pressured to 700 psi with ethylene and heated with magnetic stirring at the indicated temperatures. The extent of reaction was measured by VPC until no more of the starting olefinic halide remained. Yields were determined by using the *n*-nonane as the internal standard (10 ft × 0.25 in., 20% DC-550, 140°). Products were identified by comparison of their VPC retention times with those of authentic samples and by mass spectral and NMR analyses of samples isolated by VPC.

Reaction of (*E*)-1-Hexene-1-boronic Acid with Methyl Acrylate. (*E*)-1-Hexene-1-boronic acid (0.64 g, 5 mmol), 10 ml of methyl acrylate, and 2 ml of triethylamine were stirred magnetically at 0° in an ice bath and 1.12 g (5 mmol) of $Pd(OAc)_2$ was added. The bath was allowed to gradually come to room temperature and the reaction mixture was stirred overnight at room temperature.

The mixture was then centrifuged and the residue was washed several times with ether. The supernatant liquids were combined and put through an alumina column, eluting with 1 l. of ether. Removal of the ether, methyl acrylate, and triethylamine under reduced pressure left 0.697 g of a pale yellow oil which was identified by its NMR spectrum as essentially pure methyl (*E,E*)-2,4-nonadieneoate (82%).

Reaction of (*Z*)-1-Hexene-1-boronic Acid with Methyl Acrylate. (*Z*)-1-Hexene-1-boronic acid (0.256 g, 2 mmol), 5 ml of methyl acrylate, 1 ml of triethylamine, and 0.448 g (2 mmol) of $Pd(OAc)_2$ were allowed to react and the product was isolated as in the preceding experiment. There was obtained 0.282 g of product which, by NMR and VPC analysis, was found to be mainly (*E,Z*)-2,4-hexadienoate (no *E,E* ester was present). The residue was dissolved in ether with 0.154 g (1 mmol) of biphenyl and the yield of the *E,Z* ester was determined by VPC (5 ft × 0.25 in., 20% DEGS, 140°) to be 70%. A pure sample of the ester was isolated by VPC.

Acknowledgment. This research was supported by a grant from the National Science Foundation.

Registry No.—1-Iodo-1-hexyne, 1119-67-1; (*Z*)-1-hexene-1-boronic acid, 54354-55-1; tri-*n*-butyl borate, 688-74-4; (*E*)-1-hexene-1-boronic acid, 42599-18-8; $Pd[P(C_6H_5)_3]_2(OAc)_2$, 14588-08-0.

References and Notes

(1) R. F. Heck and J. P. Nolley, Jr., *J. Org. Chem.*, **37**, 2320 (1972).
(2) H. A. Dieck and R. F. Heck, *J. Am. Chem. Soc.*, **96**, 1133 (1974).
(3) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5518 (1968).
(4) G. Zweifel and A. B. Steele, *J. Am. Chem. Soc.*, **89**, 2753 (1967).
(5) G. Zweifel and H. Arzoumanian, *J. Am. Chem. Soc.*, **89**, 5086 (1967).
(6) H. C. Brown and S. K. Gupta, *J. Am. Chem. Soc.*, **94**, 4370 (1972).
(7) H. C. Brown, T. Hamaoka, and N. Ravindran, *J. Am. Chem. Soc.*, **95**, 6456 (1973).
(8) G. J. Martin and M. L. Martin, *Bull. Soc. Chim. Fr.*, 1636 (1936).
(9) P. Caubere, *Bull. Soc. Chim. Fr.*, 144 (1964).
(10) G. E. Ficken, H. France, and R. P. Linstead, *J. Chem. Soc.*, 3730 (1954).

Organosilicon Compounds. XX. Synthesis of Aromatic Diamines via Trimethylsilyl-Protecting Aniline Intermediates

J. Richard Pratt,[1] W. Dale Massey, Frank H. Pinkerton, and Shelby F. Thames*

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39401

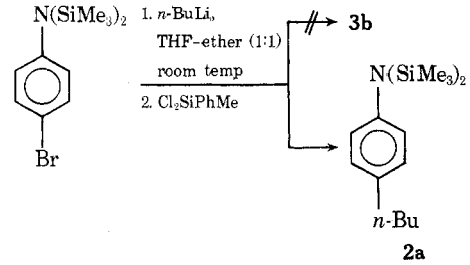
Received September 12, 1974

A synthetic approach using a trimethylsilyl protecting group was employed to produce silicon- and diketo-containing diamines. Thus, the halogen–metal interchange of *N,N*-bis(trimethylsilyl)bromoanilines with *n*-butyllithium in ether produced the corresponding lithium derivatives, which were treated with dichloro-substituted silanes or dinitriles to afford the *N,N*-bis(trimethylsilyl)silicon-containing dianilines or the corresponding lithioimines, respectively. Hydrolysis removed the trimethylsilyl-protecting groups and converted the lithioimines to the corresponding carbonyl compounds to afford the free diamines.

