The Reaction of Nitrile Oxide-Quinone Cycloadducts. III.[1] Reinvestigation of the Base-Induced Isomerization of the 1 : 1 -C=C-Adducts of Aromatic Nitrile Oxides with 2,5- and 2,6-Dialkyl-Substituted *p*-Benzoquinones

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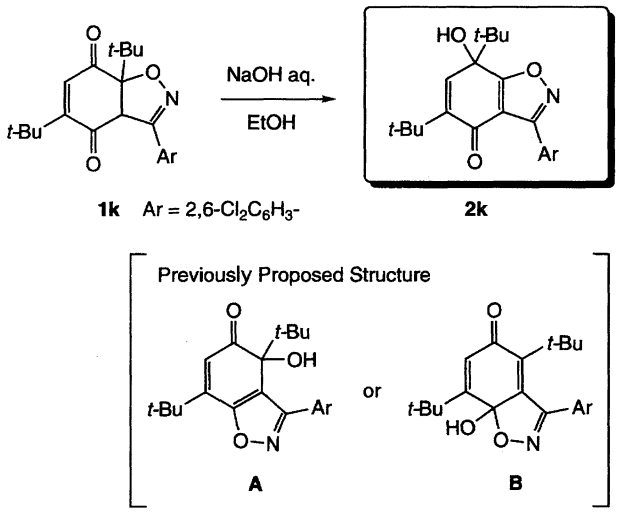
The structure of the product obtained by the base-induced isomerization of the 1,3-dipolar cycloadduct of 2,5-di-*t*-butyl-*p*-benzoquinone with 2,6-dichlorobenzonitrile oxide was determined by X-ray analysis. The *t*-butyl group at the bridgehead position of the 1,3-dipolar cycloadduct migrated to the neighboring carbonyl carbon atom. This base-induced rearrangement took place with a bulky group, i. e., Et, *i*-Pr, *t*-Bu, and Bn at the bridgehead position of nitrile oxide-quinone cycloadducts in an alcoholic media. The driving force of this reaction is considered to be due to stabilization by aromatization from isoxazoline derivatives to isoxazole-fused *p*-quinol derivatives.

Nitrile oxides are one of the typical 1,3-dipoles, and their 1,3-dipolar cycloadditions with various unsaturated bonds have been widely investigated.[2] Nevertheless, the 1,3-dipolar cycloaddition of quinones with nitrile oxides was scarcely reported,[3—8] except for ours. We have investigated the 1,3-dipolar cycloaddition of substituted *p*-benzoquinones with some aromatic nitrile oxides in detail,[1,9—14] and have revealed that 2,5- and 2,6-dialkyl-substituted *p*-benzoquinones afforded 1 : 1-C=C-adducts, isoxazoline-fused cyclohexenedione derivatives with aromatic nitrile oxides in excellent yields with a small amount of 1 : 2-adducts in some cases.[1,11] Since the bridgehead methine of the cycloadducts is an active methine, the reaction of the cycloadducts with a base was conducted in expectation of some ring transformation. Yellow ethanolic solutions of the cycloadducts were treated with an aqueous solution of sodium hydroxide. Upon the treatment, some of the cycloadducts suffered a beautiful color change to purple, and then almost instantaneously to colorless to give isomers of the cycloadducts, which were confirmed by elemental analysis and mass spectrometry. We considered two possible structures, **A** and **B** (Scheme 1), considering the stability of the intermediate anion species; the structure of the isomers was estimated to be **A** from spectroscopic data, which showed one hydroxy, one carbonyl, and no acetal carbon atom. Although the structure satisfied the IR, ^{1}H NMR, and ^{13}C NMR data, an X-ray analysis has been desired for a definite determination of the structure.[14]

In this paper, we report on a reinvestigation of the structure of the products obtained by the base-induced isomerization of the cycloadducts. A definite structure determination by a single-crystal X-ray analysis showed that the unusual *carbon-to-carbon* rearrangement of the alkyl group under a basic condition took place. A large number of rearrangements



Scheme 1. Previously proposed structure of base-induced isomerized products.

of the alkyl group under an acidic condition are known; however, those under a basic condition are rare. We thus investigated the mechanism of this unusual base-induced rearrangement in detail.

Results and Discussion

X-Ray Structure Determination. A suitable single-crystal for X-ray analysis was prepared by recrystallization of a white powder of the base-induced isomerized product **2k** obtained from the 1,3-dipolar cycloadduct **1k** of 2,5-di-*t*-butyl-*p*-benzoquinone (25DBQ) with 2,6-dichlorobenzonitrile oxide (CNO). An ORTEP drawing is depicted in Fig. 1 and selected bond distances and angles are summarized in Table 1.

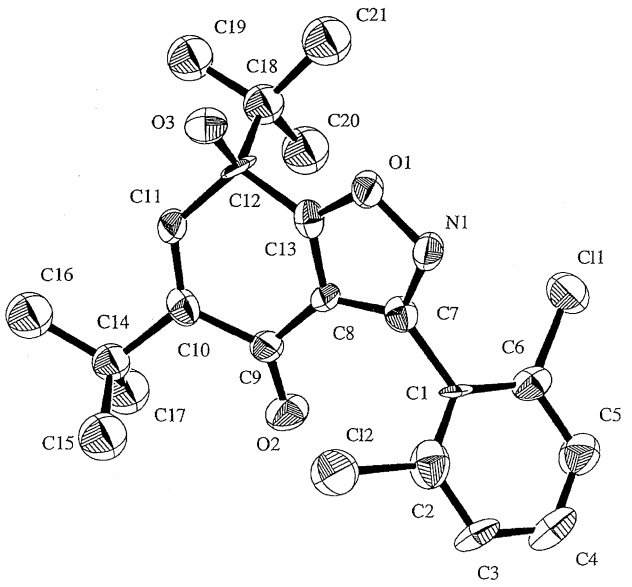


Fig. 1. ORTEP drawing of **2k**.

Table 1. Selected Bond Lengths and Angles for **2k**

a) Bond lengths (Å)			
O(1)–N(1)	1.42(1)	O(1)–C(13)	1.32(1)
O(2)–C(9)	1.23(1)	O(3)–C(12)	1.42(1)
N(1)–C(7)	1.33(1)	C(1)–C(7)	1.54(2)
C(7)–C(8)	1.40(2)	C(8)–C(9)	1.46(1)
C(8)–C(13)	1.37(2)	C(9)–C(10)	1.52(2)
C(10)–C(11)	1.36(2)	C(10)–C(14)	1.54(2)
C(11)–C(12)	1.55(2)	C(12)–C(13)	1.52(2)
C(12)–C(18)	1.58(2)		
b) Bond angles (°)			
N(1)–O(1)–C(13)	108.4(9)	O(1)–N(1)–C(7)	104.3(10)
N(1)–C(7)–C(8)	112(1)	C(7)–C(8)–C(13)	103(1)
C(9)–C(8)–C(13)	121(1)	C(8)–C(9)–C(10)	115(1)
C(9)–C(10)–C(11)	119(1)	C(10)–C(11)–C(12)	125(1)
C(11)–C(12)–C(13)	108.1(10)	O(1)–C(13)–C(8)	111(1)
C(8)–C(13)–C(12)	124(1)		

