for 24 h. The catalyst was removed by filtration of the mixture through a neutral Al_2O_3 column, and the residue was then subjected to separation by HPLC on an ODS-2 column. The composition of this mixture is listed in Table I.

General Procedure for Heterogeneous Catalytic Hydrogenation. A solution of 46 mg of 23-methylenecholesterol *i*-methyl ether (IIIf) in 5 mL of ethyl acetate was hydrogenated with 20 mg of 5% Pd-$BaSO_4$ at room temperature for 1.5 h. After removal of the catalyst, the solvent was evaporated under reduced pressure. The residue was then dissolved in 10 mL of aqueous dioxanne (containing 2 mg of *p*-toluenesulfonic acid) and heated under reflux for 1 h. The mixture was treated in the usual way to give the crude product, which was separated by HPLC on an ODS-2 column; for product composition see Table I.

Acknowledgment. Financial support for the Stanford work was provided by the National Institutes of Health (Grants GM-06840 and GM-28352). We thank Annemarie Wegmann and staff for mass spectral measurements, Dr. Lois Durham and colleagues for the 360-MHz ^1H NMR spectra (which were obtained at the Stanford NMR facility funded by NIH Grant RR-0711 and NSF Grant GP-23633), Dr. James N. Shoolery (Varian Associates) for ^{13}C measurements and assignments, and Ciba-Geigy for donation of methyl 3β-acetoxycholenate. The work at Buffalo was supported by DHHS Grants AM-26546 and AM-07368 and the Margaret L. Wendt Foundation. We acknowledge the assistance of Dr. Douglas Rohrer for collecting the X-ray data and Miss F. Elaine DeJarnette for technical assistance.

Registry No. Ib, 79396-51-3; Ic, 79396-53-5; Id, 79396-54-6; If, 82903-15-9; Ig, 71932-06-4; Ih, 82903-20-6; Ii, 82903-17-1; Ij, 82903-18-2; Il, 80082-94-6; Im, 80082-93-5; In, 83719-76-0; Io, 83719-77-1; Ip, 474-62-4; Iq, 4651-51-8; IIIf, 83719-78-2; IIIn, 83719-79-3; IIIo, 83719-80-6; IIIr, 83719-81-7; IIIs, 83719-82-8; IIIw, 69081-90-9; IIIy (23*R*), 83719-83-9; IIIy (23*S*), 83719-84-0; IIIz, 73668-96-9; Vn, 83719-85-1; isobutyl bromide, 78-77-3; methyltriphenylphosphonium bromide, 1779-49-3; (*R*)-23-ethylcholestanol, 83542-21-6; (*S*)-23 ethylcholestanol, 83572-16-1.

Oxidation of Alcohols with Dimethyl Selenide–*N*-Chlorosuccinimide Complex

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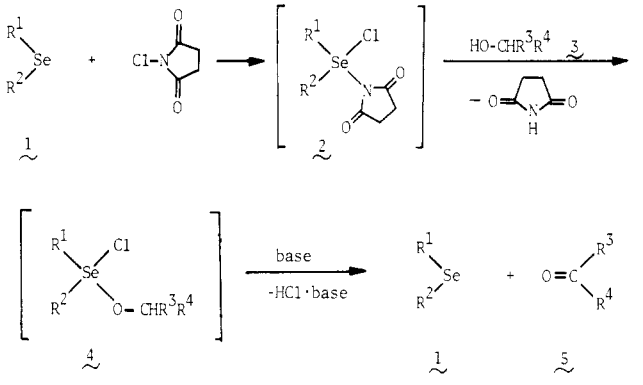
Dimethyl selenide reacts with *N*-chlorosuccinimide (NCS) to give a new complex, with which various alcohols are successfully oxidized to carbonyl compounds. Notably, this method is applicable to allylic alcohols without formation of allylic chlorides and rearranged products. β-Hydroxy selenide **8** is converted to β-oxo selenide **9** by the treatment with NCS. On the other hand, facile deselenization occurs in the case of γ-hydroxy selenide **10** under similar conditions. A plausible mechanism of the reactions is also discussed.