Two investigators[2,3] have reported the synthesis of substituted anilines by treating, e.g., *p*-bromo-*N,N*-bis(trimethylsilyl)aniline with *n*-butyllithium, followed by treating the resulting lithium derivative with chlorotrimethylsilane to afford *p*-trimethylsilyl-*N,N*-bis(trimethylsilyl)aniline. The trimethylsilyl moieties blocked the amine nitrogen atom to the effects of *n*-butyllithium, since this silicon–nitrogen bond was inert to *n*-butyllithium under the reaction conditions, yet allowed the more selective halogen–metal interchange to produce a highly reactive organolithium reagent. After the reaction with chlorotrimethylsilane, hydrolysis of the trimethylsilyl protecting groups afforded *p*-trimethylsilylaniline. This same technique was employed by Greber[4] to prepare several bis(*p*-aminophenyl)methylsiloxane oligomers. The need for aromatic diamines containing flexiblizing groups for the synthesis of thermally stable polyamides and polyimides led to the expansion of this protecting technique to prepare silicon- and diketo-containing diamine precursors.

Scheme I describes the preparation of both meta and para isomers of several silicon-containing diamines. *p*- or *m*-Bromo-*N,N*-bis(trimethylsilyl)aniline (**1** or **5**) was prepared by treating the corresponding bromoaniline (1 mol) with *n*-butyllithium (2.3 mol) in THF at room temperature, followed by chlorotrimethylsilane (2.3 mol). A maximum yield of reproducibly pure product was obtained when this excess of *n*-butyllithium–chlorotrimethylsilane was utilized. Without this excess an azeotrope, e.g., of **1** and *p*-bromo-*N*-trimethylsilylaniline, was invariably formed.

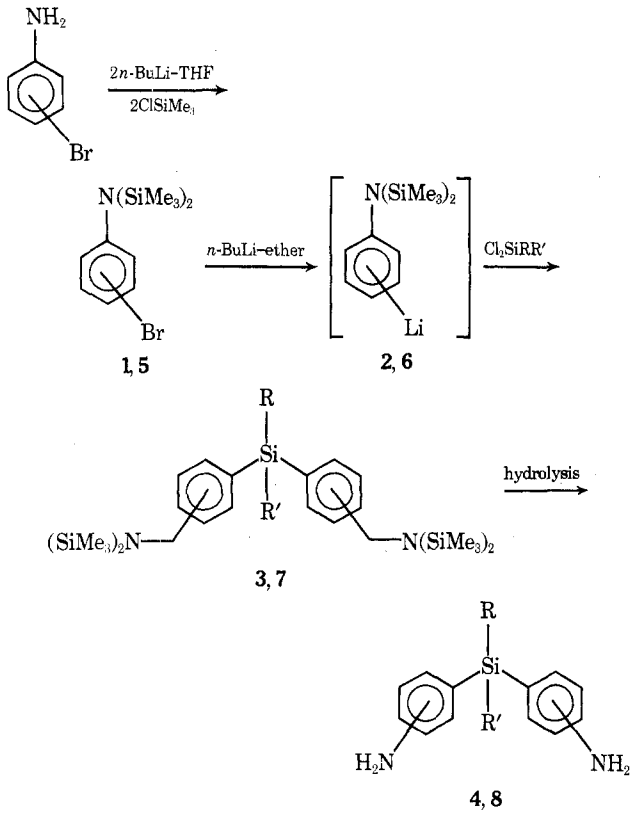
A halogen–metal interchange of the bromine atoms of **1** or **5** with *n*-butyllithium in ether at 0° was found to produce the lithium derivatives **2** or **6** most readily. These lithio species were treated in situ with the appropriately substituted dichlorosilanes to form the fully silylated diamines **3** or **7**. The attempted preparation of **2** (and subsequent conversion to **3b**) in THF–ether (1:1) at room temperature afforded 4-(*n*-butyl)-*N,N*-bis(trimethylsilyl)aniline (**2a**) in 42% yield.



