Table I. 1-Substituted N^4-[(Dimethylamino)methylene]cytosines (2) and 1-Substituted Cytosines (3)

	compd 2				compd 3			
R	yield,[a] %	solvent of recryst	molec formula[b]	mp, °C	yield, %	solvent of recryst	molec formula	mp, °C
a methyl	99	benzene-chloroform	$C_8H_{12}N_4O$	203-204[21]	98	MeOH-petroleum ether	$C_5H_7N_3O$	301-302 dec (lit.[26] 300-302)
b ethyl	99	benzene-petroleum ether	$C_9H_{14}N_4O$	147-148	99	H_2O	$C_6H_9N_3O$	244-246 (lit.[8] 245-247)
c propyl	99	toluene-petroleum ether	$C_{10}H_{16}N_4O$	142-143	96	*f*	$C_7H_{11}N_3O$	256-257.5 (lit.[8] 256-258)
d butyl	98	AcOEt-petroleum ether	$C_{11}H_{18}N_4O$	122-123	96	MeOH	$C_8H_{13}N_3O$	231-233 (lit.[8] 229-231)
e allyl	96	toluene	$C_{10}H_{14}N_4O$	133-134	99	*f*	$C_7H_9N_3O$	250.5-252 (lit.[8] 232-236)[g]
f benzyl[c]			$C_{14}H_{16}N_4O$[d]	192-193	96[e]	*f*	$C_{11}H_{11}N_3O$	300-301 dec (lit.[1] 301-303)

[a] Yield of isolated product before purification. [b] Satisfactory analytical data (±0.4% for C, H, and N) were obtained for all new compounds listed in the table. [c] The first two attempts gave 1-benzylcytosine directly in overall yields of 74% and 88%. A third attempt gave compound **2f** in 36% yield. [d] The crude product gave acceptable microanalyses, thus obviating recrystallization. [e] Hydrolysis of **2f** with concentrated ammonium hydroxide required initial gentle warming to achieve solution. [f] Physicochemical properties of the crude products were in close agreement with the literature values, thus eliminating the need for recrystallization. [g] The literature value is based upon a sample with an estimated 4.5% inert impurity.

was recrystallized from the appropriate solvent listed in Table I.

General Procedure for the Hydrolysis of Compounds of Type 2 to 1-Substituted Cytosines (3). A mixture of **2** (0.5 mmol) and concentrated ammonium hydroxide solution (10 mL) was stirred at room temperature for 17 h and then heated on a steam bath for 30 min to drive off excess ammonia. The solution was evaporated to dryness on a rotary evaporator, and the solid residue obtained was recrystallized from the appropriate solvent listed in Table I.

Spectroscopic Data. **N^4-[(Dimethylamino)methylene]-1-methylcytosine (2a)** has been described.[21] The conditions used in the present paper work equally well.

N^4-[(Dimethylamino)methylene]-1-ethylcytosine (2b): ^{1}H NMR ($(CD_3)_2SO$) δ 1.12 (t, *J* = 7.5 Hz, 3, CH_2CH_3), 3.04 (s, 3, $N(CH_3)_2$), 3.16 (s, 3, $N(CH_3)_2$), 5.88 (d, *J* = 7.5 Hz, 1, 5-H), 7.58 (d, *J* = 7.5 Hz, 1, 6-H), 8.58 (s, 1, 1′-H); mass spectrum (70 eV), *m/e* (relative intensity) 194 (M^+, 36), 151 ($M^+ + 1 - N(CH_3)_2$, 26), 150 ($M^+ - N(CH_3)_2$, 100), 122 ($M^+ - N(CH_3)_2 - CH_2CH_3$, 31), 111 (35), 44 ($N(CH_3)_2^+$, 84), 42 (61), 28 (57).

