course of the reaction.
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(22) Probably the prevailing diastereomer is that formed from two molecules of the alkyne (**1**) with the same chirality. However, the optically active (*E*)-2,2,3,7,8,8-hexamethyl-4-methylene-5-nonene recovered had the same optical purity as the starting **1**.
(23) In regard to the cyclotrimers, there is to be noted that when the 1-alkyne is used, **7** and **8** are recovered not containing deuterium atoms upon deuteriolysis. The use of 1-hexyne-*1-d* gives rise to the formation of cyclotrimers having three deuterium atoms.
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(29) Also, employing $(i\text{-Bu})_4$AlLi instead of $(i\text{-Bu})_3$Al results in a decrease of the reaction rate and an increase of the yields of cyclotrimers with respect to those of the low molecular weight products.
(30) This hypothesis seems to be confirmed by the presence of 1,2-diisobutyl-1-alkene in the reaction mixtures, even if in small amounts (ca. 3%). The formation of this alkene should be rationalized by assuming the insertion of **1** into the Ni–C bond of a dialkylnickel complex, followed by reductive elimination.
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(32) In this context, it is noteworthy that the formation of a dimeric enyne system is also improved (Table V); this process is, however, very selective toward the formation of the "head-to-tail" enyne.

Metalation of Aromatic Tertiary Diamines with *n*-Butyllithium

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We report the results obtained by direct metalation of aromatic tertiary diamines with *n*-BuLi. The reaction done in a nonpolar solvent, such as hexane, at elevated temperature (60 °C) shows the formation of both a monolithiated and a dilithiated compound, the site of lithiation being the ortho position of the benzene ring as evidenced by ^{1}H NMR data. The metalation was followed by gas chromatography by measuring the butane evolved during the reaction.

Since the work of Langer[1] on the formation of the stable equimolecular TMEDA-*n*-BuLi complex and its use either in metalation reactions or as an anionic polymerization catalyst, a number of results have been published concerning the use of essentially aliphatic tertiary polyamines[1] as complexing reagents for *n*-BuLi.

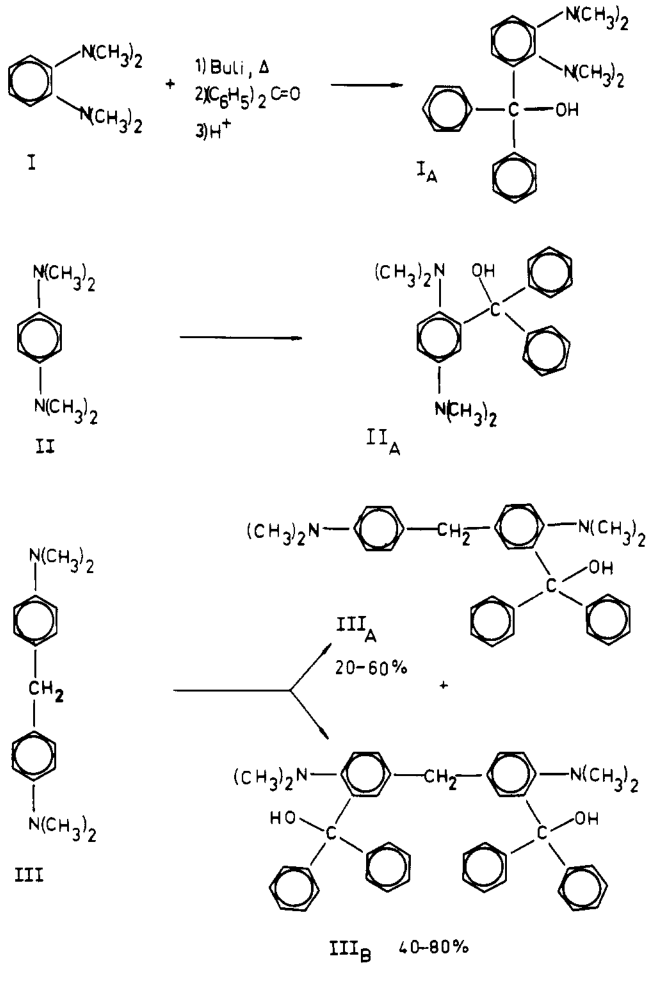
We obtained similar results when using tertiary aromatic diamines (increase of the reactivity of *n*-BuLi). The obtained coordination complexes have the following compositions. (A, BuLi)$_x$:[2] A representing the amines I, *N,N,N′,N′*-tetramethyl-*o*-phenylenediamine, II, *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine, and III, bis(*N,N*-dimethyl-4-aminophenyl)methane; and *x* being, respectively, 1, 4, and 6 [I$_c$, (BuLi, I), II$_c$, (BuLi, II)$_4$, and III$_c$, (BuLi, III)$_6$].

