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Stereochemical Studies. XLIII.[1] Novel Reactivity of Organometallic Reagents to 5,5-Ethylenedioxy-2-methyl-2-phenylcyclohexanone[2]

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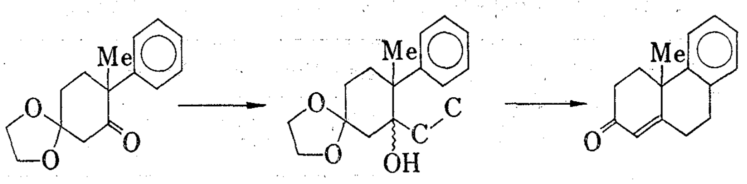
In connection with our studies on asymmetric synthesis of optically active diterpenes and steroids, introduction of a two carbon unit into the carbonyl group of 5,5-ethylenedioxy-2-methyl-2-phenylcyclohexanone (1) was examined using several kinds of organometallic reagents as nucleophiles.

Although N,N-dimethyl lithioacetamide (**4f**) could afford the desired 1,2-addition product (**8e**), other organometallic reagents (**4a**—**e**) simply behaved as bases which cleaved the ketal ring of **1**, giving the enol ether (**5**).

Use of **4f**-1,4-diazabicyclo[2,2,2]octane complex could further improve the yield of **8e** from 26% to 84%.

In the course of our studies on asymmetric synthesis of optically active diterpenes and steroids,[1,4] it became necessary for us to introduce a two carbon unit into the sterically hindered carbonyl function of 5,5-ethylenedioxy-2-methyl-2-phenylcyclohexanone (**1**)[4,5] (see **2**) for synthesizing phenanthrone derivative (**3**).



1 **2** **3**

Chart 1

Attempted nucleophilic reactions with several kinds of organometallic reagents (**4a**—**f**) uncovered that only N,N-dimethyl lithioacetamide (**4f**) could attack the carbonyl group of **1** as a nucleophile to afford the desired 1,2-addition product, and that the other organometallic reagents (**4a**—**e**) simply behaved as bases which effected a novel cleavage of the ketal group of **1**.

This report deals with our studies on reactivity of **4a**—**f** to **1**, structural elucidation of the novel compound which can be produced from **1** by a cleavage of the ketal group, and effect of tertiary amines on the reaction of **4f** with **1**.

Result and Discussion

As methods for introducing a two carbon unit into the carbonyl group of **1**, Reformatsky reaction[6] and Grignard reaction with vinylmagnesium bromide (**4b**) and allylmagnesium

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[1] Part XLII: T. Sone, S. Terashima, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), 24, 1288 (1976).

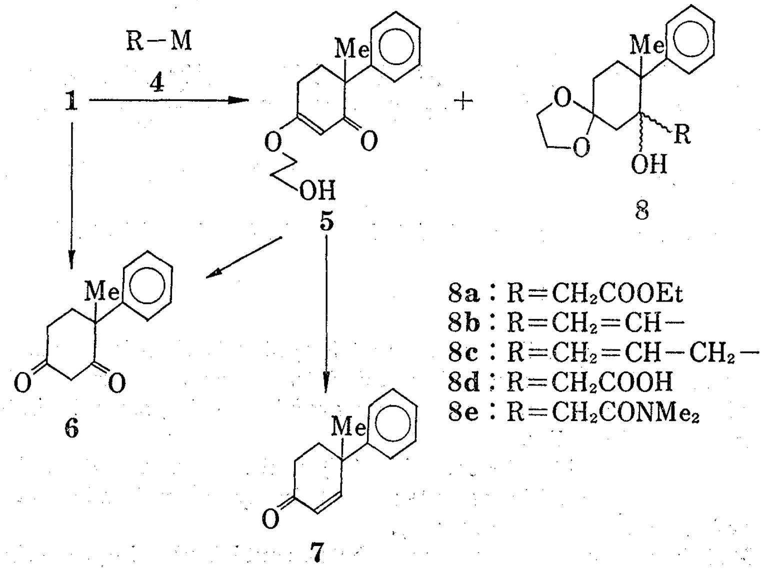
[2] A part of this work has been presented at the 94th Annual Meeting of the Pharmaceutical Society of Japan, Sendai, April, 1974, and at the Symposium of the Society of Synthetic Organic Chemistry Japan, Tokyo, November, 1974.