N^4-[(Dimethylamino)methylene]-1-propylcytosine (2c): ^{1}H NMR ($(CD_3)_2SO$) δ 0.82 (t, *J* = 7.5 Hz, 3, CH_2CH_3), 1.61 (m, *J* = 6.0, 7.5 Hz, 2, $CH_2CH_2CH_3$), 3.10 (s, 3, $N(CH_3)_2$), 3.20 (s, 3, $N(CH_3)_2$), 3.67 (t, *J* = 7.5 Hz, 2, $CH_2CH_2CH_3$), 5.87 (d, *J* = 7.5 Hz, 1, 5-H), 7.73 (d, *J* = 7.5 Hz, 1, 6-H), 8.59 (s, 1, 1′-H); mass spectrum (70 eV), *m/e* (relative intensity) 208 (M^+, 58), 166 ($M^+ + 1 - C_3H_7$, 42), 165 ($M^+ - C_3H_7$, 27), 164 ($M^+ - N(CH_3)_2$, 100), 151 (37), 123 (21), 122 ($M^+ + 1 - N(CH_3)_2 - C_3H_7$, 53), 44 ($N(CH_3)_2^+$, 63), 43 (35), 42 (37).

1-Butyl-N^4-[(dimethylamino)methylene]cytosine (2d): ^{1}H NMR ($(CD_3)_2SO$) δ 0.89 (t, *J* = 7.5 Hz, 3, $(CH_2)_3CH_3$), 1.37 (m, 4, $CH_2CH_2CH_2CH_3$), 3.0 (s, 3, $N(CH_3)_2$), 3.13 (s, 3, $N(CH_3)_2$), 3.69 (t, *J* = 7.5 Hz, 2, $CH_2(CH_2)_2CH_3$), 5.85 (d, *J* = 7.5 Hz, 1, 5-H), 7.74 (d, *J* = 7.5 Hz, 1, 6-H), 8.58 (s, 1,1′-H); mass spectrum (70 eV), *m/e* (relative intensity) 222 (M^+, 79), 178 ($M^+ - N(CH_3)_2$, 100), 166 ($M^+ + 1 - C_4H_9$, 43), 151 (65), 122 ($M^+ + 1 - N(CH_3)_2 - C_4H_9$, 79), 112 (56), 57 ($C_4H_9^+$, 49), 45 (40), 44 ($N(CH_3)_2^+$, 98), 42 (48), 41 (57).

1-Allyl-N^4-[(dimethylamino)methylene]cytosine (2e): ^{1}H NMR ($(CD_3)_2SO$) δ 3.05 (s, 3, $N(CH_3)_2$), 3.19 (s, 3, $N(CH_3)_2$), 4.36 (d, *J* = 4.5 Hz, 2, $CH_2CH{=}CH_2$), 5.10 (dd, *J* = 10.5, 1.8 Hz, 2, $CH_2CH{=}CH_2$), 5.92 (m, 1, $CH_2CH{=}CH_2$), 5.92 (d, *J* = 7.5 Hz, 1, 5-H), 7.70 (d, *J* = 7.5 Hz, 1, 6-H), 8.60 (s, 1,1′-H); mass spectrum (70 eV), *m/e* (relative intensity) 206 (M^+, 53), 162 ($M^+ - N(CH_3)_2$, 100), 44 ($N(CH_3)_2^+$, 54), 42 (52), 41 ($C_3H_5^+$, 81).

1-Benzyl-N^4-[(dimethylamino)methylene]cytosine (2f): ^{1}H NMR ($(CD_3)_2SO$) δ 3.0 (s, 3, $N(CH_3)_2$), 3.14 (s, 3, $N(CH_3)_2$), 4.90 (s, 2, $CH_2C_6H_5$), 5.90 (d, *J* = 7.5 Hz, 1, 5-H), 7.29 (s, 5, $CH_2C_6H_5$), 7.83 (d, *J* = 7.5 Hz, 1, 6-H), 8.59 (s, 1, 1′-H); mass spectrum (70 eV), *m/e* (relative intensity) 256 (M^+, 42), 212 ($M^+ - N(CH_3)_2$, 23), 91 ($C_7H_7^+$, 30), 44 ($N(CH_3)_2^+$, 18).

