not occur upon chilling, the lower layer that formed in the reaction was separated, washed with 10% NaOH, and then dissolved in ether. The resulting ether extract was then washed with base and water and was then dried over KOH pellets. The ether was removed and, in certain cases, crystallization of the resulting oil occurred upon chilling. If crystallization occurred, a recrystallization from a benzene–alcohol solvent was employed. In all cases the infrared and nmr spectra, which are not reported in this Note, agreed with the structures assigned to these compounds. However, the chemical shifts of the SCH_2N group in parts per million are recorded in Table I.

Registry No.—Ammonia, 7664-41-7.

The Reaction of Grignard Reagents with Arylthiomethylarylamines and with Tris(phenylthiomethyl)amines

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In a previous communication,[1] we have noted that Grignard reagents, in analogy with their action upon alkoxymethylamines,[2] cleave the C–S bond rather than the C–N bond in the phenylthiomethylalkylamines. The latter might be the expected cleavage if, as suggested by Grillot and Lau[3] in their study of the acid-catalyzed rearrangement of the arylthiomethylamines, the C–N bond should be a more labile bond than the C–S bond.

The study of the action of Grignard reagents on the S,N-acetals has now been extended to the N-(arylthiomethyl)arylamines, to N,N-bis(phenylthiomethyl)-aniline, and to tris(phenylthiomethyl)amine. The reaction of Grignard reagents on the two former types of compounds appears to be an excellent method of preparing N,N-dialkylanilines, while reaction with the latter compound leads to the synthesis of tertiary aliphatic amines if an excess of Grignard reagent is used.

In Table I are listed the N-alkylated anilines obtained from N-(phenylthiomethyl)N-methylaniline and N-(phenylthiomethyl)N-methyl-*p*-toluidine according to eq 1.

$$C_6H_5SCH_2N(CH_3)Ar + RMgX \longrightarrow RCH_2N(CH_3)Ar + C_6H_5SMgX \quad (1)$$

In Table II are listed the N,N-dialkylated anilines that were obtained from N,N-bis(phenylthiomethyl)-aniline according to eq 2, while in Table III are listed

$$(C_6H_5SCH_2)_2NC_6H_5 + 2RMgX \longrightarrow (RCH_2)_2NC_6H_5 + 2C_6H_5SMgX \quad (2)$$

the N-monoalkylated anilines that were obtained from N-(phenylthiomethyl)aniline, according to eq 3 and 4.

$$C_6H_5SCH_2NHC_6H_5 + 2RMgX \longrightarrow RCH_2N(MgX)C_6H_5 + C_6H_5SMgX + RH \quad (3)$$

$$RCH_2N(MgX)C_6H_5 + H_2O \longrightarrow RCH_2NHC_6H_5 + Mg(OH)X \quad (4)$$

Reaction of 3 moles of the Grignard reagent with 1 mole of tris(phenylthiomethyl)amine, according to eq 5, produces tertiary alkylmethylamines, as noted in Table IV.

$$(C_6H_5SCH_2)_3N + 3RMgX \longrightarrow (RCH_2)_3N + 3C_6H_5SMgX \quad (5)$$

In order to check the feasibility of using the reaction of tris(phenylthiomethyl)amine with Grignard reagents for the preparation of primary and secondary amines by a stepwise replacement of the thiophenoxy groups and subsequent acid hydrolysis of the unreplaced thiomethyl groups according to Scheme I and II, the Grignard reagent prepared from 0.1 mole of bromobenzene was added to 0.1 mole of tris(phenylthiomethyl)amine and the products (before acid hydrolysis) were analyzed by nmr spectroscopy. The results indicated that the reaction product was a mixture in which the components were in the following relative order of concentrations: $(PhSCH_2)_3N > (PhCH_2)_3N > (PhCH_2)_2NCH_2SPh > PhCH_2N(CH_2SPh)_2$. Thus, it seems impossible to replace selectively the thiophenoxy groups. In fact, it appears that the order of ease of replacing a single thiophenoxy group is $R_2NCH_2SPh > RN(CH_2SPh)_2 > N(CH_2SPh)_3$.