2a

The fully trimethylsilylated diamines (**3** and **7**) were readily hydrolyzed to their silicon-containing free diamines (**4** and **8**) in wet acetone or with a saturated solution of an-

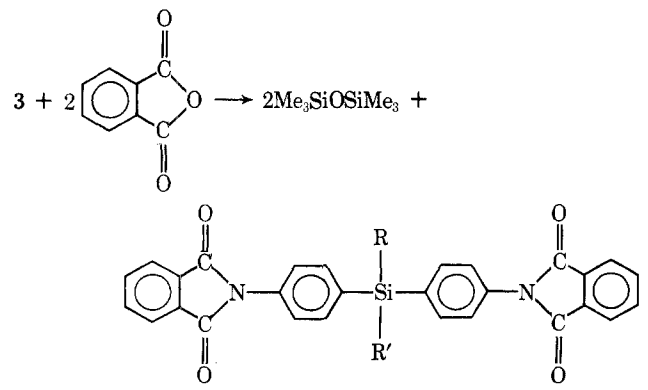
Scheme I



a, R = R′ = Me
b, R = Me; R′ = Ph
c, R = R′ = Ph
1-4 para isomeric sequence
5-8 meta isomeric sequence

hydrous HCl in ether, followed by neutralization. Pure **4a** was prepared by the hydrolysis of an analytical sample of **3a** in wet acetone, followed by drying with anhydrous $MgSO_4$ and molecular sieves and removal of all volatiles in vacuo at room temperature. This alternate procedure was required only for **4a** because of its decomposition during fractionation at reduced pressure to afford a small yield of impure **4a** and considerable resinous decomposition products. The attempted solvolysis of **3a** in refluxing ethanol or methanol afforded good yields of aniline. These findings substantiate an earlier report by Kipping and Cusa[5] of the instability of certain *p*-aminophenylsilanes.

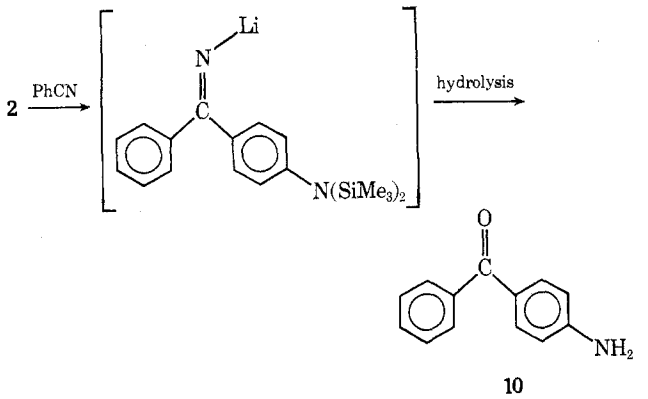
In addition, as previously reported,[6] the fully silylated diamines (**3**) were readily imidized directly to their di-



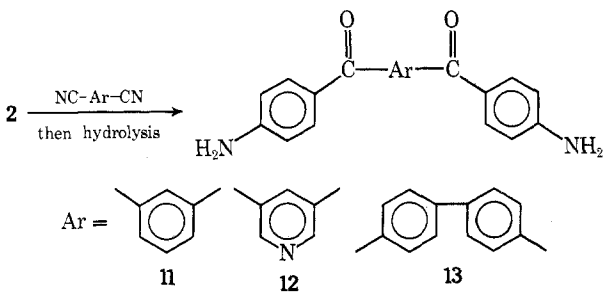
R = R′ = Me
R = Me; R′ = Ph
R = R′ = Ph

imides on treatment with 2 mol of phthalic anhydride and with loss of hexamethyldisiloxane.

Organolithium reagents are known to readily add to aromatic nitriles to form lithioimines, which can be hydrolyzed to ketones.[7] That trimethylsilyl-protected aniline organolithium reagents likewise react with nitriles was demonstrated in a model compound synthesis. *p*-Aminobenzophenone (**10**) was prepared by treating **2** with benzonitrile.

