

## Reactions of Formamidinium Salts with Organolithium Reagents

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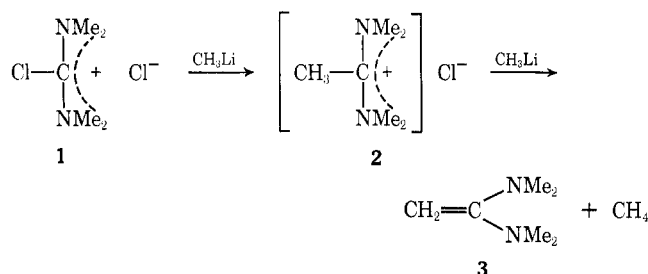
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Reaction of tetramethylchloroformamidinium chloride (**1**) with methyl lithium gave vinylidenebisdimethylamine (**3**) in good yield. Extension of this reaction to higher alkylolithiums was unsuccessful. Reactions of **1** with *tert*-butyllithium and phenyllithium proceeded by radical processes. The mechanisms of these reactions, which probably involve substituted bis(dimethylamino)methyl radicals and possibly bis(dimethylamino)carbene, are discussed.

In connection with our study of the chemistry of alkylidenebisdialkylamines (enediamines) we have been interested in developing new synthetic routes to these compounds. Two such routes have previously been described.<sup>1,2</sup> In this paper we report yet another synthesis of vinylidenebisdimethylamine (**3**) by reaction of methyl lithium with *N,N,N',N'*-tetramethylchloroformamidinium chloride (**1**). The reaction of additional organolithium reagents with this and other amidinium salts also is described.<sup>3</sup>

The reaction of methyl lithium with **1** in ether at 5° proceeded with methane evolution and formation of the enediamine **3** in 73% yield. The reaction presumably



proceeds by formation of the acetamidinium ion **2**, followed by proton abstraction by methyl lithium to give **3**. In refluxing ether, the yield of **3** was greatly diminished. Several unidentified products were noted, more high-boiling residue was formed, and the off-gases contained 25% of methyl chloride. Formation of the latter suggests halogen-metal interchange between either **1** or **2** and methyl lithium.

In contrast to the reaction of **1** with methyl lithium, the reaction with methylmagnesium iodide did not go to completion and only a small yield of **3** was obtained. We believe that the **3** which formed in the early part of the reaction complexed the Grignard reagent and prevented further reaction.

Surprisingly, attempts to extend the reaction of **1** with organolithium reagents to the synthesis of homologous enediamines were unsuccessful. Reaction of **1** with ethyllithium, *n*-butyllithium, or isopropyllithium gave complex mixtures of products containing only 10–15% of the desired enediamines as shown by nmr spectroscopy. Distillation indicated considerable tar formation. These reactions were not characterized further.

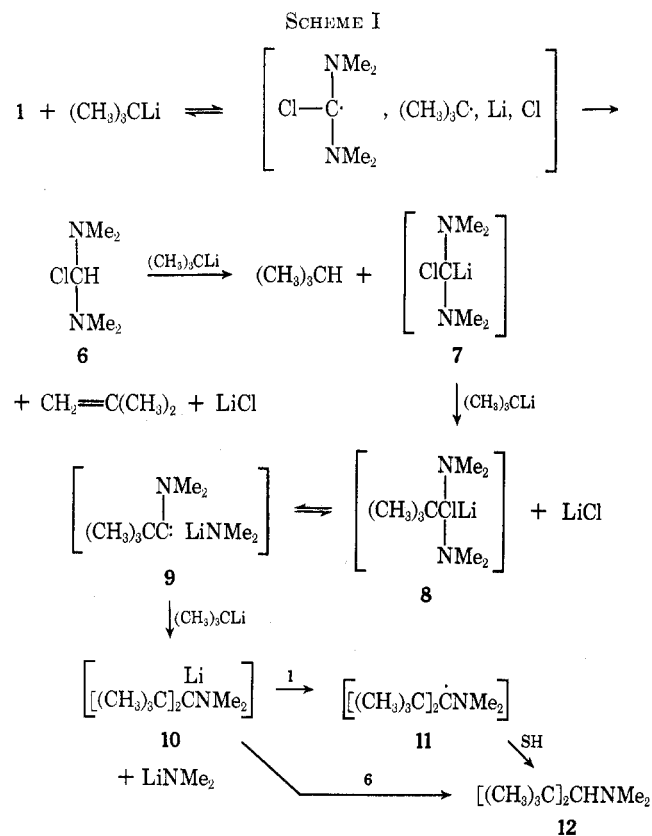
The unusual behavior of **1** with the higher organolithium reagents prompted us to investigate the reaction of **1** with *tert*-butyllithium in the hope of observing

(1) H. Weingarten and W. A. White, *J. Org. Chem.*, **31**, 2874 (1966).

