

ORGANOMETALLIC DERIVATIVES OF DIPHENYL-*N*-METHYLAMINE

BERNARD R. LALIBERTE and STEPHEN A. LEONE*

U.S. Army Materials and Mechanics Research Center Watertown, Massachusetts 02172 (U.S.A.)

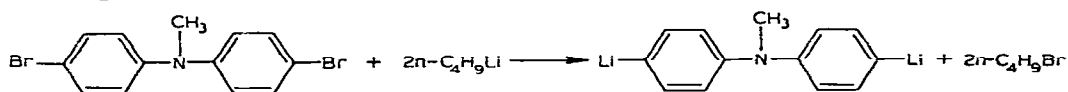
(Received October 27th, 1971)

SUMMARY

The lithium-halogen exchange reaction in two-different solvents has been used to prepare bis(4-lithiophenyl)-*N*-methylamine in high yields. Bis(4-bromophenyl)-*N*-methylamine underwent quantitative halogen-metal exchange with *n*-butyllithium in tetrahydrofuran/diethylether at -78° . An 83% conversion was accomplished in refluxing benzene. Subsequently a series of *para*-disubstituted organometallic derivatives of diphenyl-*N*-methylamine was synthesized using the reaction of the dilithio intermediate with various organometallic monohalides of Si, Ge, Sn, Pb and As. Exchange reactions were carried out between bis[4-(trimethylstannyl)phenyl]-*N*-methylamine and mercury compounds.

INTRODUCTION

Bis(4-lithiophenyl)-*N*-methylamine was prepared via a halogen-lithium exchange reaction.



Subsequently, this dilithio compound was treated with various organometallic halides to form the corresponding *para*-disubstituted organometallic derivatives of diphenyl-*N*-methylamine.



M = Si, Ge, Sn, Pb X = Cl or Br
R = CH₃ or C₆H₅

Bis[4-(diphenylarsino)phenyl]-*N*-methylamine was also synthesized.

The halogen-lithium exchange reactions were carried out under a variety of conditions.

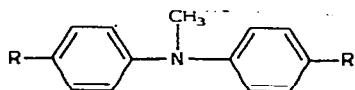
* Department of Chemistry, Merrimack College, North Andover, Massachusetts (U.S.A.).

RESULTS AND DISCUSSION

The only reported¹ conversion of bis(4-bromophenyl)-*N*-methylamine to the dilithio intermediate was carried out with lithium wire in diethyl ether/tetrahydrofuran solvent at room temperature. After derivatization of the dilithio intermediate with methyl-diphenylchlorosilane, the low yield of the resulting *para*-bis(methyl-diphenylsilyl) derivative (5.4%) and the experiment as described held little promise for general preparative utility. Bis(4-bromophenyl)-*N*-methylamine did not readily react with magnesium in tetrahydrofuran. Since the carbonation of this di-Grignard reaction produced a mixture of acids, it was not pursued further. The halogen-metal interconversion using *n*-butyllithium appeared to be more promising. Bis(2-bromophenyl)-*N*-methylamine² and the homologous *N*-ethylamine compound³ have been reported to give the *ortho*-dilithio derivative in diethyl ether at 0° in yields which exceeded 50 percent. Similar observations were made with bis(2,4-dibromophenyl)-*N*-alkylamines which in diethyl ether exchange both *ortho* positions in high yield⁴. Our results with the *para*-dibromo isomer under similar conditions showed a predominance of the monolithio intermediate accompanied by some unreacted dibromo compound. We found that the halogen-lithium interconversion was incomplete in diethyl ether solution at various temperatures and at the reflux temperature butylation (coupling) was observed.

Nearly quantitative yields, based on carbonation of the *para*-dilithio derivative can be obtained by using stoichiometric quantities in tetrahydrofuran/ether

