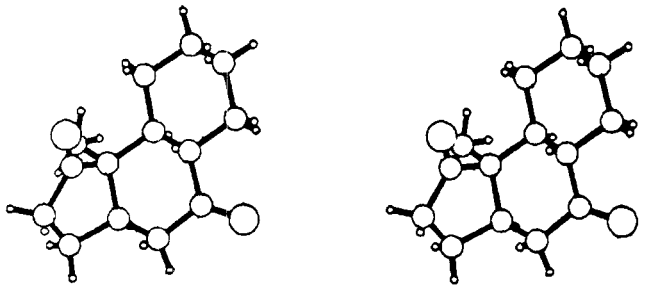

Figure 1. Stereoplot of the tricyclic dione **5**.

one portion of saturated aqueous NaCl solution, and dried over $MgSO_4$. Removal of solvents under reduced pressure, followed by chromatography over silica gel using 2% ethyl acetate in benzene, gave first 0.92 g (91%) of an alcohol **8a** (R_f 0.26): IR (CCl_4) 3600 (m), 1468 (m), 1460 (m), 1445 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.72 (s, 3 H, CH_3), 3.83 (br m, 1 H, >CHOH), 5.38 (br m, 1 H, vinyl H).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.32; H, 10.76.

After a few mixed fractions (0.020 g, 2%) there was eluted 0.060 g (6%) of a minor epimeric alcohol: IR (CCl_4) 3650 (m), 1480 (m), 1460 (m), 1455 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (s, 3 H, CH_3), 3.8 (br m, 1 H, >CHOH), 5.2 (br m, 1 H, vinyl H).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.44; H, 10.90.

1-(*tert*-Butyldimethylsilyloxy)-9bα-methyl-2,3,3aα,4,6,-7,8,9,9aα,9b-decahydro-1*H*-cyclopenta[*a*]naphthalene (8b). A mixture of 0.8 g (3.8 mmol) of the alcohol **8b** (major epimer), 1.0 g (14.7 mmol) of sublimed imidazole, 1.2 g (7.9 mmol) of *tert*-butyldimethylsilyl chloride (TBSCl),[6] and 1.6 mL of dry DMF was warmed to 40–45 °C with stirring under an argon atmosphere. After 18 h, 0.57 g (3.8 mmol) of TBSCl and 0.52 g (7.6 mmol) of imidazole were added. After 45 h, 0.29 g (1.9 mmol) of TBSCl and 0.26 g (3.8 mmol) of imidazole were added. After 78 h, the mixture was diluted with ether, washed with a 5% aqueous NaOH solution, water, and saturated aqueous NaCl solution, and dried over $MgSO_4$. Removal of solvents under reduced pressure, followed by chromatography over silica gel using cyclohexane afforded 1.18 g (97%) of the silyl ether **8b** as a colorless oil: IR (CCl_4) 1480 (m), 1250 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 0.03 (s, 6 H, $(CH_3)_2Si$), 0.53 (s, 9 H, CH_3C), 3.80 (br m, 1 H, >CHOSi), 5.2 (br m, 1 H, vinyl H).

Anal. Calcd for $C_{20}H_{36}OSi$: C, 74.93; H, 11.32. Found: C, 75.02; H, 11.26.

1-(*tert*-Butyldimethylsilyloxy)-5α-hydroxy-9bα-methyl-2,3,3aα,4,5β,5aα,6,7,8,9,9aα,9b-dodecahydro-1*H*-cyclopenta[*a*]naphthalene (9). To a stirred solution of 0.200 g (0.62 mmol) of the silyl ether **8b** in 18 mL of dry THF cooled to 0 °C under an argon atmosphere was added 2.2 mL of a commercial 0.88 M solution of borane·THF. The mixture was allowed to stir at 0 °C for 1 h and at room temperature for 1 h and quenched at 0 °C by careful dropwise addition of 0.5 mL of water. After 10 min at 0 °C, there was added dropwise 1.1 mL of a 30% aqueous H_2O_2 solution and 1.04 mL of a 3 N aqueous NaOH solution simultaneously. The mixture was allowed to stir for 1 h at 0 °C, diluted with 30 mL of water, and extracted three times with ether. The ethereal extracts were washed once with saturated aqueous NaCl solution and dried over $MgSO_4$. Removal of solvents under reduced pressure, followed by chromatography over silica gel using 10% ethyl acetate in benzene, gave 0.168 g (79%) of the alcohol **9** as a white crystalline solid: mp 88–90 °C; IR (CCl_4) 3650 (w, sh), 3425 (w, br), 1260 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.03 (s, 6 H, $(CH_3)_2Si$), 0.85 (s, 9 H, $(CH_3)_3C$), 1.03 (s, 3 H, CH_3), 3.86 (br m, 2 H, >CHOR).