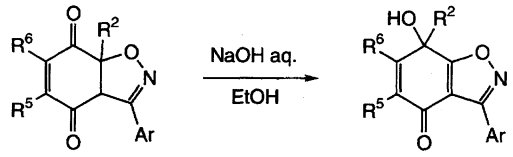
The unit cell contained two independent molecules whose structures were closely related to each other. The O(1), N(1), C(7), C(8), and C(13) atoms lay nearly on a plane. The bond lengths of C(7)–C(8) and C(8)–C(13) were 1.40(2) and 1.37(2) Å, respectively, which were the typical length of the aromatic C–C bond (1.39 Å). The bond lengths of O(1)–C(13) and N(1)–C(7) were 1.32(1) and 1.33(1) Å, respectively, which were shorter than the usual C–O (1.43 Å) and C–N (1.47—1.49 Å) single bond. The bond lengths of C(8)–C(9) and C(12)–C(13) were 1.46(1) and 1.52(2) Å, respectively, which were intermediate between the C–C single bond (1.54—1.56 Å) and the aromatic C–C bond. The bond lengths of C(9)–C(10) and C(11)–C(12) were 1.52(2) and 1.55(2) Å, respectively, which were nearly the typical C–C single bond and the C(10)–C(11) bond length of 1.36(2) Å is the C=C double bond length (1.33—1.44 Å). Consequently, this compound had the structure of 4,7-dihydrobenz[*d*]isoxazole. The C(2)–C(1)–C(7)–C(8) torsion angle of −70(1)° indicated that the benzene ring was nearly perpendicular to the isoxazole ring due to a steric hindrance of two chlorine atoms at the *o*-positions.

It was shown that one of the *t*-butyl groups in the 1,3-dipolar cycloadduct migrated from the bridgehead position to the neighboring carbonyl carbon and that aromatization from isoxazoline to isoxazole took place (Scheme 1).

Reaction of Various Cycloadducts 1 with Base. As we have reported in a previous paper,[14] this base-induced rearrangement takes place in the case of the 1,3-dipolar cycloadducts of 25DBQ and 2,6-diisopropyl-*p*-benzoquinone with CNO, and no isomerization is observed in the case of the cycloadducts having a methyl group at the bridgehead position, and even the cycloadduct of 2,6-di-*t*-butyl-*p*-benzoquinone with CNO. In order to explain the substituent effect in this base-induced reaction, we studied the reactions of various cycloadducts with sodium hydroxide. The results are given in Table 2.

In the case of cycloadducts **1a—e** having a methyl group at the bridgehead position, an instantaneous color change of their ethanolic solutions from yellow to deep purple upon the addition of aqueous sodium hydroxide was observed; however, the deep purple color of the solutions remained for a long period, and neutralization of the solution with dilute aqueous hydrochloric acid gave a complex mixture of unisolable products[15] (Entries 1—5). On the other hand, in the case of cycloadducts having a larger substituent than the methyl group, i. e., the ethyl, isopropyl, *t*-butyl, and benzyl group at the bridgehead position, except for **1l**, a deep purple color which resulted upon the addition of aqueous sodium hydroxide vanished within a few seconds (**1h—k**, **1m**, and **1n**), or at longest in about ten minutes (**1f** and **1g**), to give the corresponding rearranged products **2f—k**, **2m**, and **2n**

Table 2. Reaction of Cycloadducts **1** with Base



1 Ar = 2,6-$Cl_2C_6H_3$- **2**

Entry	Cycloadduct	R^2	R^5	R^6	2	Yield/%[a]
1[b]	**1a**	Me	Me	H	—	0
2[b]	**1b**	Me	H	Me	—	0
3	**1c**	Me	H	*i*-Pr	—	0
4	**1d**	Me	H	*t*-Bu	—	0
5	**1e**	Me	Benzo		—	0
6	**1f**	Et	Et	H	**2f**	54
7	**1g**	Et	H	Et	**2g**	86
8	**1h**	*i*-Pr	*i*-Pr	H	**2h**	89
9[b]	**1i**	*i*-Pr	H	*i*-Pr	**2i**	93
10	**1j**	*t*-Bu	Me	H	**2j**	88
11[b]	**1k**	*t*-Bu	*t*-Bu	H	**2k**	96
12[b]	**1l**	*t*-Bu	H	*t*-Bu	—	0
13	**1m**	*t*-Bu	Benzo		**2m**	48
14	**1n**	Bn	H	Bn	**2n**	85

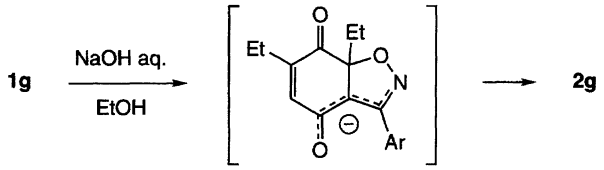
a) Isolated yield. b) Reported in Ref. 14.

upon neutralization with dilute aqueous hydrochloric acid in moderate-to-excellent yields (Entries 6—11, 13, and 14). **1l** did not afford a rearranged product, but a complex mixture[15] (Entry 12). In the case of **1l**, the *t*-butyl group on the other side of the carbonyl group sterically prevents a rearrangement of the *t*-butyl group at the bridgehead position. It is suggested that this base-induced rearrangement proceeded in those cycloadducts having a bulky substituent at the bridgehead position. The reason why the rearrangement does not proceed in the case of cycloadducts having a methyl group at the bridgehead position remains unsolved.

A mixture of **1i** and **1k** was treated with aqueous sodium hydroxide in ethanol to afford the mixture of **2i** and **2k**. No cross-migration was observed. This indicates that the alkyl group at the bridgehead position migrated in an intramolecular manner.

NMR Study of 1g with Sodium Deuteroxide. In order to observe the reaction intermediate, the ^{1}H NMR spectra of **1g** with a deuterium oxide solution of sodium deuteroxide were measured in methanol-d_4/benzene-d_6. The spectral change is shown in Fig. 2. After 5 min after the addition of sodium deuteroxide, the protons of the ethyl groups and olefin of **1g** partly remained; however, the methine proton of **1g** had completely disappeared. At this stage of the reaction, besides the signals considered to be due to the deprotonated **1g**, signals due to the rearranged product **2g** were observed. After 15 min, only signals due to the rearranged product **2g** were observed. This result reveals that, as soon as sodium deuteroxide was added, the methine proton of **1g** was abstracted to generate an anion species, which might exist as a delocalized anion leading to an alkyl rearrangement to give **2g** (Scheme 2).

Reaction of 1k with Various Bases. Either the ethanol solution of **1k** with a catalytic amount of aqueous sodium hydroxide or a THF solution of **1k** with an equimolar or a catalytic amount of potassium *t*-butoxide under a nitrogen atmosphere afforded **2k** in quantitative yield. Either solution suffered an instantaneous color change from yellow to deep purple and then to colorless. A treatment of **1k** with an equimolar amount of 1,8-bis(dimethylamino)naphthalene (proton sponge) or an excess amount of triethylamine in ethanol afforded **2k** in almost quantitative yield; however, in either case, no color change of the solution to deep purple was observed and the initial yellow color of the solution gradually became colorless. Completion of the rearrangement took a longer reaction time (55 h with proton sponge and 20 h with triethylamine). On the other hand, the reaction of **1k** with



Scheme 2.