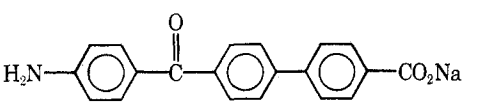


Likewise, the reaction of **2** with three aromatic dinitriles, 1,3-dicyanobenzene, 3,5-dicyanopyridine, and 4,4′-dicyanobiphenyl afforded their dilithioimines, which were hydrolyzed to the free diamines, 1,3-bis(4-aminobenzoyl)benzene (**11**), 3,5-bis(4-aminobenzoyl)pyridine (**12**), and 4,4′-bis(4-aminobenzoyl)biphenyl (**13**), respectively. Considerable by-



product formation accompanied the preparation of **12**. The reaction of **2** with 2,6-dicyanopyridine afforded a black, oily material which was not identified.

The only by-product from the preparation of **13** was 4-(4-aminobenzoyl)-4′-biphenylcarboxylic acid sodium salt.



When crude **13** was crystallized from acetone containing a few drops of dilute acid, the product displayed a carboxylic acid absorption in the ir.[8] Likewise, when precipitated from basic acetone solution, crude **13** displayed two NH_2 lines in the NMR. Repeated crystallization from pyridine–water (2:1) and acetone–water (1:1) afforded yellow crystals of pure **13**, which displayed only one NH_2 NMR absorption. The by-product would be expected to arise from incomplete addition of **2** to both nitrile moieties of 4,4′-dicyanobiphenyl, followed by acid hydrolysis of unreacted nitrile moiety to the carboxylic acid.

In summary, we have reported the reaction of two *N,N*-bis(trimethylsilyl)organolithium reagents with chlorosilanes and nitriles to produce, after hydrolysis and neutralization, new silicon- and keto-containing aromatic diamines. This technique in principle allows the synthesis of a number of isomers not obtainable by conventional electrophilic aromatic substitution reactions.

Table I[m]
Experimental Summary

Compd	Yield, %	Mp, °C	Bp, °C (mm)	nD (°C)	NMR, δ	Ir, cm^{-1}	Formula
1[n]	61		155.5–158 (23)	1.5129 (28)	7.3 (2 H, d, aryl CH ortho to Br), 6.7 (2 H, d, aryl CH ortho to N), 0.0 (18 H, s, silyl CH_3)	1252, 840 (silyl CH_3)[f]	$C_{12}H_{22}BrSi_2$
2a	42		97 (0.34)	1.4830 (25)	6.75 and 7.0 (2 H each, d each, aryl CH), 2.55 (2 H, t, methylene α to ring), 0.75–1.9 (7 H, m, remaining aliphatic protons of n-butyl), 0.05 (18 H, s, silyl CH_3)	1250, 825 (silyl CH_3), 2940 (strong, complex alkyl CH)[f]	$C_{16}H_{31}NSi_2$
3a[o]	70		154.5–155 (0.02)	1.5120 (25)	7.25 (4 H, d, aryl CH ortho to Si), 6.8 (4 H, d, aryl CH ortho to N) 0.45 (6 H, s, silyl CH_3), 0.05 (36 H, s, silyl CH_3)	1250, 815 (silyl CH_3)[f]	$C_{26}H_{50}N_2Si_5$
3b	59	93–95	202–204.5 (0.03)	1.5369 (24)	7.1–7.65 (9 H, m, silyl Ph and aryl CH ortho to Si), 6.85 (4 H, d, aryl CH ortho to N), 0.75 (3 H, s, silyl CH_3), 0.05 (36 H, s, silyl CH_3)	1246, 830 (silyl CH_3), 1425, 1105, 695 (silyl Ph)[f]	$C_{31}H_{52}N_2Si_5$
3c	60		230–234 (0.005)		7.05–7.6 (14 H, m, silyl Ph and aryl CH ortho to Si), 6.85 (4 H, d, aryl CH ortho to N), 0.05(36 H, s, silyl CH_3)	1250, 830 (silyl CH_3), 1428, 1110, 700 (silyl Ph)[i]	$C_{36}H_{54}N_2Si_5$
4a	65		*b*		7.2 (4 H, d, aryl CH ortho to Si), 6.4 (4 H, d, aryl CH ortho to NH_2), 3.35 (4 H, s, NH_2), 0.4 (6 H, s, silyl CH_3)	3408 (doublet, NH_2), 1250, 820 (silyl CH_3)[f]	$C_{14}H_{18}N_2Si$
4b	81	97–98			6.85–7.6 (9 H, m, silyl Ph and aryl CH ortho to Si), 6.35 (4 H, d, aryl CH ortho to NH_2), 3.3 (4 H, s, NH_2), 0.6 (3 H, s, silyl CH_3)	3404 (doublet, NH_2), 1249, 820 (silyl CH_3), 1425, 1105, 690 (silyl Ph)[f]	$C_{19}H_{20}N_2Si$
4c	100[a]	205.5–207			6.9–8.0 (14 H, m, aryl CH) 6.7 (4 H, d, aryl CH ortho to NH_2), 5.3 (4 H, s, NH_2)[d]	3398 (doublet, NH_2), 1410, 1089, 688 (silyl Ph)[h]	$C_{24}H_{22}N_2Si$
5	58		149 (24)	1.5115 (24)	6.65–7.35 (4 H, m, aryl CH), 0.05 (18 H, s, silyl CH_3)[c]	1254, 841 (silyl CH_3)[f]	$C_{12}H_{22}BrNSi_2$
7a	67		140 (0.01)	1.5060 (24)	6.75–7.3 (8 H, m, aryl CH), 0.5 (6 H, s, silyl CH_3), 0.0 (36 H, s, silyl CH_3)	1250, 830 (silyl CH_3)[f]	$C_{26}H_{50}N_2Si_5$
7b	63		166 (0.005)	1.5301 (25)	6.75–7.7 (13 H, m, aryl CH), 0.75 (3 H, s, silyl CH_3), 0.05 (36 H, s, silyl CH_3 of N)	1250, 835 (silyl CH_3), 1430, 1100, 700 (silyl Ph)[f]	$C_{31}H_{52}N_2Si_5$
7c	79		191–193 (0.025)	1.5518 (25)	6.85–7.8 (18 H, m, aryl CH), 0.0 (36 H, s, silyl CH_3)	1250, 820 (silyl CH_3) 1430, 1108, 700 (silyl Ph)[f]	$C_{36}H_{54}N_2Si_5$
8a	81		156–156.5 (0.02)	1.6170 (25)	6.35–7.4 (8 H, m, aryl CH), 3.3 (4 H, s, NH_2), 0.4 (6 H, s, silyl CH_3)	3400 (doublet NH_2), 1248, 808 (silyl CH_3)[f]	$C_{14}H_{18}N_2Si$
8b	82	96–97	226–229 (0.075)		6.3–7.6 (13 H, m, aryl CH), 3.15 (4 H, s, NH_2), 0.7 (3 H, s, silyl CH_3)	3413 (doublet, NH_2), 1253, 780 (silyl CH_3), 1430, 1111, 700 (silyl Ph)[f]	$C_{19}H_{20}N_2Si$
8c	70	279–280.5			6.5–7.85 (18 H, m, aryl CH), 5.05 (4 H, s, NH_2)[d]	3408 (doublet, NH_2), 1415, 1098, 688 (silyl Ph)[h]	$C_{24}H_{22}N_2Si$