An analytical sample was prepared by recrystallization from ether–petroleum ether: mp 89–90 °C.

Anal. Calcd for $C_{20}H_{38}O_2Si$: C, 70.94; H, 11.31. Found: C, 71.22; H, 11.22.

1,5α-Dihydroxy-9bα-methyl-2,3,3aα,4,5β,5aα,6,7,8,9,9aα,-9b-decahydro-1*H*-cyclopenta[*a*]naphthalene (10). A solution of 0.150 g (0.44 mmol) of the alcohol silyl ether **9** in 5 mL of methanol containing 4 mL of a 10% aqueous HCl solution was warmed to 70–80 °C for 8 h. The mixture was then diluted with water and extracted with three portions of ether. The ethereal extracts were washed with saturated NaCl solution and dried over $MgSO_4$. Removal of solvents under reduced pressure, followed by chromatography over silica gel using 30% ethyl acetate in benzene, afforded 0.094 g (95%) of the diol **10** as a white crystalline solid: mp 136–137 °C; IR ($CHCl_3$) 3640 (m, sh), 3475 (m, br), 1460 (m, sh) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (s, 3 H, CH_3), 3.96 (br m, 2 H, >CHOH).

An analytical sample was prepared by recrystallization from ether: mp 137–138 °C.

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.77; H, 10.61.

9bα-Methyl-2,3,3aα,4,5,5aα,6,7,8,9,9aα,9b-dodecahydro-1*H*-cyclopenta[*a*]naphthalene-1,5-dione (11). To a stirred solution of 0.070 g (0.31 mmol) of the diol **10** in 5 mL of dry dichloromethane was added 0.270 g (1.25 mmol) of pyridinium chlorochromate.[11] After 2 h at room temperature the mixture was diluted with 25 mL of anhydrous ether and filtered through a column of silica gel with 100 mL of anhydrous ether. Removal of solvents under reduced pressure, followed by chromatography on silica gel using 5% ethyl acetate in benzene, afforded 0.057 g (85%) of dione **11** as a white crystalline solid: mp 88–91 °C; IR (CCl_4) 1740 (s, sh), 1720 (s, sh), 1460 (m, sh) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (s, CH_3).

An analytical sample was prepared by recrystallization from cyclohexane: mp 41–42 °C.

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.29; H, 9.16.

Conversion of the Dione 11 to the Dione 5. To a stirred solution of 0.050 g (0.23 mmol) of the dione **11** in 10 mL of dry methanol was added 0.05 mL of a 0.54 M stock solution of sodium methoxide in methanol. The mixture was gently refluxed for 15 min, diluted with ether, washed with saturated NaCl solution, and dried over $MgSO_4$. Removal of solvents under reduced pressure, followed by chromatography over silica gel using 5% ethyl acetate in benzene, afforded 0.047 g (95%) of the crystalline dione **5**: mmp 74–76 °C; IR (CCl_4) 1740 (s, sh), 1720 (s, sh), 1460 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (s, CH_3).

Acknowledgment. The authors gratefully acknowledge financial support of this research by the National Science Foundation. We also thank the Kroc Medical Foundation and Medical Research Services of the Veterans Administration for their support.

Registry No. 2, 1120-73-6; **3**, 71096-87-2; **4**, isomer 1, 71096-88-3; **4**, isomer 2, 71096-89-4; **5**, 71096-90-7; **6**, 2622-21-1; **7**, 71096-91-8; **8a**, isomer 1, 71096-92-9; **8a** isomer 2, 71096-93-0; **8b**, 71096-94-1; **9**, 71096-95-2; **10**, 71096-96-3; **11**, 71096-97-4; *tert*-butyldimethylsilyl chloride, 18162-48-6; acetylcyclohexene, 932-66-1.

Supplementary Material Available: The atom numbering system used (Figure 2); additional plots including a view of packing in the unit cell (Figure 3); positional and thermal parameters (Table I); and bond distances and torsional angles (Table II) (18 pages). Ordering information is given on any current masthead page.

