The Action of Magnesium and of Grignard Reagents on Certain Benzyl Ethers. Part II.* The Action of Grignard Reagents on o-, m-, and p-Methoxy- and -Phenoxy-methylanilines.

### By Frederick G. Mann and Frederick H. C. Stewart.

It is shown that phenylmagnesium bromide reacts with o-methoxy-methylaniline to give o-benzylaniline, a reaction which is apparently general with Grignard reagents : p-methoxymethylaniline behaves similarly, but the *meta*-isomer is unaffected.

Phenylmagnesium bromide reacts with p-methoxymethyl-NN-dimethyl-aniline to form p-benzyl-NN-dimethylaniline, but the sterically hindered *ortho*-isomer is unaffected.

The mechanism and practical applications of these reactions are discussed.

In Part I * Mann and Stewart suggested that the formation of an amorphous polymer $(C_8H_8)_x$ by the action of magnesium on o-alkoxy(and -aryloxy)methylbenzyl chlorides (I) is due to the initial transitory formation of a Grignard reagent (II) which breaks down as indicated to give the highly reactive o-quinodimethane (III), which immediately polymerises.
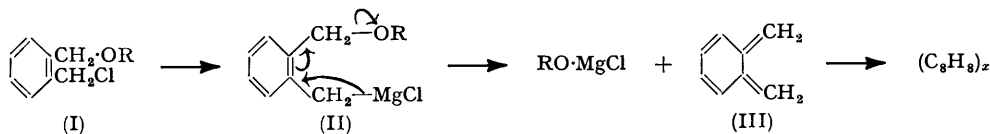
We have now investigated comparable reactions which may involve nitrogen analogues of o-quinodimethane (III) : for clarity of presentation, the reactions and their probable mechanism will be discussed first, then the preparation of the necessary starting materials, and finally the synthetical value of these reactions.

It appeared, by analogy with the reactions described in Part I, that o-methoxymethyl-aniline (IV), when treated with a Grignard reagent, *e.g.*, phenylmagnesium bromide, would first give the magnesium derivative (V), which by a mechanism similar to that illustrated above could break down to form o-quinomonomethane imine (VI). Willstätter and Pfannenstiel (*Ber.*, 1904, **37**, 4605) prepared p-quinone monoimine, $O:C_6H_4:NH$, and p-quinone di-imine, $NH:C_6H_4:NH$, but found that the o-di-imine was too reactive to be isolated although it could be obtained in ethereal solution by suitable oxidation of o-phenylene-diamine. It appeared therefore that the o-mono-imine (VI), although receiving some stabilisation from the polar form (VIA), might have approximately the same resonance energy as o-quinodimethane (III) and would be a highly reactive substance readily under-going polymerisation to (VII).

Experiment showed in fact that the amine (IV), when treated with an excess of phenyl-magnesium bromide, formed in small yield a polymeric material (as VII), but that the major product was o-benzylaniline (IX). We suggest that these results indicate that in this overall reaction the o-quinomonomethaneimine (VI) has a transient existence : a small proportion undergoes direct polymerisation, while the greater part unites with a second molecule of phenylmagnesium bromide to give (VIII) and thence on hydrolysis the amine (IX). The formation of (IX), instead of the isomeric phenyl-o-tolylamine, is probably due mainly to the fact that (VIA) represents the only significant polar form of (VI), and thus necessarily guides the addition of the Grignard reagent to (VIII) and thus to (IX).

Other examples of this terminal addition of Grignard reagents to compounds having the quinomethane system are known : for example, Julian and Magnani (*J. Amer. Chem. Soc.*, 1934, **56**, 2174) have shown that phenylmagnesium bromide adds terminally to methylene-anthrone to form 9-benzyl-10-anthranol.

* Part I, *J.*, 1954, 2826.