[3] Location: *Hongo, Bunkyo-ku, Tokyo, 113, Japan.*

[4] T. Sone, S. Terashima, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), 24, 1273 (1976).

[5] All compounds which were utilized in this work are racemic modifications.

[6] R.L. Shriner, "Organic Reactions," Vol. 1, John-Wiley and Sons, Inc., New York, 1942, p. 1.



8a : R=CH_2COOEt
8b : R=CH_2=CH−
8c : R=CH_2=CH−CH_2−
8d : R=CH_2COOH
8e : R=CH_2CONMe_2

4a : R=CH_2COOEt	M=ZnBr	**4e** : R=CH_2COOLi	M=Li
4b : R=CH_2=CH−	M=MgBr	**4f** : R=CH_2CONMe_2	M=Li
4c : R=CH_2=CH−CH_2−	M=MgBr	**4g** : R=N(iso-Pr)$_2$	M=Li
4d : R=CH_2COOEt	M=Li		

Chart 2

TABLE I. Reactions of Organometallic Reagents (**4a**—**g**) with 5,5-Ethylenedioxy-2-methyl-2-phenylcyclohexanone (**1**)

Run	Organometallic reagents (4a—g)		Reaction conditions			Reaction products[a] (%)		
	Nature	Molar ratio to **1**	Solv.	Temp. (°C)	Time (hr)	**1**	**5**	**8**
1	$BrZnCH_2COOEt$ (**4a**)	5.0	C_6H_6	80	20	63	20	0 (**8a**)
2[b]	CH_2=CH-MgBr (**4b**)	5.0	THF	65	10	68	18	0 (**8b**)
3[b]	CH_2=CH-CH_2-MgBr (**4c**)	5.0	THF	65	10	60	21	0 (**8c**)
4[b]	$LiCH_2COOEt$ (**4d**)	2.0	THF	−25	3	18	64	0 (**8a**)
5[b]	$LiCH_2COOLi$[c] (**4e**)	2.0	THF	0	2	46	27	0 (**8d**)
6[b]	$LiCH_2CONMe_2$ (**4f**)	2.0	THF	−25	3	0	58	26[d] (**8e**)
7	LiN(iso-Pr)$_2$ (**4g**)	2.0	THF	−75	1	0	80	0

[a] determined by the separation with column chromatography or preparative TLC (silica gel, solvent ether: hexane 1:2 (runs 1—5) or ether (runs 6 and 7))
[b] A THF solution of organometallic reagent was added to a cooled THF solution of **1** (reverse addition).
[c] 3.0 eq. of hexamethylphosphoramide (HMPA) to the lithium reagent was used.
[d] A combined yield of two epimers (**8eA** and **8eB**) which were separable by column chromatography or preparative TLC. The ratio of two epimers determined by weight measurement was *ca.* 7:1.

bromide (**4c**) were first examined under conditions summarized in Table I (Table I, runs 1, 2, and 3). Thin-layer chromatography (TLC) (silica gel, solvent ether) of the reaction mixtures clearly disclosed that **1** (*Rf ca.* 0.8) was very unreactive to these reagents (**4a**—**c**), and that formation of the new compound (**5**) (*Rf ca.* 0.25) was always observed.[7] After usual extractive isolation and separation, **5** was isolated as an oil in about 20% yield, and **1** was obtained in 60—68% recovery.