Oxidation of alcohols via oxasulfonium ion intermediates is a useful synthetic method;[1] however, it is one which has serious limitations: (i) it is not applicable to allylic alcohols, as it results in the formation of allylic halides; (ii) alkylthio methyl ethers are formed by Stevens rearrangement in polar solvents.[2] On the other hand, there is currently a significant interest in the development of selenium chemistry,[3] for example, oxidation of alcohols with benzeneseleninic anhydride[4] and selenium-catalyzed chlorination of olefins.[5] Nevertheless, selenium(IV) compounds have been little investigated. In contrast to sulfur analogues, they are relatively stable,[6] and therefore oxaselenium(IV) species are potentially valuable intermediates for oxidation of alcohols, as they are expected to overcome the limitations described above. We report here a new oxidation of alcohols with dimethyl selenide–*N*-chlorosuccinimide complex.

When dimethyl selenide (1) was added to a solution or suspension of NCS, a new white precipitate was formed immediately, which gradually disappeared upon addition of alcohol **3** (Scheme I). GLC analyses showed formation of a small amount of carbonyl compound **5** at this stage. The product was dramatically increased after addition of base, but long reaction times and heating were not as effective. An aqueous workup gave a clean mixture containing the carbonyl compound **5** and the starting alcohol **3**; other products were not detected. Of course, the selenide **1** could be recovered quantitatively, if necessary.

Scheme I



We examined the reactions of benzyl alcohol and *p*-nitrobenzyl alcohol in order to determine the optimum conditions (Table I). As shown in Table I, the following series of decreasing reactivities is observed: selenides, CH_3SeCH_3 > $PhSeCH_3$ > PhSePh; solvents, $C_6H_5CH_3$ >

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0022-3263/83/1948-0054$01.50/0

Table I. Optimization of Reaction Conditions[a]

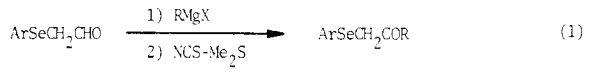
alcohol	selenide	solvent	base	% yield of the aldehyde[b]
$C_6H_5CH_2OH$	PhSePh	$CHCl_3$-$C_6H_5CH_3$[c]	Et_3N	18
$C_6H_5CH_2OH$	PhSePh	$CHCl_3$	Et_3N	15
$C_6H_5CH_2OH$	$PhSeCH_3$	$C_6H_5CH_3$	Et_3N	76
$C_6H_5CH_2OH$	CH_3SeCH_3	$C_6H_5CH_3$	Et_3N	80
$C_6H_5CH_2OH$	CH_3SeCH_3	$C_6H_5CH_3$	$NaHCO_3$	26
$C_6H_5CH_2OH$	CH_3SeCH_3	$C_6H_5CH_3$	DBU	93
$C_6H_5CH_2OH$	CH_3SeCH_3	CH_2Cl_2	Et_3N	66
$C_6H_5CH_2OH$	CH_3SeCH_3	CH_2Cl_2	$NaHCO_3$	26
$C_6H_5CH_2OH$	CH_3SeCH_3	CH_2Cl_2-Me_2SO[c]	Et_3N	5
p-$NO_2C_6H_4CH_2OH$	$PhSeCH_3$	$C_6H_5CH_3$	Et_3N	61
p-$NO_2C_6H_4CH_2OH$	CH_3SeCH_3	$C_6H_5CH_3$	Et_3N	77

[a] Room temperature for 4 h. [b] Yields were determined by GLC with internal standards or ^1H NMR. [c] 1:1 v/v.

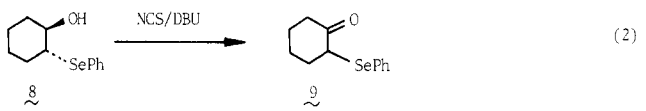
$CH_2Cl_2 > CH_2Cl_2$–Me_2SO; bases, DBU > Et_3N > $NaHCO_3$. The order of the selenides would be influenced by their nucleophilicities to form the complexes with NCS, since a precipitate was not observed in the case of diphenyl selenide. Less polar solvents are suitable for this reaction, suggesting that the reaction intermediate is oxaselenium **4** rather than selenonium salt. The complex **2** ($R^1 = R^2$ = Me) was isolable [NMR (Me_2SO-d_6) δ 2.57 (s, 6 H), 3.08 (s, 4 H)] but gradually decomposed at room temperature and therefore was used without separation in the next steps.

