with labile functional groups and sensitive stereochemical centers.

Experimental Section

General Methods. Benzene, toluene, and acetonitrile were distilled under nitrogen atmosphere from CaH_2; diethyl ether was distilled from sodium benzophenone ketyl. The construction and use of the high pressure apparatus employed in this study has been described previously.[16] IR spectra were recorded on a Perkin-Elmer Model 281 spectrometer either as a thin film (NaCl plates) or pellet (KBr). Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory, operated by the College of Chemistry, University of California, Berkely. Mass spectra were recorded on a Kratos MS-50 high resolution mass spectrometer.

General Procedure for High Pressure and Ambient Pressure Reactions. A solution of triphenylphosphine (0.25 mmol), alkyl halide or sulfonate (0.50 mmol), and solvent (0.8 mL, acetonitrile or benzene:toluene, 7:3 mole ratio) in a Teflon tube clamped at both ends was pressurized at 15 kbar (1.5 GPa) hydrostatic pressure for 24–36 h at 20–40 °C (see Tables I and II for solvent and exact conditions). The reactions were cooled (if necessary), depressurized, and concentrated under reduced pressure to afford the crude phosphonium salts which were washed with anhydrous ethyl ether. The precipitated phosphonium salts were collected, washed repeatedly with ether, and dried under vacuum. The salts showed characteristic bands at 1450–1425 cm^{-1} (s), 1120–1100 cm^{-1} (s), 1010–990 cm^{-1} (m-s), and 730–720 cm^{-1} (s).[4b,17] The control runs were performed at 1 bar pressure, 36–48 h, and 20–80 °C, with an identical ratio of reagents in each case with those described for their respective high pressure runs. The following new compounds were prepared.

1-Undecyltriphenylphosphonium bromide: failed to crystallize; IR (thin film) 1440, 1103, 995, 720 cm^{-1}. Anal. Calcd for $C_{29}H_{38}PBr$: C, 70.01; H, 7.70; Br, 16.06. Found: C, 69.53; H, 7.30; Br, 15.42.

[3-(1,3-Dioxolan-2-yl)butyl]triphenylphosphonium bromide: amorphous foam; IR (pellet) 1450, 1120, 1005, 730 cm^{-1}. Anal. Calcd for $C_{24}H_{26}O_2PBr$: C, 63.03; H, 5.73. Found: C, 62.77; H, 5.76.

(1-Phenylethyl)triphenylphosphonium bromide: mp 224–225 °C; IR (pellet) 1440, 1100, 1000, 728 cm^{-1}. Anal. Calcd for $C_{26}H_{24}PBr$: C, 69.81; H, 5.46; Br, 18.03. Found: C, 69.67; H, 5.48; Br, 18.20.

1-Pentyltriphenylphosphonium chloride: mp 171–173 °C; IR (pellet) 1448, 1115, 1005, 730 cm^{-1}. Anal. Calcd for $C_{23}H_{26}PCl$: C, 74.89; H, 7.10. Found: C, 75.00; H, 6.99.

Cyclohexyltriphenylphosphonium chloride: amorphous foam; IR (pellet) 1448, 1120, 1000, 728 cm^{-1}; mass spectrum, exact mass calcd for $C_{24}H_{26}PCl$ minus HCl m/e 344.1726, found m/e 344.1699.

2-Butyltriphenylphosphonium methanesulfonate: mp 183–185 °C; IR (pellet) 1438, 1100, 995, 720 cm^{-1}. Anal. Calcd for $C_{23}H_{25}O_3SP$: C, 66.97; H, 6.11; S, 7.77. Found: C, 66.26; H, 6.64; S, 7.74.

1-Decyltriphenylphosphonium *p*-toluenesulfonate: mp 94–96 °C; IR (pellet) 1452, 1125, 1005, 730 cm^{-1}. Anal. Calcd for $C_{35}H_{43}O_3SP$: C, 73.14; H, 7.54; S, 5.58. Found: C, 72.89; H, 7.54; S, 5.79.

2-Butyltriphenylphosphonium *p*-toluenesulfonate: mp 197–199 °C; IR (pellet) 1445, 1115, 1015, 728 cm^{-1}. Anal. Calcd for $C_{39}H_{31}O_3SP$: C, 70.99; H, 6.37. Found: C, 70.77; H, 6.32.

Concentration-Dependent High Pressure Reactions. *n*-Butyltriphenylphosphonium Bromide. A solution of triphenylphosphine (1.5 mmol), *n*-butyl bromide (0.5 mmol), and 7:3 benzene:toluene (0.8 mL) was pressurized at 15 kbar, 20 °C, for 24 h. The sample was depressurized and the crude phosphonium salt processed as described above to afford 165 mg (82%) of *n*-butyltriphenylphosphonium bromide; mp 240–241 °C (lit.[9] mp 242–243 °C).