It must be emphasised that the magnesium derivative (V), like the Grignard reagent (II) (cf. Part I), may have only a very transient existence, since its formation may be immediately followed by decomposition to (VI).
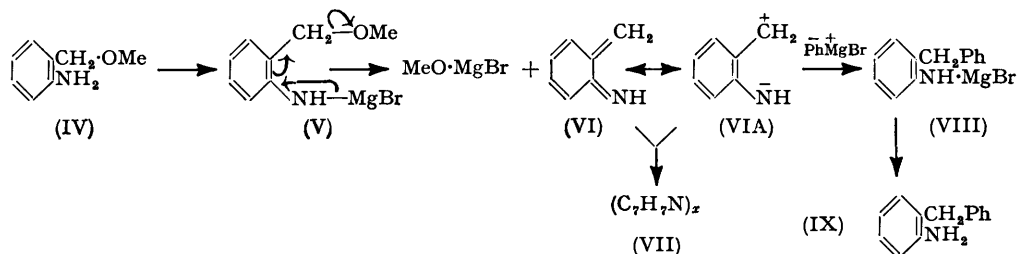
If the above mechanism is accepted, four corollaries follow : (*a*) the amine (IV) should undergo a similar reaction with any other normal Grignard reagent; (*b*) an aryloxymethyl analogue of (IV) should give the same product with the same Grignard reagent; (*c*) the *p*-isomer of (IV) should give the *p*-isomer of (IX), since the same mechanism can now apply, with the intermediate formation of *p*-quinonomonomethane monoimine (as VI); (*d*) the *m*-isomer of (IV) should initially give the *m*-isomer of (V), but since our mechanism cannot now operate, this isomer would be stable until the hydrolysis stage, in which the original amine would be regenerated.

(*a*) We find that the amine (IV), when treated with *n*-propyl-, *iso*propyl-, and 2-phenylethyl-magnesium bromide and with benzylmagnesium chloride gives *o-n*-butylaniline, *o-iso*butylaniline, *o*-3-phenylpropylaniline and *o*-2-phenylethylaniline respectively in high yield, accompanied by some polymeric material in all cases. Other examples are given below.

(*b*) *o*-Phenoxymethylaniline (as IV), when treated with *iso*propylmagnesium bromide, also gave *o-iso*butylaniline. In this case the formation of the polymer was appreciably greater than when (IV) was used.

(*c*) When *p*-methoxymethylaniline was treated with *iso*propyl- and phenyl-magnesium bromide, *p-iso*butylaniline and *p*-benzylaniline respectively were formed, in each case accompanied by a hard resin, undoubtedly the *para*-analogue of the polymer (VII), and formed in considerably greater proportion than that in the *ortho*-series.

(*d*) When *m*-methoxymethylaniline was treated with an excess of phenylmagnesium bromide under the same conditions as the above *ortho*- and *para*-isomers, and the mixture then hydrolysed, the unchanged aniline was recovered in 97% yield.

It is noteworthy that the amine (IV) when treated with lithium aluminium hydride forms chiefly *o*-toluidine with a small quantity of resinous material. Benzyl alkyl ethers
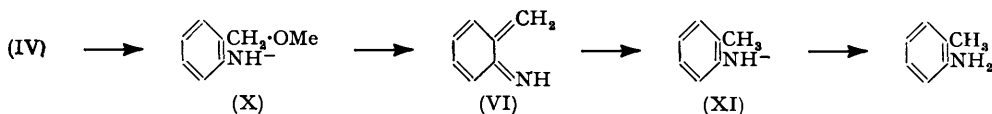
are usually unaffected by this reagent (cf. Part I), and it is probable therefore that the anion (X) produced initially by the hydride ions also gives *o*-quinonomonomethane imine (VI), which then by addition of hydride ion gives (XI), and hence on hydrolysis *o*-toluidine.

The reaction of Grignard reagents with tertiary amines of type (IV) is of particular interest, as the mechanism must now show significant differences. Robinson and Robinson (*J.*, 1923, **123**, 532) have shown that tertiary aminomethylene ethers of type (XII) react with Grignard reagents thus :

$$\text{(XII)} \quad R_2N \cdot CH_2 \cdot OR' + R'' \cdot MgBr = R_2N \cdot CH_2 R'' + R'O \cdot MgBr$$
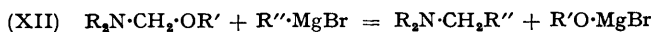
By this reaction they prepared many tertiary amines, including *N*-substituted piperidines and piperazines, the yields being usually *ca.* 50% : Mason and Zief (*J. Amer. Chem. Soc.*, 1940, **62**, 1450) similarly prepared several *N*-substituted morpholines, in yields of 40—60%.

