303 mg (60%) of amino alcohol **12**, identical with that described above.

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Registry No.—**1**, 22776-74-5; **2**, 26768-57-0; **5**, 26269-35-2; **6**, 53516-37-3; **7a**, 69631-64-7; **7b**, 69631-65-8; **8a**; 69631-66-9; **8b**, 69631-67-0; **9a**, 69668-45-7; **9b**, 69631-68-1; **12**, 69631-69-2; **13**, 69631-70-5; **14**, 69631-71-6; **15**, 69653-38-9; **16**, 69631-72-7; **17**, 69631-73-8; **18a**, 69631-74-9; **18b**, 69631-75-0; **19**, 69631-76-1; **20**, 69631-77-2; acetyl hypobromite, 4254-22-2; dihydropyran, 25512-65-6.

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Ortho Lithiation via a Carbonyl Synthon

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The use of the imidazolidine ring as an ortho-directing group in aryl and aralkyl metalation is described. This carbonyl synthon directs lithiation to the ortho position nearly quantitatively and affords the corresponding aromatic aldehyde on mild acid hydrolysis. Thus, lithiation of 1,3-dimethyl-2-phenylimidazolidine (**1**) with *n*-butyllithium–TMEDA, quenching with methyl iodide, and hydrolysis with 2 N HCl gave *o*-tolualdehyde (**3**) in 95% yield. The generality of this technique is discussed.

In recent years an increasing number of examples of heteroatom-facilitated ortho metalation have appeared. This process is a potentially valuable technique in synthetic organic chemistry because it allows one to prepare ortho-disubstituted aromatic compounds completely free of the isomeric meta or para isomers. The functional groups which are capable of directing metalation encompass a wide variety of structural types, including amides, amines, ethers, and halides.[1,2] One of the major limitations of the currently available directing groups is their poor versatility for further chemical transformations. One functional group which is especially difficult to obtain from these directing groups is an aromatic aldehyde. The only directing group which is easily transformed into an aromatic aldehyde is aryloxazoline.[3,4] This transformation is accomplished in two steps: formation of the quaternary salt, followed by $NaBH_4$ reduction (Scheme I).[5] We wish to report the use of the imidazolidine ring as a directing group for aromatic metalation. Not only does this group provide ortho lithiation regiospecifically and nearly quantitatively, it also gives rise to the corresponding aromatic aldehyde by mild acid hydrolysis.

The known 1,3-dimethyl-2-phenylimidazolidine (**1**) was prepared in 77% yield from benzaldehyde and *N,N'*-dimethylethylenediamine. Lithiation of an ethereal solution of **1** using 3 equiv of *n*-butyllithium *N,N,N',N'*-tetramethylethylenediamine (TMEDA) at 25 °C for 7 h gave the *o*-lithio derivative **2** in nearly quantitative yield, as shown by quenching experiments. Use of less than 3 equiv of organometallic reagent gave lower yields of **2**. When the anion solution was quenched with methyl iodide and hydrolyzed with 2 N HCl for 10 min at 25 °C *o*-tolualdehyde (**3**) was isolated in 95% yield. Similarly, quenching **2** with D_2O gave a 95% yield of *o*-deuteriobenzaldehyde (**4**). In order to examine the versatility and generality of this synthetic method we have quenched anion **2** with a variety of electrophiles. The results of these experiments are summarized in Table I.

The use of *n*-butyl bromide as the electrophile gave *o*-*n*-butylbenzaldehyde (**5**) in the moderate yield of 45%. If *sec*-butyl bromide was used, none of the expected *o*-*sec*-butyl-