(11) E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 2647 (1975).

β-Lithioenamines from β-Chloroenamine. A Convenient Preparation Method of Hindered Ketones

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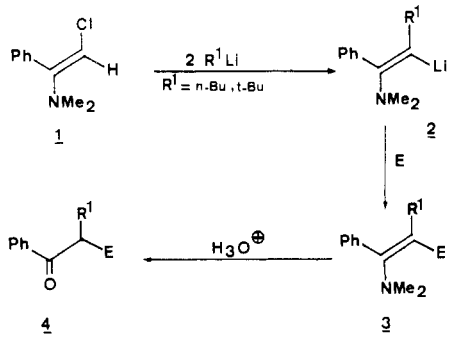
We have recently reported that the reaction of alkyllithium reagents with β-bromoenamines produces β-lithioenamines by a halogen–metal exchange reaction.[1] In

Table I. β-Lithioenamines 2: Synthesis and Reactions[a]

R^1Li (reaction time)	E (reagent)	isolated product: enamine 3	isolated product: ketone 4	isolated yield,[b] %	bp, °C/mmHg or (mp °C)
n-BuLi (8 h)	H (H_2O)	$PhC(NMe_2)=CH(n\text{-}Bu)$		50	88/0.8
	H (H_2O)[c]		PhCOn-Am	66	105/1
	D (D_2O)	$PhC(NMe_2)=CD(n\text{-}Bu)$		60	88/0.8
	D (D_2O)[c]		$PhCOCHD(n\text{-}Bu)$	60	55/0.25
	Me (MeI)	$PhC(NMe_2)=CMe(n\text{-}Bu)$		70	60/0.4
	Me (MeI)[c]		$PhCOCHMe(n\text{-}Bu)$	70	77/0.5
t-BuLi (3 h)	D (D_2O)	$PhC(NMe_2)=CD(t\text{-}Bu)$		68	80/0.5
	Me (MeI)	$PhC(NMe_2)=CMe(t\text{-}Bu)$		75	68/0.3
	Me (MeI)[c]		$PhCOCHMe(t\text{-}Bu)$	75	77/0.5
	Br (Br_2)[c]		$PhCOCHBr(t\text{-}Bu)$	50	(74)

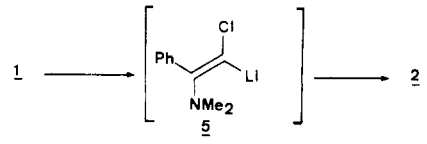
[a] The IR, NMR, and mass spectral data are fully compatible with the structure shown. Purity was established by gas chromatography. [b] No attempt was made to optimize these yields. [c] Intermediate enamine 3 was not isolated but was hydrolyzed into ketone 4.

the present note, we wish to describe a novel route to the lithioenamine 2 by a one-pot reaction utilizing the β-



chloroenamine 1 as the starting material. β-Lithioenamines 2, prepared by the reaction of enamine 1 with 2 equiv of alkyllithium, may be readily trapped by the electrophiles H_2O, D_2O, MeI, Br_2, giving either enamine 3 or ketone 4 by hydrolysis of 3 (see Table I).

Halogen substitution by group R^1 of the alkyllithium reagents may be explained by the initial formation of compound 5 by metalation of enamine 1.[2] Such a property



was already observed with vinyl chlorides[3,4] and α-chloro epoxides.[5]

In conclusion, we have developed a novel procedure which may be useful in the synthesis of sterically hindered ketones or the corresponding enamines. In fact, this process allows us to carry out the following transformation:

Insertion of the first group R^1 takes place according to a nucleophilic mode and that of the second group E according to an electrophilic mode. Introduction of a sterically hindered group such as the *tert*-butyl group may be obtained without any problem during the nucleophilic step.

Experimental Section[6]

2-Chloro-1-(dimethylamino)-1-phenylethylene (1).[7] To a stirred solution of 7.72 g (50 mmol) of chloroacetophenone in 150 mL of dry ether was added a solution of 6.83 g (33 mmol) of tris(dimethylamino)arsine in 80 mL of dry ether at 5 °C under N_2. The reaction mixture was stirred at 5 °C for 2 h and then stored at −20 °C overnight. After the solution was warmed to room temperature, As_2O_3 precipitated as white solid and was collected by filtration, 3.3 g (100%). After evaporation, the filtrate was distilled to give 7.8 g (86%) of enamine 1: IR 1597 cm^{-1}; E/Z[8] = 90/10; ^1H NMR δ (*E* isomer) 7.32 (br s, 5 H), 5.15 (s, 1 H), 2.49 (s, 6 H), (*Z* isomer) 7.32 (br s, 5 H), 5.10 (s, 1 H), 2.80 (s, 6 H).

