NSERC Postgraduate scholar.

Registry No. 1, 65857-68-3; (1*R*-*endo*)-3-bromo-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one, 10293-06-8; 2-bromo-3,4-dihydro-1-(2*H*)-naphthalenone, 13672-07-6; 2,4′-dibromoacetophenone, 99-73-0; 2-bromocycloheptanone, 766-65-4; 2α-bromocholestan-3-one, 23737-88-4; 16α-bromo-3-methoxyestra-1,3,5(10)-trien-17-one, 10324-68-2; 2-bromo-2,4-dimethylpentan-3-one, 3212-63-3; 2-bromocyclohexanone, 822-85-5; 2-chlorocyclohexanone, 822-87-7; 2-chloro-2-methylcyclohexanone, 10409-46-8; 2-chloroacetophenone, 532-27-4; sodium diethylphosphite, 2303-76-6.

Synthesis of (Aryloxy)propanolamines via a Palladium-Promoted Oxyamination

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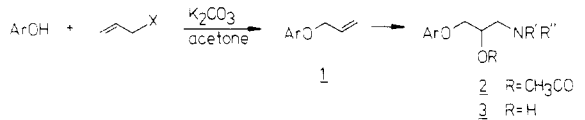
We recently reported a method for direct vicinal oxyamination of alkenes utilizing palladium.[1] An important aspect on the reaction is the high stereospecificity resulting in an overall cis oxyamination. The addition to certain alkenes is also regioselective. In this work we have taken advantage of the regioselectivity of the reaction and applied the oxyamination to transformation of allyl aryl ethers **1** into (aryloxy)propanolamines **3**. Compounds **3** are an important class of biologically active substances with β-adrenergic receptor blocking effects.[2] The oxyamination reaction now also proceeds with primary amines, an improvement over our previous report. It has previously been reported that oxyamination of phenyl allyl ether with stoichiometric amounts of a (*tert*-butylimido)osmium reagent gives **3** (R′ = H, R″ = *t*-Bu).[3]

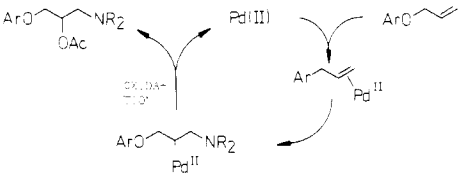
The procedure, which has generally been used to prepare (aryloxy)propanolamines **3**, involves reaction of an epihalohydrin with a phenoxide, followed by amination of the product obtained, which is either a 3-arylpropene oxide[2a,2d] or a 1-halo-3-arylpropen-2-ol,[2e] or a mixture of both. Another common method utilizes 5-(hydroxymethyl)-2-phenyl-1,3-oxazolidine.[2f,2g] Here, we have utilized a mild, direct vicinal oxyamination of **1**, which proceeds through an aminopalladation oxidation sequence. The allyl aryl ethers **1** are obtained by allylation of the corresponding phenol in high yield[4] (Scheme I).

Oxyamination of the double bond in **1** at −50 °C, using the aminopalladation–oxidation sequence described previously,[1] gives the aminoacetate **2**. Hydrolysis of **2**, which is quantitative, yields the desired amino alcohol **3**. Secondary amines gave fair to good yields of oxyamination products (Table I). It was found that lead tetraacetate is the most efficient oxidant for oxyamination of olefins **1**. This is in contrast to the oxidation of styrene, where *N*-bromosuccinimide (NBS) as the oxidant gave the best yields.[1]

Scheme I

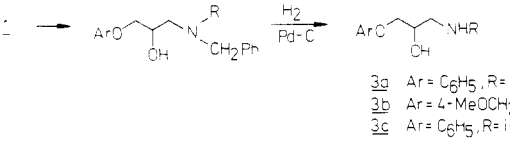


Scheme II



We have now succeeded in obtaining oxyamination products from primary amines. In our previous study we were only able to isolate aziridines when primary amines were used. We have now found that the formation of aziridines is depressed on addition of a silver salt. However, the amino acetates **2** obtained in this way from primary amines are not conveniently isolated due to acetyl migration from oxygen to nitrogen.[6] The crude product from these reactions was therefore hydrolyzed[7] with base to afford the corresponding amino alcohol **3**. Thus, oxyamination of allyl phenyl ether with isopropylamine followed by hydrolysis gave **3c** in 50% yield.