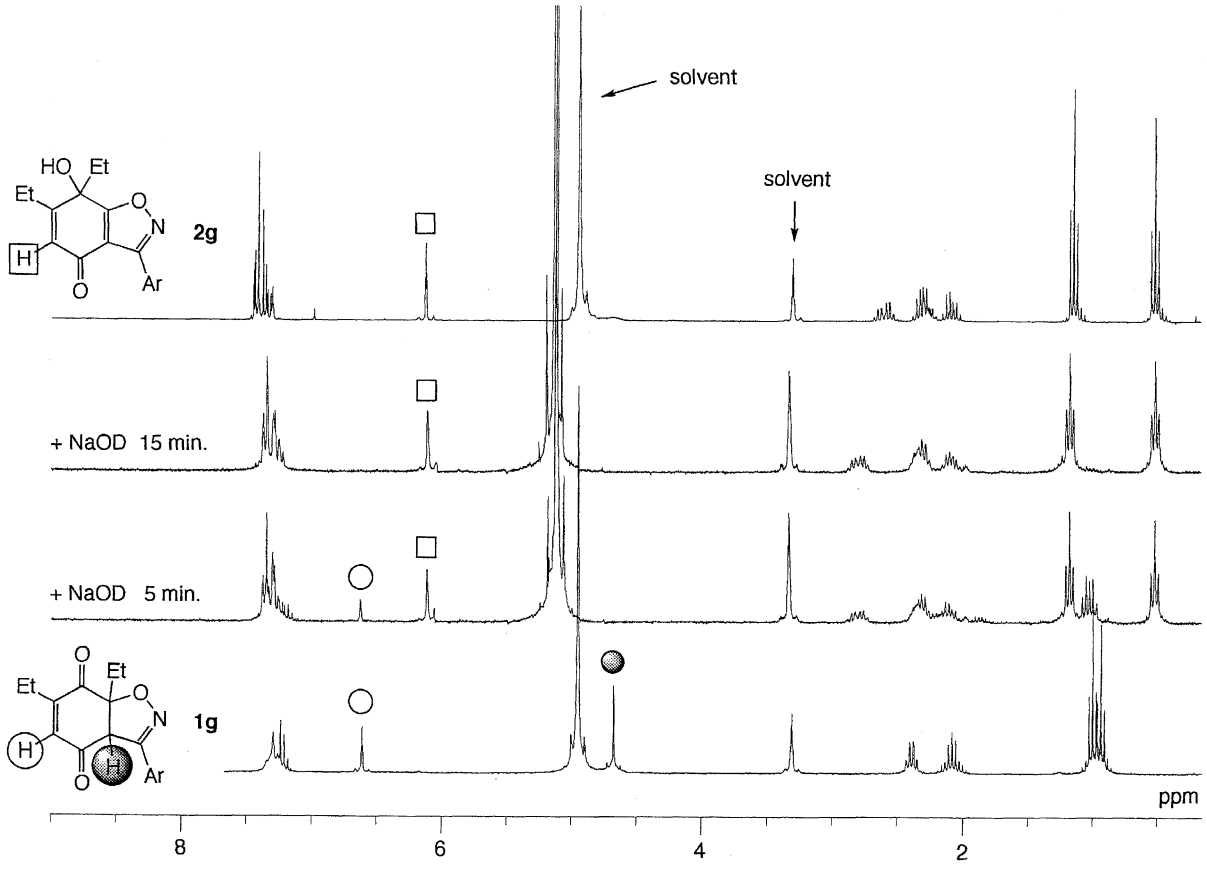


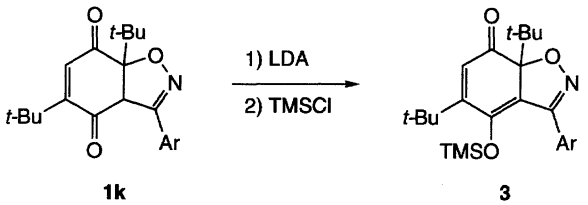
Fig. 2. ^{1}H NMR spectral change for the reaction of **1g** with NaOD/D_2O in CD_3OD/C_6D_6.

lithium diisopropylamide (LDA) at room temperature in THF under a nitrogen atmosphere brought about an instantaneous color change of the solution from yellow to deep purple, but the deep purple color remained for a prolonged period and no formation of **2k** was observed upon neutralization with dilute aqueous hydrochloric acid.

These results indicate that not only strong bases, but also week bases such as amine, effect the rearrangement, even though the reaction rate is slow and that a catalytic amount of base is enough for the base-induced rearrangement. Also, because in a THF solution the reaction of **1k** with LDA did not give the rearrangement product **2k**, it is suggested that alcohol acted as a proton source and gave the alcoholic hydrogen to the anionic species generated by the rearrangement reaction. In the case of the reaction of **1k** with potassium *t*-butoxide in THF, the *t*-butoxide ion extracted an active methine proton from cycloadduct **1k** to form *t*-butyl alcohol as a proton source.

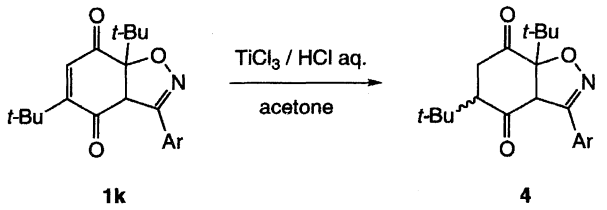
As suggested, that an anionic species is generated at the initial stage of a reaction of **1k** with a base, we attempted to trap the anionic species with an electrophile. The treatment of **1k** with LDA at −78 °C in THF and then with chlorotrimethylsilane as an electrophile afforded a trimethylsilyl enol ether derivative **3** (Scheme 3). At −78 °C the reaction of **1k** with sodium methoxide in ethanol gave a deep-purple solution, and the color was sustained for a long period. The anionic species generated from **1k** by proton abstraction was stable and no rearrangement took place at −78 °C. The anionic species is considered to exist in a deprotonated form based on the fact of the formation of the silyl enol ether **3**.

Reaction of C=C Bond Reduced Product 4 with Sodium Hydroxide. The C=C bond of the cyclohexenedione ring in **1k** was reduced with titanium(III) trichloride to give **4** according to the literature.[16] The relative configuration of **4** was still unknown, but it was obtained as a sole stereoisomer (Scheme 4). In the reaction of **4** with aqueous sodium hydroxide in ethanol, a color change of the solution from colorless to yellow was observed, but **4** was recovered in



1k **3**

Scheme 3.



1k **4**

Scheme 4.