The former authors point out that, although compounds of type (XII) have the usual properties of normal covalent compounds, their behaviour as above indicates a potential ionisation, formulated as $R_2\overset{+}{N}{:}CH_2 \cdots\cdots \overset{-}{O}R'$.

It might appear therefore that *o*-methoxymethyl-*NN*-dimethylaniline (XIII) and its *para*-isomer (XIV) could also give an analogous reaction with Grignard reagents, since they are in effect vinylogues of compounds of type (XII). In the case of the *para*-compound (XIV), Robinson's (extended) reaction would entail an intermediate ionisation phase involving a resonance cation stabilised by the two main polar forms (XV) and (XVA). In the presence of phenylmagnesium bromide, therefore, this cation—acting necessarily as (XVA)—should form *p*-benzyl-*NN*-dimethylaniline (XVI). We find that the aniline (XVI)
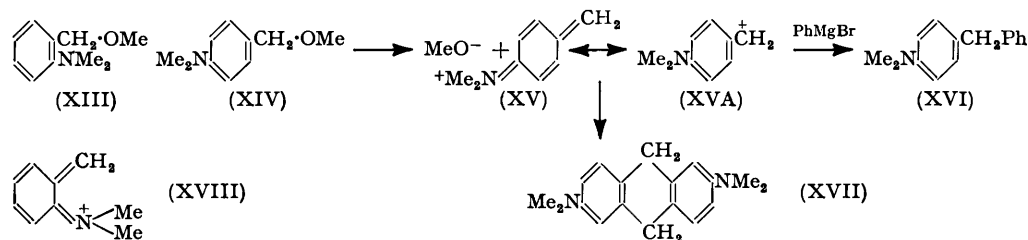

is in fact produced in 84% yield, and additional evidence for the suggested mechanism is the simultaneous formation in small yield of 2 : 6-bisdimethylamino-9 : 10-dihydro-anthracene (XVII), which almost certainly arises by self-condensation of the cation (XV–XVA) with proton elimination. No resin could be detected as a product of this reaction.

The dihydroanthracene (XVII) was also synthesised, for identification, by hydrogenation of 2 : 6-bisdimethylaminoanthracene, prepared by the reduction of *p*-dimethylamino-benzaldehyde with tin and hydrochloric acid (Albano, *Anal. Asoc. Quím. Argentina*, 1946, **34**, 18); it is noteworthy that Albano considers that this reduction involves the inter-mediate formation of a *p*-quinonoid cation, $^+Me_2N{:}C_6H_4{:}CH(OH)$, analogous to (XV).

Further evidence that this type of reaction involves a cation stabilised predominantly by the polar form (XV) is provided by the *ortho*-amine (XIII), which by analogy should thus produce the cationic intermediate (XVIII). An additional factor, namely, steric inhibition of resonance, enters here, however. The *para*-amine (XIV) is of course free from steric hindrance and, for example, very readily forms a methiodide : the *ortho*-amine (XIII) in contrast shows marked hindrance, for it is virtually unaffected when its solution in methyl iodide is boiled for 15 hours. Similar steric hindrance is shown by *o*-ethyldimethylaniline (von Braun and Neumann, *Ber.*, 1916, **49**, 1286; cf. Brown and Cahn, *J. Amer. Chem. Soc.*, 1950, **72**, 2939). The result of this steric effect in (XIII) is that the cation (XVIII), in which the charged dimethylamino-group and the benzene ring would be coplanar, cannot exist. The influence of the quinonoid cation appears to be essential for this type of re-action, for we find that the *ortho*-amine (XIII) is unaffected by phenylmagnesium bromide, in striking contrast to the *para*-amine (XIV).