Scheme I

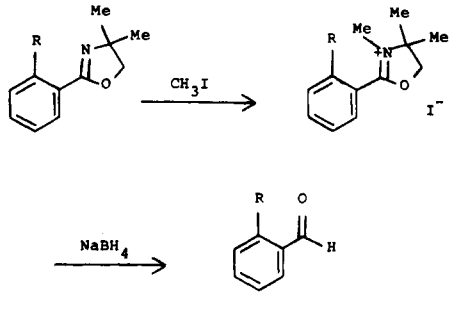

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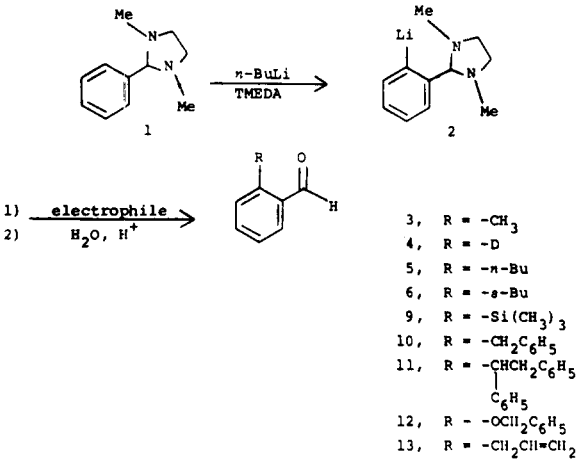
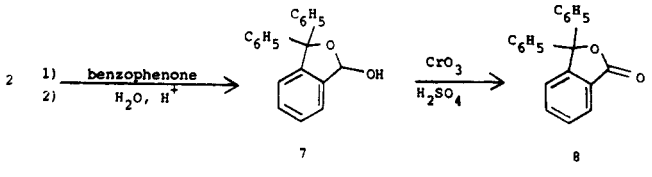
Table I. Quenching of Anion 2 with Electrophiles

product	[electrophile],[a] mmol	reaction time	yield,[b] %	obsd mp, °C	lit. mp, °C	ref
3	CH_3I (48)	10 min	95[c]	2,4-DNP, 191–194	195	9
4	D_2O (50)	3 h	95[c]	2,4-DNP, 237–239	237	9
5	*n*-BuBr (24)	24 h	45	semicarbazone, 137–139	139–140	10
6	*sec*-BuBr (24)	20 h	0			
8	benzophenone (9)	2 h	63[d]	118–119	116–117	1
9	$(CH_3)_3SiCl$ (33)	18 h	50	*p*-nitrophenylhydrazone, 192–193	192–193.5	11
11	$C_6H_5CH_2Br$ (33)	18 h	30	2,4-DNP, 148–149		
12	$C_6H_5CH_2Br$ (100)[e]	3 h	21	2,4-DNP, 173–175		
13	$CH_2{=}CHCH_2Br$ (100)	4 h	0[f]			

[a] All reactions were run on a scale of 3 mmol of 1. [b] Unless otherwise noted, yields are based on the weight of product isolated by chromatography. [c] NMR yield. [d] After oxidation with Jones reagent. [e] Inverse addition. [f] Normal or inverse addition.



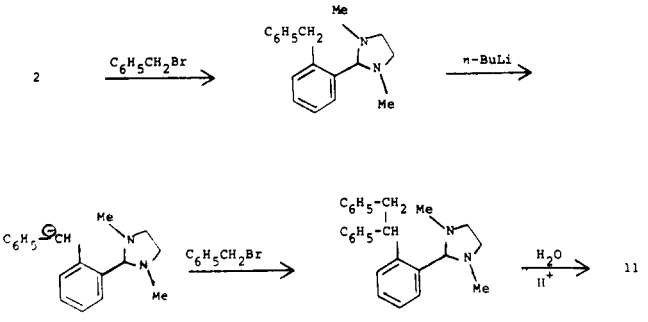
benzaldehyde (**6**) was observed. Only benzaldehyde was isolated from the reaction mixture. These results suggest that the major limitation of this directing group is steric hindrance to attack on the electrophile. Molecular models suggest that this is primarily due to the *N*-methyl groups. In these two examples there is probably competition from dehydrohalogenation reactions. However, in the absence of such competing



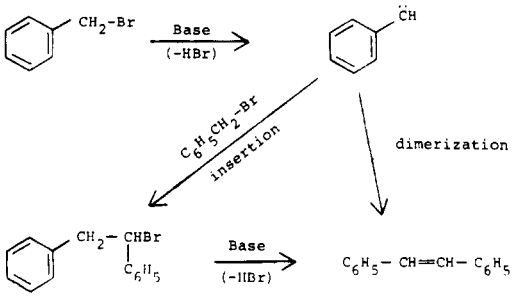
side reactions, steric hindrance does not appear to be a major concern. Quenching anion **2** with benzophenone gave hemiacetal **7** after the usual aqueous acidic workup. The crude hemiacetal was oxidized with Jones reagent to give the known lactone **8** in 63% overall yield from **1**. This yield compares very favorably with the product yields observed when the *o*-lithio derivatives of a wide variety of aromatic containing directing groups are quenched with benzophenone.[6] Treatment of **2** with chlorotrimethylsilane gave *o*-trimethylsilylbenzaldehyde (**9**) in 50% yield.

