, CCl_4) δ 1.65 (3 H, m, CH_3C=C), 3.40 (2 H, s, CH_2SePh), 4.61 (2 H, s, CH_2=C), and 5.38 (1 H, br s, $W_{1/2}$ = 9.2 Hz, CH=C).

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

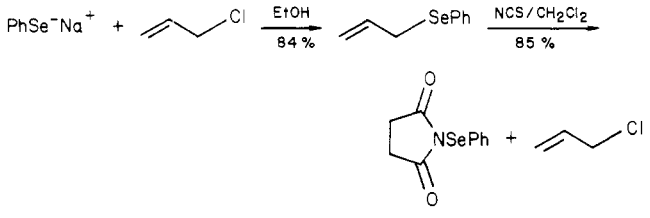
(8) Although PhSeCl is not in the catalytic cycle, it serves as a catalyst because the reaction of NCS with **6** or **7**, which are produced by reaction between PhSeCl and β-pinene, generates *N*-(phenylseleno)succinimide (**5**).

(9) There are three possible reasons for the incomplete transposition of the double bond. (a) Impure starting allylic phenylselenides. Allylic phenylselenides undergo 1,3 shifts easily [Sharpless, K. B.; Lauer, R. F. *J. Org. Chem.* **1972**, *37*, 3973]. Therefore, it is often difficult to isolate pure regioisomers of allylic phenylselenides (e.g., **9**, see note *d* in Table I). (b) Possible instability of the initially formed allylic chlorides (e.g., upon heating, **2** rearranges to **3**. See ref 2). (c) Direct attack by chloride ion at the carbon bearing the oxidized phenylseleno moiety. This type of process could account for the selective formation of the *E* chloride **14** (i.e. no neryl chloride was detected) in the reaction with geranyl phenyl selenide (**12**, Table I).

Scheme III



Scheme IV



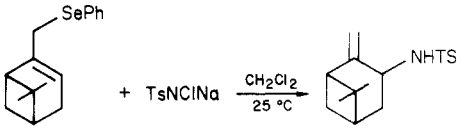
position of the double bond. A likely mechanism for this reaction is as follows: NCS reacts with the selenium moiety to give (alkylphenylsuccinimido)selenonium chlorides, which in turn undergo a 2,3-like rearrangement which leads to the allylic chlorides. It will be noticed that there is a similarity between these reactions and those of the corresponding 2,3 shifts observed for allylic phenylselenoxides.[10]

Cohen and co-workers have reported the reaction of allylic phenylsulfides with NCS shown in Scheme III. The reaction takes a completely different course than that described here for the selenium analogues.[11]

The facility of the reaction between allylic phenylselenides and NCS (e.g., reaction 3, Scheme I) suggested the efficient route to *N*-(phenylseleno)succinimide (**5**) shown in Scheme IV.[12] A number of interesting applications have been found for *N*-(thiophenyl)succinimide, and *N*-(thiophenyl)phthalimide,[13] and now that the corresponding selenium analogue is available, it seems likely that it will find uses as well.[15]

Allylic phenylselenides are potentially valuable in organic synthesis due primarily to the ease with which they undergo substitutive allylic rearrangements following oxidations at the selenium atom. We had previously established these rearrangements for oxygen[10] and carbon,[14] and the present work has extended this class of reactions to include chlorine.

Finally, we wish to describe a single experiment which demonstrates that nitrogen can also be included in this list. It was found that 10-(phenylseleno)-β-pinene (**6**) afforded 3-(*p*-toluenesulfonamido)-β-pinene (**15**) in 44% yield upon reaction with 2.5 equiv of anhydrous Chloramine-T in methylene chloride.



Acknowledgment. We are grateful to the National Science Foundation (CHE74-21260), Hoffmann-LaRoche, and Eli Lilly for financial support.

Registry No. 1, 127-91-3; 2, 71564-06-2; 3, 30897-76-8; 4, 5707-04-0; 5, 68395-72-2; 6, 71518-08-6; 7, 71518-09-7; 8, 71518-10-0; 9, 71518-11-1; 10, 42886-46-4; (*E*)-11, 71518-12-2; (*Z*)-11, 71518-13-3; 12, 71518-14-4; 13, 471-10-3; 14, 5389-87-7; 15, 57981-21-2; NCS, 128-09-6; diphenyl diselenide, 1666-13-3; allyl chloride, 107-05-1; allyl phenylselenide, 14370-82-2; TsNClNa, 127-65-1.