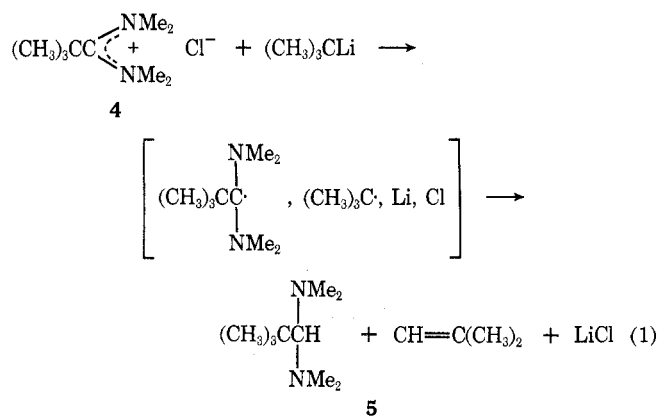
(2) J. D. Wilson, C. F. Hobbs, and H. Weingarten, *ibid.*, **35**, 1542 (1970).

(3) After this work was completed, the reaction of cyclononatriene anion with **1** to give 10,10-bis(dimethylamino)nonafulvene was reported: K. Hafner and H. Tappe, *Angew. Chem.*, **81**, 564 (1969).

simpler chemistry. This reaction yielded isobutene and isobutane in nearly equal quantities, the monoamine **12** (81%) (Scheme I), tetrakis (dimethylamino)



methane (10%), and smaller amounts of tris (dimethylamino)methane and tetrakis (dimethylamino)ethylene. The reaction was shown not to involve simple ionic displacement by *tert*-butyllithium on **1** to give the pivalamidinium salt **4** as an intermediate. Treatment of **4**

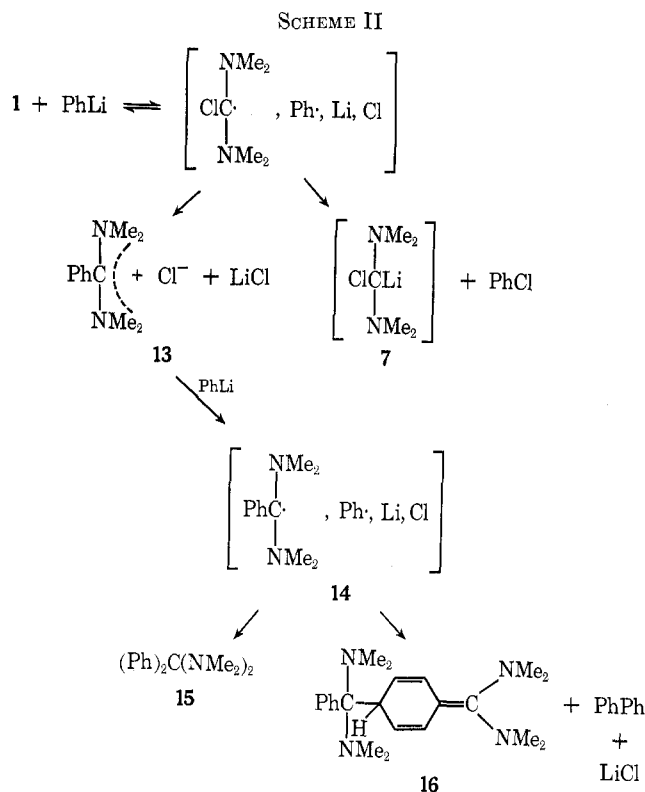


with *tert*-butyllithium afforded the reduction product **5** in addition to considerable intractable residue; none of the products observed in the reaction of **1** with *tert*-butyllithium were observed. Furthermore, a careful check of the reaction mixture of **1** with *tert*-butyllithium showed no evidence of **5**.

The reduction of **4** to **5** is best explained by electron transfer to give radical intermediates<sup>4</sup> which then undergo hydrogen transfer to products, as shown in eq 1. This suggests that a similar process may occur in the reaction of **1** with *tert*-butyllithium to give *N,N,N',N'*-tetramethylformamidinium chloride (**6**) as an intermediate. Indeed, when **6** was treated with *tert*-butyllithium, the same array of products was obtained as in the reaction of **1** with *tert*-butyllithium. The chief difference in the two reactions was that more tetrakis(dimethylamino)methane and less tris(dimethylamino)methane were obtained with **1** than with **6**.