Preparative scale reaction of triphenylphosphine (11.4 mmol) and *n*-butyl bromide (11.4 mmol) in 7:3 benzene:toluene (5 mL) at 15 kbar pressure, 20 °C for 36 h, afforded, after usual ethyl ether processing, 4.15 g (91%) of *n*-butyltriphenylphosphonium bromide.

2-Butyltriphenylphosphonium Bromide. Acetonitrile (0.8 mL) was charged with triphenylphosphine (0.5 mmol) and 2-butylbromide (0.5 mmol) and then subjected to 15 kbar pressure, 40 °C for 36 h. Depressurization, followed by workup described above, yielded 110 mg (55%) of 2-butyltriphenylphosphonium bromide; mp 234–238 °C (lit.[10] mp 235–238 °C).

Cyclopentylphosphonium Bromide. Treatment of triphenylphosphine (0.25 mmol) with excess cyclopentyl bromide (10.0 mmol) in acetonitrile (0.2 mL) at 15 kbar pressure, 20 °C for 36 h, afforded, after ether processing, 81 mg (79%) of cyclopentyltriphenylphosphonium bromide; mp 260–261 °C (lit.[11] mp 262–263 °C).

Registry No. Ph_3P, 603-35-0; *n*-$C_{10}H_{21}CH_2Br$, 693-67-4; *n*-$C_9H_{19}CH_2OTs$, 5509-08-0; *n*-butyltriphenylphosphonium bromide, 1779-51-7; 1-undecyltriphenylphosphonium bromide, 60669-22-9; 1-butyl-3-(1,3-dioxolanyl)triphenylphosphonium bromide, 71864-02-3; 1-pentyltriphenylphosphonium chloride, 35171-60-9; 2-butyltriphenylphosphonium bromide, 3968-92-1; cyclopentyltriphenylphosphonium bromide, 7333-52-0; cyclohexyltriphenylphosphonium chloride, 91949-56-3; (1-phenylethyl)triphenylphosphonium bromide, 30537-09-8; (1-(ethoxycarbonyl)-ethyl)triphenylphosphonium bromide, 30018-16-7; 1-butyltriphenylphosphonium methanesulfonate, 91949-57-4; 2-butyltriphenylphosphonium methanesulfonate, 91949-58-5; 1-decyltriphenylphosphonium *p*-toluenesulfonate, 91949-59-6; 2-butyltriphenylphosphonium *p*-toluenesulfonate, 91949-60-9; *n*-butyl bromide, 109-65-9; 2-(2-bromoethyl)-2-methyl-1,3-dioxolane, 37865-96-6; 1-pentyl chloride, 543-59-9; *sec*-butyl bromide, 78-76-2; cyclopentyl bromide, 137-43-9; cyclohexyl chloride, 542-18-7; 1-phenylethyl bromide, 585-71-7; ethyl 2-bromopropanoate, 535-11-5; *n*-butyl methanesulfonate, 1912-32-9; *sec*-butyl methanesulfonate, 16156-54-0; *sec*-butyl *p*-toluenesulfonate, 715-11-7.

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Further Evidence for Nitrenium Ion Intermediacy in *N*-Phenylhydroxylamine Rearrangement to Aminophenol

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N-Arylhydroxylamines (AH) are highly reactive products formed by metabolic oxidation of primary arylamines.[1,2] In aqueous solution, at neutral pH,[3] they are readily oxidized to nitrosobenzenes, nitrobenzenes, *p*-nitrosophenols, and azo- and azoxybenzenes.

In the absence of O_2, the stability of *N*-phenylhydroxylamine (PHA) and substituted *N*-phenylhydroxylamines is greatly enhanced,[3] except in the strongly acidic region where AH's undergo O_2-independent rearrangement to the corresponding aminophenol.[4] The mechanism of this rearrangement in aqueous solution has not been clearly elucidated. Both bimolecular[5] and unimolecular[6] pathways have been suggested. Attempts to resolve this controversy through ^{18}O-labeling studies have been inconclusive. Rearrangement of ^{18}O-labeled *N*-

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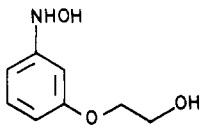
Table I. Pseudo-First-Order Rate Constants for the Degradation of 1 and 2 in Sulfuric Acid Solution at 25 °C[a-c]