Representative results are summarized in Table II. Primary and secondary alcohols were easily oxidized to the corresponding carbonyl compounds in good yields (entries 1–8). Similarly, facile oxidatio of allylic alcohols occurred without formation of chlorinated or rearranged products which were possible byproducts (entries 9–12). Success in the oxidation of allylic alcohols may be attributed to the fact that nucleophilic attack of chlorine is suppressed by the interaction with the selenium atom.[7] In other words, the equilibrium of oxaselenium **6** and selenonium **7** is moved to the left (Scheme II). While 1,2-diketone and α-keto ester moieties were prepared from α-hydroxy ketone and ester precursors (entries 13, 14), this method was not applicable to the β-hydroxy ester, affording dehydrated product instead of β-keto ester (entry 15). Furthermore, 1,2-diol was readily oxidized to give diketone in good yield (entry 16).

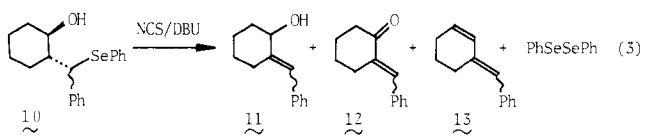
Due to the mechanistic interest and the utility of keto selenides in synthetic chemistry, we have undertaken a study of oxidation of hydroxy selenides. Baudat reported the conversion of α-seleno aldehydes to the corresponding ketones with Me_2S·NCS (eq 1);[8] however, dimethyl sulfide



(1)



(2)

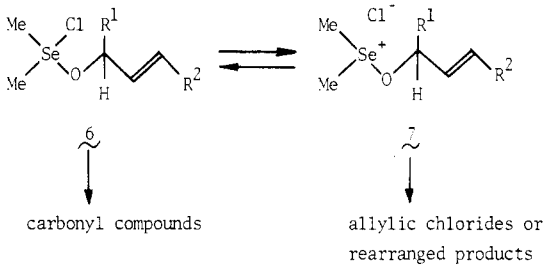


(3)

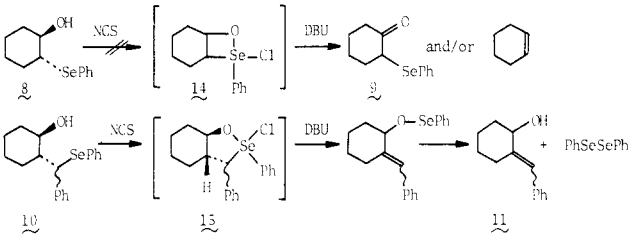
might be unnecessary, if our method was possible in this system. Indeed, β-hydroxy selenide **8** was oxidized to β-oxo selenide **9** by treatment with NCS in 81% yield (eq 2). In contrast, γ-hydroxy selenide **10** (a mixture of threo and erythro, 1:2) was exclusively deselenized to give allylic alcohol **11** (cis/trans, 3:7) and diphenyl diselenide in 97% and 40% yields, respectively, under similar conditions. When this reaction was carried out for a longer time, the yield of **11** was gradually decreased (~75%), and formation of enone **12** (~15%) and diene **13** (~5%) was observed (eq 3).

The differences between **8** and **10** can reasonably be explained as follows. β-Hydroxy selenide **8** was oxidized intermolecularly, since intramolecular reaction should proceed via an unfavorable four-membered ring **14**, which might be changed to cyclohexene rather than β-oxo selenide **9** (Scheme III). Reich has reported the reaction of β-hydroxy selenide with *tert*-butyl hypochlorite, where olefin synthesis via a four-membered ring was not possible.[9] In the case of γ-hydroxy selenide **10**, oxaselenium(IV)

Scheme II



Scheme III



Scheme IV

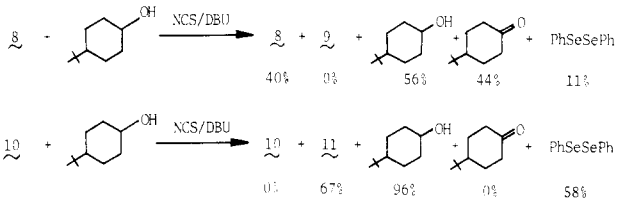


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Table II. Oxidation of Alcohols with Dimethyl Selenide-NCS Complex[a]