An alternative method for obtaining secondary oxyamines **3**, via the benzyl derivatives, was also used. Thus, oxyamination utilizing an *N*-alkylbenzylamine, followed by hydrogenolysis (Pd/C) of the benzyl group in the amino alcohol obtained, affords secondary oxy amines **3a–c** (eq 1). This route to secondary oxy amines should be useful



in cases where a protecting group is desired on the oxygen or nitrogen atoms. Another synthetic application of this procedure is in asymmetric oxyamination using an amine with an optically active benzyl group (e.g., α-methylbenzyl) which can be removed at the end.[8]

The inhibition of aziridine formation on addition of a silver salt needs some comment. We previously observed[1a] that it was not possible to inhibit formation of an aziridine by protonating the amino group β to palladium. To account for these results we suggested that a β-chloro amine is first formed, which on treatment with base would give the aziridine. The present results provide strong support for such a mechanism under acidic conditions. In fact, we were able to isolate β-chloro amines in several cases using the general procedure in the absence of a silver salt.

In principle, the oxyamination can be considered to be a catalytic reaction since palladium(II) is regenerated in the oxidative cleavage of the palladium–carbon bond (Scheme II). However, the palladium(II) regenerated is

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(7) The base hydrolysis proceeds via the amide: $RCH(OAc)CH_2NHR \rightarrow RCH(OH)CH_2N(Ac)R \rightarrow RCH(OH)CH_2NHR$ (cf. ref 6). In fact, it was difficult to isolate the amino acetate without O → N acetyl migration.

(8) Preliminary results show that oxyamination of allyl phenyl ether with optically active *N*-methyl-1-phenethylamine gives an optical yield of approximately 20–30%: Bäckvall, J. E.; Björkman, E. E.; Byström, S.; Solladié-Cavallo, A. *Tetrahedron Lett.*, in press.

0022-3263/82/1947-1126$01.25/0

Table I. Palladium-Promoted Oxyamination of Aryl Allyl Ethers

starting material	amine	method	product (% yield)[a]	characterization
4-$MeC_6H_4OCH_2CH{=}CH_2$	Et_2NH	A	4-$MeC_6H_4OCH_2CH(OAc)CH_2NEt_2$ (54)	*b*
3-Me-$C_6H_4OCH_2CH{=}CH_2$	Et_2NH	A	3-$MeC_6H_4OCH_2CH(OAc)CH_2NEt_2$ (68)	*b*
2-Me-$C_6H_4OCH_2CH{=}CH_2$	Et_2NH	A	2-$MeC_6H_4OCH_2CH(OAc)CH_2NEt_2$ (64)	*b*
2-Me-$C_6H_4OCH_2CH{=}CH_2$	Me_2NH	B	2-$MeC_6H_4OCH_2CH(OAc)CH_2NMe_2$ (69)	*c*
3,5-diMe-$C_6H_3OCH_2CH{=}CH_2$	Et_2NH	A	3,5-di$MeC_6H_3OCH_2CH(OAc)CH_2NEt_2$ (61)	*c*
3,5-diMe-$C_6H_3OCH_2CH{=}CH_2$	Me_2NH	B	3,5-di$MeC_6H_3OCH_2CH(OAc)CH_2NMe_2$ (63)	*c*
3,4-di$MeC_6H_3OCH_2CH{=}CH_2$	Et_2NH	A	3,4-di$MeC_6H_3OCH_2CH(OAc)CH_2NEt_2$ (68)	*d*
4-MeO-$C_6H_4OCH_2CH{=}CH_2$	Et_2NH	A	4-$MeOC_6H_4OCH_2CH(OAc)CH_2NEt_2$ (51)	*e*
4-Cl-$C_6H_4OCH_2CH{=}CH_2$	Et_2NH	A	4-$ClC_6H_4OCH_2CH(OAc)CH_2NEt_2$ (60)	*c*
$C_6H_5OCH_2CH{=}CH_2$	Et_2NH	A	$C_6H_5OCH_2CH(OAc)CH_2NEt_2$ (49)	*f*
$C_6H_5OCH_2CH{=}CH_2$	Me_2NH	B	$C_6H_5OCH_2CH(OAc)CH_2NMe_2$ (71)	*f*
$C_6H_5OCH_2CH{=}CH_2$	BzNHMe	B	$C_6H_5OCH_2CH(OAc)CH_2N(Bz)Me$ (55)	*g*
$C_6H_5OCH_2CH{=}CH_2$	BzNH-*i*-Pr	B	$C_6H_5OCH_2CH(OAc)CH_2N(Bz)$-*i*-Pr (55)	*g*
$C_6H_5OCH_2CH{=}CH_2$	*i*-$PrNH_2$	B[h]	$C_6H_5OCH_2CH(OH)CH_2NH$-*i*-Pr (50)[i]	*j*
$C_6H_5OCH_2CH{=}CH_2$	*t*-$BuNH_2$	B[h]	$C_6H_5OCH_2CH(OH)CH_2N$-*t*-Bu (39)[i]	*k*
4-$MeOCH_2CH_2C_6H_4OCH_2CH{=}CH_2$	BzNHMe	B	4-$MeOCH_2CH_2C_6H_4OCH_2CH(OAc)CH_2N(Bz)Me$ (59)	*g*
4-$MeOCH_2CH_2C_6H_4OCH_2CH{=}CH_2$	*i*-$PrNH_2$	B[h]	4-$MeOCH_2CH_2C_6H_4OCH_2CH(OH)CH_2NH$-*i*-Pr (46)[i]	*l*