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Registry No. 1, 71-30-7; **2a**, 77738-01-3; **2b**, 79044-10-3; **2c**, 79044-11-4; **2d**, 79044-12-5; **2e**, 79044-13-6; **2f**, 79044-14-7; **3a**, 1122-47-0; **3b**, 25855-37-2; **3c**, 22919-46-6; **3d**, 25855-40-7; **3e**, 25855-43-0; **3f**, 60722-54-5; *N,N*-dimethylformamide dimethyl acetal, 4637-24-5; *N,N*-dimethylformamide diethyl acetal, 1188-33-6; *N,N*-dimethylformamide dipropyl acetal, 6006-65-1; *N,N*-dimethylformamide diallyl acetal, 61296-25-1; *N,N*-dimethylformamide dibutyl acetal, 18503-90-7; *N,N*-dimethylformamide dibenzyl acetal, 2016-04-8.

Selective Halogen-Lithium Exchange in Some Secondary and Tertiary (Bromophenyl)alkyl Halides[1]

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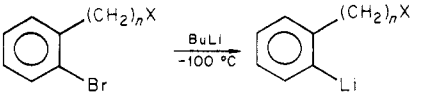
Parham et al.[3] discovered that when each of certain primary (*o*-bromophenyl)alkyl halides (1) is treated with



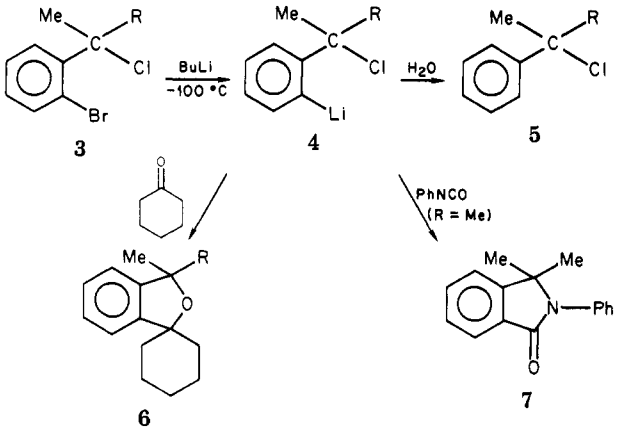
1	2
a, *n* = 1; X = Cl	a, *n* = 1; X = Cl
b, *n* = 2; X = Br	b, *n* = 2; X = Br
c, *n* = 3; X = Br	c, *n* = 3; X = Br
d, *n* = 3; X = Cl	d, *n* = 3; X = Cl

butyllithium at −100 °C there ensues a preferential halogen–lithium exchange of the *aryl* halogen. The resulting

(1) This research was supported in part by Grants DAHCO4-74-GD128 and DAAG29-77-G-0170 of the U.S. Army Research Office.
(2) Deceased May 21, 1976.
(3) Parham, W. E.; Jones, L. D.; Sayed, Y. *J. Org. Chem.* **1975**, *40*, 2394.

0022-3263/81/1946-4804$01.25/0

Scheme I[a]



[a] a, R = H; b, R = Me.

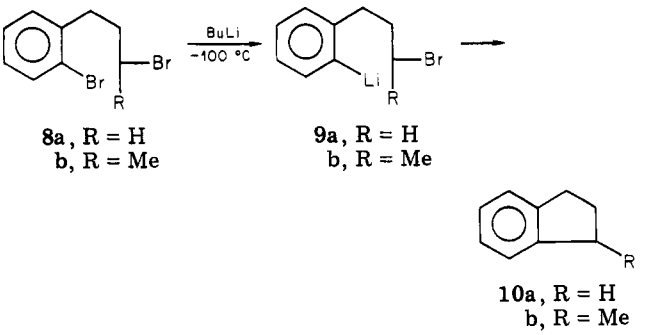
organolithium reagents (2) can (with the exception of **2c**) be caused to react with added electrophiles to produce useful synthetic intermediates. alternatively, conditions can be selected so that the halogen-bearing alkyl side chain may act as an internal electrophile (except in **2a**),[4] bringing about what has been referred to as the Parham cyclialkylation.[5,6] In this way **2b** afforded good yields of benzocyclobutene[3,7] and **2c** and **2d** similar yields of indan.[3]