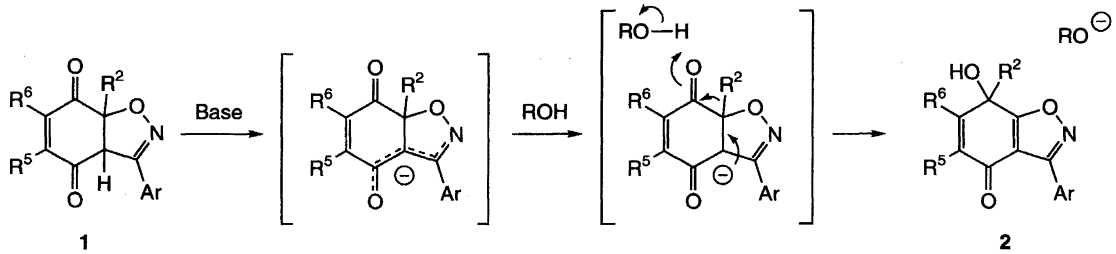
quantitative yield upon neutralization with dilute aqueous hydrochloric acid. It is appeared that the C=C bond of the cyclohexenedione ring at **1k** is necessary for a base-induced rearrangement.

Reaction Mechanism. A base-induced rearrangement is considered to proceed via an intermediacy of anionic species formed by the abstraction of the active methine proton of the cycloadducts **1** with a base (Scheme 5). In the case of cycloadducts having a bulky substituent at the bridgehead position, except for **1l**, the substituent migrates from the bridgehead position to the neighboring carbonyl carbon and a proton transfers from the hydroxy group of alcohol or water to the carbonyl oxygen to form neutral rearranged products **2**.

In this reaction, secondary and even tertiary alkyl groups migrate *from-carbon-to-carbon* under basic conditions. Alkyl migrations under basic conditions are scarce and the Favorskii reaction,[17] benzilic acid rearrangement,[18—24] and α-ketol rearrangement[18,25—28] are known. This base-induced rearrangement may be regarded as an analogue of a benzilic acid rearrangement and an α-ketol rearrangement. These two reactions take place via an intermediate **C**, in which the oxido anion is located at the α-position of the carbonyl group (Scheme 6). The substituent Z in **C** migrates to the neighboring carbonyl carbon atom. However, in our base-induced rearrangement, a delocalized anion intermediate leads to an alkyl shift to the neighboring carbonyl carbon. The driving force of this reaction is considered to be due to stabilization by aromatization from isoxazoline (cycloadduct) to isoxazole-fused *p*-quinol (rearranged product) together with extending conjugation with cyclohexadienone.

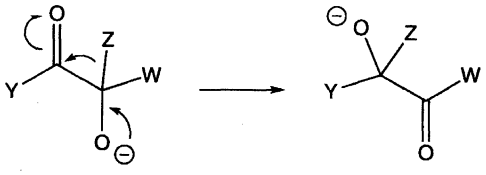
Experimental

General. The melting points were measured with a Yazawa micro melting-point measuring apparatus type BY-1 and were uncorrected. IR spectra were measured with a JASCO IR-700 spectrometer. ^{1}H NMR (270 MHz) and ^{13}C NMR (67.8 MHz) spectra were measured with a JEOL JNM GX-270 spectrometer in chloroform-*d* unless otherwise noted and chemical shifts were reported in ppm from internal tetramethylsilane. High-resolution mass spectra



1 **2**

Scheme 5. Proposed mechanism of base-induced rearrangement of **1**.



C

Scheme 6.

were measured with a JEOL JMS-DX303 spectrometer. Column chromatography was performed with Silica Gel 60 (Kanto Chemical Co., Inc.). Fremy's salt was prepared according to a published method.[29] Benzene, hexane, and diethyl ether were distilled from sodium. Dichloromethane, triethylamine, benzyl bromide, and 2, 6-dichloroanisole were distilled from calcium hydride prior to use. Tetrahydrofuran was distilled from benzophenone and sodium under a nitrogen atmosphere before use. Other reagents were obtained from commercial sources and used without further purification, unless otherwise noted.

Preparation of *p*-Benzoquinones. 2-Isopropyl-6-methyl-*p*-benzoquinone,[30] 2,6-diethyl-*p*-benzoquinone,[31] and 2-*t*-butyl-1,4-naphthoquinone[32] were prepared by the reported methods.

2,5-Diethyl-*p*-benzoquinone. 2,5-Diethyl-*p*-benzoquinone was prepared from 2,5-diethylphenol[33] by a modification of the method reported by Teuber and Rau[34] and recrystallized from pentane. Yield 49%, yellow plates, mp 76.5—78 °C; IR (KBr) 2974, 1651 (C=O), 1613, 1427, 1387, 1317, 1244, 1126, 929 cm^{-1}; ^1H NMR δ = 1.14 (t, J = 7 Hz, 6H), 2.45 (dq, J = 2, 7 Hz, 4H), 6.54 (t, J = 2 Hz, 2H); ^{13}C NMR δ = 11.7, 21.8, 131.9, 150.5, 188.1. Found: C, 73.40; H, 7.39%. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37%.

2,5-Diisopropyl-*p*-benzoquinone (7). 2,5-Diisopropyl-*p*-benzoquinone was synthesized according to Scheme 7.

2,5-Diisopropylnitrobenzene (5): 1,4-Diisopropylbenzene (18.0 g, 0.11 mol) was dropped into a vigorously stirred mixture of concd sulfuric acid (16 ml) and acetic acid (9 ml) at −3 °C during 3 min. A mixture (cooled to 0 °C with dry-ice) of conc. sulfuric acid (16 ml) and nitric acid (d = 1.38, 8 ml) was added dropwise to the emulsified mixture at −15 °C to −20 °C over a period of 2.5 h. After the addition was completed, stirring was continued for 0.5 h. The mixture was then poured into ice-water (100 ml) and extracted with hexane (100 ml×3). The hexane layer was washed with water (150 ml×2), saturated aqueous sodium hydrogencarbonate (100 ml×3), and saturated aqueous sodium chloride (100 ml) and dried over sodium sulfate. After evaporation of the solvent, the crude products were purified by column chromatography (benzene : hexane = 1 : 19) and distilled under reduced pressure to give 2,5-diisopropylnitrobenzene (**5**) as a pale yellow oil (4.71 g, 22 mmol, 22%). Bp 98—99 °C (1.5 Torr; 1 Torr = 133.322 Pa); IR (NaCl) 2966, 2872, 1526, 1460, 1412, 1366, 1278, 1068, 837, 784 cm^{-1}; ^1H NMR δ = 1.26 (d, J = 7 Hz, 6H), 1.28 (d, J = 7 Hz, 6H), 2.94 (sep, J = 7 Hz, 1H), 3.37 (sep, J = 7 Hz, 1H), 7.39 (s, 2H), 7.54 (s, 1H); ^{13}C NMR δ = 23.6, 28.2, 33.4, 121.4, 127.3, 130.8, 139.7, 147.6, 149.6. HRMS Found: m/z 207.1255. Calcd for $C_{12}H_{17}NO_2$: M, 207.1259.