Determination of the structure of **5** was examined by the following spectral data and its chemical behavior. IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 3300 (OH), 1600 (1,3-diketone enol ether). NMR (in CCl_4):

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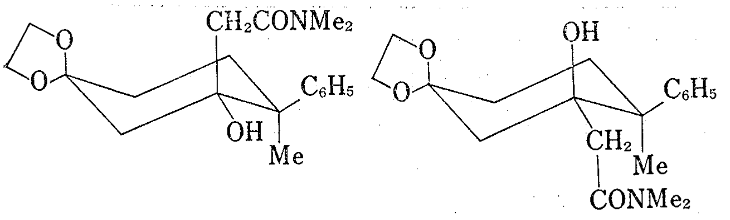
[7] Formation of the reaction products other than **5**, was not observed by TLC analysis of the reaction mixtures.

1.34 (3H, s, C–C$\underline{H}_3$), 1.7—2.5 (4H, m, –C$\underline{H}_2$C$\underline{H}_2$–), 3.14 (1H, s, O$\underline{H}$), 3.80 (4H, s, OC$\underline{H}_2$C$\underline{H}_2$OH), 5.37 (1H, s, =C$\underline{H}$–CO), 7.16 (5H, s, $C_6\underline{H}_5$). UV $\lambda_{max}^{95\%EtOH}$ nm: 253 (log ε 4.17) (cyclohexane-1,3-dione enol ether).[8] Mass Spectrum *m/e*: 246 (M^+), 218, 204. Treatment of **5** with dilute hydrochloric acid in aqueous ethanol afforded 4-methyl-4-phenylcyclohexane-1,3-dione (**6**), which was identified with an authentic sample independently prepared from **1**. Reduction of **5** with lithium aluminum hydride (LAH) in tetrahydrofuran (THF) at 0°, followed by acidic treatment, gave a 60% yield of 4-methyl-4-phenyl-2-cyclohexenone (**7**). This was also identified with an authentic sample[4] by spectral and chromatographic comparisons. According to the spectral and chemical properties described above, the structure of **5** is definitely assigned as 2-(2-hydroxyethoxy)-6-methyl-6-phenyl-2-cyclohexanone.

Next, reactions of ethyl lithioacetate[9] (**4d**) (run 4) and lithium lithioacetate[10] (**4e**) (run 5) were examined as shown in Table I. These lithium reagents could be generated *in situ* by treating ethyl acetate or acetic acid with lithium diisopropylamide (**4g**). However, these reactions were again found to be useless for giving the desired 1,2-addition products (**8a** and **8d**), and afforded **5** in 64% and 27% yields with recovery of **1** (18% and 46% recovery).

Since all attempts for introducing a two carbon unit into **1** turned out to be unsuccessful, the addition reaction with **4f**[11] was finally undertaken. When **1** was treated with a THF solution of **4f** under the condition shown in Table I (run 6), the desired 1,2-addition product (**8e**) was obtained in 26% yield, with concomitant formation of **5** in 58% yield. Although **8e** consists of two kinds of epimers (**8eA** 23% yield; **8eB** 3% yield) and the structures of these epimers have been clearly established as shown in Chart 3 by considering their spectral differences and the addition mechanism,[4] the yield of **8e** is expressed by the combination of those of **8eA** and **8eB** in this report.



8eA 8eB

Chart 3

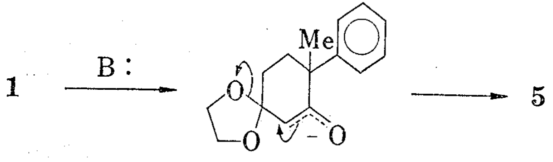


Chart 4

As shown in Chart 4, the formation of **5** from **1** can be construed by the reaction mechanism in which **4a**—**f** behave as bases that abstract a proton α to the carbonyl group and the formed stabilized carbanion opens the ketal ring. This might be due to the steric hindrance to the carbonyl group caused by the neighboring methyl and phenyl groups. When **1** was treated with a strong base such as **4g** at −75° (Table I, run 7), **5** could be produced as the sole reaction product in 80% yield. This result might further support the proposed formation mechanism for **5**.