The purpose of the present investigation was to examine the selective halogen–lithium exchange of dihalides resembling 1, except that the haloalkyl group was secondary or tertiary instead of primary, and to study possible synthetic applications of the organolithium reagents generated. It was recognized that substitution reactions of the S_N2 type would be more difficult than those in the primary alkyl halide series (1).[8]

o-Bromo-α-methylbenzyl chloride (**3a**)[9] was subjected to halogen–lithium exchange with butyllithium at −100 °C in the usual way[3] (Scheme I). Within 15 min exchange of the bromine atom by lithium was complete, as evidenced by ^{1}H NMR examination of samples withdrawn from the reaction mixture and quenched.[3] In another experiment *o*-lithio-α-methylbenzyl chloride (**4a**) was hydrolyzed to α-methylbenzyl chloride[10] (**5a**) in 65% yield (from **3a**). Reaction of **4a** with cyclohexanone followed by spontaneous cyclization afforded the expected phthalan (**6a**), also in 65% yield.

With the homologous tertiary halide, *o*-bromo-α,α-dimethylbenzyl chloride (**3b**), the exchange of the bromine atom under the usual conditions was complete in 1 h, and hydrolysis afforded cumyl chloride (**5b**) in 73% yield. Reaction of the new organolithium reagent (**4b**) with cyclohexanone to yield the phthalan **6b** (25% yield) or with phenyl isocyanate to yield the phthalimidine **7** (29% yield) proved less satisfactory.

Since the formation of a five-membered ring occurs with great ease in the Parham cyclialkylation (**8a** → **10a**),[3] it seemed logical that the first attempt to apply the cyclization to a secondary halide should be made by using 4-(2-bromophenyl)-2-bromobutane (**8b**) as the starting material. While **8b** was unknown, it was prepared easily from 4-(2-bromophenyl)-2-butanone as described by Hauser et al.[11] When treated with butyllithium at −100 °C, **8b** readily underwent bromine–lithium exchange of the bromine on the benzene ring, but the resulting organolithium reagent (**9b**), unlike **9a**, did not appear to cyclize at −100 °C. When temperature was allowed to rise to 20 °C and maintained there for 3 h, 1-methylindan (**10b**) was produced in a yield of 46%.[12] This is in contrast to a yield of 82% of indan (**10a**), after 15 min at −100 °C, reported[3] for the primary halide **8a**.



8a, R = H
b, R = Me

9a, R = H
b, R = Me

10a, R = H
b, R = Me

Except for *o*-bromobenzyl bromide,[3] alkylbenzenes having halogen (Cl or Br) in the side chain and bromine in the nucleus undergo halogen–lithium exchange with butyllithium at −100 °C preferentially with the aromatic bromine. Our preliminary results indicate that of the resulting organolithium reagents those having secondary or tertiary halogen in the side chain will prove less useful synthetically than those having primary halogen (**2**).

Experimental Section

All reactions involving organolithium reagents were carried out under an atmosphere of dry nitrogen. Tetrahydrofuran was dried by distillation from lithium aluminum hydride or calcium hydride and stored over 4-Å molecular sieves. Hexane (practical) was dried by storage over 4-Å molecular sieves. Elemental analyses were performed by MHW Laboratories. Melting points were determined in capillaries by using a Mel-Temp melting point block and were not corrected.