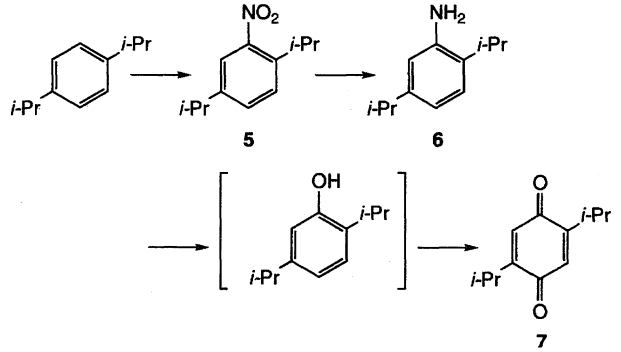
2,5-Diisopropylaniline (6): 2,5-Diisopropylnitrobenzene (**5**) (15.78 g, 76 mmol) in methanol (900 ml) was catalytically reduced with hydrogen over 5% Pd–C (4.0 g) for 24 h. After removal of the catalyst and evaporation, the residual yellow oil was purified by column chromatography (toluene) and distilled under reduced pressure to give 2,5-diisopropylaniline (**6**) as a pale yellow oil (7.32 g, 41 mmol, 54%). Bp 88.5—89 °C (1.2 Torr); IR (NaCl) 3464, 3374, 2960, 2870, 1621, 1572, 1509, 1460, 1427, 1301, 862, 811 cm^{-1}; ^1H NMR δ = 1.21 (d, J = 7 Hz, 6H), 1.24 (d, J = 7 Hz, 6H), 2.78 (sep, J = 7 Hz, 1H), 2.85 (sep, J = 7 Hz, 1H), 3.54 (br, 2H), 6.54 (d, J = 2 Hz, 1H), 6.65 (dd, J = 2, 8 Hz, 1H), 7.05 (d, J = 8 Hz, 1H); ^{13}C NMR δ = 22.3, 23.9, 27.4, 33.5, 113.8, 117.0, 125.2, 130.0, 143.1, 147.1. HRMS Found: m/z 177.1518. Calcd for $C_{12}H_{19}N$: M, 177.1518.

2,5-Diisopropyl-*p*-benzoquinone (7): 2,5-Diisopropylaniline (**6**) (7.02 g, 39 mmol) was suspended in concd sulfuric acid (50 ml) and water (12 ml) and cooled by the addition of ice (20 g). To the resulting suspension with stirring by a mechanical stirrer, sodium nitrite solution (3.00 g, 43 mmol in 7 ml of water) was added dropwise at 0 °C for 30 min. After the addition was completed, stirring was continued for 5 min. The cold diazonium solution was dropped into boiling 10% sulfuric acid (200 ml) and the resulting products were steam distilled at the same time. The distillate was extracted with diethyl ether (100 ml×3) and dried over sodium sulfate. After evaporation of the solvent, the crude products were purified by column chromatography (chloroform : hexane = 1 : 1) to give the mixture of 2,5-diisopropylphenol and 2,5-diisopropyl-*p*-benzoquinone as an orange oil (3.18 g).

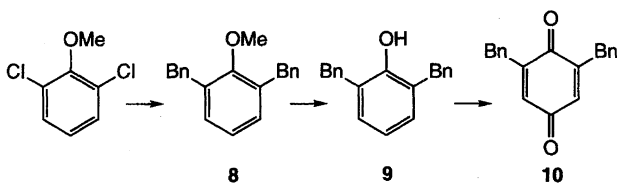
2,5-Diisopropyl-*p*-benzoquinone (**7**) was prepared from the above-mentioned mixture by a modification of the method reported by Teuber and Rau[34] and recrystallized from hexane. Yield 41% (based on **6**), yellow needles, mp 43—44 °C; IR (KBr) 2964, 2936, 1645 (C=O), 1609, 1467, 1386, 1316, 1245, 1065, 932 cm^{-1}; ^1H NMR δ = 1.13 (d, J = 6.9 Hz, 12H), 3.03 (sep, J = 6.9 Hz, 2H), 6.51 (s, 2H); ^{13}C NMR δ = 21.4, 26.4, 130.7, 154.1, 187.8. Found: C, 75.07; H, 8.46%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

2,6-Dibenzyl-*p*-benzoquinone (10). 2,6-Dibenzyl-*p*-benzoquinone (**10**) was synthesized according to Scheme 8.

2,6-Dibenzylanisole (8): Benzylmagnesium bromide was prepared from magnesium turnings (3.66 g, 151 mmol) and benzyl bromide (18.0 ml, 151 mmol) in diethyl ether (60 ml). To a suspension of dichloro[1,3-bis(diphenylphosphino)propane]nickel(II)[35] (0.162 g, 0.30 mmol) and 2,6-dichloroanisole (8.0 ml, 60 mmol) in diethyl ether (60 ml), the Grignard reagent was added for 0.5 h at 0 °C under a nitrogen atmosphere. The resulting solution was allowed



Scheme 7. Synthesis of 2,5-diisopropyl-*p*-benzoquinone (**7**).



Scheme 8. Synthesis of 2,6-dibenzyl-*p*-benzoquinone (**10**).

to warm to room temperature and stirred for 5 h and then refluxed for 12 h. The mixture was cooled in an ice bath and hydrolyzed with 10% hydrochloric acid (100 ml). The organic layer was separated and the aqueous layer was extracted with diethyl ether (100 ml×3). The combined extracts were washed with water (100 ml) and dried over magnesium sulfate. After evaporation of the solvent, the crude products were purified by column chromatography (ethyl acetate : hexane = 1 : 20) and recrystallized from hexane to give 2, 6-dibenzylanisole (**8**) (13.39 g, 46 mmol, 78%) as colorless cubes. Mp 46.5—48 °C; IR (KBr) 3064, 3024, 2942, 1493, 1463, 1451, 1432, 1248, 1083, 1010, 770, 724, 695 cm^{-1}; ^1H NMR δ = 3.59 (s, 3H), 4.04 (s, 4H), 6.96—7.30 (m, 13H); ^{13}C NMR δ = 35.8, 61.1, 124.1, 125.9, 128.4, 128.9, 129.3, 134.1, 141.0, 156.6. Found: C, 87.16; H, 7.15%. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99%.

2,6-Dibenzylphenol (9): To a solution of 2,6-dibenzylanisole (**8**) (1.73 g, 6.0 mmol) in CH_2Cl_2 (60 ml) at −78 °C, boron tribromide (0.57 ml, 6.0 mmol) in CH_2Cl_2 (6 ml) was added dropwise for 10 min. After the addition was completed, stirring was continued for 10 min. The mixture was allowed to warm to room temperature and stirred for 2 h. Then, the reaction mixture was hydrolyzed with water (12 ml) and extracted with diethyl ether (60 ml×3) and dried over sodium sulfate. After evaporation of the solvent, the residue was recrystallized from hexane to afford 2,6-dibenzylphenol (**9**) (1.11 g, 4.0 mmol, 67%) as colorless needles. Mp 32.5—33.5 °C; IR (KBr) 3530 (OH), 3026, 1601, 1494, 1452, 1165, 1079, 764, 731, 696 cm^{-1}; ^1H NMR δ = 3.95 (s, 4H), 4.60 (s, 1H), 6.81—7.30 (m, 13H); ^{13}C NMR δ = 36.6, 120.6, 126.4, 127.1, 128.6, 128.7, 129.3, 139.6, 152.1. Found: C, 87.37; H, 6.63%. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61%.