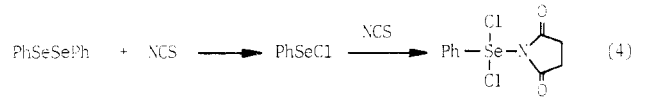
entry	alcohol	product	% yield[b]
1	$PhCH_2OH$	PhCHO	93
2	p-$NO_2C_6H_4CH_2OH$	p-$NO_2C_6H_4CHO$	77[c]
3	$CH_3(CH_2)_6OH$	$CH_3(CH_2)_5CHO$	82
4	$CH_3(CH_2)_9OH$	$CH_3(CH_2)_8CHO$	68
5	$CH_3(CH_2)_3CH(OH)CH_3$	$CH_3(CH_2)_3COCH_3$	60
6	$CH_3(CH_2)_3CH(OH)C_2H_5$	$CH_3(CH_2)_3COC_2H_5$	58
7	cyclopentanol	cyclopentanone	77
8	cyclohexanol	cyclohexanone	72
9	t-PhCH=$CHCH_2OH$	t-PhCH=CHCHO	70
10	t-PhCH=CHCH(OH)Ph	t-PhCH=CHCOPh	81[c]
11	carveol	carvone	76
12	$CH_2=C(SiMe_3)CH(OH)Ph$	$CH_2=C(SiMe_3)COPh$	100[c]
13	PhCH(OH)COPh	PhCOCOPh	93[c]
14	$PhCH(OH)CO_2Et$	$PhCOCO_2Et$	94[c]
15	$PhCH(OH)CH_2CO_2Et$	t-PhCH=$CHCO_2Et$	34[c]
16	PhCH(OH)CH(OH)Ph	PhCOCOPh	99[c,d]

[a] Solvent, $C_6H_5CH_3$; base, DBU; room temperature for 4 h. [b] Yields were determined by GLC with internal standards, unless otherwise noted. [c] Isolated yields. [d] The oxidant (2 equiv).

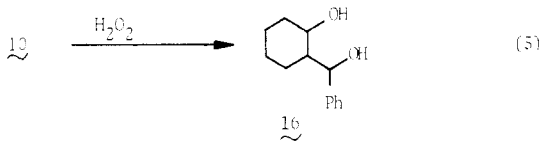
intermediate **15** could be formed intramolecularly, which would lead predominantly to selenenic ester by the abstraction of the β proton followed by the elimination of phenylselenenyl group to give allylic alcohol **11**.

To test this hypothesis, we examined the reaction of **8** and **10** in the presence of equimolar amount of 4-*tert*-butylcyclohexanol (cis/trans, 1:3.4; Scheme IV). The cyclohexanol was converted to cyclohexanone, and **8** was recovered unchanged in the former case, which suggests undoubtedly intermolecular oxidation. On the other hand, allylic alcohol **11** was formed without oxidation of the cyclohexanol, showing the intramolecular deselenization of **10**. Thus, the mechanism proposed above could be confirmed on the basis of these results.

It has been reported that diphenyl diselenide reacted with NCS to give selenide dichloride (eq 4),[5] with which



(4)



(5)

allylic alcohol **11** could be oxidized to enone **12**.[10] Diene **13** was also derived from **11** by dehydration.[11] It is noteworthy that deselenization of γ-hydroxy selenide with NCS provides an alternative method for oxidative elimination of the phenylselenenyl group, because difficulties were encountered in the synthesis of trisubstituted allylic alcohols.[12] In fact, oxidation of **10** with hydrogen peroxide gave diol **16** in 71% yield (eq 5).

In summary, effective oxidation of alcohols with dimethyl selenide–NCS complex is accomplished under mild conditions, affording a clean reaction mixture. Except for β-hydroxy esters, this method has a wide applicability to various alcohols including allylic ones. Utilization of this complex for other synthetic reactions is under investigation.