H_2SO_4 concentration, M	$k_{obsd} \times 10^3$, s^{-1}	
	1[d]	2[d]
0.01	2.6	3.6
0.05	2.9	2.9
0.10	2.8	2.9

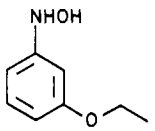
[a] $\mu = 0.5$ ($NaClO_4$). [b] Reactions were carried out as described in the Experimental Section. [c] Reaction was monitored by HPLC using a Waters (Milford, MA) μ-Bondapak C-18 column (300 × 4.6 mm i.d.; 10-μm particle) using a mobile phase of 10 mM phosphate buffer (pH 5.8): methanol (9:1). A flow rate of 2 mL/min^{-1} was maintained and the column effluent was monitored spectrophotometrically at 280 nm. [d] Initial concentration of 1 or 2 = 3.3×10^{-4} M.

hydroxy-2-fluorenylacetamide proceeds with retention of the label,[7] suggesting an intramolecular mechanism whereas reaction of ^{16}O-labeled AH's in $H_2{}^{18}O$ occurs with ^{18}O-incorporation into the resulting aminophenol,[8] indicating an intermolecular process. Recently, Sone et al.[9] reported a large negative Hammett reaction coefficient ($\rho = -3.2$) for H_2SO_4-catalyzed rearrangement of meta-substituted *N*-phenylhydroxylamines supporting the contention that reaction proceeds via an S_N1-type pathway. Similarly, Kohnstam et al.[10] have supported a mechanism based on unimolecular decomposition of the O-protonated hydroxylamine based on kinetic solvent isotope measurements.

To help resolve this controversy, *N*-[3-(2-hydroxyethoxy)phenyl]hydroxylamine, **1**, and *N*-(3-ethoxyphenyl)-hydroxylamine, **2**, were synthesized and their chemistry studied in aqueous sulfuric acid solution.



1

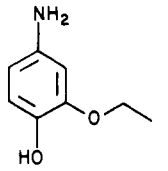


2

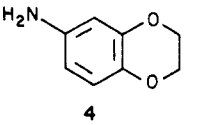
If rearrangement were to proceed via an S_N2 mechanism, the hydroxyl group in 1 may be capable of providing intramolecular catalytic rate enhancement of AH degradation, while 2 is not capable of participating in such anchimerically assisted rearrangements. Kinetic measurements as well as product identification could aid in the detection of such catalysis, if it were to occur.

At 25 °C, in sulfuric acid solutions (0.01, 0.05, and 0.10 M; ionic strength maintained at 0.5 with sodium perchlorate) the reaction of 1 and 2 (in the absence of O_2) follows apparent first-order kinetic behavior for at least 4 half lives. From HPLC tracings, it appears that under anaerobic conditions, reaction products can be totally accounted for in terms of the Bamberger rearrangement pathways. Exclusion of O_2 is essential in avoiding intervention by parallel oxidation and condensation reactions.[3] Above pH 1.7, however, redox and condensation reactions predominate, and therefore, studies above this pH were not pursued. As shown in Table I, no significant difference in the rates of degradation of 1 vs. 2 was observed in these H_2SO_4 solutions. The degradation products are characterized from spectroscopic data and elemental analysis. 2 degrades to the corresponding aminophenol **3**. The melting point of the isolated degradation product (210 °C) corresponds with that of isomer **3** as prepared by an alternative route.[11] 1 is transformed to 6-aminobenzo-1,4-dioxane, **4**. Physical constants and spectral data (^1H NMR, IR, and mass spectra) were identical with those of **4** obtained from a commercial source,[12] confirming this isomer as the reaction product.

Differentation between aminophenols and benzodioxans was based primarily on comparison of their elemental analyses and electron impact mass spectra. The aminophenol **3** shows a weak molecular ion (*m/e* 153) as the base peak and the characteristic loss of M – NH_2 (*m/e* 137) and M – NH_2 – OH (*m/e* 120) fragments, whereas the benzodioxan mass spectrum is characterized by a prominent molecular ion (*m/e* 151) and an M – NH_2 (*m/e* 135) fragment. Calculated elemental analyses for **3** and **4** were sufficiently different to also be useful in structure elucidation.

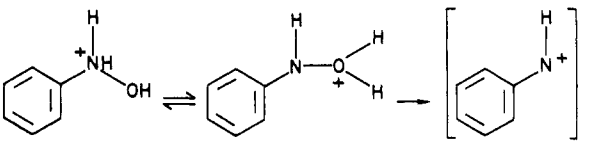


3



4

At the pHs studied (0.7, 1.0, and 1.7), the hydroxylamine exists ostensibly as the hydroxylammonium cation **5** (pK_a of 1 and 2 estimated[9] to be 2.7 from Hammett reactivity coefficients). Thus, the pH-independent behavior of the rearrangement in this acidity range is consistent[9] with the postulated protonation of the AH prior to the rate-determining step with ensuing loss of water to form a nitrenium ion intermediate **6**. Attempts to study the reaction at pH <1.7, where pH dependency was anticipated, were unsuccessful due to competition by dominant side reactions.