The most surprising finding of this work was the reactivity of **2** toward benzyl bromide and allyl bromide. Addition of benzyl bromide to an ethereal solution of anion **2** did not give the expected *o*-benzylbenzaldehyde (**10**). Instead, 2-(1,2-diphenylethyl)benzaldehyde (**11**) was isolated in 30% yield. This product presumably arises by the sequence of reactions outlined in Scheme II. An attempt was made to suppress the formation of **11** by an inverse addition of reactants. Addition of an ethereal solution of **2** to a large excess of benzyl bromide in anhydrous ether gave a 21% yield of *o*-benzyloxybenzaldehyde (**12**) rather than the expected *o*-benzylbenzaldehyde (**10**). This product presumably arises by an initial reaction of anion **2** with molecular oxygen. The reaction was run under nitrogen atmosphere and all reagents and solvents were purified and stored under nitrogen. The fact that this product was not observed during the normal addition was probably due to the much smaller amount of solvent and reagents used. No attempt was made to eliminate this product by rigorously degassing solvent and reagents.

Scheme II



Scheme III



Quenching anion **2** with benzyl bromide produces a large number of products according to analysis by thin-layer chromatography. We have attempted to identify some of these products in order to explain the low yield of compound **11**. The inverse addition reaction was repeated on a large scale and the crude reaction mixture was purified initially by fractional distillation. Further purification by preparative layer chromatography and sublimation gave a 2% yield of *trans*-stilbene and a 1.2% yield of bibenzyl. It is well known that the reaction of numerous organometallic reagents with alkyl halides can proceed by electron-transfer reactions.[13,14] The intervention of radical intermediates is especially important in reactions of organolithium reagents. The formation of bibenzyl is therefore readily explained by an electron-transfer process involving the formation of relatively stable benzyl radicals. *trans*-Stilbene is probably formed from phenylcarbene by one of the two routes outlined in Scheme III. We were interested

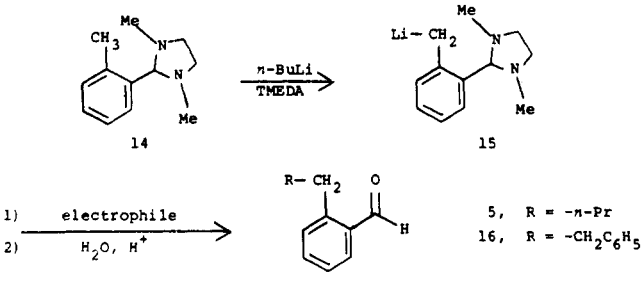
Table II. Quenching of Anion 15 with Electrophiles

product	[electrophile],[a] mmol	reaction time, h	yield,[b] %	obsd mp, °C	lit. mp, °C	ref
5	*n*-PrBr (33)	1	90	semicarbazone, 137–139	139–140	10
16	$C_6H_5CH_2Br$ (33)	1	72	2,4-DNP, 176–178	178–179	12

[a] All reactions were run on a scale of 3 mmol of **14**. [b] Yield of aldehyde isolated by chromatography.

in determining whether phenylcarbene was formed by reaction of benzyl bromide with excess *n*-butyllithium or with anion **2**. A control reaction was run in which an ethereal solution of *n*-butyllithium/TMEDA was added to a large excess of benzyl bromide in anhydrous ether. Workup of the reaction by the above procedure gave a 19.5% yield of bibenzyl. There was no evidence for the formation of stilbene. Thus it appears that phenylcarbene is formed primarily from sterically hindered anion **2**. Finally, addition of allyl bromide to **2** by either the normal or inverse model of addition gave, after aqueous acidic workup, only benzaldehyde. While no attempt was made to identify any of the other reaction products it seems reasonable to assume that the failure of this reaction to produce *o*-allylbenzaldehyde (**13**) is also due to the formation of free radical and carbene intermediates.

It has been demonstrated with *o*-toluamides[7,8] and *o*-methylaryloxazolines[3,4] that deprotonation of the aromatic



methyl group can be accomplished in high yields. Similarly we have found that 1,3-dimethyl-2-*o*-tolylimidazolidine (**14**) is easily converted to the corresponding lithio derivative **15**, and that **15** readily undergoes alkylation with alkyl halides. The results of these experiments are shown in Table II. Alkylation of **15** with benzyl bromide gave *o*-phenethylbenzaldehyde (**16**) in 72% yield, while alkylation using *n*-propyl bromide gave **5** in 90% yield. These results indicate that alkylation of **15** is influenced by steric factors to a much smaller degree than is lithio derivative **2**.