[a] Isolated yield. [b] Characterized as the alcohol.[10] [c] Characterized only by IR and NMR. [d] Anal. Calcd for $C_{17}H_{27}NO_3$: C, 69.59; H, 9.28; N, 4.77. Found: C, 69.43; H, 9.25; N, 4.93. [e] Characterized as the alcohol.[11] [f] Reference 1a. [g] Characterized by IR, NMR, and debenzylation to the secondary amine, cf. Table II. [h] Amination at −70 °C. [i] Hydrolytic workup; attempts to isolate the acetate resulted in acetyl migration. [j] Mp 91–93 °C (lit.[2a] mp 92–93 °C). [k] Reference 12; NMR ($CDCl_3$) δ 3.97 (br, 3, CH_2O, CHO), 2.75 (m, 2, CH_2N), 1.13 (s, 9, CMe_3). [l] Mp 45–47 °C (lit.[13] mp 45–48 °C).

Table II. Debenzylation of N-Benzylic (Aryloxy)propanolamines[a]

starting material	product	% yield	mp, °C
$C_6H_5OCH_2CH(OH)CH_2N(Bz)Me$	3a	98	89–91 (ether/pentane)
4-$MeOCH_2CH_2C_6H_4OCH_2CH(OH)CH_2N(Bz)Me$	3b	95	85–93 (ether/pentane)
$C_6H_5OCH_2CH(OH)CH_2N(Bz)$-*i*-Pr	3c	75	90–93[b] (cyclohexane)

[a] Debenzylation by hydrogenation (Pd/C) at room temperature under atmospheric pressure of hydrogen. [b] Lit.[2a] 92–93 °C.

obviously too deactivated by amine (probably in the form of $(R_2NH)_2PdX_2$ where X = Cl or OAc) to be capable to coordinating an olefin under the reaction conditions employed here.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 421 spectrometer. NMR spectra were obtained with a Varian EM-360 or a Bruker WP 200 FT spectrometer. GLC analyses were performed on a 6 ft × 1/8 in. steel column packed with 20% Apiezon L with 10% KOH on Chromosorb W (60/80 mesh). $(PhCN)_2PdCl_2$ was prepared according to Kharasch.[9] Tetrahydrofuran was distilled over potassium/benzophenone under nitrogen. Lead tetraacetate containing 20% acetic acid was obtained from Merck Schuchard. All olefins were prepared according to Tarbell.[4]

General Procedure for Oxyamination of Aryl Allyl Ethers. Procedure A. A solution of 0.5 mL of appropriate aryl allyl ether in 5 mL of anhydrous THF was added to $(PhCN)_2PdCl_2$ (0.383 g, 1 mmol) under nitrogen atmosphere at 0 °C. After the mixture was stirred for 10 min, the temperature was decreased to −50 °C and 4 mmol of the appropriate amine in THF (2 mL) was added during a 5–10-min period. The temperature was kept at −50 °C for 1 h and then 300 mg of acetic acid was added, followed by $Pb(OAc)_4$ (0.6 g (70–80%), 1 mmol). The solution was kept at −50 °C for a few minutes and then allowed to slowly warm to room temperature. After 2.5 h the reaction mixture was made alkaline by adding 6 mL of 2 M NaOH. After 10 min 10 mL of ether and 0.1 g of KBH_4 were added, and the mixture was stirred for another 20 min. The palladium black and other precipitates were filtered off and washed with ether. The organic layer was separated and extracted with 1 M HCl (3 × 5 mL). The aqueous phase was washed with ether, made alkaline (pH 11), and extracted with ether (3 × 10 mL). The organic phase was then washed with brine and dried over K_2CO_3. Purification, if required, was accomplished by preparative TLC.