The complexes show catalytic properties in the anionic polymerization of isoprene[2] and other unsaturated hydrocarbons.[3] The evolution of these complexes with time or under heating leads to the formation of an organometallic compound which may be monolithiated or dilithiated, heating being an accelerating factor for the metalation of the phenyl group.

Results and Discussion

The obtained organolithium compounds have been characterized by proton NMR spectroscopy after condensation with benzophenone to the corresponding alcohol (Scheme I) and as the organometallic product in the case of III. Results are given in Table I.

Scheme I



The 12 equivalent protons of the two *N,N*-dimethylamino groups give rise to a singlet at 2.7–2.88 ppm according to the amine. In the presence of the diphenylcarbinol group, a new singlet appears near 2.30–2.35 ppm. These two peaks have the same intensity, and the integration corresponds to 6 H. This upfield chemical shift (0.4–0.5 ppm) has been assigned to a shielding effect[4] of the diphenylcarbinol group at the ortho position of the benzene ring, and we may conclude to an ortho metalation. This structure is the most compatible with the

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Table I. Proton Nuclear Magnetic Resonance Spectra of the Diamines and the Carbinols from Metalated Amines[a]

		chemical shifts				
compd	registry no.	$N(CH_3)_2$	HOC–Ar–$N(CH_3)_2$	Ar	Ar–COH	$(Ar)_2CH_2$
N,N,N′,N′-tetramethyl-1,2-phenylenediamine	704-01-8	2.78 (s)		6.95 (s)		
N,N,N′,N′-tetramethyl-2,3-diaminotriphenylcarbinol (I_A)	68317-78-2	2.76 (s)	2.32 (s)	6.95 (m)	8.9 (s)	
N,N,N′,N′-tetramethyl-1,4-diaminophenylenediamine	100-22-1	2.76 (s)		6.55 (s)		
N,N,N′,N′-tetramethyl-2,5-diaminotriphenylcarbinol (II_A)	68317-79-3	2.70 (s)	2.30 (s)	6.55 (s)	9.0 (s)	
bis(*N,N*-dimethyl-4-aminophenyl)methane	106-61-1	2.88 (s)		7.18 (q)		3.72 (s)
(*N,N,N′,N′*-tetramethyl-3-diphenylcarbinol-4,4′-diamino)diphenylmethane (III_A)	68317-80-6	2.86 (s)	2.31 (s)	7.18 (m)	8.85 (s)	3.63 (s)
bis(*N,N*-dimethyl-3-diphenylcarbinol-4-aminophenyl)methane (III_B)	68317-81-7		2.35 (s)	7.18 (s)	8.80 (s)	3.60 (s)

[a] All peaks are relative to Me_4Si in parts per million in CCl_4 solvent. Splittings are as follows: s = singlet, q = quadruplet, and m = multiplet. Ar = benzene ring. Anal. I_A Calcd for $C_{23}H_{26}N_2O$: C, 79.73; H, 7.56; N, 8.08. Found: C, 79.61; H, 7.43; N, 7.97. Anal. II_A Calcd for $C_{23}H_{26}N_2O$: C, 79.73; H, 7.56; N, 8.08. Found: C, 79.54; H, 7.45; N, 8.22. Anal. III_A Calcd for $C_{30}H_{32}N_2O$: C, 82.53; H, 7.38; N, 6.42. Found: C, 82.09; H, 7.40; N, 6.97. Anal. III_B Calcd for $C_{43}H_{42}N_2O_2$: C, 83.46; H, 6.84; N, 4.53. Found: C, 83.38; H, 6.92; N, 5.06. The isotopic exchange with D_2O confirms the broad signal of the hydroxyl group at δ = 8.80–9.0 ppm.

observed chemical shift. A similar result has been noted by Hauser et al.[5] in the metalation of *N,N*-dimethyl-*p*-toluidine. These authors attributed the singlet at 2.29 ppm to the protons of the dimethylamino group with a diphenylcarbinol group in the ortho position. Lepley et al.[6] and Slocum et al.[7] reported similar results for the lithiation of *N,N*-dimethylaniline.

The structure of the product was confirmed by synthesis and isolation of III_A and III_B, corresponding, respectively, to a monometalation and a dimetalation; the NMR spectrum of III_A shows two unsplit peaks at 2.86 and 2.31 ppm with area ratios of 6.0:6.0 protons, respectively. In the spectrum of III_B we note the absence of the singlet at 2.86 ppm and the presence of an unsplit peak at 2.35 ppm with an intensity of 12 H.