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(10) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 7154. Sharpless, K. B.; Young, M. W.; Lauer, R. F. *Tetrahedron Lett.* **1973**, 1979.

(11) Mura, A. J., Jr.; Bennett, D. A.; Cohen, T. *Tetrahedron Lett.* **1975**, 4433.

(12) The procedure for preparation of **5** is as follows. Diphenyl diselenide (3.12 g, 10 mmol) was dissolved in 20 mL of absolute ethanol. Sodium borohydride (768 mg, 20.3 mmol) was added carefully, while stirring magnetically under nitrogen, until the bright yellow solution turned colorless. The reaction mixture was cooled in an ice bath and allyl chloride (1.68 g, 22 mmol) was added. The ice bath was removed and the reaction mixture was stirred at ambient temperature for 5 h. Extraction with hexane and distillation afforded 3.31 g (84%) of allyl phenylselenide, bp 75–76 °C (0.3 mm). It seems very likely that the standard molar scale Grignard preparation of diphenyl diselenide [Sharpless, K. B.; Young, M. W. *J. Org. Chem.* **1975**, *40*, 947] could be easily modified (i.e., addition of allyl chloride to the PhSeMgBr instead of air oxidation) to produce allyl phenyl selenide directly. NCS (2.19 g, 16.4 mmol) was added to a magnetically stirred ice-cooled solution of allyl phenylselenide (3.31 g, 16.8 mmol) in 30 mL of dry methylene chloride under nitrogen atmosphere. The ice bath was removed after 30 min and the reaction mixture was stirred for an additional 1.5 h at room temperature. Concentration of the solvent to about 5 mL and addition of 17 mL of dry hexane gave 3.54 g (97% pure by NMR, but gave correct C, H analysis, mp 114–120 °C, 82% yield) of (phenylseleno)succinimide, which is sensitive to moisture but is otherwise stable: NMR (60 MHz, $CDCl_3$) δ 2.78 (4 H, s) and 7.2–7.9 (5 H, m). A signal due to the methylene protons of succinimide appears at 2.71 ppm if the product is contaminated by succinimide.

(13) Mukaiyama, T.; Kobayashi, S.; Kumamoto, T. *Tetrahedron Lett.* **1970**, 5115. Kumamoto, T.; Kobayashi, S.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 866.

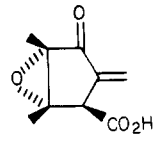
(14) Sharpless, K. B.; Gordon, K. M.; Lauer, R. F.; Patrick, D. W.; Singer, S. P.; Young, M. W. *Chem. Scr.* **1975**, *8A*, 9.

(15) (a) Dr. L. K. Truesdale (Allied Chemical Co., Morristown, N.J.) has prepared a variety of *N*-(arylseleno)succinimides using our procedure (see ref 12). He has also prepared *N*-(phenylseleno)phthalimide by the same procedure[12] except that *N*-chlorophthalimide was used in place of *N*-chlorosuccinimide. (b) For some interesting synthetic applications of both *N*-(phenylseleno)succinimide and *N*-(phenylseleno)phthalimide see Nicolaou, K. C.; Claremon, D. A.; Barnette, W. E.; Seitz, S. P. *J. Am. Chem. Soc.* **1979**, *101*, 3704.

Stereospecific Total Synthesis and Absolute Configuration of (+)-Methylenomycin A

Summary: Starting from 2,3-dimethyl-1-oxocyclopent-2-ene-4-carboxylic acid (**4**), a stereospecific synthesis of (+)-methylenomycin A (**1**) was accomplished and its absolute configuration was determined via X-ray crystallographic techniques.

Sir: Methylenomycin A (**1**) and B are two antibiotics recently reported by Arai and co-workers.[1] Compound



1

1 bears structural similarities to a whole family of medicinally important cyclopentanone natural products, including the pentenomycins,[2] xanthocidin,[3] and sarkomy-

(1) T. Haneishi, N. Kitahara, Y. Takiguchi, M. Arai, and S. Sugawara, *J. Antibiot.*, **27**, 386 (1974).

(2) K. Umino, N. Takeda, Y. Ito, and T. Okuda, *Chem. Pharm. Bull.*, **22**, 1233 (1974).

(3) K. Asahi, J. Nagatsu, and S. Suzuki, *J. Antibiot.*, **19**, 195 (1966); K. Asahi and S. Suzuki, *Agric. Biol. Chem.*, **34**, 325 (1970).

0022-3263/79/1944-4210$01.00/0