Procedure B. This procedure is similar to that of procedure A except for the following changes: AgOAc (334 mg, 2 mmol) was added before the addition of acetic acid and lead tetraacetate. In the case where a primary amine was used as a nucleophile, the crude product after extraction was hydrolyzed with base (vide infra).

Spectral Data on Amino Acetates 2. 1-(Diethylamino)-2-acetoxy-3-(4-methylphenoxy)propane: NMR ($CDCl_3$) δ 7.2–6.7 (m, 4), 5.23 (m, 1, CHOAc), 4.15 (2, AB part of ABX, CH_2O), 2.85–2.15 (m, 6, CH_2N), 2.06 (s, 3, CH_3), 1.04 (t, 3, CH_3); IR (neat) 2960, 2925, 2860, 2800, 1740, 1610, 1590, 1460, 1370, 1325, 1300, 1230, 1160, 1050, 820, 680 cm^{-1}.

1-(Diethylamino)-2-acetoxy-3-(3-methylphenoxy)propane: NMR ($CDCl_3$) δ 7.3–6.5 (m, 4), 5.14 (m, 1, CHOAc), 4.15 (2, AB part of ABX, CH_2O), 2.8–2.3 (m, 6, CH_2N), 2.28 (s, 3, CH_3), 2.02 (s, 3, CH_3) 0.98 (t, 6, CH_3); IR (neat) 2960, 2920, 2860, 1740, 1600, 1585, 1490, 1465, 1370, 1290, 1235, 1160, 1055, 775 cm^{-1}.

1-(Diethylamino)-2-acetoxy-3-(2-methylphenoxy)propane: NMR ($CDCl_3$) δ 7.28–6.65 (m, 4), 5.23 (m, 1, CHOAc), 4.15 (2, AB part of ABX, CH_2O), 2.85–2.3 (m, 6, CH_2N), 2.27 (s, 3, CH_3), 2.05 (s, 3, CH_3), 1.02 (t, 6, CH_3); IR (neat) 2960, 2930, 2870, 2820, 1740, 1600, 1510, 1490, 1460, 1370, 1290, 1235, 1120, 1050, 750 cm^{-1}.

1-(Dimethylamino)-2-acetoxy-3-(2-methylphenoxy)-propane: NMR ($CDCl)_3$ δ 7.3–6.7 (m, 4), 5.4 (m, 1, CHOAc), 4.15 (2, AB part of ABX, CH_2O), 2.9–2.35 (m, 2, CH_2N), 2.27 (s, 6, CH_3), 2.18 (s, 3, CH_3), 2.05 (s, 3, CH_3); IR (neat) 2970, 2940, 2860, 2820, 2760, 1740, 1600, 1495, 1460, 1370, 1230, 1120, 1040, 750 cm^{-1}.

1-(Diethylamino)-2-acetoxy-3-(3,5-dimethylphenoxy)-propane: NMR ($CDCl_3$) δ 6.7–6.4 (m, 3), 5.20 (m, 1, CHOAc), 4.15 (2, AB part of ABX, CH_2O), 2.85–2.2 (m, 6, CH_2N), 2.25 (s,

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6, CH_3), 2.05 (s, 3, CH_3), 0.98 (t, 6, CH_3); IR (neat) 2960, 2920, 2870, 2810, 1740, 1595, 1460, 1370, 1320, 1295, 1235, 1170, 1060, 830, 690 cm^{-1}.

1-(Dimethylamino)-2-acetoxy-3-(3,5-dimethylphenoxy)-propane: NMR ($CDCl_3$) δ 6.6 (br, 3), 5.28 (m, 1, CHOAc), 4.15 (m, 2, CH_2O), 2.56 (d, 2, CH_2N), 2.28 (s, 12, four CH_3 groups), 2.06 (s, 3, CH_3); IR (neat) 2970, 2940, 2920, 2860, 2820, 2770, 1740, 1610, 1590, 1505, 1455, 1370, 1295, 1235, 1170, 1155, 1070, 1050, 1035, 830 cm^{-1}.