Table I
(Continued)

Compd	Yield, %	Mp, °C	Bp, °C (mm)	nD (°C)	NMR, δ	Ir, cm^{-1}	Formula
10	85[j]	106–107[k]			7.5 (5 H, s, aryl CH), 7.4 (2 H, d, aryl CH ortho to carbonyl), 6.7 (2 H, d aryl CH ortho to NH_2), 5.0 (2 H, broad s, NH_2)[e]	3350 (doublet, NH_2), 1628 (broad and strong carbonyl)[h]	$C_{13}H_{11}NO$
11	89[l]	216.5–217.5			7.4–8.0 (8 H, m, aryl CH ortho to carbonyl, aryl CH of center ring), 6.65 (4 H, d, aryl CH ortho to NH_2), 6.15 (4 H, s, NH_2)	3340 (doublet, NH_2), 1620 (broad and strong carbonyl)[h]	$C_{20}H_{16}N_2O_2$
12	18	292–294			8.95 (2 H, d, H_2 and H_6 Py), 8.1 (1 H, t, H_4 Py), 7.65 (4 H, d, aryl CH ortho to carbonyl), 6.7 (4 H, d, aryl CH ortho to NH_2), 6.3 (4 H, s, NH_2)[d]	3350 (doublet, NH_2), 1645 (strong carbonyl), 1600 (aryl C=C)[g]	$C_{19}H_{15}N_3O_2$
13	50	237–239			7.5–8.1 (12 H, m, biphenyl CH and aryl CH ortho to carbonyl), 6.7 (4 H, d, aryl CH ortho to NH_2), 6.2 (4 H, s, NH_2)[d]	3350 (doublet, NH_2), 1621 (broad carbonyl)[h]	$C_{26}H_{20}N_2O_2$