2,6-Dibenzyl-*p*-benzoquinone (10). 2,6-Dibenzyl-*p*-benzoquinone (**10**) was prepared from 2,6-dibenzylphenol (**9**) by a modification of the method reported by Teuber and Rau[34] and recrystallized from hexane. Yield 42%, yellow cubes, mp 76.5—78 °C; IR (KBr) 3032, 1656 (C=O), 1620, 1495, 1453, 1306, 1185, 1129, 940, 895, 754, 701 cm^{-1}; ^1H NMR δ = 3.74 (s, 4H), 6.28 (s, 2H), 7.11—7.36 (m, 10H); ^{13}C NMR δ = 35.4, 126.9, 128.8, 129.3, 133.1, 136.5, 148.7, 187.1, 187.8. Found: C, 83.06; H, 5.57%. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59%.

Preparation of the Cycloadducts of *p*-Quinones with 2,6-Dichlorobenzonitrile Oxide. The cycloadducts **1a**, **1b**, **1d**, **1e**, **1i**, **1j**, **1k**, and **1l** were previously prepared.[11] Other cycloadducts were synthesized by the same method.

1c: The cycloadduct **1c** was isolated by fractional crystallization of the mixture of methyl side adduct **1c** and isopropyl side adduct from benzene/hexane. Yield 27%, yellow needles, mp 125—127 °C; IR (KBr) 2970, 2932, 2876, 1682 (C=O), 1434, 1373, 1269, 1243, 1199, 1181, 966, 910, 778, 732 cm^{-1}; ^1H NMR δ = 1.16 (d, J = 6.9 Hz, 6H), 1.74 (s, 3H), 3.15 (sep, J = 6.9 Hz, 1H), 4.43 (s, 1H), 6.61 (s, 1H), 7.36 (br, 3H); ^{13}C NMR δ = 20.5, 21.0, 21.1, 28.3, 66.1, 86.5, 126.1, 128.2, 131.7, 134.3, 135.1, 135.6, 151.1, 161.6, 187.3, 191.0. Found: C, 57.97; H, 4.26; N, 4.20%. Calcd for $C_{17}H_{15}NO_3Cl_2$: C, 57.97; H, 4.29; N, 3.98%.

1f: Yield 88%, yellow orange cubes, mp 143—145 °C; IR (KBr) 2980, 2938, 2882, 1690 (C=O), 1429, 1302, 1222, 1189, 1130, 916, 869, 786, 728, 547 cm^{-1}; ^1H NMR δ = 1.00 (dd, J = 8 Hz, 3H), 1.11 (t, J = 7 Hz, 3H), 2.08 (dq, J = 8, 15 Hz, 1H), 2.27 (dq, J = 8, 15 Hz, 1H), 2.30—2.55 (m, 2H), 4.65 (s, 1H), 6.83 (t, J = 2 Hz, 1H), 7.35 (br, 3H); ^{13}C NMR δ = 7.7, 11.2, 22.8, 28.1, 62.9, 90.3, 126.3, 128.3, 131.8, 135.2, 135.6, 137.2, 151.0, 155.7, 188.8, 191.9. Found: C, 58.01; H, 3.99; N, 4.18%. Calcd for $C_{17}H_{15}NO_3Cl_2$: C, 57.97; H, 4.29; N, 3.98%.

1g: Yield 73%, yellow needles, mp 139—141.5 °C; IR (KBr) 2970, 2936, 2876, 1691 (C=O), 1669 (C=O), 1617, 1461, 1434, 1297, 1274, 1209, 1195, 930, 888, 776 cm^{-1}; ^1H NMR δ = 1.00 (dd, J = 7 Hz, 3H), 1.15 (t, J = 8 Hz, 3H), 2.08 (dq, J = 7, 14 Hz, 1H), 2.28 (dq, J = 7, 14 Hz, 1H), 2.56 (q, J = 8 Hz, 2H), 4.59 (s, 1H), 6.66 (s, 1H), 7.37 (br, 3H); ^{13}C NMR δ = 7.8, 11.4, 23.3, 28.1, 63.0, 90.0, 126.3, 128.2, 131.7, 135.1, 135.7, 136.0, 136.1, 151.2, 157.3, 187.8, 192.2. Found: C, 58.13; H, 4.23; N, 4.09%. Calcd for $C_{17}H_{15}NO_3Cl_2$: C, 57.97; H, 4.29; N, 3.98%.

1h: Yield 51%, yellow plates, mp 123—124 °C; IR (KBr) 2972, 2938, 2878, 1678 (C=O), 1464, 1433, 1295, 1216, 1191, 1046, 923, 779 cm^{-1}; ^1H NMR δ = 0.90 (d, J = 7 Hz, 3H), 1.07 (d, J = 7 Hz, 3H), 1.095 (d, J = 7 Hz, 3H), 1.102 (d, J = 7 Hz, 3H), 2.72 (qq, J = 7 Hz, 1H), 2.92 (qq, J = 7 Hz, 1H), 4.70 (s, 1H), 6.83 (s, 1H), 7.31—7.41 (m, 3H); ^{13}C NMR δ = 15.8, 17.0, 20.6, 21.6, 27.4, 32.7, 59.9, 93.0, 126.2, 128.0, 128.2, 131.7, 135.1, 135.5, 136.7, 151.0, 159.1, 188.7, 194.3. Found: C, 60.11; H, 5.03; N, 3.52%. Calcd for $C_{19}H_{19}NO_3Cl_2$: C, 60.01; H, 5.04; N, 3.68%.

1m: Yield 90%, a pale yellow powder, mp 168—169.5 °C; IR (KBr) 2968, 1693 (C=O), 1593, 1432, 1289, 1258, 1191, 912, 867, 783, 731 cm^{-1}; ^1H NMR δ = 1.09 (s, 9H), 5.10 (s, 1H), 7.22—8.11 (m, 7H); ^{13}C NMR δ = 25.9, 36.7, 61.7, 96.7, 126.6, 126.7, 126.8, 127.7, 127.9, 131.6, 133.0, 134.6, 135.1, 135.5, 135.6, 136.5, 152.0, 187.4, 195.2. Found: C, 62.51; H, 4.13; N, 3.59%. Calcd for $C_{21}H_{17}NO_3Cl_2$: C, 62.70; H, 4.26; N, 3.48%.

1n: Yield 62%, yellow cubes, mp 111—113 °C; IR (KBr) 3064, 3030, 2922, 1677 (C=O), 1559, 1495, 1453, 1431, 1270, 1195, 782, 699, 416 cm^{-1}; ^1H NMR δ = 3.38 (d, J = 14 Hz, 1H), 3.48 (d, J = 14 Hz, 1H), 3.72 (d, J = 17 Hz, 1H), 3.82 (d, J = 17 Hz, 1H), 4.64 (s, 1H), 6.27 (s, 1H), 7.08—7.31 (m, 13H); ^{13}C NMR δ = 35.9, 40.8, 62.6, 89.6, 126.0, 127.2, 127.7, 128.0, 128.9, 129.0, 129.3, 130.4, 131.7, 133.0, 135.5, 137.7, 151.5, 154.2, 187.4, 192.1. Found: C, 67.82; H, 3.75; N, 2.80%. Calcd for $C_{27}H_{19}NO_3Cl_2$: C, 68.08; H, 4.02; N, 2.94%.