Synthesis of Starting Materials.—*o*-Methoxymethylaniline (IV) was originally prepared by Thiele and Dimroth (*Annalen*, 1899, **305**, 110) who converted *o*-nitrobenzyl chloride (XIX) by sodium methoxide into methyl *o*-nitrobenzyl ether (XX) and reduced this by
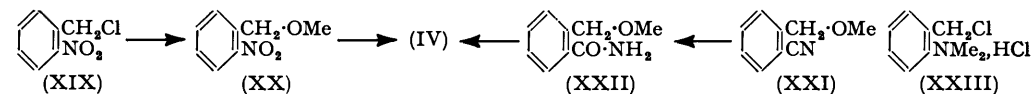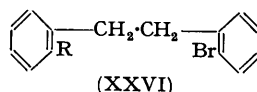

alkaline ferrous sulphate to the aniline (IV); this method is however unsuitable for large-scale work. We find it advantageous to convert *o*-methoxymethylbenzonitrile (XXI) (Mann and Stewart, *J.*, 1954, 2819) by hydrogen peroxide into the benzamide (XXII) which by the Hofmann reaction furnishes the aniline (IV), in 80—85% yield from (XXI).

p-Methoxymethylaniline has been prepared by Romeo (*Gazzetta*, 1905, **35**, 111) using Thiele and Dimroth's method (above) : the reduction stage is far more conveniently carried

out by using iron filings and sodium chloride solution (Rozina, *Zhur. Priklad. Khim.*, 1950, **23**, 1110), and the *meta*-isomer (as IV) has now been similarly prepared. It is significant that the action of sodium methoxide on *o*- and *p*-nitrobenzyl chloride (as XIX) always gives considerable quantities of the corresponding dinitrostilbenes, whereas in the *meta*-series the methyl ether (as XX) is obtained in high yield owing to the almost complete absence of stilbene formation. Furthermore, the *meta*-nitro-ether (as XX) on reduction gave the aniline (as IV) in 82% yield with no resinous by-products, whereas the *p*-aniline derivative (as IV) was formed consistently in 55% yield accompanied by much resin.

Failure attended attempts to prepare *o*-methoxymethyl-*NN*-dimethylaniline (XIII) by methylation of *o*-dimethylaminobenzyl alcohol, obtained by the lithium aluminium hydride reduction of methyl *NN*-dimethylanthranilate. Ultimately the aniline was obtained by treating a cold benzene solution of the alcohol with thionyl chloride, whereby the benzyl chloride was presumably stabilised by formation of the hydrochloride (XXIII), which, on treatment with an excess of sodium methoxide, furnished the aniline (XIII). The *para*-isomer of (XIII) was similarly prepared.

Synthetical Application of Above Reactions.—The action of Grignard reagents on *o*- and *p*-methoxymethylanilines (as IV) can clearly give rise to numerous *o*- and *p*-alkyl (and arylalkyl)anilines, respectively, for many of which (particularly in the *ortho*-series) a convenient synthesis has not previously been available. In addition to examples quoted above, the action of 1- and 2-naphthyl-magnesium bromides on (IV) gave 1-*o*-aminobenzyl- and 2-*o*-aminobenzyl-naphthalene (XXIV) respectively. The reaction is apparently unin-

fluenced by steric hindrance in the Grignard reagent, for mesitylmagnesium bromide gave *o*-aminobenzylmesitylene (XXV) in 85% yield.
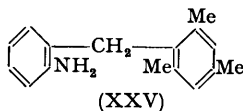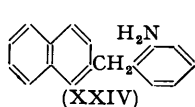
Two classes of compounds otherwise very difficult to obtain may be specified. As an example of a mixed-halogen derivative, *o*-bromobenzylmagnesium bromide, $Br \cdot C_6H_4 \cdot CH_2 \cdot MgBr$, reacts with (IV) to give 2-amino-2'-bromodibenzyl (XXVI; R = NH_2), which can be readily converted, for example, into 2-bromo-2'-iododibenzyl (XXVI; R = I).