The most attractive feature of this new directing group is the ease with which it is converted into an aldehyde. The great versatility of the aldehyde functional group suggests that the imidazolidine ring could be a very useful ortho-directing group in organic synthesis.

Experimental Section

General. IR spectra were recorded on a Perkin-Elmer 457 spectrometer as KBr pellets (solids) or as thin films (liquids). NMR spectra were recorded on either a Perkin-Elmer R20A or a Varian EM 360A spectrometer, using $CDCl_3$ as solvent and Me_4Si as internal standard. Melting points were obtained on a Mel-Temp melting point apparatus and are uncorrected. Elemental analyses were by Galbraith Laboratories, Knoxville, Tenn.

All preparative layer chromatography was done on Analtech silica gel plates. All column chromatography was done on silica gel in a homemade medium-pressure (60–100 psi) liquid chromatograph. *n*-Butyllithium (1.6 M in hexane) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were purchased from Aldrich Chemical Co. The TMEDA was distilled from sodium metal and stored over Linde 4 Å molecular sieves. Diethyl ether was distilled from sodium metal immediately before use.

Preparation of *o*-Lithio Derivative 2. General Procedure for Quenching 2 with Electrophiles. A solution of 528 mg (3 mmol) of 1 and 1.35 mL (9 mmol) of TMEDA in 20 mL of anhydrous ether was treated with 5.7 mL of a 1.6 M solution of *n*-butyllithium in hexane (9 mmol) under a nitrogen atmosphere. The solution was stirred for 7 h at 25 °C and quenched with one of the electrophiles listed in Table I. After being stirred for the time indicated in Table I, the mixture was hydrolyzed with 50 mL of 2 N HCl for 10 min at 25 °C. The mixture was extracted with three 25-mL portions of $CHCl_3$, and the combined organic extracts were dried ($MgSO_4$) and concentrated to give crude product as an oil.

***o*-Tolualdehyde (3).** Quenching anion **2** with methyl iodide and workup by the general procedure above gave **3** as a pale yellow oil. NMR integration indicated 95% alkylation.

***o*-Deuteriobenzaldehyde (4).** The crude product obtained by quenching anion **2** with D_2O and workup by the procedure above was dissolved in 5 mL of CH_2Cl_2 and filtered through a short column of silica gel. The filtrate was concentrated to give 323 mg (100% material balance) of **4** as a colorless liquid. NMR integration indicated deuterium incorporation in excess of 95%.

***o*-*n*-Butylbenzaldehyde (5).** Quenching anion **2** and *n*-butyl bromide and workup by the general procedure outlined above gave crude **5** as a dark green oil. Purification by preparative layer chromatography (CCl_4 as eluent) gave 219 mg (45%) of **5** as a pale yellow oil.

***o*-Trimethylsilylbenzaldehyde (9).** Quenching anion **2** with chlorotrimethylsilane and workup by the general procedure outlined above gave crude **9** as a brown oil. Purification by preparative layer chromatography (CCl_4 as eluent) gave 267 mg (50%) of **9** as a pale yellow oil.

Preparation of γ-Lactone 8. After benzophenone was added to the solution of anion **2** and stirred for 2 h, the turquoise mixture was treated with 20 mL of H_2O and stirred to dissolve the solid precipitate. The mixture was adjusted to pH 6 with glacial acetic acid and then to pH 1 with 2 N HCl, and washed with two 50-mL portions of ether to remove unreacted benzophenone and butyldiphenylcarbinol byproduct. The mixture was extracted with two 30-mL portions of $CHCl_3$, and the organic extracts were dried (Na_2SO_4) and concentrated to give 750 mg of hemiacetal **7** as a maroon oil.

The hemiacetal was dissolved in 50 mL of acetone and oxidized with 2 mL of 4 N Jones reagent. After 15 min, 1.0 g of sodium bisulfite was added and stirring was continued until the orange color of the reagent had disappeared. The acetone solution was decanted from the solid and the solid was washed with an additional 25 mL of acetone. The combined acetone fractions were concentrated to a volume of 5 mL and dissolved in 50 mL of ether. The ether solution was washed with two 25-mL portions of 0.1 N NaOH, dried (Na_2SO_4), and concentrated to give 608 mg of a crystalline solid. Recrystallization from CCl_4–hexane gave 472 mg of **8** as an off-white solid, mp 118–119 °C (lit.[1] mp 116–117 °C). The mother liquor was concentrated and the residue was purified by preparative layer chromatography (benzene as eluent) to give an oil, which was crystallized from CCl_4–hexane to give an additional 66 mg of **8**, mp 115–116 °C, to raise the total overall yield ot 63%.