General Procedure for the Base-Induced Rearrangement of Cycloadducts 1. To a solution of a cycloadduct **1** (1 mmol) in ethanol (50 ml), a 10% aqueous sodium hydroxide solution (0.4 ml) was added, and the resulting mixture was stirred for 1—10 min. The solution was then poured into dilute hydrochloric acid (100 ml). The resulting precipitate was collected by filtration and recrystallized from hexane/benzene to give **2**.

Rearranged products **2i** and **2k** were previously reported.[14]

2f: Pale brown cubes, mp 174—176 °C; IR (KBr) 3324 (OH), 2970, 2934, 2876, 1679 (C=O), 1598, 1455, 1426, 1332, 1194, 1087, 1056, 1028, 869, 787 cm^{-1}; ^1H NMR δ = 0.78 (t, J = 7 Hz, 3H), 1.10 (t, J = 7 Hz, 3H), 2.05—2.39 (m, 4H), 2.87 (br, 1H), 6.44 (s, 1H), 7.35—7.46 (m, 3H); ^{13}C NMR δ = 8.0, 12.7, 21.5, 32.7, 70.4, 114.3, 126.2, 128.0, 131.5, 135.3, 135.4, 140.6, 140.7, 142.3, 155.4, 178.8, 180.4. Found: C, 57.94; H, 4.22; N, 3.78%. Calcd for $C_{17}H_{15}NO_3Cl_2$: C, 57.97; H, 4.29; N, 3.98%.

2g: Pale brown cubes, mp 153—154 °C; IR (KBr) 3350 (OH), 2970, 2936, 2880, 1657 (C=O), 1457, 1433, 1284, 1137, 881, 787, 739 cm^{-1}; ^1H NMR δ = 0.58 (t, J = 7.6 Hz, 3H), 1.19 (t, J = 7.3 Hz, 3H), 2.06—2.66 (m, 4H), 3.56 (br, 1H), 6.12 (t, J = 1.7 Hz, 1H), 7.34—7.45 (m, 3H); ^{13}C NMR δ = 7.9, 11.8, 21.4, 31.6, 73.1, 114.6, 126.1, 126.3, 128.0, 131.6, 135.1, 135.4, 155.0, 162.0, 179.9. Found: C, 57.85; H, 4.00; N, 3.87%. Calcd for $C_{17}H_{15}NO_3Cl_2$: C, 57.97; H, 4.29; N, 3.98%.

2h: Colorless needles, mp 196—197 °C; IR (KBr) 3332 (OH), 2964, 2874, 1677 (C=O), 1593, 1454, 1429, 1306, 1194, 1074, 1046, 998, 920, 786 cm^{-1}; ^1H NMR δ = 0.91 (d, J = 6.9 Hz, 3H), 1.04 (d, J = 6.9 Hz, 3H), 1.09 (d, J = 6.9 Hz, 3H), 1.11 (d, J = 6.9 Hz, 3H), 2.47 (qq, J = 6.9 Hz, 1H), 2.89 (s, 1H), 3.02

(qq, J = 6.9 Hz, 1H), 6.47 (s, 1H), 7.34—7.46 (m, 3H); ^{13}C NMR δ = 16.7, 21.7, 22.4, 26.1, 37.3, 72.7, 114.8, 126.3, 128.0, 128.1, 131.5, 135.2, 135.4, 137.9, 147.3, 155.4, 178.9, 179.9. Found: C, 60.12; H, 4.98; N, 3.46%. Calcd for $C_{19}H_{19}NO_3Cl_2$: C, 60.01; H, 5.04; N, 3.68%.

2j: Colorless cubes, mp 217—220 °C; IR (KBr) 3342 (OH), 2972, 1680 (C=O), 1592, 1453, 1429, 1308, 1196, 1127, 1079, 996, 909, 780 cm^{-1}; ^{1}H NMR δ = 1.12 (s, 9H), 1.96 (d, J = 2 Hz, 3H), 2.67 (s, 1H), 6.69 (q, J = 2 Hz, 1H), 7.37—7.45 (m, 3H); ^{13}C NMR δ = 15.2, 25.2, 39.9, 75.0, 114.5, 126.3, 127.9, 128.0, 131.5, 135.1, 135.5, 136.7, 141.7, 155.2, 179.6, 180.8. Found: C, 59.28; H, 4.63; N, 3.76%. Calcd for $C_{18}H_{17}NO_3Cl_2$: C, 59.03; H,4.68; N, 3.82%.

2m: A pale yellow powder, mp 211.5—212.5 °C; IR (KBr) 3460 (OH), 2968, 2874, 1670 (C=O), 1599, 1563, 1459, 1431, 1290, 1195, 1150, 1049, 992, 913, 788, 755 cm^{-1}; ^{1}H NMR δ = 1.00 (s, 9H), 2.99 (br, 1H), 7.26—8.12 (m, 7H); ^{13}C NMR δ = 25.6, 41.4, 78.1, 115.4, 126.4, 126.7, 127.7, 128.1, 128.6, 131.6, 132.0, 133.1, 135.0, 135.9, 142.7, 155.7, 178.9, 180.5. Found: C, 62.77; H, 4.56; N, 3.33%. Calcd for $C_{21}H_{17}NO_3Cl_2$: C, 62.70; H, 4.26; N, 3.48%.

2n: Colorless needles, mp 192—195 °C; IR (KBr) 3486 (OH), 3060, 3030, 1667 (C=O), 1455, 1433, 1111, 1048, 792, 778, 747, 701 cm^{-1}; ^{1}H NMR δ = 3.15 (br, 1H), 3.53 (d, J = 13 Hz, 1H), 3.68 (d, J = 13 Hz, 1H), 3.82 (dd, J = 1, 17 Hz, 1H), 4.06 (dd, J = 1, 17 Hz, 1H), 5.66 (t, J = 1 Hz, 1H), 6.82—6.86 (m, 2H), 7.13—7.38 (m, 11H); ^{13}C NMR δ = 35.8, 45.8, 73.5, 115.0, 125.9, 127.2, 127.7, 128.0, 128.6, 129.0, 129.3, 129.4, 129.8, 131.6, 132.6, 135.1, 135.5, 136.6, 155.1, 158.7, 178.8, 179.0. Found: C, 67.83; H, 3.96; N, 2.71%. Calcd for $C_{27}H_{19}NO_3Cl_2$: C, 68.08; H, 4.02; N, 2.94%.

Reaction of 1k with Various Bases. With Catalytic Amount of Sodium Hydroxide: To a solution of **1k** (0.204 g, 0.5 mmol) in ethanol (25 ml), 10% aqueous sodium hydroxide solution (0.04 ml, 0.1 mmol) was added and the resulting mixture was stirred for 2 h. Then the mixture was poured into dilute hydrochloric acid (150 ml). The resulting precipitate was collected by filtration to give crude **2k** (0.204 g, 100%).