Lithium–Bromine Exchange with *o*-Bromo-α-methylbenzyl Chloride (3a). (a) Preparation of α-Methylbenzyl Chloride (5a). The reaction of **3a** (4.39 g, 20 mmol)[9] with 20 mmol of butyllithium was carried out at −100 °C essentially as described for **1a**.[3] After 15 min the organolithium reagent (**4a**) was poured into 100 mL of water. The layers were separated, and the aqueous phase was extracted with ether (3 × 100 mL). The combined organic solutions were dried and concentrated, and the residue (3.28 g) was distilled, affording 1.83 g (65%) of α-methylbenzyl chloride: bp 42.5–44 °C (2.2 torr) [lit.[10] bp 90–91 °C (33 torr)]; ^{1}H NMR[13] ($CDCl_3$) δ 2.83 (d, J = 7 Hz, 3, CH_3), 5.13 (q, J = 7 Hz, 1, benzylic methine), 7.15–7.60 (m, 5, Ar H).

(b) Conversion to 3′-Methylspiro[cyclohexane-1,1′-phthalan] (6a). The lithiation of 4.39 g (20 mmol) of **3a** was carried out as in part a except that to the organolithium reagent **4a** was added a solution of cyclohexanone (2.94 g, 30 mmol) in 20 mL of tetrahydrofuran at such a rate that the temperature did not exceed −100 °C. The solution was kept at −100 °C for 1 h and then warmed to room temperature over 2 h. The mixture was poured into water (100 mL), and the layers were separated. the aqueous layer was extracted with ether (3 × 75 mL). The combined organic solutions were washed (3 × 50 mL) with a

(4) *o*-Lithiobenzyl chloride (**2a**) reacts intermolecularly to afford dihydroanthracene.
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(12) The yield corrected for the organolithium reagent removed in testing the progress of the reaction is 46%.
(13) Identical with that of an authentic sample.[10]
(14) The procedure for removal of excess carbonyl compound is that of: Shriner, R. L.; Fuson, R. C.; Curtin, D. Y. "The Systematic Identification of Organic Compounds", 5th ed.; Wiley: New York, 1946; p 163.

mixture of 40% sodium bisulfite and ethanol (4/1 v/v).[13] The organic phase was dried and concentrated and the residue distilled, affording 2.63 g (65%) of phthalan **6a** as a colorless oil: bp 78–80 °C (0.25–0.30 torr); ^{1}H NMR ($CDCl_3$) δ 1.20–2.70 (m, 13, CH_3, cyclohexyl CH_2's), 5.36 (q, J = 7 Hz, 1, benzylic methine), 7.10–7.50 (m, 4, Ar H).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.85; H, 8.88.

***o*-Bromo-α,α-dimethylbenzyl Chloride (3b).** *o*-Bromo-α,α-dimethylbenzyl alcohol[15] (11.0 g, 51 mmol) was protected from moisture, cooled to 0 °C, and magnetically stirred while dry hydrogen chloride was bubbled through it for 5.5 h. The mixture was poured into ice–water and the organic layer taken up in ether. The ether solution was washed with saturated sodium bicarbonate solution, dried, and concentrated. Distillation of the residue afforded 8.0 g (67%) of **3b** as a colorless oil: bp 58–62 °C (0.02 torr);[16] ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 6, CH_3), 7.04–7.75 (m, 4, Ar H).

Anal. Calcd for $C_9H_{10}BrCl$: C, 46.29; H, 4.32; halogen, 30.36 (as Cl). Found: C, 46.65; H, 4.33; halogen, 30.51 (as Cl).