The results with both **1** and **6** can be explained by the reactions depicted in Scheme I. In the case of **1**, electron transfer from *tert*-butyllithium affords radical species which undergo hydrogen transfer to give **6**. Proton abstraction from **6** affords **7**,<sup>5</sup> or the carbene derived from **7** by loss of lithium chloride. Reaction of **7**, or of the bis(dimethylamino)carbene, with *tert*-butyllithium<sup>6</sup> affords the adduct **8**, which can eliminate lithium dimethylamide either by concerted reaction with *tert*-butyllithium or *via* a carbene complex, **9**, to give **10**. The conversion of **10** to **12** can be envisioned as occurring either by direct proton abstraction from some acidic species, say **6**, or by electron transfer to **1**, giving the radical **11** which can abstract hydrogen to give **12**. The lithium dimethylamide which is liberated in the above process can react with both **1** and **6** in known reactions to give tetrakis(dimethylamino)methane<sup>7</sup> and tris(dimethylamino)methane,<sup>8</sup> respectively. The observation that the dominant by-product in the case of **1** is tetrakis(dimethylamino)methane, whereas in the case of **6** it is tris(dimethylamino)methane, is consistent with this interpretation. Tetrakis(dimethylamino)ethylene is most likely formed by the attack of **7** on the formamidinium salt **1**.<sup>5,9</sup>

We next turned our attention to the reaction of **1** with phenyllithium, a system in which hydrogen transfer should be more difficult than with the alkyl-lithium reagents. Reaction of **1** with phenyllithium in ether gave the expected product, the diphenylmethanediamine **15** (Scheme II), in high yield. However, when the reaction was repeated in benzene or pentane, only 28% of **15** was found, and, in addition, chlorobenzene, biphenyl, chlorobiphenyl, a small amount of tetrakis(dimethylamino)ethylene, and a product identified as the dimer **16** were formed. The formation of **16** together with chlorobenzene, biphenyl, and chlorobiphenyl indicates the incursion of radical processes in this reaction and can best be explained by the reactions



depicted in Scheme II. Electron transfer from phenyllithium to **1** produces radical intermediates, which can react to give either the benzamidinium salt **13** or chlorobenzene and the unstable lithium exchange product **7**. The latter probably accounts for the tetrakis(dimethylamino)ethylene observed.<sup>5</sup> Electron transfer from a second mole of phenyllithium to **13** affords phenyl radical and radical **14**; these can dimerize to give biphenyl and **16**, respectively, or cross-couple to yield **15**. The formation of **15** *via* **13** by an alternate ionic process cannot be ruled out.

The coupling of radical **14** to give **16** is reminiscent of the dimerization of the triphenylmethyl radical to give an analogous methylenecyclohexadiene structure.<sup>10</sup> Although dimer **16** was too unstable to permit its isolation, its structure could be deduced from its partial nmr spectrum in the mixture and from its chemical reactions outlined in Scheme III. The nmr spectrum clearly showed vinyl protons and two sets of dimethylamino groups with chemical shifts and proton ratios consistent with the proposed structure; additional features of the spectrum were masked by signals from other components in the mixture.

Upon standing, or more rapidly upon heating, **16** decomposed to give the benzylidenediamine **17** (Scheme III). This same product was obtained, with less tar formation, upon catalytic hydrogenation of the reaction mixtures containing **16**. This behavior is consistent with cleavage of **16** to the radical **14**, which can then abstract hydrogen from solvent or other species in the reaction mixture, or from the hydrogenation catalyst.

Addition of water to reaction mixtures containing **16** caused its immediate disappearance with formation of *N,N*-dimethylbenzamide, dimethylamine, and **17**. Ex-

(4) Radical formation in alkyl halide-alkyllithium reactions is well documented: G. A. Russell and D. W. Lamson, *J. Amer. Chem. Soc.*, **91**, 3967 (1969), and references cited therein.

(5) N. Wiberg and J. W. Buchler, *Z. Naturforsch.*, **B**, **19**, 953 (1964).

(6) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, pp 40-41, 60-61.

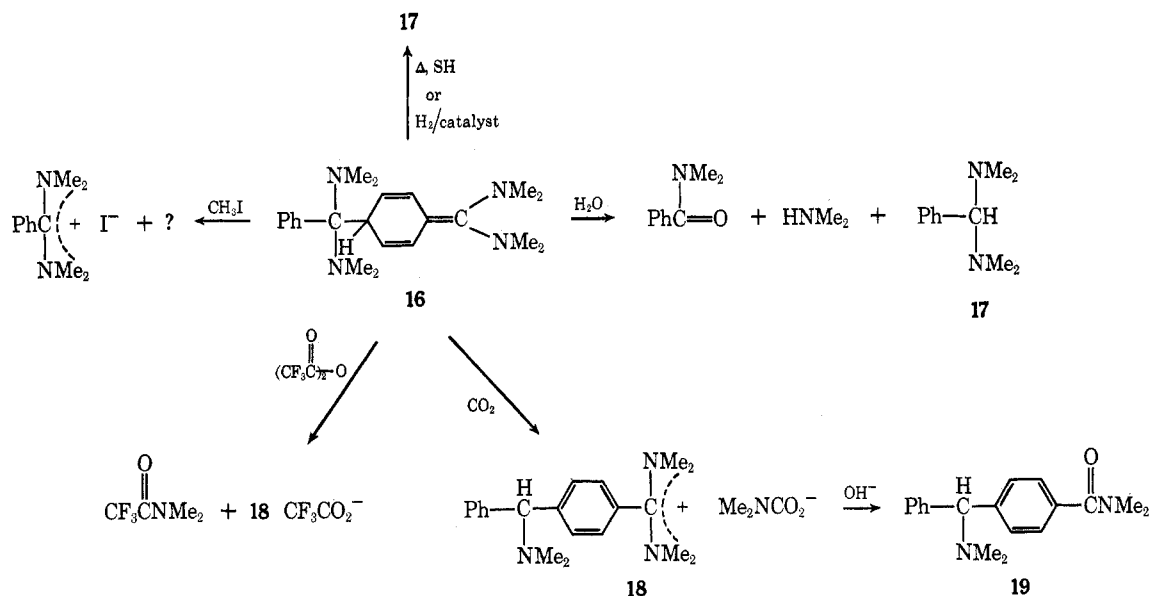
(7) H. Weingarten and W. A. White, *J. Amer. Chem. Soc.*, **88**, 2885 (1966).