Experimental Section

Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded with a Hitachi 215 spectrophotometer. ^1H NMR spectra were obtained from a JEOL PMX-60, and chemical shifts are reported in parts per million on the δ scale from internal tetramethylsilane. Mass spectra were taken with a Hitachi RMU-6D mass spectrometer. Microanalyses were determined on a Yanagimoto CHN-Corder, Type II. GLC analyses were performed on a KOR-70 equipped with an FID and on a G-80 with a TCD and with using a 2 m × 3 mm i.d. column of 10% OV-17 or 10% SE-30 on Chromosorb W. Column chromatography was carried out on Wakogel C-300 (silica gel).

Materials. Reagent grade solvents were purified by standard techniques and kept over a drying agent. Selenides **1** were prepared by the known methods. Dimethyl selenide:[13] bp 58 °C; NMR ($CDCl_3$) δ 2.00 (s). Methyl phenyl selenide:[14] bp 47–50 °C (3 torr); NMR ($CDCl_3$) δ 2.23(s, 3 H), 7.23(m, 5 H). Diphenyl selenide:[15] bp 88–93 °C (2 torr). 1-Phenyl-2-(trimethylsilyl)-2-propen-1-ol was obtained by the reaction of benzaldehyde witn (α-lithiovinyl)trimethylsilane:[16] bp 96 °C (4 torr); IR (neat) 3350, 1585 cm^{-1}; NMR ($CDCl_3$) δ 0.08 (s, 9 H), 2.28 (s, 1 H, OH), 5.27 (m, 1 H), 5.50 (m, 1 H), 5.87 (m, 1 H), 7.27(m, 5 H). *trans*-2-(Phenylseleno)cyclohexanol (**8**) was prepared by the reported method:[17] bp 190 °C (5 torr, Kugelrohr); IR (neat) 3650–3150, 1580 cm^{-1}; NMR ($CDCl_3$) δ 0.95–1.95 (m, 6 H), 1.95–2.52 (m, 2 H), 2.65 (br s, 1 H, OH), 2.53–3.65 (m, 2 H), 7.15–7.43 (m, 2 H), 7.43–7.82 (m, 3 H). *trans*-2-[1-(Phenylseleno)benzyl]cyclohexanol (**10**) was formed by the reaction of cyclohexene oxide with the lithium salt of benzyl phenyl selenide:[18] bp 160 °C (5 torr); IR (neat) 3650–3130, 1580 cm^{-1}; NMR ($CDCl_3$) δ 0.67–2.24 (m, 10 H), 2.81–3.37 (m, 1 H), 4.74 (d, J = 3.0 Hz, 0.33 H), 4.90 (d, J = 4.5 Hz, 0.67 H), 6.77–7.70 (m, 10 H). Other chemicals were purchased or prepared by well-known methods.

General Procedure for Oxidation of Alcohols. Dimethyl selenide (**1**, $R^1 = R^2$ = Me; 0.82 g, 7.5 mmol) in dry toluene (10 mL) was added to a stirred suspension of *N*-chlorosuccinimide (1.00 g, 7.5 mmol) in toluene (30 mL) under N_2 with cooling in an ice bath. White precipitate was formed immediately, and stirring was continued for 1 h at 0 °C. To the mixture was added alcohol **3** (5.0 mmol) in toluene (10 mL), and the resulting solution was stirred for 1 h at 0 °C and then allowed to warm to room temperature for 1 h. 1,8-Diazabicyclo[5.4.0]undec-7-ene (1.37 g,

(10) Enone **12** was obtained in 24% yield by the treatment of **11** with NCS–PhSeSePh (2:1) and then DBU (toluene, room temperature, 6 h).
(11) Facile dehydration of **11** was observed in the course of preparative GLC.
(12) Reich, H. J.; Shah, S. K.; Chow, F. *J. Am. Chem. Soc.* **1979**, *101*, 6648.
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9.0 mmol) was added to the mixture. After the mixture was stirred for 4 h at room temperature, the reaction was quenched with water (20 mL), and the mixture was extracted with ether. The extract was washed with brine, dried over sodium sulfate, and concentrated in vacuo to give carbonyl compound **5**, which was purified by column chromatography, if necessary. The products were identified with authentic samples. The complex of dimethyl selenide and NCS was easily isolated (97%) in ether instead of toluene; however, it was very hygroscopic and gradually decomposed at room temperature.