Typical Procedure for the Preparation of Enamines 3. 1-(Dimethylamino)-2-deuterio-1-phenyl-1-hexene. To a stirred solution of 0.91 g (5 mmol) of enamine 1 in 10 mL of THF was added dropwise a solution of 8.5 mL (11 mmol) of *n*-butyllithium (1.3 M in hexane) at −70 °C under N_2. The reaction time is noted in Table I. The reaction mixture was quenched with D_2O. After the solution was warmed to room temperature, the reaction mixture was then extracted with ether, dried ($MgSO_4$), and distilled, leaving 0.61 g (60%) of the enamine: bp 88 °C (0.8 mm); IR 1620 cm^{-1}; ^1H NMR δ 7.25 (br s, 5 H), 2.5 (s, 6 H), 1.9–0.85 (m, 9 H).

Typical Procedure for the Preparation of Ketones 4. 1-Phenyl-2,3,3-trimethyl-1-butanone. To a stirred solution of 0.91 g (5 mmol) of enamine 1 in 10 mL of THF was added dropwise a solution of 12 mL (12 mmol) of *tert*-butyllithium (1 M in pentane) at −70 °C under N_2. The reaction time is noted in Table I. A solution of 1.42 g (10 mmol) of methyl iodide in 2 mL of THF was added at −70 °C, and then the reaction mixture was allowed to warm to room temperature with stirring. The reaction mixture was treated with 5 mL of 10% aqueous HCl (hydrolysis required 4 h at 40 °C) and then extracted with ether, dried ($MgSO_4$), and distilled, leaving 0.72 g (75%) of the ketone: bp 77 °C (0.5 mm); IR 1680 cm^{-1}; ^1H NMR δ 7.9 (m, 2 H), 7.4 (m, 3 H), 3.4 (q, 1 H), 1.16 (d, 3 H), 1.0 (s, 9 H).

Registry No. (*E*)-1, 71129-92-5; (*Z*)-1, 71130-01-3; 2 (R′ = Bu), 71129-93-6; 2 (R′ = *t*-Bu), 71129-94-7; 3 (R′ = Bu; E = H), 71129-95-8; 3 (R′ = Bu; E = D), 71129-96-9; 3 (R′ = Bu; E = Me), 71129-97-0; 3 (R′ = *t*-Bu; E = D), 71129-98-1; 3 (R′ = *t*-Bu; E = Me), 71129-99-2; 4 (R′ = Bu; E = H), 942-92-7; 4 (R′ = Bu; E = D), 71130-00-2; 4 (R′ = Bu; E = Me), 17180-39-1; 4 (R′ = *t*-Bu; E = Br), 33119-75-4; 4 (R′ = *t*-Bu; E = Me), 57847-43-5.

(1) L. Duhamel and J. M. Poirier, *J. Am. Chem. Soc.*, **99**, 8356 (1977).
(2) By using only 1 equiv of *n*-butyllithium reagent, we observe formation of a half-equivalent of lithioenamine 2. Formation of 5 should be the slow step followed by a fast nucleophilic substitution of halogen which gives 2.
(3) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **6**, 41 (1967).
(4) G. Köbrich and F. Ansari, *Chem. Ber.*, **100**, 2011 (1967).
(5) H. Molines, J. M. Normant, and C. Wakselman, *Tetrahedron Lett.*, 951 (1974).
(6) All boiling points and melting points are uncorrected. Infrared spectra (IR) were recorded on a Perkin-Elmer 377 (thin film). ^1H NMR spectra were obtained on a Perkin-Elmer R 12. The chemical shifts (δ values) are given in parts per million relative to Me_4Si as the internal standard in $CDCl_3$ solutions. THF was freshly distilled from $LiAlH_4$.
(7) P. Duhamel, L. Duhamel, and J. M. Poirier, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **270**, 957 (1970).
(8) The stereochemistry of enamine 1 was determined by the ^1H NOE effect.