(8) H. Brederick, F. Effenberger, and T. Brendle, *Angew. Chem.*, **78**, 147 (1966).

(9) D. M. Lemal and K. I. Kawano, *J. Amer. Chem. Soc.*, **84**, 1761 (1962).

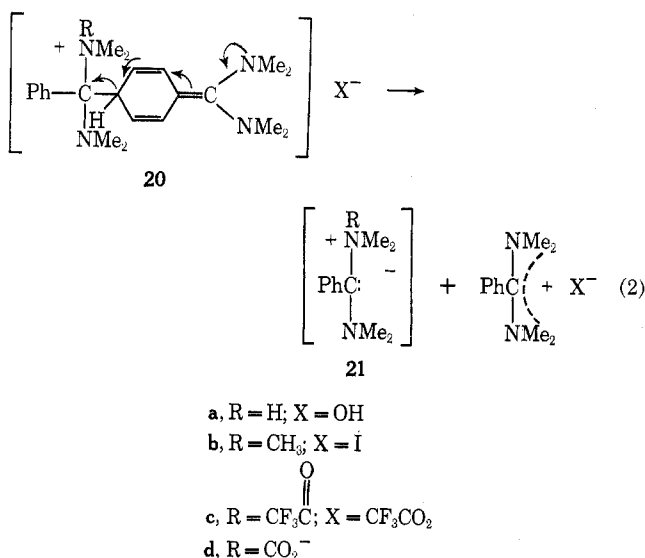
(10) H. Lankamp, W. T. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968).

## SCHEME III



periments with deuterium oxide showed that deuterium was incorporated only in **17** and only at the benzylic carbon. Treatment of **16** with methyl iodide gave *N,N,N',N'*-tetramethylbenzamimidinium iodide as the only isolable product. Addition of carbon dioxide or trifluoroacetic anhydride to solutions containing **16** precipitated ionic products, presumably salts of the amidinium cation **18**, which were converted to the aminoamide **19** by mild basic hydrolysis. Smaller amounts of *N,N*-dimethylbenzamide also were isolated in the latter two cases. In addition, *N,N*-dimethyltrifluoroacetamide was isolated from the reaction of **16** with trifluoroacetic anhydride.

The above results can be explained by reaction of **16** with the reagents,  $\text{RX}$ , to give **20**, which can fragment in two ways. Fragmentation in the manner indicated



by arrows, eq 2, affords the ylide **21** and the benzamimidinium salt. This is apparently the preferred pathway for **20a** and **20b**. In the case of water, **21a** rearranges by proton transfer to the benzyldenediamine (**17**), and the benzamimidinium salt (X = OH) is hydrolyzed to *N,N*-dimethylbenzamide and dimethylamine by hy-

droxide ion. With methyl iodide, the benzamimidinium salt (X = I) is isolated, but the fate of the proposed ylide **21b** is not known. This same fragmentation probably takes place to a limited extent with both trifluoroacetic anhydride and carbon dioxide, since some *N,N*-dimethylbenzamide is isolated after hydrolysis. However, the main fragmentation in the latter two cases occurs at the benzyl carbon-nitrogen bond of **20c** and **20d** to give the amidinium cation **18** and *N,N*-dimethyltrifluoroacetamide and *N,N*-dimethylcarbamate, respectively.