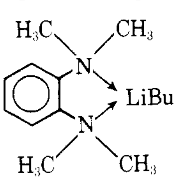
It is also noteworthy that the CH_2 group at 3.60–3.72 ppm between the two aromatic rings has not been metalated; its ^1H NMR signal remains unaltered in the spectrum after reaction with BuLi.

The hydroxyl group is confirmed by a broad signal at 8.80–9.0 ppm.

The monolithiated compound III_A is slightly soluble in benzene. Its ^1H NMR spectrum in C_6D_6 shows two singlets at 2.53 and 2.20 ppm with area ratios of 6.0:6.0, respectively. The first signal has been attributed to the 6 H of the $N(CH_3)_2$ group of the unmetalated moiety of the molecule, and the second peak to the 8 H of the $N(CH_3)_2$ group after metalation in the ortho position of the benzene ring.

The kinetic study of the metalation reaction has been followed at 25 and 55 °C by gas chromatography by measuring the butane evolved during the reaction (Figure 1).

In contrast to amine I, amines II and III show increasing rates of metalation with temperature; this phenomenon may be explained by the higher stability of the cyclic coordination complex I_c. Such a complex is not possible with II and III.



I_c

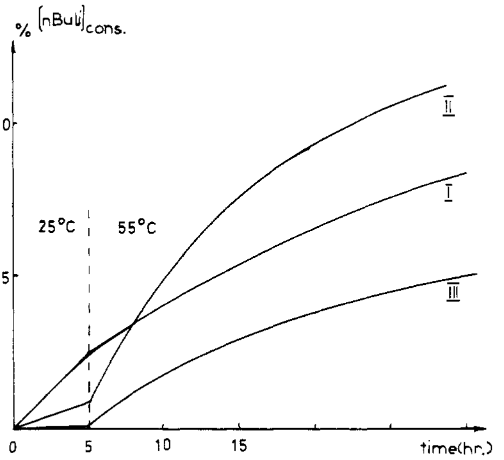


Figure 1. Kinetic curves of the metalation reaction of the amines: I, *N,N,N′,N′*-tetramethyl-*o*-phenylenediamine; II, *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine; and III, bis(*N,N*-dimethyl-4-aminophenyl)methane. [Amine]/[*n*-BuLi]$_0$ = 1; [*n*-BuLi]$_0$ = 4.8 × 10^{-2} mol L^{-1}. Dotted line: on the left the kinetic measurements are done at 25 °C, and on the right they have been done at 55 °C.

Since we were interested in the preparation of a dilithiated compound, we have studied with care the metalation of the bis(*N,N*-dimethyl-4-aminophenyl)methane. The resulting dimetallic compound has been used as an effective difunctional anionic polymerization catalyst for conjugated dienes, acrylic and methacrylic nitriles, and esters,[8] so we tried to increase the yield of this dilithium compound. But whatever the experimental conditions, we never obtained a pure dilithiated compound. The mixture contained at least 20% of a monolithiated product, the overall yield of the reaction being 25–35%. These attempts show that the formation of the dilithiated compound is favored by using a large excess of BuLi (see Experimental Section).

Experimental Section

Chemicals. Bis(*N,N*-dimethyl-4-aminophenyl)methane and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (Eastman Kodak) were purified by crystallization from hexane. *N,N,N′,N′*-Tetramethyl-*o*-phenylenediamine (Eastman Kodak) was dried over calcium hydride and distilled under vacuum. *n*-BuLi (Fluka, 20% in hexane) was analyzed by the Watson and Eastham method[9] for active lithium content before use. Hexane was dried over sodium wire. The overall yields are based on initial diamine.

Metalation Reaction. (*N,N,N′,N′*-Tetramethyl-2,3-diaminophenyl)lithium and (*N,N,N′,N′*-Tetramethyl-2,5-diaminophenyl)lithium. A hexane solution (20 mL) of *n*-BuLi (2 × 10^{-2} mol) was heated to 55 °C under argon. A solution of 2 × 10^{-2} mol of the corresponding diamine in 150 mL of dry hexane was then introduced. This mixture was kept under agitation at 55 °C during 48 h. The organolithium compound precipitate was filtered off and washed five times with anhydrous hexane. It appeared as a pale yellow fine powder (overall yield 50–60%).

5,5′-Bis[(*N*,*N*-dimethyl-2-aminophenyl)lithium]methane. Preparation A. The diamine (10^{-2} mol) and *n*-BuLi (2×10^{-2} mol) were mixed in dry *n*-hexane (150 mL) and heated to 60 °C during 48 h with agitation.