[a] Based on the hydrochloride salt, mp 134–135°. [b] See Experimental Section for **4a**. [c] Cyclohexane standard. [d] DMSO-d_6. [e] Acetone-d_6. [f] Neat. [g] Nujol. [h] KBr. [i] Hexane solution, 5%. [j] Based on the crude hydrochloride salt, mp 240–256°. [k] The NMR showed 2 mol of water per mole of **10**; the literature reports the melting point of **10** as 121–124°, undoubtedly the anhydrate. [l] Based on the crude hydrochloride salt. [m] Satisfactory analytical data for carbon and hydrogen (and nitrogen for **8b**) were reported for all new compounds listed in Table I except **3c**, which was a high-boiling oil. [n] Reference 3. [o] Reference 11.

Experimental Section

General. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer. NMR spectra were determined on a Varian A-60D spectrometer using tetramethylsilane as the internal standard in CCl_4, unless otherwise specified, at concentrations of approximately 30% by weight and are reported in parts per million. Analyses were performed by Chemalytics, Inc., Tempe, Ariz. All reactions employing *n*-butyllithium were carried out under anhydrous nitrogen in glassware previously dried for several hours at 110°. The free diamines were recrystallized under sparging nitrogen to prevent discoloration.

Table I provides an experimental summary of all compounds prepared. In addition, a detailed procedure of several typical reactions has been included.

4-Bromo-*N,N*-bis(trimethylsilyl)aniline (1). To a solution of *p*-bromoaniline (68.8 g, 0.40 mol) in 400 ml of freshly distilled THF[9] was added *n*-butyllithium (418 ml, 0.92 mol, a 15% excess) of 2.2 *M* in hexane dropwise at 0°. After a reaction period of 2–3 hr, during which the solution was allowed to warm to room temperature, chlorotrimethylsilane (117 ml, 0.92 mol, a 15% excess) was added dropwise, and the solution was stirred overnight. Filtration of the LiCl was conducted in a drybox under anhydrous nitrogen or, while exposed to the atmosphere, as rapidly as possible into freshly dried, lukewarm glassware.

Distillation afforded 77.3 g (61%) of **1**, bp 155.5–158° (23 mm), n^{28}D 1.5129. The literature[3] reports the preparation via ethylmagnesium bromide exchange in 43% yield, bp 106° (1.2mm), n^{25}D 1.5140.

Bis[*N,N*-bis(trimethylsilyl)-3-aminophenyl]diphenylsilane (7c). To a solution of **5** (86.6 g, 0.275 mol) in 500 ml of anhydrous ether[10] was added *n*-butyllithium (125 ml, 0.275 mol) of 2.2 *M* in hexane dropwise at 0°. After stirring for 2 hr at 0°, redistilled dichlorodiphenylsilane (34.6 g, 0.135 mol) was added dropwise, and the resulting mixture was stirred overnight and then refluxed for 1 hr. The LiCl was removed by filtration and the ether removed in vacuo. Distillation afforded 70.4 g (79%) of **7c**, bp 191–193° (0.025 mm), n^{25}D 1.5518.

Bis(3-aminophenyl)diphenylsilane (8c). A sample of **7c** in ether was hydrolyzed with sparging HCl gas for 2 min, and then neutralized with 5% aqueous NaOH solution under sparging nitrogen. After filtration, washing with water, and recrystallization from acetone under sparging nitrogen, a 70% yield of **8c**, mp 279–280.5°, was obtained.

Bis(4-aminophenyl)dimethylsilane (4a). A solution of **3a** (12.9 g, 0.024 mol) and water (3.5 g, 0.192 mol, a 100% excess) in 100 ml of acetone was stirred at room temperature overnight. The solution was then stirred for 24 hr with anhydrous $MgSO_4$ and for 12 hr with molecular sieves. Filtration and removal of the acetone in vacuo gave a pale tan oil which analyzed correctly and whose proposed structure corresponded to spectral data (see Table I).

This material could not be recrystallized; vacuum distillation afforded a small yield of broad-boiling **4a**, accompanied by considerable decomposition.