SCHEME I

$$RMgX + (PhSCH_2)_3N \xrightarrow[-PhSMgX]{} RCH_2N(CH_2SPh)_2 \xrightarrow[\substack{-2PhSH\\ -2CH_2O}]{H^+} RCH_2NH_2$$

SCHEME II

$$2RMgX + (PhSCH_2)_3N \xrightarrow[-2PhSMgX]{} (RCH_2)_2NCH_2SPh \xrightarrow[-PhSH,\ -CH_2O]{H^+} (RCH_2)_2NH$$

Experimental Section

Infrared spectra obtained on a Perkin-Elmer Infracord and nmr spectra obtained on a Varian A-60 spectrometer for the compounds prepared in this study are in agreement with the structures assigned.

The method used in the preparation of the N-(arylthiomethyl)-arylamines and of the N,N-bis(phenylthiomethyl)aniline has been reported by Grillot and Schaffrath[4] while the synthesis of tris(phenylthiomethyl)amine has been described by Pollak and Grillot.[5] The preparation of N-*n*-propyl-N-methylaniline is typical of the preparation of all the amines studied. The Grignard reagent was prepared from 24 g (1 g-atom) of magnesium turnings in 100 ml of dry tetrahydrofuran (THF) to which was added over a period of 2 hr a solution of 48 g (0.44 mole) of ethyl bromide in 50 ml of THF. At the completion of the addition of ethyl bromide, the reaction mixture was refluxed for an additional 30 min.

To the thus prepared Grignard reagent was gradually added a solution of 93 g (0.4 mole) of N-phenylthiomethyl-N-methylaniline[4] in 50 ml of THF. A vigorous exothermic reaction ensued. At the end of the addition, the reaction mixture was stirred for 1 hr. Following the usual work-up (See the Experimental Section entitled Reactions of Phenylthiomethylamines with Grignard Reagents in ref 1), 47.5 g (79.5% of theory) of N-*n*-propyl-N-methylaniline was obtained as a colorless liquid that boiled at 58–60° (1–2 mm). Pertinent data concerning all the amines prepared in this study appear in Tables I, II, III, and IV (p 2893).

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[1] I. E. Pollak, A. D. Trifunac, and G. F. Grillot, *J. Org. Chem.*, **32**, 272 (1967).

[2] G. M. Robinson and R. Robinson, *J. Chem. Soc.*, **123**, 532 (1923).

[3] G. F. Grillot and P. T. S. Lau, *J. Org. Chem.*, **30**, 28 (1965).

[4] G. F. Grillot and R. E. Schaffrath, *ibid.*, **24**, 1035 (1959).

[5] I. E. Pollak and G. F. Grillot, *ibid.*, **32**, 2891 (1967).

TABLE I

N-ALKYL-N-ARYLMETHYLAMINES FROM N-ARYL-N-PHENYLTHIOMETHYL-N-METHYLAMINES AND GRIGNARD REAGENTS ACCORDING TO EQ 1

RMgX	Ar	RCH_2	Registry no.	Yield, %	Mp, °C	Bp (mm), °C
C_2H_5MgBr	C_6H_5	n-C_3H_7	13395-54-5	80		58–60 (1–2)[a]
n-C_4H_9MgBr	C_6H_5	n-C_5H_{11}	3299-39-6	83		107–108 (4–5)[b]
C_6H_5MgBr[f]	C_6H_5	$C_6H_5CH_2$	614-30-2	85		108–112 (1–2)[c]
p-$(CH_3)_2NC_6H_4MgBr$	C_6H_5	p-$(CH_3)_2NC_6H_4CH_2$	7137-77-1	86	68–70[d]	
p-$(CH_3)_2NC_6H_4MgBr$	p-$CH_3C_6H_4$	p-$(CH_3)_2NC_6H_4CH_2$	10509-65-6	77		180–181 (1–2)[e]