That **8e** could be produced from **1** when **4f** was used as a nucleophile, might be verified by the explanation that difference in the balance between nucleophilicity and basisity of **4f** is larger than those of other organometallic reagents examined here.

Aiming to improve the yield of **8e**, that is, to further increase nucleophilicity of **4f**, the addition reaction of **4f** to **1** was examined in the presence of several kinds of tertiary amines

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8) "Organic Electronic Spectral Data," Vol. II, Ed. by H.E. Ungnade, Interscience Publishers, Inc., New York, p. 191. UV spectrum of 3-methoxy-5,5-dimethyl-2-cyclohexenone was reported to show λ_{max}^{EtOH} nm: 249 (log 4.21).

9) M.W. Rathke and A. Lindert, *J. Am. Chem. Soc.*, **93**, 2318 (1971).

10) P.E. Pfeffer and L.S. Silbert, *J. Org. Chem.*, **35**, 262 (1970).

11) D.S. Crouse and D. Seebach, *Chem. Ber.*, **101**, 3113 (1968).

such as tetramethylethylenediamine (TMEDA), 1,8-bis(dimethylamino)naphthalene (Proton sponge), 1,8-diazabicyclo[5,4,0]-7-undecene (DBU), and 1,4-diazabicyclo[2,2,2]octane (DABCO). These tertiary amines are reported to increase nucleophilicity of organolithium reagent by forming organolithium-tertiary amine complex.[12]

A THF solution of **4f**-tertiary amine complex was prepared by adding tertiary amine to a THF solution of **4f** at −70°, and by stirring the whole solution at −70° for 10 min. Results obtained by changing amine component and relative ratio of tertiary amine to **4f**, are shown in Table II. It is obvious that use of **4f**-tertiary amine complex can clearly increase nucleophilicity of **4f**, and higher yield of **8e** than that without tertiary amine can be always observed. The best result was obtained when DABCO (1.0 eq. to **4f**) was used as a tertiary amine additive (Table II, run 4).

Table II. Reactions of N,N-Dimethyl lithioacetamide (**4f**)–Tertiary Amine Complexes with 5,5-Ethylenedioxy-2-methyl-2-phenylcyclohexanone (**1**)[a]

Run	Tertiary amines		Reaction products[b] (%)	
	Nature	Molar ratio to **4f**	**8e**[c]	**5**
1	TMEDA	1.0	37	40
2	Proton sponge	1.0	42	43
3	DBU	1.0	45	40
4	DABCO	1.0	50	38
5	DABCO	0.5	42	42
6	DABCO	1.5	46	32

a) 2.0 eq. of **4f** to **1** was used. Reaction conditions were the same as those for run 6 in Table I.
b) separated by column chromatography or preparative TLC (silica gel, solvent ether)
c) A combined yield of two epimers (**8eA** and **8eB**) which were separable by column chromatography or preparative TLC. The ratio of two epimers determined by weight measurement was *ca.* 7:1.

Table III. Effects of Reaction Time for N,N-Dimethyl lithioacetamide (**4f**)-DABCO Complex Formation on the Yield of the 1,2-Addition Product[a] (**8e**)

Run	Reac. time for **4f**–DABCO complex formation (min)	Reaction products[b] (%)	
		8e[c]	**5**
1	10	50	38
2	60	74	13
3	90	84	7
4	120	82	6

a) 2.0 eq. of **4f** to **1** was used. Reaction conditions were the same as those for run 6 in Table I.
b) separated by column chromatography or preparative TLC (silica gel, solvent ether)
c) A combined yield of two epimers (**8eA** and **8eB**) which were separable by column chromatography or preparative TLC. The ratio of two epimers determined by weight measurement was *ca.* 7:1.