1-Phenyl-2-(trimethylsilyl)propenone: bp 110 °C (3 torr, Kugelrohr); IR (neat) 1650 cm^{-1}; NMR ($CDCl_3$) δ 0.21 (s, 9 H), 6.01 (d, J = 2.4 Hz, 1 H), 6.10 (d, J = 2.4 Hz, 1 H), 7.20–7.60 (m, 3 H), 7.70–7.97 (m, 2 H).

Oxidation of β-Hydroxy Selenide 8. To a stirred solution suspension of NCS (1.00 g, 7.5 mmol) in dry toluene (30 mL) was added **8** (1.28 g, 5.0 mmol) in toluene (10 mL) under N_2 with cooling in an ice bath. After the mixture was stirred for 1 h at 0 °C, DBU (1.37 g, 9 mmol) was added to the mixture, and stirring was continued for 6 h at room temperature. Oily residue obtained by a workup as above was chromatographed on silica gel to give 1.02 g (81%) of 2-(phenylseleno)cyclohexanone (**9**): bp 115 °C (3 torr, bath temperature); IR (neat) 1700, 1570 cm^{-1}; NMR ($CDCl_3$) δ 1.42–2.53 (m, 7 H), 2.60–3.31 (m, 1 H), 3.80–4.07 (m, 1 H), 7.10–7.43 (m, 3 H), 7.43–7.73 (m, 2 H). The compound **9** was identified with an authentic sample prepared from lithium cyclohexanone enolate and phenylselenenyl bromide.

Oxidation of γ-Hydroxy Selenide 10. When this reaction was carried out under conditions similar to those for **8** for 7 h after addition of DBU, 2-benzylidenecyclohexanol (**11**) and diphenyl diselenide were obtained in 97% and 40% yields (preparative TLC), respectively. For the product **11**: IR (neat) 3600–3150, 1625, 1600, 1570 cm^{-1}; NMR ($CDCl_3$) δ 1.07–3.67 (m, 9 H), 4.07–4.37 (m, 0.7 H), 4.72–7.90 (m, 0.3 H), 6.33 (m, 0.3 H), 6.53 (br s, 0.7 H), 6.87–7.75 (m, 5 H); mass spectrum (70 eV), m/e 188 (M^+). The reaction for 14 h after addition of DBU gave a complicated mixture, which was chromatographed on silica gel and then purified by preparative GLC to afford **11** (75%), 2-benzylidenecyclohexanone (**12**, 15%), 3-benzylidenecyclohexene (**13**, 5%), and diphenyl diselenide (~50%). Enone **12**: IR (neat) 1680, 1600, 1570 cm^{-1}; NMR ($CDCl_3$) δ 1.45–2.32 (m, 4 H), 2.32–3.18 (m, 4 H), 7.12–7.62 (m, 6 H); mass spectrum (70 eV), m/e 186 (m^+). Diene **13**: IR (neat) 1600 cm^{-1}; NMR ($CDCl_3$) δ 1.45–2.98 (m, 6 H), 5.82–6.35 (m, 2 H), 7.25 (m, 6 H); mass spectrum (70 eV), m/e 170 (M^+).

Cross-reaction of **8** or **10** was carried out as follows. 4-*tert*-Butylcyclohexanol was added to a stirred solution of **8** or **10** (5.0 mmol) and NCS (0.60 g, 4.5 mmol) in dry toluene (30 mL) with cooling. After addition of DBU (0.76 g, 5.0 mmol) and stirring of the mixture for 5 h at room temperature, the reaction was quenched and worked up as usual. Yields of the products were determined by GLC and NMR.