[a] J. von Braun and G. Kirschbaum, *Chem. Ber.*, **52,** 1729 (1919), reported bp 225° (760 mm), while J. Meisenheimer, *et al.*, *Ann. Chem.*, **449,** 196 (1926), reported bp 107–110° (20 mm). Its picrate melts at 107–109°. J. Meisenheimer, *et al.*, found it to melt at 109°, while B. K. Singh, *J. Chem. Soc.*, **109,** 791 (1916), reported mp 106–107°. [b] R. Grewe and W. von Bonin, *Chem. Ber.*, **94,** 234 (1961), reported bp 170° (12 mm). [c] The picrate melts at 106–108°. The following melting and boiling points have been reported: mp 109° (B. K. Singh, footnote *a*) and 127° (J. Meisenheimer, *et al.*, footnote *a*); bp 171° (13 mm) (C. Courtot and A. Dondelinger, *Bull. Soc. Chim. France*, (4) **37,** 116 (1925), and 162–163° (8 mm) (R. D. Desai, *J. Indian Inst. Sci.*, **7,** 250 (1924); *Chem. Zentr.*, I, 1298 (1925)). [d] Recrystallized from alcohol. *Anal.* Calcd for $C_{16}H_{20}N_2$: C, 79.96; H, 8.39; N, 11.66. Found: C, 80.08; H, 8.58; N, 11.21. [e] *Anal.* Calcd for $C_{17}H_{22}N_2$: C, 80.27; H, 8.72; N, 11.01. Found: C, 80.05; H, 8.70; N, 10.93. [f] Infrared spectrum in concordance with Sadtler's Standard Infrared Spectra No. 15288.

TABLE II

N,N-DIALKYLANILINES FROM N,N-BIS(PHENYLTHIOMETHYL)ANILINE AND GRIGNARD REAGENTS ACCORDING TO EQ 2

RMgX	RCH_2	Registry no.	Yield, %	Mp, °C	Bp (mm), °C
n-C_4H_9MgBr	n-C_5H_{11}	6249-76-9	84		95–102 (1–2)[a]
n-$C_5H_{11}MgBr$	n-C_6H_{13}	4430-09-5	85		138–140 (5–6)[b]
$CH_2{=}CHCH_2MgBr$	$CH_2{=}CHCH_2CH_2$	13369-16-9	81		90–93 (5–6)[c]
$(CH_3)_2CHMgBr$	$(CH_3)_2CHCH_2$	13369-17-0	77		78–83 (5–6)[d]
C_6H_5MgBr[g]	$C_6H_5CH_2$	91-73-6	86	67–70[e]	210–218 (1–2)[f]

[a] K. H. Slotta and W. Franke, *Ber.*, **B66,** 104 (1933), reported the boiling point of N,N-di-(*n*-amyl)aniline as 280–284° (760 mm), while R. Foster and D. L. Hammick, *J. Chem. Soc.*, 2685 (1954), reported bp 164° (15 mm). [b] The reported boiling points of N,N-di-(*n*-hexyl)aniline are 172–173° (15 mm) (K. H. Slotta and W. Franke, see footnote *a*), 188–189° (30 mm) (R. Foster and D. L. Hammick, see footnote *a*), and 130–135° (0.5 mm) (J. Willenz, *J. Chem. Soc.*, 1677 (1955). [c] *Anal.* Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.41; H, 9.64; N, 6.75. [d] A. Studer, *Ann. Chem.*, **211,** 235 (1882), reported bp 245–250° (760 mm) for N,N-diisobutylaniline. [e] Melting point of solid that crystallized from oil; lit. mp 71–72° (E. Wedekind, *Ber.*, **32,** 521 (1899). [f] The reported boiling point of dibenzylaniline is 226° (10 mm) (C. Courtot and P. Petitcolas, *Bull. Soc. Chim. France*, (4) **39,** 461 (1926)). The melting point of 1,3,5-trinitrobenzene adduct, obtained as deep red needles from alcohol, is 91.5–92.5°. The melting point of this adduct has been reported as 86–87° by J. J. Sudborough, *J. Chem. Soc.*, **109,** 1346 (1916). [g] Infrared spectrum in concordance with Sadtler's Standard Infrared Spectra No. 17392.