Finally, in order to further improve the yield of **8e**, the reaction time which was needed for preparing the complex from **4f** and DABCO was changed as shown in Table III. It is evident that the formation speed of **4f**-DABCO complex is fairly slow at −70°, and that about 1.5 hr are necessary for the maximum formation of the complex. Aging the complex

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[12] *a*) J.M. Mallan and R.L. Bebb., *Chem. Rev.*, **69**, 693 (1969); *b*) D.R. Dimmel and S. Huang, *J. Org. Chem.*, **38**, 2758 (1973); *c*) K. Ohshima, H. Takahashi, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **95**, 2693 (1973).

for 1.5 hr at −70° before being allowed to react with **1** gave a 84% yield of **8e** and a 7% yield of **5** (Table III, run 3).

As mentioned above, the introduction of a two carbon unit into the carbonyl group of **1**, has now become possible in more than 80% yield, and the difficulties which we initially encountered, have been completely solved.

Experimental[13]

Reactions of Organometallic Reagents (4a—g) with 5,5-Ethylenedioxy-2-methyl-2-phenylcyclohexanone (1)——a) Table I, Run 1: A solution of **1**[4] (123 mg, 0.50 mmole) in benzene (3 ml) was added to a benzene solution (5 ml) containing zinc powder (165 mg, 2.5 mg atom) and ethyl bromoacetate (0.42 g, 2.5 mmole). The whole mixture was stirred under reflux for 20 hr, then diluted with ice-water. The benzene layer was separated, and the lower aqueous phase was further extracted with ether. The combined organic extracts were washed with satd. NaCl, and dried over anhyd. $MgSO_4$. Filtration and evaporation *in vacuo*, followed by purification by column chromatography (silica gel, solvent, ether: hexane 1: 2), gave **5** as a pale yellow oil (25 mg, 20%) and **1** as an oil (77 mg, 63% recovery). Spectral data of **5** have already been described in result and discussion part. The recovered **1** was identified with the authentic starting material by spectral (IR) and chromatographic (TLC) comparisons.

b) Table I, Run 4: A THF solution of **4g** (2.0 mmole) was prepared by adding 1.5M butyllithium solution (hexane) (1.3 ml, 2.0 mmole) to a THF solution (2 ml) of diisopropylamine (200 mg, 2.0 mmole) at −70° under nitrogen atmosphere, and by stirring the whole mixture under the same condition for 30 min. A THF solution (2 ml) of ethyl acetate (176 mg, 2.0 mmole) was added to the THF solution of **4g** prepared above, at −70°, and the whole solution was stirred at −70° for 1.5 hr, to give a THF solution of **4d**.

To a THF solution (3 ml) of **1** (246 mg, 1.0 mmole) cooled at −25—−30°, was added the THF solution **4d** with stirring. The mixture was stirred at −25° for 3 hr, then diluted with satd. NH_4Cl (2 ml). After warming up to room temperature, the upper organic phase was separated, and the lower aqueous phase was extracted with ether. The combined organic layers were washed with satd. NH_4Cl, and satd. NaCl, then dried over anhyd. $MgSO_4$. Filtration and evaporation *in vacuo*, gave a residue, which was purified by column chromatography (silica gel, solvent ether: hexane 1: 2) to afford oily **5** (45 mg, 18%) and **1** (160 mg, 64%). The structures of these compounds were comfirmed by spectral comparisons with the samples obtained in a).

c) Table I, Run 6: A THF solution (10 ml) of N,N-dimethyl acetamide (0.87 g, 10 mmole) was added to a solution of **4g** (10 mmole) in THF (10 ml) prepared in a similar manner to that described in b), under nitrogen atmosphere at −70°, and the whole mixture was stirred under the same condition for 1.5 hr.

A THF solution of **4f** thus obtained, was added to a solution of **1** (1.23 g, 5.0 mmole) in THF (50 ml) at −25° under nitrogen atmosphere. The reaction mixture was stirred at −25° for 3 hr, then diluted with satd. NH_4Cl. The organic layer was separated, and the lower aqueous phase was extracted with ether. The combined organic layers were washed with satd. NH_4Cl and satd. NaCl, and finally dried over anhyd. $MgSO_4$. Filtration and evaporation *in vacuo* gave an oily residue, which was separated by column chromatography (silica gel, solvent ether), to afford **8eA** as a crystalline solid (375 mg, 23%), **8eB** as a pale yellow oil (54 mg, 3%), and **5** the a pale yellow oil (715 mg, 58%).