Experimental Section<sup>11</sup>

*N,N,N',N'*-Tetramethylchloroformamidinium Chloride (**1**) with Methylolithium.—To a stirred slurry of 51 g (0.30 mol) of **1**<sup>12</sup> in 100 ml of ether was added 0.63 mol of methylolithium in 244 ml of ether. The temperature of the mixture was kept at 5–10° during the addition and for an additional 2 hr afterward. The mixture was filtered and the filtrate was distilled to obtain 25.0 g (73%) of vinylidenebisdimethylamine (**3**), bp 95–105° (745 mm), identical (vpc and nmr) with authentic material.<sup>1</sup> During the addition of the methylolithium, gas was evolved which was collected; mass spectroscopy indicated 95% of methane, 1.5% of methyl chloride, and minor (<1%) components.

When the reaction was repeated in refluxing ether, only 36% of **3** was obtained. The evolved gas, 60% of theory, contained 74% of methane and 25% of methyl chloride.

*N,N,N',N'*-Tetramethylchloroformamidinium Chloride with *tert*-Butyllithium.—The formamidinium salt **1**,<sup>12</sup> 17.1 g (0.10 mol), was added in small portions to 0.22 mol of *tert*-butyllithium (1.54 M in pentane) at a rate sufficient to maintain gentle reflux. The gas which evolved was collected and was shown by mass spectroscopy to consist of a 1:1.3 mixture of butenes and isobutane. The mixture was stirred for an additional 6 hr at room temperature and then filtered, and the solvent was removed from the filtrate by distillation. The product was distilled as rapidly as possible at 1 mm into a Dry Ice cooled receiver. Fractional distillation afforded 7.6 g (81% based on *tert*-butyllithium) of 1-*tert*-butyl-2,2,*N,N*-tetramethylpropylamine (**12**): bp 75° (16

(11) Melting points are corrected; boiling points are uncorrected. All manipulations and reactions involving amidinium salts and organolithium reagents were carried out in an atmosphere of dry nitrogen. Vpc analyses were carried out on a F & M 720 dual column programmed temperature gas chromatograph using 8 ft × 0.25 in. o.d. columns packed with 0.2% OV-17 on 60–80 mesh GLC-110 (glass beads, Chemical Research Services, Inc., Addison, Ill.).

(12) H. Eilingsfeld, G. Neubauer, M. Seefelder, and H. Weindinger, *Chem. Ber.*, **97**, 1232 (1964).

mm);  $n_D^{25}$  1.4464; nmr ( $C_6D_6$ )  $\tau$  7.40 (s, br, 6,  $-NMe_2$ ), 7.94 (s, 1,  $>CH$ ), and 8.95 (s, 18,  $Me_2C$ ).

*Anal.* Calcd for  $C_{11}H_{25}N$ : C, 77.11; H, 14.71; N, 8.18; mol wt, 171. Found: C, 76.63; H, 14.70; N, 8.33; mol wt, 171.

Treatment of 12 with dry hydrogen chloride in ether gave the HCl salt: mp 181–182° (EtOAc- $CH_2CN$ ); nmr ( $CD_3CN$ )  $\tau$  0.60 (m, 1,  $N^+H$ ), 6.83 (d,  $J = 0.3$  Hz), and 6.86 (d,  $J = 5.5$  Hz) (total 7,  $H_{CN}+H$  and  $HN^+Me_2$ ), and 8.67 (s, 18,  $Me_2C^-$ ). The HCl salt was converted to the hexafluorophosphate, mp 212° dec (acetone).

*Anal.* Calcd for  $C_{11}H_{25}F_6NP$ : C, 41.64; H, 8.26; N, 4.42; P, 9.76. Found: C, 41.82; H, 8.22; N, 4.26; P, 9.76.

A small forerun from the fractional distillation of 12 consisted predominantly of 12 along with a minor amount of tris(dimethylamino)methane. The latter was identified (vpc, nmr) by comparison with an authentic sample.<sup>1</sup>

The semisolid residue from the fractional distillation of 12 was filtered to obtain a solid product and the filtrate. The solid was recrystallized from pentane to obtain 0.5 g (10% based on *tert*-butyllithium) of tetrakis(dimethylamino)methane: mp 122–124°; nmr ( $C_6D_6$ )  $\tau$  7.35 (s); mmp with authentic sample,<sup>7</sup> 121–123°. The filtrate from above was subjected to preparative-scale vpc to isolate the major unidentified component, which was shown by vpc and nmr to be tetrakis(dimethylamino)ethylene:<sup>13</sup> mass spectrum (70 eV)  $m/e$  200, 185, 142, 85, and 44.

***N,N,N',N'-2,2-Hexamethylpropionamidinium Iodide (4) with tert-Butyllithium.***—A total of 11.4 g (0.04 mol) of amidinium salt 4<sup>14</sup> was added in small portions over a period of 10 min to 0.04 mol of *t*-butyllithium in 28 ml of pentane. The reaction mixture was allowed to stand overnight and then was filtered. The filtrate was distilled to obtain 1.2 g (20% of *N,N,N',N'-2,2*-hexamethyl-1,1-propanediamine (5): bp 57° (13 mm);  $n_D^{25}$  1.4381; nmr ( $C_6D_6$ )  $\tau$  7.12 (s, 1,  $>CH$ ), 7.54 (s, 12,  $-NMe_2$ ), and 8.97 (s, 9,  $-CMe_3$ ). Hydrolysis of diamine 5 in dilute hydrochloric acid yielded pivalaldehyde, identical (vpc and nmr) with an authentic sample.