TABLE III

N-ALKYLANILINES FROM N-PHENYLTHIOMETHYLANILINES AND GRIGNARD REAGENTS ACCORDING TO EQ 3 AND 4

RMgX	RCH_2	Registry no.	Yield, %	Mp, °C	Bp (mm), °C
n-C_4H_9MgBr	n-C_5H_{11}	2655-27-8	75		140–141 (18)[a]
C_6H_5MgBr[d]	$C_6H_5CH_2$	103-32-2	89	33–36[b]	114–118 (1–2)[c]

[a] J. von Braun and R. Murjahn, *Ber.*, **59,** 1205 (1926), reported the boiling point of *n*-amylaniline as 130° (11 mm). [b] Melting point of crystals obtained by chilling the oil. [c] F. G. Willson and T. S. Wheeler, "Organic Syntheses," Coll. Vol. I, H. Gilman and A. H. Blatt, Ed., 2nd ed, John Wiley and Sons, Inc., N. Y., 1941, p 102, reported the melting point of benzylaniline as 36° and its boiling point as 298–300°, 190° (16 mm), and 178–180° (12 mm). [d] Infrared spectrum in concordance with Sadtler's Standard Infrared Spectra No. 2323.

TABLE IV

TRIALKYLAMINES FROM TRIS(PHENYLTHIOMETHYL)AMINE AND GRIGNARD REAGENTS ACCORDING TO EQ 5

RMgX	RCH_2	Registry no.	Yield, %	Mp, °C	Bp (mm), °C
n-C_4H_9MgBr[e]	n-C_5H_{11}	621-77-2	81		90–95 (1–2)[a]
$(CH_3)_2CHMgBr$	$(CH_3)_2CHCH_2$	1116-40-1	79		183 (760)[b] 115 (80)
C_6H_5MgBr[f]	$C_6H_5CH_2$	620-40-6	91	87–89[c]	
$(CH_3)_3CMgCl$	$(CH_3)_3CCH_2$	13369-22-7	0[d]		

[a] Tri-*n*-amylamine has been reported as boiling at 240–245° (760 mm), A. Mailhe, *Ann. Chim.* (*Paris*), (9) **13,** 193 (1920); 130° (14 mm), A. Skita and F. Keil, *Monatsch. Chem.*, **53/54,** 760 (1929); 127° (11 mm), E. T. Borrows, *et al.*, *J. Chem. Soc.*, 201 (1947); 109° (5 mm), A. I. Vogel, *ibid.*, 1832 (1948). [b] Boiling point reported as 184–186° by R. Sachtleben, *Ber.*, **11,** 734 (1878). [c] Recrystallized from alcohol, F. R. Goss, C. K. Ingold, and I. S. Wilson, *J. Chem. Soc.*, 2457 (1926), found mp 92.5°. Hydrochloride salt melts at 210–225°; R. Panebianco, *Gazz. Chim. Ital.*, **8,** 357 (1878), reported melting point of this salt as 208°, while P. Spica, *ibid.*, **10,** 515 (1880), reported its melting point as 227–228°. [d] Upon work-up, no trisneopentylamine could be isolated. Trimethylamine was probably formed by reduction of the tris(phenylthiomethyl)amine by the Grignard reagent.[1] [e] Infrared spectrum in concordance with Sadtler's Standard Infrared Spectra No. 6375. [f] Infrared spectrum in concordance with Sadtler's Standard Infrared Spectra No. 18406.