1-(Diethylamino)-2-acetoxy-3-(3,4-dimethylphenoxy)-propane: NMR ($CDCl_3$) δ 7.6–6.55 (m, 3), 5.20 (m, 1, CHOAc), 4.15 (2, AB part of ABX, CH_2O), 2.85–2.3 (m, 6, CH_2N), 2.30 (s, 3, CH_3), 2.26 (s, 3, CH_3), 2.05 (s, 3, CH_3), 1.01 (t, 6, CH_3); IR (neat) 2960, 2920, 2870, 2800, 1740, 1610, 1500, 1450, 1370, 1235, 1205, 1165, 1050, 810 cm^{-1}.

1-(Diethylamino)-2-acetoxy-3-(4-methoxyphenoxy)-propane: NMR ($CDCl_3$) δ 6.9 (s, 4, Ar), 5.20 (m, 1, CHOAc), 4.15 (2, AB part of ABX, CH_2O), 3.80 (s, 3, CH_3O), 2.8–2.3 (m, 6, CH_2N), 2.05 (s, 3, CH_3), 1.03 (t, 6, CH_3); IR (neat) 2960, 2930, 2870, 2830, 1740, 1510, 1460, 1370, 1230, 1040, 820, 750 cm^{-1}.

1-(Diethylamino)-2-acetoxy-3-(4-chlorophenoxy)propane: NMR ($CDCl_3$) δ 7.3–6.7 (m, 4), 5.20 (m, 1, CHOAc), 4.15 (2, AB part of ABX, CH_2O), 2.7–2.25 (m, 6, CH_2N), 2.05 (s, 3, CH_3), 1.03 (t, 6, CH_3); IR (neat) 2960, 2920, 2870, 2800, 1740, 1600, 1490, 1450, 1370, 1230, 1060, 1040, 820 cm^{-1}.

1-(Benzylmethylamino)-2-acetoxy-3-phenoxypropane: NMR ($CDCl_3$) δ 7.5–6.8 (m, 10, aromatic), 5.37 (m, 1, CHOAc), 4.15 (m, 2, CH_2O), 3.55 (br s, 2, $PhCH_2$), 2.65 (d, 2, CH_2N), 2.28 (s, 3, CH_3N), 2.03 (s, 3, CH_3); IR (neat) 3050, 3020, 2940, 2840, 2780, 1735, 1595, 1585, 1490, 1450, 1365, 1230, 1170, 1070, 1045, 1020, 970, 750 cm^{-1}.

1-(Benzylmethylamino)-2-acetoxy-3-[4-(2-methoxyethyl)phenoxy]propane: NMR ($CDCl_3$) 7.6–6.8 (m, 9), 5.36 (m, 1, CHOAc), 4.15 (m, 2, CH_2), 3.58 (s, 2, $PhCH_2$), 3.5 (concealed t, 2, CH_2), 3.35 (s, 3, CH_3O), 3.0–2.5 (m, 4, CH_2N, CH_2 in CH_2CH_2), 2.23 (s, 3, CH_3N), 2.05 (s, 3, CH_3); IR (neat) 3080, 3050, 3020, 2970, 2920, 2860, 2840, 2820, 1740, 1620, 1580, 1510, 1450, 1330, 1230, 1115, 1045, 970, 740, 700 cm^{-1}.

1-(Isopropylbenzylamino)-2-acetoxy-3-phenoxypropane: NMR ($CDCl_3$) δ 7.5–6.7 (m, 10), 5.15 (m, 1, CHOAc), 4.0 (m, 2, CH_2), 3.63 (br s, 2, $PhCH_2$), 3.3–2.5 (m, 3, CHN, CH_2N), 2.00 (s, 3, CH_3), 0.99 (d, 6, CH_3); IR (neat) 3050, 3020, 2960, 2920, 2870, 2830, 1735, 1595, 1585, 1490, 1455, 1365, 1230, 1270, 1050, 1030, 965, 750 cm^{-1}.