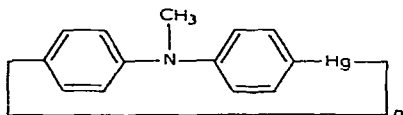
TABLE I

DATA AND ANALYSES OF DIPHENYL-*N*-METHYLAMINE DERIVATIVES,

No.	Product R	Yield (%)	M.p. (°C)	Mol. Wt. found (calcd.)	Analyses found (calcd.) (%)			
					C	H	N	Metal
1	COOH	100	306 (dec.)		66.60 (66.41)	4.89 (4.83)	5.09 (5.16)	
2	(CH ₃) ₃ Sn	57	95-98	491(C ₆ H ₆) (509)	44.70 (44.85)	5.77 (5.74)	2.78 (2.75)	46.51 (46.65)
3	(C ₆ H ₅) ₃ Si	63	267	704(CHCl ₃) (700)	84.23 (84.07)	6.05 (5.90)	1.90 (2.00)	8.03 (8.03)
4	(C ₆ H ₅) ₃ Ge	66	260-261	794(C ₆ H ₆) (789)	74.32 (74.59)	5.10 (5.24)	1.73 (1.78)	18.56 (18.40)
5	(C ₆ H ₅) ₃ Sn	48	222-224		66.91 (66.78)	4.74 (4.70)	1.47 (1.59)	26.75 (26.94)
6	(C ₆ H ₅) ₃ Pb	57	210-212	1021(C ₆ H ₆) (1058)	55.74 (55.61)	3.91 (4.03)	1.39 (1.32)	39.00 (39.16)
7	(C ₆ H ₅) ₂ As	35	84	639 ^a (639)	69.61 (69.49)	5.03 (4.89)	2.00 (2.19)	23.67 (23.43)
8	<i>n</i> -Bu		^b		85.28 (85.37)	9.77 (9.89)	4.92 (4.74)	

^a Molecular ion from mass spectrum. ^b B.p. 150°/0.075 mm.

The exchange reaction of the *para*-bis(trimethylstannyl) compound with phenylmercuric chloride did not yield bis[4-(phenylmercuric)-phenyl]-*N*-methylamine. The reaction was found to proceed in a 1/1 molar ratio. The pure colorless product obtained has a high melting point and is insoluble in most common organic solvents with the exception of pyridine and *N,N*-dimethylformamide. The elemental analysis is consistent with the empirical formula $C_{13}H_{11}HgN$ and X-ray diffraction confirms a crystalline structure. The following structure is therefore proposed for this compound.



Attempts to obtain the molecular weight through a mass spectrum were not successful.

Similar reactions have been reported by Wittig for both *o*-dilithiobenzene⁶ and 2,2'-dilithiobiphenyl⁷ with $HgCl_2$ to give a high melting cyclic hexamer of *o*-phenylenemercury, $(-C_6H_4-Hg-)_6$ and a cyclic tetramer of diphenylenemercury, $(-C_6H_4-C_6H_4-Hg-)_6$ respectively.

EXPERIMENTAL

All the reactions described were carried out in anhydrous conditions under argon. Tetrahydrofuran was dried over lithium aluminum hydride and distilled under argon. Thiophene-free benzene was used after azeotropic removal of moisture; *n*-butyllithium (1.5 *M*) in hexane was obtained from Foote Mineral Co. All chemicals, with the exception of bis(4-bromophenyl)-*N*-methylamine⁸ were commercial and purified wherever necessary by established procedures. Molecular weights were determined with a Mechrolab Osmometer Model 301A. Decomposition temperatures were obtained with a DuPont Model Differential Thermal Analyzer. Capillary melting points (uncorrected) were obtained on a Thomas Hoover Apparatus. Infrared spectra were obtained using a Perkin-Elmer 137 spectrophotometer. Mass spectra were obtained on Model 21-110B, Consolidated Electronics Corporation, and measured at 70 eV. Elemental analyses were carried out by Galbraith Laboratories Inc., Knoxville, Tennessee.

(1). *Bis*(4-carboxyphenyl)-*N*-methylamine via carbonation of bis(4-lithiophenyl)-*N*-methylamine

(A). *Tetrahydrofuran*. A solution of bis(4-bromophenyl)-*N*-methylamine (6.82 g; 0.02 mole) in 125 ml of tetrahydrofuran was added dropwise to a magnetically stirred solution of *n*-butyllithium (hexane) (26.7 ml; 0.04 mole) in 25 ml of diethyl ether during a 30 min period at -78° . After an hour, the contents were poured over a dry-ice/diethyl ether slurry with vigorous stirring. After the solvents evaporated, the residue was dissolved in water and filtered. The filtrate was carefully acidified with dilute sulfuric acid. The precipitated dicarboxylic acid was filtered and washed thoroughly with water then washed once with cold ethanol. The yield (5.4 g) was quanti-

tative. Purification by crystallization from tetrahydrofuran/ethanol did not alter the decomposition temperature.

(B). *Benzene*. A solution of the bis(4-bromophenyl)-*N*-methylamine (0.02 mole) in 95 ml of benzene was dropped rapidly into a magnetically stirred solution of *n*-butyllithium (hexane) (0.04 mole). Turbidity set in after a short time (ca. 10 min) at gentle reflux followed by copious precipitation during the remainder of the heating period of 1.5 h. After cooling to room temperature, the contents were carbonated as described above in (A) giving 4.5 g (83%) of the diacid. Infrared spectra and decomposition temperatures of the diacid products obtained by both methods were identical.