The filter cake from the reaction was dissolved in water and treated with sodium hexafluorophosphate to precipitate 2.5 g of tetramethylammonium hexafluorophosphate, mp  $>360^\circ$ .

*Anal.* Calcd for  $C_4H_{12}F_6NP$ : C, 21.92; H, 5.52; F, 52.03; N, 6.39; P, 14.13. Found: C, 22.24; H, 5.56; F, 51.81; N, 6.46; P, 14.04.

***N,N,N',N'-Tetramethylformamidinium Chloride (6) with tert-Butyllithium.***—The formamidinium salt 6,<sup>15</sup> 10.9 g (0.08 mol), was added in small portions with cooling to 0.08 mol of *tert*-butyllithium in 52 ml of pentane. The mixture was allowed to stand overnight and then was filtered. Distillation of the filtrate gave 2.4 g (21% based on 6) of tris(dimethylamino)methane, 1.9 g (42% based on *tert*-butyllithium) of 12, and a higher boiling residue. Nmr analysis of the residue indicated the presence of tetrakis(dimethylamino)ethylene; a trace of tetrakis(dimethylamino)methane was also indicated but this was not confirmed.

***N,N,N',N'-Tetramethylchloroformamidinium Chloride with Phenyllithium. A. In Ether.***—A total of 3.4 g (0.02 mol) of 1 was added in small portions with stirring to 0.04 mol of phenyllithium in 34 ml of ether. The mixture was cooled to 5° during the addition, which required 45 min. The mixture then was allowed to warm to room temperature and stand overnight. The mixture was filtered and the filtrate was distilled to obtain 3.6 g (71%) of  $\alpha,\alpha$ -diphenyl-*N,N,N',N'*-tetramethylmethanediamine (15): bp 130° (0.3 mm); mp 129.5–131.5° (acetone); nmr ( $C_6D_6$ )  $\tau$  2.85 (m, 10, aromatic) and 8.04 (s, 12,  $NMe_2$ ).

*Anal.* Calcd for  $C_{17}H_{22}N_2$ : C, 80.30; H, 8.72; N, 11.02. Found: C, 80.07; H, 8.91; N, 11.00.

Hydrolysis of 15 in dilute hydrochloric acid yielded benzo-phenone, mp 48.5–49.5°, mmp 49.0–49.5°.

Substantially the same results as above were observed when the order of addition was reversed.

**B. In Benzene.**—A solution of 0.04 mol of phenyllithium in 34 ml of ether was placed in a small round-bottom flask and the ether was evaporated under vacuum with warming to 50°. The dry residue<sup>16</sup> was slurried with 50 ml of benzene and the slurry was added in portions to 3.42 g (0.02 mol) of 1 and 10 ml of benzene with stirring. After an induction period of 5–15 min, the mixture turned dark red and evolved heat. The mixture was stirred for an additional 2 hr and then filtered.

Nmr spectroscopic analysis of the filtrate indicated approximately equal amounts of 15 and a product subsequently identified as the dimer, 16: nmr  $\tau$  7.55 (s, 12,  $NMe_2$ ), 7.46 (s, 12,  $NMe_2$ ), and 4.05 (m, 4, vinyl). A small peak at  $\tau$  7.39 was assigned to tetrakis(dimethylamino)ethylene on the basis of spiking experiments. The aromatic region of the spectrum was too complex for analysis. Vpc coupled with mass spectroscopic analysis showed the following products (estimated yield) to be present: chlorobenzene (20%), biphenyl (10–15%), and chlorobiphenyls (7–10%). Substantially the same results were obtained when pentane solvent was used in place of benzene.

The solvent was removed from the filtrate by distillation up to a pot temperature of 120°. Nmr analysis of the residue showed complete disappearance of 16 and the appearance of a new compound subsequently identified as benzylidenebisdimethylamine (17).<sup>17</sup> This same transformation occurred, although at a slower rate, when the filtrate was allowed to stand at room temperature. Distillation of the residue afforded 1.4 g (28%) of 15 and 1.0 g (28%) of 17: bp 50–53° (0.55 mm);  $n_D^{25}$  1.5098; nmr ( $C_6D_6$ )  $\tau$  2.79 (s, 5, aromatic), 6.62 (s, 1,  $ArCH^-$ ), and 7.86 (s, 12,  $NMe_2$ ). Hydrolysis of 17 in dilute hydrochloric acid yielded benzaldehyde (nmr and vpc identical with those of an authentic sample).