Hydrolysis of 1-(Isopropylbenzylamino)-2-acetoxy-3-phenoxypropane. The amino acetate (266 mg, 0.78 mmol) was dissolved in 3 mL of 5 M KOH–CH_3OH and refluxed for 30 min. After cooling, the mixture was neutralized (pH ~5) with 2 M HCl, and the methanol was removed under vacuum. The mixture was made alkaline (pH ~11) with 2 M NaOH and extracted with ether (3 × 10 mL). The organic phase was washed with brine and dried over K_2CO_3. Evaporation of the ether gave 228 mg (98%) of 1-(isopropylbenzylamino)-3-phenoxypropan-2-ol: NMR ($CDCl_3$) δ 7.4–6.7 (m, 10, aromatic), 3.9 (br s and m, 3, CH_2O, CHO), 3.6 (AB q, 2, only two strong lines visible, $PhCH_2$), 2.93 (m, 1, CH), 2.57 (m, 2, CH_2N), 1.06, 1.00 (2 d, 6, CH_3); IR (neat) 3420, 2960, 1595, 1495, 1245 cm^{-1}.

The following amino alcohols were obtained in quantitative yields (95–100%) by the same hydrolysis procedure.

1-(Benzylmethylamino)-3-phenoxypropan-2-ol: NMR ($CDCl_3$) δ 7.5-6.6 (m, 10, aromatic), 4.0 (m, 1, CHO), 3.96 (br s, 2, CH_2O), 3.6 (AB q, 2, only two strong lines visible, $PhCH_2$), 3.33 (br, 1, OH), 2.60–2.55 (2, AB part of ABX, CH_2N), 2.26 (s, 3, CH_3N); IR (neat) 3420, 2930, 1595, 1585, 1450, 1240, 1040 cm^{-1}.

1-(Benzylmethylamino)-3-[4-(2-methoxyethyl)phenoxy]-propan-2-ol: NMR ($CDCl_3$) δ 7.4–6.5 (m, 9, aromatic), 4.2–3.8 (concealed m, 1, CHO), 3.90 (br s, 2, CH_2O), 3.55 (concealed t, 2, CH_2), 3.6 (AB q, 2, only two strong lines visible, $PhCH_2$), 3.35 (s, 3, CH_3O), 2.73 (t, 3, CH_2), 2.50 (d, 2, CH_2N), 2.20 (s, 3, CH_3); IR (neat) 3440, 2920, 1610, 1510, 1245, 1115 cm^{-1}.

Debenzylation of 1-(Benzylmethylamino)-3-(aryloxy)-propan-2-ols. The amino alcohol (0.4 mmol) and palladium on carbon (50 mg, 10% Pd) in ethanol (2 mL) were stirred under hydrogen (1 atm) for 15 h. The results are given in Table II. **3a**: NMR ($CDCl_3$) δ 7.47–6.73 (m, 5, aromatic), 4.2–3.8 (concealed m, 1, CHO), 3.97 (br s, 2, CH_2O), 3.07–2.30 (br m, 6, CH_2N, CH_3, NH).

3b: NMR ($CDCl_3$) δ 7.20–6.60 (q, 4, aromatic), 4.0–3.8 (br m, 3, CH_2O, CHO) 3.5 (t, 2, CH_2), 3.33 (s, 3, CH_3O), 3.13 (br s, 1, OH), 2.70 (concealed m, 7, CH_2, CH_2N, CH_3N). **3c**: NMR ($CDCl_3$) δ 7.4–6.6 (m, 5, aromatic), 4.2–3.8 (concealed m, 1, CHO), 3.96 (br s, 2, CH_2O), 3.2–2.4 (m, 4, CH_2N, CHN, OH), 1.06 (d, 6, CH_3).

3c from Direct Oxyamination with Isopropylamine. Procedure B was used. After reduction with KBH_4 and removal of palladium black, the organic layer was concentrated in vacuo. The remaining residue was dissolved in 10 mL of 5 M KOH–CH_3OH, refluxed for 30 min, and then neutralized with 2 M HCl. The methanol was removed in vacuo and ether (20 mL) and 1 M HCl (10 mL) was added to the residue. The aqueous phase was separated and the organic layer was extracted with 1 M HCl (3 × 10 mL). The combined aqueous phases were washed with ether (10 mL) made alkaline and extracted with ether (4 × 10 mL). Drying (K_2CO_3) and evaporation of the ether gave 0.105 g (50%) of white crystals, mp 91–93 °C (cyclohexane).

1-(Isopropylamino)-3-[4-(2-methoxyethyl)phenoxy]-propan-2-ol. The same procedure was used (5 mmol scale). The crude product was purified by preparative TLC to give 0.62 g (46%) of a yellow oil which gave white crystals from cyclohexane/pentane: mp 45–47 °C; NMR ($CDCl_3$) δ 7.2–6.7 (q, 4, aromatic), 3.96 (m, 3, CH_2O, CHO), 3.56 (t, 2, CH_2), 3.35 (s, 3, CH_3O), 2.82 (m, 5, CH_2, CH_2N, CHN), 1.09 (d, 6, CH_3).