8eA: mp 149—150° (recrystallized from ether–hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3490 (OH), 1623 ($CONMe_2$). NMR (in $CDCl_3$): 1.47 (3H, s, $C\underline{H}_3$), 1.5—2.9 (8H, m, $4\times C\underline{H}_2$), 2.38, 2.75 (6H, doubled s, $N(C\underline{H}_3)_2$), 4.30 (1H, s, $O\underline{H}$), 3.96 (4H, s, $OC\underline{H}_2C\underline{H}_2O$), 7.1—7.7 (5H, m, $C_6\underline{H}_5$). These spectral data were completely the same as those of the authentic sample obtained in the previous report.[4]

8eB: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3330 (OH), 1614 ($CONMe_2$). NMR (in $CDCl_3$): 1.43 (3H, s, $C\underline{H}_3$), 1.5—2.6 (8H, m, $4\times C\underline{H}_2$), 2.84, 2.89 (6H, doubled s, $N(C\underline{H}_3)_2$), 3.86 (4H, s, $OC\underline{H}_2C\underline{H}_2O$), 6.20 (1H, br s, $O\underline{H}$), 7.1—7.7 (5H, m, $C_6\underline{H}_5$). These spectral behaviors of this oil were identical with those of the authentic optically active compound obtained in the previous report.[4]

5: This was identified with the sample obtained in a) by spectral comparisons.

d) Table I, Run 7: To a THF solution (1 ml) of **4g** (1.0 mmole), prepared by using diisopropylamine (101 mg, 1.0 mmole) and 1.5M butyllithium solution (hexane) (0.67 ml, 1.0 mmole) according to the same procedure as that described in b), was added a THF solution (3 ml) of **1** (123 mg, 0.50 mmole) at −75° with

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[13] All melting points are uncorrected. Infrared (IR) spectra were measured with spectrometers, JASCO Infrared Spec- trometer Model DS-402G and JASCO IRA-1 Grating Infrared Spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded with spectrometers, JNM-PS 100 Spectrometer (100 Mc) and Hitachi R-24 High Resolution NMR Spectrometer (60 Mc). All signals are expressed by the ppm downfield from tetramethylsilane used as an internal standard (δ value). Following abbreviations are used: singlet (s), dou- blet (d), triplet (t), quartet (q), multiplet (m), broad (br). Ultraviolet (UV) spectra measurements were carried out with a spectrometer, Hitachi Model EPS-3T Recording Spectrophotometer. Mass spectra were measured with a spectrometer, JEOL JMS SG-2 Mass Spectrometer.

stirring. After stirring at −75° for 1 hr, the whole was diluted with satd. NH_4Cl (1 ml) and ether (10 ml), then the temperature of the mixture was raised up to room temperature. The upper organic phase was separated, washed with satd. NaCl, and finally dried over anhyd. $MgSO_4$. Filtration and evaporation *in vacuo*, followed by purification with preparative TLC (silica gel, solvent ether), gave **5** as a yellow oil (98.9 mg, 80%). This sample was identified with the authentic compound obtained in a) by spectral comparisons.