Bromine–Lithium Exchange of *o*-Bromo-α,α-dimethylbenzyl Chloride (3b). (a) Conversion to α,α-Dimethylbenzyl Chloride (5b). Following the usual precautions,[3] we treated 4.67 g (20 mmol) of **3b** in 130 mL of tetrahydrofuran and 30 mL of hexane at −100 °C with 20 mmol of butyllithium and maintained the mixture at the same temperature for 1 h. The resulting yellow slurry was poured into cold 5% hydrochloric acid and the organic material extracted with ether (3 × 100 mL). The ether solution was dried and concentrated to afford 3.47 g of oil which, upon examination by ^{1}H NMR, appeared to be 73% **5b** (comparison with an authentic sample[17]). Vacuum distillation of the oil was accompanied by severe decomposition but yielded 0.46 g of **5b**: bp 49–54 °C (2.2–2.8 torr) [lit.[16] bp 65–68.5 °C (6.5–7.0 torr)]; ^{1}H NMR ($CDCl_3$) δ 2.00 (s, 6, CH_3), 7.20–7.70 (m, 5, Ar H).

(b) Conversion to 3′,3′-Dimethylspiro[cyclohexane-1,1′-phthalan] (6b). The organolithium reagent (**4b**) was prepared from 4.67 g (20 mmol) of **3b** at −100 °C, was treated with 2.94 g (30 mmol) of cyclohexanone as in the preparation of the lower homologue (**6a**), and was worked up in the same way, except that before the final distillation the crude product was refluxed for 1 h in 20% alcoholic potassium hydroxide solution. This mixture was diluted with 150 mL of water and extracted with ether. The ether extract was dried and concentrated, and the residue was distilled to afford 1.06 g (25%) of **6b**: bp 87–90 °C (1.0–0.9 torr) [lit.[15] bp 56–58 °C (0.08 torr)];[18] ^{1}H NMR ($CDCl_3$) δ 1.52 (s, 6, CH_3), 1.72 (br s, 10, cyclohexyl CH_2's), 6.98–7.30 (m, 4, Ar H).

(c) Conversion to 3,3-Dimethyl-*N*-phenylphthalimidine (7). The organolithium reagent (**4b**) was prepared from 4.67 g (20 mmol) of **3b**, and a solution of phenyl isocyanate (2.62 g, 22 mmol) in 25 mL of hexane was added over a period of 5 min. The reaction mixture which rapidly lost its cloudy appearance was stirred at −100 °C for 15 min and then warmed to 25 °C over 1.5 h. The reaction mixture was poured into water and the product taken up in ether.

The ethereal solution was dried and concentrated, and the semisolid residue was crystallized from chloroform–ligroin as yellow crystals: 1.64 g (35%); mp 186–190 °C. One recrystallization afforded 1.36 g (29%) of faintly yellow crystals of **7**: mp 191–192.5 °C (lit.[19] mp 189–190 °C); ^{1}H NMR ($CDCl_3$) δ 1.52 (s, 6, CH_3), 7.20–8.02 (m, 9, Ar H); IR ($CHCl_3$) 1680 cm^{-1} (C=O).

4-(*o*-Bromophenyl)-2-butanol. To a stirred solution of 21.12 g (93 mmol) of 4-(*o*-bromophenyl)-2-butanone[10] in 200 mL of 2-propanol was added a suspension of sodium borohydride (1.90 g, 50 mmol) in 50 mL of 2-propanol, and the mixture was refluxed for 24 h with stirring. After the solution cooled, 45 mL of water and then 13 mL of acetic acid were added. The mixture was concentrated under reduced pressure and the residue partitioned between water and ether. The ether solution was dried and concentrated. Distillation of the residue through a 10-cm column gave a low-boiling forerun followed by 9.28 g (43.5%) of a colorless oil: bp 87.5–89 °C (0.10 torr); ^{1}H NMR ($CDCl_3$) δ 1.23 (d, J = 6 Hz, 3, Me), 1.78 (m, 2, CH_2CHOH), 2.22 (bs, 1, OH, exchangeable), 2.86 (m, 2, CH_2AR), 3.86 (m, 1, CHOH), 6.90–7.64 (m, 4, Ar H); IR (neat), 3350 cm^{-1} (OH).