Earlier attempts to isolate **4a** following the ethanolysis of **3a** afforded an 89% yield of aniline; an attempted methanolysis of **3a** gave aniline also.[11]

1,3-Bis(4-aminobenzoyl)benzene (11). To a solution of **1** (30.0 g, 0.095 mol) in 600 ml of anhydrous ether was added *n*-butyllithium (40 ml, 0.095 mol) of 2.4 *M* in hexane at 0°. After the reaction mixture was allowed to stir for 2 hr at room temperature, the solution was again cooled to 0° and 1,3-dicyanobenzene (6.1 g, 0.048 mol) in 60 ml of anhydrous THF was added over a 10-min period. The resulting blood-red solution was allowed to stir for 4 hr at room temperature before it was hydrolyzed with excess aqueous 3 *N* HCl to yield 16.4 g (89%) of crude hydrochloride salt. A sample of this material was neutralized with 10% aqueous NaOH and recrystallized from ethanol–water (9:1) under sparging nitrogen to afford pure **11**, mp 216.5–217.5°.

Attempted Preparation of 2 in THF. Isolation of 4-(*n*-Butyl)-*N,N*-bis(trimethylsilyl)aniline (2a). To a solution of **1** (90.0 g, 0.285 mol) in 400 ml of anhydrous THF–ether (1:1) was added *n*-butyllithium (119 ml, 0.285 mol) of 2.39 *M* in hexane dropwise at 0°. The solution was allowed to stir at room temperature for 4 hr before dichloromethylphenylsilane (27.2 g, 0.143 mol) was added dropwise. After stirring overnight the LiCl was removed by filtration and the solvents were removed in vacuo. Fractionation afforded 35.4 g (42%) of **2a**, bp 97° (0.34 mm), n^{25}D 1.4830.

Acknowledgment. The authors express their thanks to NASA, Langley Research Center, for Grant No. 25-005-005-008.

Registry No.—**1**, 5089-33-8; **2a**, 54120-39-7; **3a**, 41992-38-5; **3b**, 42077-73-6; **3c**, 41992-39-6; **4a**, 54120-40-0; **4b**, 54120-41-1; **4c**, 3454-24-8; **5**, 54120-42-2; **7a**, 54120-43-3; **7b**, 54120-44-4; **7c**, 54120-45-5; **8a**, 54120-46-6; **8b**, 54181-91-8; **8c**, 54120-47-7; **10**, 1137-41-3; **11**, 54120-48-8; **12**, 54120-49-9; **13**, 54120-50-2; 1,3-dicyanobenzene, 626-17-5; 3,5-dicyanopyridine, 1195-58-0; 4,4′-dicyanobiphenyl, 1591-30-6; *p*-bromoaniline, 106-40-1; chlorotrimethylsilane, 75-77-4; dichlorodiphenylsilane, 80-10-4; dichloromethylphenylsilane, 149-74-6; dichlorodimethylsilane, 75-78-5.

References and Notes

(1) Taken in part from the Ph.D. Dissertation of J. R. Pratt, University of Southern Mississippi, 1974.
(2) W. Broser and W. Harrer, *Angew. Chem.*, **77**, 1139 (1965); *Angew. Chem., Int. Ed. Engl.*, **4**, 1081 (1965).
(3) D. R. M. Walton, *J. Chem. Soc. C*, 1706 (1966).
(4) G. Greber, *J. Prakt. Chem.*, **313**, 461 (1971).
(5) F. S. Kipping and N. W. Cusa, *J. Chem. Soc.*, 1088 (1935).
(6) J. R. Pratt and S. F. Thames, *Synthesis*, **4**, 223 (1973).
(7) F. C. Schaefer, "Chemistry of the Cyano Groups", Z. Rappoport, Ed., Interscience, New York, N.Y., 1970, p 276.
(8) The crude material displayed a broad carboxylic dimer stretch at 2950 cm^{-1} and a strong acid carbonyl stretch at 1630 cm^{-1}. Both absorptions disappeared after recrystallization from acetone in the presence of dilute base.
(9) Redistilled from $LiAlH_4$ or CaH_2 under nitrogen and stored over molecular sieves.
(10) Stored over sodium ribbon.
(11) F. H. Pinkerton, Dissertation, University of Southern Mississippi, 1971, p 173.