With Potassium *t*-Butoxide: To a solution of **1k** (0.204 g, 0.5 mmol) in THF (5 ml), potassium *t*-butoxide (0.1 mol dm^{-3} solution in THF, 0.5 ml, 0.05 mmol) was added and the resulting mixture was stirred for 5 min under a nitrogen atmosphere. The mixture was then poured into dilute hydrochloric acid (50 ml). The resulting precipitate was collected by filtration to give crude **2k** (0.204 g, 100%).

With Proton Sponge: To a solution of **1k** (0.205 g, 0.5 mmol) in ethanol (25 ml), 1,8-bis(dimethylamino)naphthalene (0.107 g, 0.5 mmol) in ethanol (2 ml) was added and the resulting mixture was stirred for 55 h. The mixture was then poured into dilute hydrochloric acid (100 ml). The resulting precipitate was collected by filtration to give crude **2k** (0.204 g, 100%).

With Triethylamine: To a solution of **1k** (0.208 g, 0.5 mmol) in ethanol (25 ml), triethylamine (0.7 ml, 5 mmol) was added and the resulting mixture was stirred for 20 h. The mixture was then poured into dilute hydrochloric acid (100 ml). The resulting precipitate was collected by filtration to give crude **2k** (0.215 g, 103%).

With Lithium Diisopropylamide (LDA): To a solution of **1k** (0.082 g, 0.2 mmol) in THF (10 ml), lithium diisopropylamide (2 mol dm^{-3} solution in heptane/THF/ethylbenzene, 0.15 ml, 0.3 mmol) was added and the resulting mixture was stirred for 0.5 h under a nitrogen atmosphere. The mixture was then poured into dilute hydrochloric acid (100 ml) and extracted with chloroform (50 ml×3). The extract was dried over magnesium sulfate and the solvent was evaporated to give a complicated mixture as a brown oil.

Reaction of 1k with LDA/TMSCl. To a solution of **1k** (0.123 g, 0.3 mmol) in THF (5 ml), lithium diisopropylamide (2 mol dm^{-3} solution in heptane/THF/ethylbenzene, 0.2 ml, 0.4 mmol) was added at −78 °C under a nitrogen atmosphere. After stirring for 10 min, chlorotrimethylsilane (0.1 ml, 0.8 mmol) was added and the resulting mixture was stirred for 1 h at −78 °C, and then 1 h at room temperature. The mixture was quenched with saturated aqueous ammonium chloride (5 ml). The organic layer was separated, washed with saturated aqueous sodium chloride (5 ml), and dried over sodium sulfate. After evaporation of the solvent, the crude products were purified by column chromatography (ethyl acetate : hexane = 1 : 5) to give **3** (0.091 g, 63%) as a yellow oil. IR (CCl_4) 2962, 1693 (C=O), 1581, 1559, 1430, 1367, 1253, 1194, 1071, 852 cm^{-1}; ^{1}H NMR δ = 0.39 (s, 9H), 1.149 (s, 9H), 1.154 (s, 9H), 4.88 (s, 1H), 7.25—7.39 (m, 3H); ^{13}C NMR δ = 3.4, 25.6, 30.3, 36.5, 37.4, 63.3, 97.8, 127.1, 128.6, 131.2, 135.4, 150.4, 156.6, 167.5, 191.8, 199.3.

Reduction of 1k with Titanium(III) Trichloride. To a solution of **1k** (2.04 g, 5.0 mmol) in acetone (100 ml), titanium(III) trichloride (20% solution in aqueous hydrochloric acid, 6.5 ml, 10.5 mmol) was added. After stirring for 24 h, the resulting mixture was poured into saturated aqueous sodium chloride (500 ml) and extracted with diethyl ether (150 ml×3). The extract was dried over magnesium sulfate and the solvent was evaporated. The residue was recrystallized from benzene/hexane to give **4** (1.55 g, 3.8 mmol, 76%) as a sole diastereomer. Colorless needles, mp 191—193 °C (decomp); IR (KBr) 2962, 2912, 1718 (C=O), 1476, 1431, 1368, 1316, 1095, 940, 902, 851, 782 cm^{-1}; ^{1}H NMR δ = 0.98 (s, 9H), 1.22 (s, 9H), 2.47—2.54 (m, 1H), 2.73—2.85 (m, 2H), 4.79 (s, 1H), 7.29—7.40 (m, 3H); ^{13}C NMR δ = 25.5, 27.2, 32.4, 37.3, 38.5,

Table 3. X-Ray Crystallographic Data for **2k**

	2k
(a) Crystal data	
Empirical formula	$C_{21}H_{23}NO_3Cl_2$
Formula weight	408.32
Crystal dimension/mm	0.3 × 0.3 × 0.1
Crystal system	Orthorhombic
Space group	$Pca2_1$ (No. 29)
a/Å	18.272(2)
b/Å	9.235(4)
c/Å	24.339(3)
V/Å^3	4106(1)
Z	8
D_{calcd}/g cm^{-3}	1.321
μ (Mo $K\alpha$)/cm^{-1}	3.36
F(000)	1712
(b) Data collection	
Scan method	$\omega/2\theta$
Scan rate/deg min^{-1}	16
$2\theta_{max}$/deg	55
No. of unique reflections	5274
Transmission factor	0.9397—0.9996
(c) Structure solution and refinements	
No. of data used	2222 ($I > 3\sigma(I)$)
No. of variables	406
R; R_w	0.069; 0.055
Goodness of fit indicator	2.82

55.0, 63.3, 94.8, 127.5, 128.2, 131.1, 151.3, 199.5, 202.9. Found: C, 61.46; H, 6.15; N, 3.19%. Calcd for $C_{21}H_{25}NO_3Cl_2$: C, 61.47; H, 6.14; N, 3.41%.

X-Ray Crystallographic Studies of 2k. A single crystal of **2k** was obtained by careful recrystallization from hexane. Cell-parameter measurements and reflection data collection were carried out at room temperature on a Rigaku AFC 7R four-circle diffractometer using Mo $K\alpha$ radiation monochromated by graphite (λ = 0.71069 Å). The orientation matrices and unit-cell parameters were derived from a least-squares fit of 21 ($31.8° < 2\theta < 37.1°$) machine-centered reflections. No significant decay in the intensities of three standard reflections was observed during data collections. The intensity data were corrected for the Lorentz and polarization effects and for absorption (empirical, Ψ scans). The crystallographic data are summarized in Table 3.

Structure solution and refinements were performed using the teXsan crystallographic software package.[36] The positions of the non-hydrogen atoms were determined by direct methods (SIR-88[37]) and subsequent Fourier syntheses. The carbon atoms of the *t*-Bu groups were refined isotropically. All other non-hydrogen atoms were refined anisotropic thermal parameters by full-matrix least-squares techniques. The OH hydrogen was found in the difference Fourier map, while the other hydrogen atoms were placed at the calculated positions. All hydrogen atoms were included in the final stages of refinements with fixed parameters. Refinements of the structure with an opposite polarity did not result in lower *R* values.

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