(2). *Bis*[4-(trimethylstannyl)phenyl]-*N*-methylamine

To the dilithio species prepared in 83% yield as described in (B), trimethyltin chloride (7.0 g, 0.035 mole) was added in one portion with vigorous stirring at room temperature. A mild exothermic reaction ensued and lithium chloride precipitated instantly. After stirring for several hours, the mixture was filtered and the solvent was removed *in vacuo*. The residue, 8.56 g, solidified and was washed with cold methanol to remove an oily by-product. The yellowish solid 5.1 g (57%) melted at 92–97°. Crystallization from hot methanol gave colorless glistening plates.

(3). *Bis*[4-(triphenylsilyl)phenyl]-*N*-methylamine

A solution of triphenylchlorosilane (11.6 g; 0.04 mole) in 100 ml of tetrahydrofuran was added dropwise to a solution of the *para*-dilithio compound (0.02 mole) prepared as described in (A), during a period of 30 min. The reaction was maintained at –78° for 1 h and slowly allowed to rise to room temperature. The solvent was removed under vacuum. The residue was washed well with water, ethanol, and hexane. Purification was accomplished by crystallization from tetrahydrofuran/hexane.

(4). *Bis*[4-(triphenylgermyl)phenyl]-*N*-methylamine

Using triphenylgermyl bromide with the dilithio reagent as described in (B) gave the crude *para*-bisgermyl compound. Purification was accomplished by crystallization from methylene chloride/isopropyl alcohol.

(5). *Bis*[4-(triphenylstannyl)phenyl]-*N*-methylamine

Same as described for the bis(trimethylstannyl) derivative. The residue was washed with hexane, m.p. 190–195°. An analytical sample was prepared by crystallization from hot cyclohexane.

(6). *Bis*[4-(triphenylplumbyl)phenyl]-*N*-methylamine

As described in (B) but with 2 h reflux in benzene. The residue was washed with diethyl ether, m.p. 206–210°, 57% yield. Analytical sample was obtained by crystallization from hot cyclohexane.

(7). *Bis*[4-(diphenylarsino)phenyl]-*N*-methylamine

Diphenylchloroarsine, 0.04 mole, was added to the 4,4'-dilithio reagent (0.02 mole) prepared as described in (A). The reaction was maintained at –78° for 1 h and then allowed to rise to room temperature. The solvent was concentrated

in vacuo, benzene was added and the insoluble salts were removed by filtration. Benzene was removed *in vacuo*. Purification of the residual material was accomplished by repeated crystallization from a diethyl ether/petroleum ether solution at -5° .

(8). *Bis[4-n-butylphenyl]-N-methylamine*

The exchange was carried out as described in (4) except that the temperature was maintained at -10° for 30 min. The reaction mixture was concentrated under vacuum and redissolved in benzene and filtered to remove lithium bromide. The filtrate was again concentrated, placed on a column packed with neutral alumina and eluted with benzene. The product obtained was distilled, b.p. $150^{\circ}/0.075$ mm, to give 4.2 g (71%) of coupling product, n_D^{25} 1.5615.

(9). *4-Bromo-4'-carboxydiphenyl-N-methylamine*

(a). *In diethyl ether*. The bis(4-bromophenyl)-*N*-methylamine (0.02 mole) was added in portions to a stirred solution of *n*-butyllithium (hexane) (0.04 mole) in 125 ml of diethyl ether at 0° during a period of 30 min. After further stirring for 30 min one-third of the reaction mixture was withdrawn and carbonated as described previously. The acidic product obtained (1.5 g) was analyzed⁹ by DSC and found to contain about 5% of the diacid. The yield of the monoacid is about 75%.

(b). *In tetrahydrofuran*. The use of equimolar amounts of the reactants under the identical conditions for the preparation of bis(4-carboxyphenyl)-*N*-methylamine as described in (4) provided a quantitative yield of the monoacid, 4-bromo-4'-carboxydiphenyl-*N*-methylamine. An analytical sample was obtained by recrystallization from tetrahydrofuran/ethanol.