5a 5b 6

The fact that 1 and 2 react at the same rate suggests that both compounds proceed through the same rate-determining step and that intramolecular catalysis is not operative in the rearrangement of substituted *N*-phenylhydroxylamines under these conditions. Rather, the data supports the contention that formation of a nitrenium ion (**6**) is rate determining and that attack by available nucleophiles occurs in a fast subsequent step. The proximity of the pendent hydroxyl group in 1 coupled with the increase in solvent structure (in strongly acidic solution) accounts for formation of **4** rather than the corresponding aminophenol. When intramolecular nucleophilic sites are unavailable (as in 2), the anticipated aminophenol **3** is formed. Thus, the internal nucleophile provided in 1 only serves to trap the intermediate nitrenium ion, once formed, without effecting the rate of rearrangement.

Experimental Section

Synthesis. a. *m*-Nitrophenoxyethanol. *n*-Nitrophenol (2.8 g, 25 mmol), ethylene carbonate (1.8 g, 20 mmol), and tetra-

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ethylammonium bromide (1 g, 5 mmol) were heated at 180 °C for 1 h. The resulting mixture was dissolved in methylene chloride and first extracted repeatedly with 10% NaOH solution until the washings were colorless and then with 10 mL of water. The methylene chloride layer was dried over anhydrous Na_2SO_4 and concentrated to yield the product which was crystallized in petroleum ether (2.5 g, 68% yield; mp 92 °C; lit.[13] mp 86–87.5 °C).

b. *N*-[3-(2-Hydroxyethoxy)phenyl]hydroxylamine, 1. *m*-Nitrophenoxyethanol (1 g, 6 mmol) and ammonium chloride (0.7 g, 13 mmol) were suspended in a mixture of ethanol (10 mL) and water (3 mL). The mixture was stirred and deoxygenated with argon for 15 min. Zinc dust (0.7 g, 11 mmol) was then added over a 3-min period and the mixture was stirred for an additional 7 min.[11] Water (5 mL) was added, the suspension filtered, and the cake washed with methylene chloride. The aqueous layer was extracted with methylene chloride, and the CH_2Cl_2 layers were combined and washed sequentially with water (10 mL) and saturated NaCl solution. The CH_2Cl_2 layer was dried over Na_2SO_4 and then reduced in volume to 5 mL. Chloroform (10 mL) and petroleum ether (10 mL) were added, and the solution was deoxygenated with argon and cooled to 0 °C. Pale yellow crystals formed which were recovered by filtration and recrystallized from petroleum ether to give colorless crystals (0.3 g, 30% yield; mp 73–74 °C).

Anal. Calcd for $C_8H_{11}NO_3$: C, 56.80; H, 6.50; N, 8.28. Found: C, 56.90; H, 6.82; N, 8.60.

c. *m*-Ethoxynitrobenzene. *m*-Nitrophenol (3 g, 20 mmol), anhydrous potassium carbonate (2 g, 15 mmol), and iodoethane (2.35 g, 15 mmol) were dissolved in 20 mL of dry acetone and the solution was heated at reflux for 2 days. Water (10 mL) was added and the acetone removed by distillation. The aqueous layer remaining was extracted with $CHCl_3$. The $CHCl_3$ layers were washed with 10% NaOH until the washings were colorless. The $CHCl_3$ layer was dried over Na_2SO_4, and the $CHCl_3$ layer was removed to yield 2.5 g (75% yield) of yellow crystals (mp 34 °C; lit.[14] mp 34 °C).

d. *N*-(*m*-Ethoxyphenyl)hydroxylamine, 2. *m*-Ethoxynitrobenzene (1 g, 6 mmol) and ammonium chloride (0.8 g, 16 mmol) were added to 10 mL of 95% ethanol and 3 mL of water. After deoxygenating the solution with argon for 15–20 min, zinc dust (0.8 g, 13 mmol) was added.[11] The yellow solution was stirred for 15 min (and become colorless). Water (5 mL) was added, the suspension was filtered, and the resulting filter cake was washed with chloroform (25 mL). The aqueous layer was extracted with $CHCl_3$, and the $CHCl_3$ layers were combined, washed with saturated NaCl solution (10 mL), and dried over Na_2SO_4. The dried $CHCl_3$ layer was evaporated to 5 mL, hexane (20 mL) was added, and the solution was cooled to 0 °C. Colorless crystals (0.26 g, 28% yield; mp 69 °C) were formed, filtered, and washed with hexane. Anal. Calcd for $C_8H_{11}NO_2$: C, 62.75; H, 7.19; N, 9.15. Found: C, 63.05; H, 7.27; N, 9.30.