B. In a dry flask a solution of *n*-BuLi (2×10^{-2} mol) in 25 mL of *n*-hexane was stirred and heated to 60 °C. Then a solution of the amine (10^{-2} mol) in 100 mL of hexane was added dropwise over a period of 24 h. This addition was followed by an additional 48 h of heating to 60 °C.

C. The same conditions as in B were used, but the addition of the amine solution was done over a period of 72 h followed by an additional 48 h of heating at 60 °C.

D. The mixture obtained in A was heated with a solution of *n*-BuLi (2×10^{-2} mol) at 60 °C during 48 h.

In all cases, after reaction the mixture was cooled to room temperature and the organolithium precipitate was filtered off and washed with anhydrous hexane. The product appeared as a pale yellow powder. Its molar composition was as follows: method A, RLi_1 = 65% and RLi_2 = 35%; method B, RLi_1 = 60% and RLi_2 = 40%; method C, RLi_1 = 33% and RLi_2 = 67%; method D, RLi_1 = 20% and RLi_2 = 80%. The overall yield was 25–35% based on initial amine.

Synthesis of the Carbinols from Metalated Amines. General Procedure. A 10^{-2}-mol amount of the organolithium product was added to an excess of benzophenone (3×10^{-2} mol) dissolved in 20 mL of ether. The resulting mixture was stirred for 4 h and then acidified with 0.1 N HCl. The organic layer was extracted with ether; the aqueous layer was made basic with 0.1 N sodium hydroxide and extracted with ether. The latter extract was dried over magnesium sulfate, and the ether was distilled. The solid residue was fractionated by chromatography on a silica gel column (silica gel 60, Merck) with a hexane/ethyl acetate (9:1) mixture. The analytical data are given with Table I.

Kinetic Apparatus. The kinetic study has been done under vacuum (10^{-5} mmHg) in a series of sealed U-tubes (Figure 2). Amine, BuLi, solvent, and internal standard (*n*-pentane) were mixed in a. Every 2 h the solvent, pentane, and the butane which is formed during metalation are distilled from a to b cooled with liquid nitrogen. After sealing c and separation of tube b, the mixture was analyzed by gas chromatography with a Perkin-Elmer F 17 chromatograph under the following conditions: column (120 in.) was filled with Chromosorb AW, 80–100 mesh, impregnated with 3% OV 17 stationary phase; column temperature 25 °C; injection temperature 150 °C; detection temperature 200 °C.

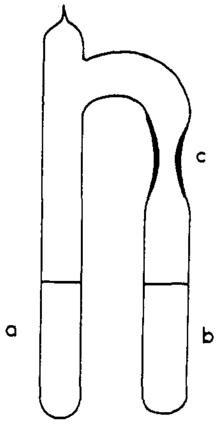


Figure 2. Kinetic apparatus.

Registry No.—(*N*,*N*,*N*′,*N*′-Tetramethyl-2,3-diaminophenyl)lithium, 68317-82-8; (*N*,*N*,*N*′,*N*′-tetramethyl-2,5-diaminophenyl)lithium, 68317-83-9; 5,5′-bis[(*N*,*N*-dimethyl-2-aminophenyl)lithium]methane, 68317-84-0; benzophenone, 119-61-9.

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Versatile Polymer-Bound Hydrogenation Catalysts. Rhodium(I)-Catalyzed Hydrogenation

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The bidentate ligand anthranilic acid has been anchored to polystyrene beads (Amberlite XAD-4) and the Rh(I) complex has been prepared. The polymer is a hydrogenation catalyst of exceptional activity, long-term stability, and considerable insensitivity to poisoning. Hundreds of catalytic cycles per metal atom are demonstrated without substantial loss of activity. The rhodium catalyst reduces a variety of olefinic and aromatic hydrocarbons and carbonyl, nitrile, and nitro functional groups. Catalytic activity depends upon retention of beads; if fragmentation occurs, the activity is considerably diminished. ESCA studies clearly demonstrate the rhodium to have a +1 formal oxidation state.

Anchoring ligands to insoluble polymeric supports, followed by complexation with transition metals, results in polymers having catalytic potential.[1-3] These metal complexes, hybrids of homogeneous and heterogeneous approaches, are attractive because they often permit the activity of soluble catalysts and the ease of product separation inherent in heterogeneous catalysts. In referring to this class of catalysts the names "polymer bound", "hybrid phase", or "supported" are common.

The choice of the ligand to be anchored is usually based on attempts to create environments analogous to those in the most active homogeneous catalysts. Because of the preponderance of phosphine complexes in homogeneous catalysts, most polymer-bound catalysts to date have involved these

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