(10). *4-Bromo-4'-(trimethylstannyl)diphenyl-N-methylamine*

To the remainder of the above reaction (a) trimethylstannyl chloride (5.1 g; 0.026 mole) in 50 ml diethyl ether was added dropwise over a 15 min period and stirred for 2.5 h at 0° . After standing overnight at room temperature, the reaction was filtered from inorganic salts and the filtrate was concentrated *in vacuo*. The dark residual oil was redissolved in hexane and filtered to remove remaining salts. After removal of the solvent, 5.43 g of crude product was obtained. Fractional distillation of 4.67 g gave 2.06 g, b.p. $155-165^{\circ}/0.1$ mm which crystallized after several days, m.p. 44° (40% yield based on monolithium intermediate). An analytical sample was prepared as needles by recrystallization from petroleum ether with chilling.

A higher distillation fraction, 1.34 g, b.p. $165^{\circ}/0.1$ mm contained the bis-(trimethylstannyl) derivative, which crystallized quickly, m.p. $90-92^{\circ}$.

(11). *4-Bromo-4'-(triphenylsilyl)diphenyl-N-methylamine*

A similar reaction conducted in 200 ml of diethyl ether at -45° with triphenylsilyl chloride afforded nearly identical results as described above. Diethyl ether was removed *in vacuo*, the residue was extracted with benzene and filtered to remove lithium salts. Benzene was removed *in vacuo* and the residue was fractionally crystallized with hexane/tetrahydrofuran (1/1). The first crop gave 10% bis(triphenylsilyl) derivative, and the later crops contained the mono(triphenylsilyl) derivative, 80%, m.p. $140-152^{\circ}$. An analytical sample of the bromotriphenylsilyl compound was obtained by recrystallization from hexane/tetrahydrofuran (10/1).

(12). *4-Bromo-4'-(triphenylplumbyl)diphenyl-N-methylamine*

The reaction described under (6) carried out with 1 h of reflux instead of 2 gave only 20% of the bislead compound and 53% of crude monobromolead compound m.p. 120–130°. The crude product was further purified by elution with hexane/benzene (9/1) on a column packed with neutral alumina to give a colorless sample m.p. 139–142°. This solid was finally recrystallized from hot hexane to yield soft needles.

Exchange reactions(13). *Bis[4-(chloromercuri)phenyl]-N-methylamine*

A solution of mercuric chloride (2.13 g; 7.86 mole) and bis[4-(trimethylstannyl)phenyl]-N-methylamine (2.00 g; 3.94 mole) in 100 ml of dry acetone was heated to reflux for 30 min. The product was filtered and washed with hot ethanol and ether. The yield obtained after vacuum drying was 2.31 g (95%).

(14). *Bis[4-(acetoxymcuri)phenyl]-N-methylamine*

The same reaction as described in (13) conducted with mercuric acetate gave 2.73 g (99%) of crystalline product.

(15). *Oligomeric 4,4'-diphenylenemercuri-N-methylamine*

Using phenylmercuric chloride in a similar reaction and refluxing the mixture 4 h gave, after washing with benzene and acetone 1.5 g of crystalline product, m.p. 310° (dec.).

ACKNOWLEDGEMENT

The authors wish to thank Dr. C. R. Desper for his cooperation by running the X-ray powder diffraction pattern of the mercury compounds. Also, we wish to thank Dr. W. E. Davidsohn for his interest and helpful suggestions. This paper reports research undertaken at the Army Materials and Mechanics Research Center, Watertown, Massachusetts, and was sponsored under Project No. 1T061101A91A. We are indebted to Mr. Maurice Basinet of the U.S. Army Natick Laboratories for the mass spectra.

The findings in this report are not to be construed as an official position of the Department of the Army.

REFERENCES

- 1 M. J. Napoli, *U.S. Pat.*, 3, 308, 144 (1967).
- 2 G. Baum, H. A. Lloyd and C. Tamborski, *J. Org. Chem.*, 29 (1964) 3410.
- 3 H. Gilman and E. A. Zeuch, *J. Amer. Chem Soc.*, 82 (1960) 2522.
- 4 R. E. Jones and D. Wasserman, *U.S. Pat.*, 3, 065, 251 (1962).
- 5 A. E. Borisov, A. I. Borisova and L. V. Ludryaveteva, *Izv. Akad. Nauk SSR, Ser. Khim.*, 10 (1968) 2287.
- 6 G. Wittig and F. Bickelhaupt, *Chem. Ber.*, 91 (1958) 883.
- 7 G. Wittig and G. Lehmann, *Chem. Ber.*, 90 (1957) 875.
- 8 K. Fric, *Justus Liebigs Ann. Chem.*, 346 (1906) 213.
- 9 C. B. Murphy, *Anal. Chem.*, (1968) 380–391R.