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Registry No. **1** (Ar = 4-MeC_6H_4), 23431-48-3; **1** (Ar = 3-MeC_6H_4, 1758-10-7; **1** (Ar = 2-MeC_6H_4), 936-72-1; **1** (Ar = 3,5-diMeC_6H_3), 20531-93-5; **1** (Ar = 3,4-diMeC_6H_3), 51788-72-8; **1** (Ar = 4-$MeOC_6H_4$), 13391-35-0; **1** (Ar = 4-ClC_6H_4), 13997-70-1; **1** (Ar = C_6H_5), 1746-13-0; **1** (Ar = 4-$MeOCH_2CH_2C_6H_4$), 80448-05-1; **2** (Ar = 4-MeC_6H_4; R′ = R″ = Et), 80448-06-2; **2** (Ar = 3-MeC_6H_4; R′ = R″ = Et), 80448-07-3; **2** (Ar = 2-MeC_6H_4; R′ = R″ = Et), 80448-08-4; **2** (Ar = 2-MeC_6H_4; R′ = R″ = Me), 80448-09-5; **2** (Ar = 3,5-diMeC_6H_3; R′ = R″ = Et), 80448-10-8; **2** (Ar = 3,5-diMeC_6H_3; R′ = R″ = Me), 80448-11-9; **2** (Ar = 3,4-diMeC_6H_3; R′ = R″ = Et), 80448-12-0; **2** (Ar = 4-$MeOC_6H_4$; R′ = R″ = Et), 80448-13-1; **2** (Ar = 4-ClC_6H_4; R′ = R″ = Et), 41965-58-6; **2** (Ar = C_6H_5; R′ = R″ = Et), 38302-63-5; **2** (Ar = C_6H_5; R′ = R″ = Me), 73687-90-8; **2** (Ar = C_6H_5; R′ = Me; R″ = CH_2Ph), 80448-14-2; **2** (Ar = C_6H_5; R′ = *i*-Pr; R″ = CH_2Ph), 80448-15-3; **2** (Ar = 4-$MeOCH_2CH_2C_6H_4$; R′ = Me; R″ = CH_2Ph), 80448-16-4; **3a**, 39631-73-7; **3b**, 80448-17-5; **3c**, 7695-63-8; **3** (Ar = C_6H_5; R′ = H; R″ = *t*-Bu), 64980-40-1; **3** (Ar = 4-$MeOCH_2CH_2C_6H_4$; R′ = H; R″ = *i*-Pr), 51384-51-1; **3** (Ar = C_6H_5; R′ = Me; R″ = CH_2Ph), 80448-18-6;)3 (Ar = 4-$MeOCH_2CH_2C_6H_4$; R′ = Me; R″ = CH_2Ph), 80448-19-7; **3** (Ar = C_6H_5; R′ = *i*-Pr; R″ = CH_2Ph), 22820-39-9; diethylamine, 109-89-7; dimethylamine, 124-40-3; benzylmethylamine, 103-67-3; benzylisopropylamine, 102-97-6; isopropylamine, 75-31-0; *tert*-butylamine, 75-64-9.

High-Yield Synthesis of 1-Isopropyl-7-methylbicyclo[4.3.0]non-6-ene by a Cationic Olefin Cyclization-Rearrangement Process[1]

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Cationic olefin cyclizations have been extensively studied,[2] and the results indicate a wide variety in both yields and complexity of the products formed. We have found a related and somewhat unusual cyclization where the

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(2) For reviews of this general area, see: Johnson, W. S. *Bioorg. Chem.* **1976**, *5*, 51. Johnson. W. S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 9. VanTamelen, E. E. *Acc. Chem. Res.* **1975**, *8*, 152. Harding, K. E. *Bioorg. Chem.* **1973**, *2*, 248. Goldsmith, D. *Fortschr. Chem. Org. Naturst.* **1971**, *29*, 363. VanTamelen, E. E. *Acc. Chem. Res.* **1968**, *1*, 111. Johnson, W. S. *Ibid.* **1968**, *1*, 1. Johnson, W. S. *Trans. N. Y. Acad. Sci.* **1967**, *29*, 1001.

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