2-(1-Hydroxybenzyl)cyclohexanol (16). Hydrogen peroxide (30%, 4.7 mL) in THF (5 mL) was added over 30 min to a stirred solution of γ-hydroxy selenide **10** (1.50 g, 4.3 mmol) in THF (20 mL) under N_2 with cooling in an ice bath, and stirring was continued for an additional 4.5 h at 0 °C. After addition of water (20 mL), the reaction mixture was extracted with ether, washed with sodium carbonate and brine, and dried over sodium sulfate. Evaporation of the solvent gave 0.63 g (71%) of **16**: mp 125–126 °C (ether); IR (Nujol) 3650–3100 cm^{-1}; NMR ($CDCl_3$) δ 0.73–2.20 (m, 9 H), 3.53 (m and s, 3 H, 2 OH and CH), 4.53 (d, J = 11.0 Hz, 1 H), 7.27 (m, 5 H); mass spectrum (70 eV), m/e 206 (M^+). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.66; H, 8.81.

Registry No. **1** (R^1 = R^2 = Me), 593-79-3; **1** (R^1 = Me; R^2 = Ph), 4346-64-9; **1** (R^1 = R^2 = Ph), 1132-39-4; **2** (R^1 = R^2 = Me), 83845-67-4; **8**, 35446-84-5; **9**, 50984-16-2; **10** (isomer 1), 83845-68-5; **10** (isomer 2), 83915-67-7; (*E*)-**11**, 50648-70-9; (*Z*)-**11**, 83845-69-6; **12**, 5682-83-7; **16**, 83915-68-8; $PhCH_2OH$, 100-51-6; *p*-$NO_2C_6H_4CH_2OH$, 619-73-8; $CH_3(CH_2)_6OH$, 111-70-6; $CH_3(CH_2)_9OH$, 112-30-1; $CH_3(CH_2)_3CH(OH)CH_3$, 626-93-7; $CH_3(CH_2)_3CH(OH)C_2H_5$, 589-82-2; *t*-PhCH=$CHCH_2OH$, 4407-36-7; *t*-PhCH=CHCH(OH)Ph, 62668-02-4; PhCH(OH)COPh, 119-53-9; $PhCH(OH)CO_2Et$, 774-40-3; $PhCH(OH)CH_2CO_2Et$, 5764-85-2; PhCH(OH)CH(OH)Ph, 492-70-6; PhCHO, 100-52-7; *p*-$NO_2C_6H_4CHO$, 555-16-8; $CH_3(CH_2)_5CHO$, 111-71-7; $CH_3(CH_2)_8CHO$, 112-31-2; $CH_3(CH_2)_3COCH_3$, 591-78-6; $CH_3(CH_2)_3COC_2H_5$, 106-35-4; *t*-PhCH=CHCHO, 14371-10-9; *t*-PhCH=CHCOPh, 614-47-1; CH_2=$C(SiMe_3)COPh$, 83845-70-9; PhCOCOPh, 134-81-6; $PhCOCO_2Et$, 1603-79-8; *t*-PhCH=$CHCO_2Et$, 4192-77-2; cyclopentanol, 96-41-3; cyclohexanol, 108-93-0; carveol, 99-48-9; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; carvone, 99-49-0; 1-phenyl-2-(trimethylsilyl)-2-propen-1-ol, 51666-96-7; (α-lithiovinyl)trimethylsilane, 51666-94-5; cyclohexene oxide, 286-20-4; α-lithiobenzyl phenyl selenide, 56253-58-8; *N*-chlorosuccinimide, 128-09-6.

Reaction of Phenylhydroxylamine with Bisulfite. A Possible Model for Amine-Mediated Carcinogenesis

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Under anaerobic conditions, phenylhydroxylamine reacts with the model nucleophile (bi)sulfite to form aniline, *o*- and *p*-aminophenol, and *o*- and *p*-aminobenzenesulfonate. Evidence is presented suggesting that all products result from intermediates formed from nucleophilic attack of both bisulfite and sulfite on the arylhydroxylamine with subsequent covalent addition–elimination processes leading to products. Such a scheme offers a possible alternative pathway for describing the mechanism for carcinogenic arylation of nucleic acid residues by arylhydroxylamines not requiring the intermediacy of short-lived free radicals or nitrenium ions.

In aqueous systems (in the absence of biological materials) at physiological pH, arylhydroxylamines undergo a series of reactions in the presence of O_2, resulting in their conversion to the corresponding 4-nitrosophenol, nitroso, nitro, and azoxy compounds. Under anaerobic conditions at similar pH, the arylhydroxylamine is stable.[5] The

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