**Reactions of Dimer 16.**—The following experiments were carried out to further elucidate the structure of 16. In each case the reaction of 1 with phenyllithium was repeated and the experiments were conducted on a fresh sample of filtered reaction mixture.

**A. Hydrogenation.**—The filtrate was hydrogenated over platinum oxide catalyst at 50 psig and room temperature for 3 hr. The nmr spectrum of the product showed that complete conversion of 16 to 17 had occurred.

**B. Hydrolysis.**—For brevity, only the experiment with deuterium oxide is described. Deuterium oxide was added dropwise to the filtrate and the reaction was monitored by nmr spectroscopy. Compound 16 disappeared during the addition while 17, *N,N*-dimethylbenzamide, and dimethylamine were produced. The mixture was treated with concentrated hydrochloric acid in the cold to hydrolyze 17 and 15 to benzaldehyde and benzophenone, respectively. The mixture was extracted with ether and the ether was removed by evaporation. The residue was separated by vpc into its components, which were examined by mass spectroscopy to determine deuterium content. No deuterium could be found in the *N,N*-dimethylbenzamide, whereas the benzaldehyde was 32% deuterated; it was determined from the cracking pattern that all of the deuterium was on the carbonyl carbon.

**C. Methyl Iodide.**—The filtrate was treated with 2.8 g (0.02 mol) of methyl iodide and allowed to stand for 12 hr. During this period a slow disappearance of 16 was noted (nmr) along with the formation of a solid precipitate. The latter was collected by filtration and dissolved in water, and sodium hexafluorophosphate was added to precipitate 0.6 g (9% based on 1) of *N,N,N',N'*-tetramethylbenzamidium hexafluorophosphate: mp 109.5–110.5° (EtOAc); nmr ( $CD_3CN$ )  $\tau$  2.37 (m, 5, aromatic) and 6.88 (s, 12,  $C^+NMe_2$ ).

*Anal.* Calcd for  $C_{11}H_{17}F_6N_2P$ : C, 41.00; H, 5.32; F, 35.37; N, 8.70; P, 9.61. Found: C, 40.93; H, 5.04; F, 35.07; N, 8.72; P, 9.52.

Hydrolysis of the salt in dilute sodium hydroxide gave *N,N*-dimethylbenzamide.

**D. Carbonation.**—Addition of gaseous carbon dioxide to the filtrate resulted in the immediate and selective disappearance of 16 and the formation of a sticky precipitate. The supernatant was decanted, the precipitate was taken up in water, and the aqueous solution was extracted with ether. Acidification of the aqueous solutions caused evolution of carbon dioxide, whereas basification gave dimethylamine and an oil which was extracted with ether. The ether extract was treated with dilute hydrochloric acid and the mixture was continuously extracted with ether to remove neutral products. Evaporation of the ether gave 0.08 g of *N,N*-dimethylbenzamide. The aqueous acid solution was made basic (6 *N* NaOH) and the oil which separated was taken up in ether. The ether solution was dried ( $MgSO_4$ ) and the ether was evaporated under a stream of nitrogen to obtain 0.3 g (10%) of *N,N,N',N'*-tetramethyl- $\alpha$ -amino- $\alpha$ -phenyl-*p*-toluamide (19): nmr ( $CD_3CN$ )  $\tau$  2.61 (m, 9, aromatic), 5.86 (s, 1,  $N-CHAr$ ), 7.12 (s, 6,  $Me_2NC=O$ ), and 7.88 (s, 6,  $>CNMe_2$ ); mass spectrum (70 eV)  $m/e$  282, 238, 205, 165, 134, and 72.

(13) H. Weingarten and W. A. White, *J. Org. Chem.*, **31**, 3427 (1966).

(14) C. F. Hobbs and H. Weingarten, *ibid.*, **33**, 2385 (1968).

(15) Z. Arnold, *Collect. Czech. Chem. Commun.*, **24**, 760 (1959).

(16) A small residue of ether could not be removed, as shown by nmr.

(17) H. Weingarten and W. A. White, *J. Org. Chem.*, **31**, 4041 (1966).

Compound 19 was dissolved in 20 ml of glacial acetic acid and hydrogenated over 0.1 g of platinum oxide at 50 psig and 75° for 8 hr. The acetic acid was evaporated and the residual amide was hydrolyzed by refluxing it in 10 ml of concentrated hydrochloric acid for 16 hr. The mixture was diluted with water and extracted with ether. The ether was evaporated to obtain  $\alpha$ -phenyl-*p*-toluic acid: mp 156–157°; mmp with authentic sample (prepared by hydrogenation of 4-benzoylbenzoic acid in acetic acid over palladium-charcoal at 65° and 50 psig), 158–160°.