Reaction of 2 with Benzyl Bromide. Normal Addition. Preparation of 2-(1,2-Diphenylethyl)benzaldehyde (11). The crude product obtained by quenching anion **2** with benzyl bromide and workup by the general procedure outlined above was concentrated for 24 h at a pressure of 0.5 mm Hg to remove excess benzyl bromide, affording a viscous green oil. Purification by medium-pressure column chromatography (hexane-0.5% acetone as eluent) gave 260 mg (30%) of **11** as a viscous pale yellow oil: NMR δ 10.13 (s, 1), 7.95–6.88 (m, 14), 5.49 (t, 1, J = 8 Hz), 3.47–3.20 (m, 2); IR 1690 cm^{-1} (C=O).

A sample of **11** was converted to the 2,4-DNP derivative for further characterization, mp 148–149 °C.

Anal. Calcd for $C_{27}H_{22}N_4O_4$: C, 69.52; H, 4.75; N, 12.01. Found: C, 69.53; H, 4.87; N, 12.06.

Reaction of 2 with Benzyl Bromide. Inverse Addition. Preparation of *o*-Benzyloxybenzaldehyde (12). The solution of anion **2** prepared by the general metalation procedure was added dropwise over a 30-min period to a solution of 12 mL (0.1 mol) of benzyl bro-

mide in 150 mL of anhydrous ether. The general workup procedure was then followed to give a yellow liquid which was concentrated for 18 h at a pressure of 0.5 mm Hg to remove excess benzyl bromide, affording a dark amber liquid. Purification by preparative layer chromatography (CCl_4 as eluent) gave 134 mg (23%) of **12** as a pale yellow oil: NMR δ 10.61 (s, 1), 8.00–6.90 (m, 9), 5.18 (s, 2); IR 1690 cm^{-1} (C=O).

A sample of **12** was converted to the 2,4-DNP for further characterization, mp 173–175 °C.

Anal. Calcd for $C_{20}H_{16}N_4O_5$: C, 61.22; H, 4.11; N, 14.28. Found: C, 61.08; H, 4.10; N, 14.26.

Large-Scale Reaction of 2 with Benzyl Bromide. Inverse Addition. Isolation of *trans*-Stilbene and Bibenzyl. A solution of 4.22 g (24 mmol) of **1** and 10.80 mL (72 mmol) of TMEDA in 150 mL of anhydrous ether was treated with 45.6 mL of a 1.6 M solution of *n*-butyllithium in hexane (72 mmol). The solution was stirred for 7 h at 25 °C and added dropwise over a 50-min period to a solution of 25 mL (0.21 mol) of benzyl bromide in 350 mL of anhydrous ether. The resultant mixture was stirred for 1.5 h and hydrolyzed with 2 N HCl for 1 h at 25 °C. The ether layer was washed successively with 100 mL of H_2O, 100 mL of 5% $NaHCO_3$, and 100 mL of H_2O, dried (Na_2SO_4), and concentrated to give a brown liquid. Excess benzyl bromide was removed by distillation, bp 60–66 °C (2 mm Hg) (lit.[15] bp 114 °C (15 mm Hg)).

Continued distillation at 0.1 mm Hg yielded two fractions: fraction A, bp 85–115 °C, 698 mg of a brown oil; fraction B, bp 115–125 °C, 1.687 g of an oily solid. Fraction A was purified by preparative layer chromatography (hexanes as eluent) to give 453 mg of an oily solid. This solid was washed with a small amount of *tert*-butyl alcohol and sublimed at 45 °C and 0.025 mm Hg to give 152 mg (1.2%) of bibenzyl as a colorless crystalline solid, mp 52–55 °C (lit.[15] mp 52.5 °C). Fraction B was washed with a small amount of *tert*-butyl alcohol to give 439 mg of a crystalline solid. This solid was further purified by preparative layer chromatography (hexanes as eluent) and sublimation at 45°C and 0.025 mm Hg to give 259 mg (2%) of *trans*-stilbene as a colorless crystalline solid, mp 119–123 °C (lit.[15] mp 124 °C).