Anal. Calcd for $C_{10}H_{13}BrO$: C, 52.42; H, 5.72; Br, 34.88. Found: C, 52.59; H, 5.98; Br, 35.16.

4-(*o*-Bromophenyl)-2-bromobutane (8b). A solution of 13.75 g (60 mmol) of 4-(*o*-bromophenyl)-2-butanol in 50 mL of ether was cooled in an ice bath and stirred while 16.3 g (60 mmol) of phosphorus tribromide was added over a period of 15 min. The ice bath was removed and stirring continued for 21 h. The reaction mixture was poured into a mixture of 200 g ice and 100 mL of saturated sodium bicarbonate solution. When the ice melted, the phases were separated, and the aqueous phase was extracted with ether. The combined organic phases were dried and concentrated. Distillation of the residue through a 10-cm column gave a fraction as a colorless oil: 7.5 g (43%); bp 86–88 °C (0.07–0.08 torr);[20] ^{1}H NMR ($CDCl_3$) δ 1.70 (d, J = 6 Hz, 3, CH_3), 2.10 (m, 2, CH_2CHBr), 2.90 (m, 2, CH_2Ar), 4.10 (m, 1, CHBr), 6.90–7.60 (m, 4, Ar H).

Anal. Calcd for $C_{10}H_{12}Br_2$: C, 41.13; H, 4.14; Br, 54.73. Found: C, 41.16; H, 4.26; Br, 54.91.

Bromine–Lithium Exchange of 8b. 1-Methylindan (10b). A solution of 4.38 g (15 mmol) of **8b** in 100 mL of tetrahydrofuran and 25 mL of hexane was cooled to −100 °C and 17 mmol of butyllithium added at such a rate that the temperature did not exceed −97 °C. The progress of the exchange and cyclization reaction was monitored by ^{1}H NMR analysis of quenched samples. Exchange was complete after only 15 min, but no cyclization was observed after a total of 30 min at −100 °C. The temperature was next allowed to rise to −78 °C and remain there for 1 h. The evidence was that very little cyclization had occurred. The temperature was allowed to rise to 25 °C (45 min) and remain there for 3 h. The mixture was poured into water, the organic layer separated, and the water extracted with ether. The combined organic phases were dried and concentrated. The residue was distilled, yielding 0.75 g (38%)[12] of colorless oil: bp 61–62 °C (5.7 torr) (lit.[21] bp 183–185 °C); ^{1}H NMR ($CDCl_3$) δ 1.26 (d, J = 6 Hz, 3, CH_3), 1.60–2.30 (m, 2, CH_2 at C-2), 2.84 (m, 2, $ArCH_2$), 3.16 (m, 1, CH), 7.16 (s, 4, ArH).

Registry No. 3a, 57739-76-1; **3b**, 7073-71-4; **4a**, 79044-15-8; **4b**, 79044-16-9; **5a**, 672-65-1; **5b**, 934-53-2; **6a**, 79044-17-0; **6b**, 59043-55-9; **7**, 53890-83-8; **8b**, 79044-18-1; **10b**, 767-58-8; cyclohexanone, 108-94-1; *o*-bromo-α,α-dimethylbenzyl alcohol, 7073-69-0; phenyl isocyanate, 103-71-9; 4-(*o*-bromophenyl)-2-butanol, 67130-96-5; 4-(*o*-bromophenyl)-2-butanone, 3506-68-1.

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(18) Although the boiling point recorded here is higher than that reported earlier, the ^{1}H NMR is identical with that recorded in this laboratory for a sample of **6b** obtained by cyclization of 1-[2-(α-hydroxyisopropyl)phenyl]cyclohexan-1-ol.[15]

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(20) The analytical sample obtained by redistillation of a portion boiled at 69–71 °C (0.03 torr).

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Regioselective Oxidations of Primary Alcohols in 1,4-Diols

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Numerous oxidative methods are currently available for the selective oxidation of secondary alcohols in primary, secondary diols.[1-5] However, since electronic stabilization

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