Kinetic Studies. Reactions were carried out in a 50-mL flask fitted with a thermostatted water jacket and inlet and outlet for argon gassing and provided with a pH electrode. Metal free[15] H_2SO_4 solution [20 mL of 0.01, 0.05, or 0.1 M, μ = 0.5 ($NaClO_4$)] was introduced into the reaction vessel which was then flushed with argon for 30 min; thereafter a positive pressure of Ar was maintained over the contents of the flask. A methanolic solution (1 mL of a solution containing 1 mg of 1 or 2 dissolved in 1 mL of methanol that had been previously deoxygenated with Ar) was added to the H_2SO_4 solution and the reaction monitored by HPLC as a function of time. Components were separated on a Waters (Milford, MA) μ-Bondapak C-18 column (300 × 4.6 mm i.d.) using a mobile phase of phosphate buffer (10 mM; pH 5.8):methanol (90:10). A flow rate of 2 mL/min was maintained and the column effluent monitored spectrophotometrically at 280 nm.

Degradation of 1 produced a single product identified to be 4 by comparison of mass and NMR spectra with an authentic sample of material and from elemental analysis. Anal. Calcd for $C_8H_9NO_2$: C, 63.58;, H, 5.96; N, 9.27. Found: C, 63.40; H, 5.89; N, 8.90. ^1H NMR ($CDCl_3$) δ 6.81 (1 H, br d), 6.25 (1 H, br s), 6.15 (1 H br d), 4.19 (4 H, s), 3.42 (2 H, br s, NH_2).

Degradation of 2 produced a single product identified from melting point (210 °C; lit.[11] mp 210–212 °C), by comparison of mass spectral and ^1H NMR data with authentic material, and from elemental analysis to be 3. Anal. Calcd for $C_8H_{11}NO_2$: C, 62.75; H, 7.19; N, 9.15. Found: C, 62.48, H, 7.18; N, 8.84. ^1H NMR (Me_2SO-d_6) δ 6.85–6.40 (3 H, m), 4.20 (1 H, br s, OH), 3.35 (2 H, br t), 3.12 (2 H, br t), 1.92 (2 H, br s).

Registry No. 1, 91861-92-6; 2, 91861-93-7; 3, 55483-70-0; 4, 22013-33-8; *m*-nitrophenol, 554-84-7; ethylene carbonate, 96-49-1; iodoethane, 75-03-6; *m*-nitrophenoxyethanol, 16365-26-7; *m*-ethoxynitrobenzene, 621-52-3.

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Direct Transformation of Ergosterol to (22*S*,23*E*)-6β-Methoxy-3α,5-cyclo-5α-ergost-23-en-22-ol, a Key Intermediate for the Synthesis of Brassinolide

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Brassinolide (**1a**) is a plant growth promoting steroidal lactone, first isolated from rape pollen.[1] Brassinolide contains a lactone group in ring B, and 22*R*,23*R* oxygen functions associated with a 24*S* methyl group in the side chain. Until now, at different laboratories,[2-6] brassinolide (**1a**) and its possible biological precursor castasterone (**2**) have been synthesized starting with a C_{22} steroid. A key intermediate in the first synthesis[2] of **1a** is (22*S*,23*E*)-6β-methoxy-3α,5-cyclo-5α-ergost-23-en-22-ol (**3a**), whose side chain was constructed by lithium alanate alkylation of (20*S*)-6β-methoxy-3α,5-cyclo-5α-pregnane-20-carboxaldehyde derived from stigmasterol (**4**). We now describe the first synthesis of **3a** by the direct modification of the side chain of ergosterol (**4**). Up to now only the C-24 epimer of brassinolide was obtained from ergosterol.[7,8]

Ergosterol was reduced,[9,10] with lithum dissolved in ethylamine to a 3:2 mixture of (22*E*)-ergosta-5,22-dien-3β-ol (**5a**) and (22*E*)-5α-ergosta-7,22-dien-3β-ol (**6a**). The mixture of **5a** and **6a** was esterified with *p*-toluenesulfonyl chloride[8] in dry pyridine and the mixture of tosylates **5b** and **6b** was treated with methanol and pyridine[11] to afford

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