**E. Trifluoroacetic Anhydride.**—Trifluoroacetic anhydride was added dropwise to the filtrate until 16 just disappeared (nmr monitor). The viscous precipitate which formed was separated from the supernatant by decantation. The supernatant was shown to contain *N,N*-dimethyltrifluoroacetamide<sup>18</sup> by vpc and

mass spectroscopy (*m/e* 171). The viscous precipitate was taken up in acetonitrile, the solution was extracted with pentane, and the acetonitrile was evaporated. The residue was dissolved in 2 *N* sodium hydroxide and the mixture was extracted with ether. The ether was evaporated, the residue was separated by vpc, and the components were examined by mass spectroscopy; the presence of *N,N*-dimethylbenzamide and compound 19 (major component) was confirmed.

**Registry No.**—3, 815-62-3; 5, 30482-28-1; 12, 30482-29-2; 12 HCl, 30482-30-5; 12 hexafluorophosphate, 30471-97-7; 15, 19111-89-8; 16, 30482-32-7; 17, 13880-55-2; 19, 30482-34-9; tetramethylammonium hexafluorophosphate, 558-32-7; *N,N,N',N'*-tetramethylbenzamidinium hexafluorophosphate, 30482-36-1.

(18) E. R. Bissell and M. Finger, *J. Org. Chem.*, **24**, 1256 (1959).

## Notes

### $\alpha,\alpha,\alpha$ -Tris(dimethylamino)toluene, a New *gem*-Triamine

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Recently there has been considerable interest in the synthesis<sup>1–5</sup> and reactions<sup>4–8</sup> of *gem*-triamines. The majority of *gem*-triamines thus far synthesized have been N derivatives of methanetriamine with hydrogen as the substituent on the central carbon. Although a higher homolog, 1,1,1-tripiperidinoethane, has been twice reported,<sup>9,10</sup> both assignments subsequently were shown to be in error.<sup>11</sup> More recently, *gem*-triamines with trifluoromethyl<sup>12</sup> and chlorodifluoromethyl<sup>13</sup> groups on the central carbon have been reported.<sup>14</sup> An attempt to synthesize an aryl-substituted *gem*-triamine,  $\alpha,\alpha,\alpha$ -tris(dimethylamino)toluene, by the amination of *N,N*-dimethylbenzamide with tetrakis(dimethylamino)titanium was unsuccessful.<sup>1</sup>

We now have found that  $\alpha,\alpha,\alpha$ -tris(dimethylamino)-toluene can be simply and conveniently prepared by the reaction of phenyllithium with hexamethylguanidinium chloride,<sup>15</sup> the latter being prepared in novel fashion by an exchange reaction between tetramethylchloroformamidinium chloride and tetrakis(dimethylamino)methane. The structure of  $\alpha,\alpha,\alpha$ -tris(dimethylamino)-toluene was proven by its nmr spectrum and elemental analysis, and by hydrolysis in dilute acid to the *N,N,N',N'*-tetramethylbenzamidinium ion, which underwent further hydrolysis to *N,N*-dimethylbenzamide upon basification.

#### Experimental Section<sup>16</sup>

***N,N,N',N',N'',N''*-Hexamethylguanidinium Chloride.**—A solution of 3.42 g (0.020 mol) of *N,N,N',N'*-tetramethylchloroformamidinium chloride<sup>17</sup> in a minimum amount of acetonitrile was added slowly to an acetonitrile solution of 3.95 g (0.021 mol) of tetrakis(dimethylamino)methane.<sup>18</sup> The reaction was sufficiently exothermic to cause reflux of the acetonitrile. The solution was allowed to cool and ether was added to precipitate the hexamethylguanidinium chloride, yield 6.72 g (94%), nmr (CD<sub>3</sub>CN)  $\tau$  7.06 (s). Addition of sodium hexafluorophosphate solution to an aqueous solution of the guanidinium chloride precipitated the hexafluorophosphate, mp 342–347° dec, nmr (CD<sub>3</sub>CN)  $\tau$  7.16 (s).

**Anal.** Calcd for C<sub>7</sub>H<sub>15</sub>F<sub>6</sub>N<sub>3</sub>P: C, 29.07; H, 6.27; F, 39.42; N, 14.53; P, 10.71. Found: C, 29.07; H, 6.44; F, 39.58; N, 14.14; P, 10.69.

**$\alpha,\alpha,\alpha$ -Tris(dimethylamino)toluene.**—To a slurry of 5.0 g (0.028 mol) of *N,N,N',N',N'',N''*-hexamethylguanidinium chloride in 35 ml of ether was added dropwise 22.8 ml (0.028 mol) of phenyllithium (1.226 *M* in ether). The mixture was refluxed for 2 hrs and then cooled and filtered. Ether was removed from the filtrate by distillation. The dark crystalline residue was taken up in pentane and filtered. The filtrate was freed of pentane by evaporation to obtain 3.93 g (52%) of  $\alpha,\alpha,\alpha$ -tris(dimethyl-

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