4-Methyl-4-phenylcyclohexane-1,3-dione (6)——a) **6** from **5**: A mixture of **5** (49 mg, 0.20 mmole) and 10% HCl (0.5 ml) in ethanol (2 ml) was heated under reflux for 10 min, then evaporated *in vacuo* to afford a residue. The residue was dissolved in benzene, and the benzene solution was extracted with 10% NaOH. The aqueous alkaline solution was acidified with 10% HCl, and extracted with ether. The combined ethereal extracts were washed with satd. NaCl, and dried over anhyd. $MgSO_4$. Filtration and evaporation *in vacuo* gave crude **6** as colorless crystals (30 mg, 75%), mp 147—155°. Recrystallization from ethanol gave pure sample as colorless prisms, mp 154—156°. IR ν_{max}^{KBr} cm^{-1}: 1735, 1710, 1610 (cyclohexane-1,3-dione). NMR (in DMSO-d_6): 1.40 (3H, s, C$\underline{H}_3$), 2.1—2.3 (4H, m, 2×C$\underline{H}_2$), 5.00 (2H, s, COC$\underline{H}_2$CO), 7.25 (5H, s, $C_6\underline{H}_5$). *Anal.* Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.18; H, 7.05.

b) **6** from **1**: A mixture of **1** (123 mg, 0.50 mmole) and 10% HCl (1 ml) in ethanol (4 ml) was heated under reflux for 10 min, and then concentrated *in vacuo* to afford a residue. The residue was dissolved in benzene and the benzene solution was extracted with 10% NaOH. The combined alkaline extracts were acidified with 10% HCl, and extracted with ether. The ethereal extracts were washed with satd. NaCl and dried over anhyd. $MgSO_4$. Filtration and evaporation *in vacuo* afforded crude **6** as a solid (85 mg, 85%). Recrystallization from ethanol gave pure **6** as colorless prisms, mp 153—155°. This was identified with the sample obtained from **5** by comparing their spectral (IR and NMR) data and by measuring mixed melting point, mmp 153—154°.

4-Methyl-4-phenyl-2-cyclohexenone (7)——LAH (38 mg, 1.0 mmole) was added to a THF solution (2 ml) of **5** (123 mg, 0.50 mmole) with stirring in an ice bath, and the heterogeneous solution was stirred for 30 min at the same temperature. After dilution with ether (20 ml), the formed metal complex was decomposed by the addition of water (0.1 ml). Filtration and evaporation *in vacuo* gave a residue which was dissolved in ethanol (2 ml). 10% HCl (1 ml) was added to the ethanolic solution, and the whole was heated under reflux for 1 hr. After evaporation *in vacuo*, a residual solution was diluted with benzene. The benzene layer was separated, and successively washed with satd. $NaHCO_3$ and satd. NaCl, and finally dried over anhyd. $MgSO_4$. Filtration and evaporation *in vacuo*, followed by purification with preparative TLC (silica gel, solvent ether: hexane 1: 4, three developments), gave pure **7** as a pale yellow oil (37 mg, 60%). Spectral (IR) and chromatographic (TLC) behavior of this oil were identical with those of the authentic sample.[4]

Reactions of N,N-Dimethyl Lithioacetamide (4f)-Tertiary Amine Complexes with 5,5-Ethylenedioxy-2-methyl-2-phenylcyclohexanone (1) (Table II and III)——a) Table II, Run 4: A THF solution (2 ml) of DABCO (224 mg, 2.0 mmole) was added to a solution of **4f** (2.0 mmole) in THF (4 ml) which was prepared from N,N-dimethyl acetamide (174 mg, 2.0 mmole) according to the same procedure as that described in Table I run 6, with stirring at −70°, and the whole solution was stirred at −70° for 10 min. The THF solution of **4f**-DABCO complex thus prepared, was added to a solution of **1** (246 mg, 1.0 mmole) in THF (10 ml) with stirring at −25° under nitrogen atmosphere. The whole mixture was stirred at −25° for 3 hr, then worked up in a similar manner to the case for Table I run 6, giving **8eA** as a crystalline solid (147 mg, 44%), mp 148.5—150°, oily **8eB** (20 mg, 6%), and **5** as a pale yellow oil (93 mg, 38%). These products were respectively identified with the authentic samples by comparing their spectral (IR) and chromatographic (TLC) behaviors.

b) Table III, Run 3: The experimental procedure was completely the same as that for a) except for the reaction time which was consumed for the preparation of **4f**-DABCO complex. Full detail of the procedure was also described on the reaction with optically active **1** in the previous paper.[4]

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