Reaction of *n*-Butyllithium with Benzyl Bromide. Isolation of Bibenzyl. A solution of 22.8 mL of 1.6 M *n*-butyllithium (36 mmol) and 5.40 mL (36 mmol) of TMEDA in 75 mL of anhydrous ether was added dropwise over a 1-h period to a solution of 12.5 mL (0.1 mol) of benzyl bromide in 150 mL of anhydrous ether. The resultant mixture was stirred for 1.5 h and hydrolyzed with 2 N HCl for 1 h at 25 °C. The ether layer was washed successively with 100 mL of H_2O, 100 mL of 5% $NaHCO_3$, and 100 mL of H_2O, dried (Na_2SO_4), and concentrated to give a pale yellow liquid. Excess benzyl bromide was removed by distillation, bp 61–66 °C (2 mm Hg) (lit.[15] bp 114 °C (15 mm Hg)).

Continued distillation at 0.05 mm Hg yielded only a single fraction, bp 80–119 °C, as an oily solid. This solid was washed with a small amount of *tert*-butyl alcohol and dried to give 1.27 g (19.5%) of bibenzyl as a colorless crystalline solid, mp 52–53.5 °C (lit.[15] mp 52.5 °C).

1,3-Dimethyl-2-*o*-tolylimidazolidine (14). A solution of 11.5 mL (0.1 mL) of *o*-tolualdehyde, 10.6 mL (0.11 mol) of *N,N'*-dimethylethylenediamine, and a catalytic amount of *p*-toluenesulfonic acid in 300 mL of benzene was heated to reflux with removal of water via a Dean-Stark trap. The theoretical amount of water (1.8 mL) was removed after 5 h. The solution was cooled and concentrated to give a light brown oil. Distillation gave 15.6 g (84%) of **14** as a colorless liquid: bp 84–87 °C (1.6 mm Hg); NMR δ 7.70–7.13 (m, 4), 3.70 (s, 1), 3.50–3.23 (m, 2), 2.70–2.52 (m, 2), 2.44 (s, 3), 2.18 (s, 6).

Anal. Calcd for $C_{12}H_{18}N_2$: C, 75.74; H, 9.54; N, 14.72. Found: C, 76.19; H, 9.74; N, 15.08.

Preparation of *o*-Lithio Derivative 15. General Procedure for Quenching 15 with Electrophiles. A solution of 570 mg (3 mmol) of **14** and 1.35 mL (9 mmol) of TMEDA in 20 mL of anhydrous ether was treated with 5.7 mL of a 1.6 M solution of *n*-butyllithium in hexane (9 mmol) under a nitrogen atmosphere. After stirring 1.5 h at 25 °C the solution was quenched with one of the electrophiles listed in Table II, stirred for 1 additional h, and hydrolyzed with 50 mL of 2 N HCl for 10 min at 25 °C. The mixture was extracted with three 25-mL portions of ether, and the combined ether extracts were dried (Na_2SO_4) and concentrated to give crude product as an oil.

2-(2-Phenethyl)benzaldehyde (16). Quenching anion **15** with benzyl bromide and workup by the procedure described above gave 1.07 g of crude **16**. Purification by medium-pressure column chromatography (CCl_4–1% acetone as eluent) gave 456 mg (72%) of **16** as a colorless oil.

***o*-*tert*-Butylbenzaldehyde (5).** Quenching anion **15** with *n*-propyl bromide and workup by the procedure described above gave 571 mg of crude **5**. Purification by preparative layer chromatography (CCl_4–1% acetone as eluent) gave 440 mg (90%) of **5** as a pale yellow oil.

Registry No.—**1,** 23229-37-0; **2,** 69621-94-9; **3,** 529-20-4; **3** · DNP, 1773-44-0; **4,** 66154-03-8; **4** · DNP, 69621-95-0; **5,** 59059-42-6; **5** · semicarbazone, 69621-96-1; **6,** 31036-46-1; **7,** 69621-97-2; **8,** 596-29-2; **9,** 17887-55-7; **9** · *p*-nitrophenylhydrazone, 17922-39-3; **11,** 69621-98-3; **11** · DNP, 69621-99-4; **12,** 5896-17-3; **12** · DNP, 69622-00-0; **13,** 62708-42-3; **14,** 69622-01-1; **15,** 69622-02-2; **16,** 32832-96-5; **16** · DNP, 69622-03-3; methyl iodide, 74-88-4; water-d_2, 7789-20-0; butyl bromide, 109-65-9; *sec*-butyl bromide, 78-76-2; benzophenone, 119-61-9; trimethylsilyl chloride, 75-77-4; benzyl bromide, 100-39-0; 2-propenyl bromide, 106-95-6; porpyl bromide, 106-94-5; bibenzyl, 103-29-7; *trans*-stilbene, 103-30-0; *N,N'*-dimethylethylenediamine, 110-70-3.

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