Dipole Stabilized Carbanions. Reactions of Benzoate Esters with Lithium 2,2,6,6-Tetramethylpiperidide

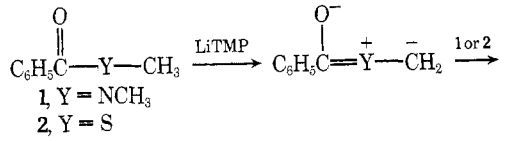
Charles J. Upton and Peter Beak*

Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801

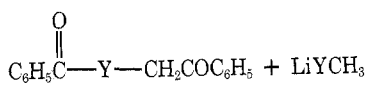
Received October 15, 1974

The reactions of benzyl benzoate (**3**), allyl benzoate (**5**), and vinyl benzoate (**12**) with lithium 2,2,6,6-tetramethylpiperidide at −78° in tetrahydrofuran give, respectively, benzoin benzoate (**4**), α-benzoyl allyl benzoate (**6**) and α-benzoyl-β-methyl vinyl benzoate (**7**), and α-benzoyl vinyl benzoate (**13**) via formation of a carbanion adjacent to oxygen followed by nucleophilic attack of the anion on the starting ester. However, methyl, ethyl, and the propyl and butyl benzoates, **15** and **17–22**, in the presence of the same base lose an ortho proton from the ring to provide, after benzoylation, the *o*-benzoylbenzoates **16** and **23–28** in a synthetically useful reaction. Related proton abstractions lead to substitution of benzophenone ortho to the carbonyl and to benzoylation of benzyl β,β-diphenylacrylate adjacent to the carbonyl group. It does not appear that the potential dipole stabilization of the ester function is sufficient, under these conditions and in the absence of additional stabilization, to direct proton abstraction to the carbon adjacent to oxygen.

The novel abstraction of a proton from the methyl groups of *N,N*-dimethylbenzamide and methyl thiobenzoate by lithium 2,2,6,6-tetramethylpiperidide (LiTMP) to generate the transient nitrogen- and sulfur-substituted dipole-stabilized carbanions **1** and **2** has been communicated.[1] Our interest in the possible generality of such species



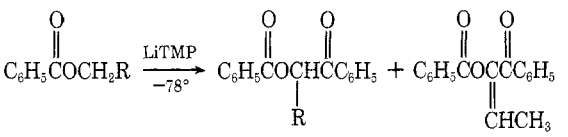
1, Y = NCH_3
2, Y = S



as well as their synthetic potential[2] prompted investigation of the reaction of benzoate esters with LiTMP. The present report establishes that formally dipole stabilized carbanions can be produced by abstraction of a proton from benzoate esters which have additional activation provided by unsaturation. In the absence of such activation, removal of an ortho proton occurs and the ultimate product is an *o*-benzoylbenzoate.

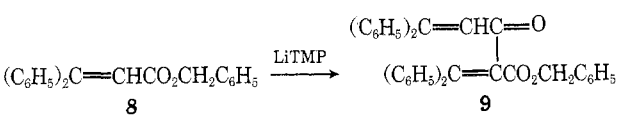
Results and Discussion

Benzyl Benzoate, Allyl Benzoate, and Vinyl Benzoate. The reaction of benzyl benzoate (**3**) with LiTMP[3] in tetrahydrofuran at −78° for 10 min provides benzoin benzoate (**4**) in 65% yield (77% conversion). A similar reaction of allyl benzoate (**5**) gives α-benzoyl allyl benzoate (**6**) and α-benzoyl-β-methyl vinyl benzoate (**7**) in a 4:1 ratio in 53% yield (75% conversion). The structural assignments for **6** and **7** are based on spectral and analytical properties. It appeared possible that **7** was produced by isomerization of **6**, since the conversion of **6** to **7** occurs on treatment of a mixture of these compounds with 10 mol % potassium *tert*-butoxide in *tert*-butyl alcohol. However, attempts to increase the yield of **6** and **7** or to alter their ratio by reaction with a twofold excess of LiTMP followed by quenching 20 min after mixing or by inverse addition of LiTMP to **5** produced no significant change in the yield or the ratio. The formation of **4** from **3** can also be observed in 50% yield at −78° if lithium diisopropylamide is the base.



3, R = C_6H_5 **4**, R = C_6H_5 **7**
5, R = CH=CH_2 **6**, R = CH=CH_2

The reactions of benzyl methyl phthalate, dibenzyl phthalate, benzyl acrylate, and benzyl β,β-diphenylacrylate (**8**) with LiTMP were investigated in an effort to achieve an intramolecular cyclization.[4] However, only in the case of **8** was a characterizable product obtained and it proved to be **9**, formed in 25% yield at both −78 and 25°. Clearly, **9** results from an intermolecular sequence which is probably initiated by removal of the vinyl proton from **8**.[5] The structure of **9** is based on its analytical and spectral properties, as well as its conversion to dibenzhydrylacetone after cata-



8 **9**