The introduction of the *iso*butyl group into the benzene ring has previously proved very difficult. But *o*-*iso*butylaniline (XXVII; R = NH_2), prepared by means of *iso*propyl-magnesium bromide, has been converted *via* the diazonium derivative into *o*-*iso*butyl-iodobenzene (XXVII; R = I), the Grignard derivative of which on carboxylation furnished the hitherto unknown *o*-*iso*butylbenzoic acid (XXVII; R = CO_2H).

EXPERIMENTAL

All products were colourless unless otherwise stated.

o-*Methoxymethylaniline* (IV).—(*a*) *o*-Methoxymethylbenzonitrile (XXI) (15 g.) was added to a solution of ethanol (27 c.c.), 25% aqueous sodium hydroxide (3 c.c.), and hydrogen peroxide (42 c.c.; 100-vol.). The reaction started at once, and the temperature was kept at 40—50° for 1 hr. by cooling, and then for 3 hr. by gentle warming. The solution was neutralised with sulphuric acid and concentrated in a vacuum, whereupon o-*methoxymethylbenzamide* (XXII) separated (16·3 g., 97%); this had m. p. 101—102° (from water) (Found : C, 65·6; H, 6·3; N, 8·7. $C_9H_{11}O_2N$ requires C, 65·4; H, 6·6; N, 8·5%).

(*b*) Bromine (3·9 c.c.) and the powdered amide (10·7 g.) were cautiously added in this order to sodium hydroxide (15·5 g.) in water (130 c.c.) at 0°. The solution was stirred until clear, heated at 70—80° for 30 min., cooled and extracted with ether. Distillation gave the aniline (IV), b. p. 106—108°/11 mm. (6·8 g., 76%). Thiele and Dimroth (*loc. cit.*) give b. p. 123—124°/30 mm. It gave a *benzoyl* derivative, needles, m. p. 74·5°, from ethanol (Found : C, 74·7; H, 6·0; N, 5·5. $C_{15}H_{15}O_2N$ requires C, 74·7; H, 6·2; N, 5·8%).

p-*Methoxymethylaniline.*—Methyl *p*-nitrobenzyl ether was prepared from *p*-nitrobenzyl

chloride by Romeo's method (*loc. cit.*) in 46% yield, accompanied by 4 : 4'-dinitrostilbene, m. p. 286—288°, in 40% yield. A mixture of iron " pin-dust " (20 g.) and 5% aqueous sodium chloride (100 c.c.) was boiled under reflux for 30 min., and then the methyl ether (10 g.) added slowly during 1 hr. Boiling was continued for 3 hr. more, and the mixture was cooled and filtered. The residue and the filtrate were extracted with ether, which on distillation gave the aniline as an oil, b. p. 131—132°/11 mm., 147—148°/23 mm. (4·5 g., 55%). It gave a benzoyl derivative, m. p. 108—109°. Romeo (*loc. cit.*) gives b. p. 164—167°/40 mm. and m. p. 111—113° for these compounds respectively.

m-*Methoxymethylaniline.*—(*a*) A solution of *m*-nitrobenzyl chloride (18·5 g.) in methanol (125 c.c.) was added to one from sodium (2·6 g.) in methanol (65 g.), which was then boiled under reflux for 2 hr., concentrated, poured into water, and extracted with ether. Distillation gave *methyl* m-*nitrobenzyl ether* as a pale yellow liquid, b. p. 138—140°/11 mm. (Found : N, 8·5. $C_8H_9O_3N$ requires N, 8·4%) : 12·9 g., 72%. No 3 : 3'-dinitrostilbene was detected.

(*b*) This nitro-ether, reduced as was the *para*-isomer, afforded m-*methoxymethylaniline*, b. p. 130—131°/11 mm. (Found : C, 69·7; H, 8·2; N, 10·5. $C_8H_{11}ON$ requires C, 70·0; H, 8·0; N, 10·2%) (82%); the initial distillation left only an insignificant non-resinous residue. The amine gave a *benzoyl* derivative, m. p. 76—77°, from benzene–light petroleum (Found : C, 74·5; H, 5·8; N, 5·8. $C_{15}H_{15}O_2N$ requires C, 74·7; H, 6·2; N, 5·8%).

m-*Methoxymethylbenzamide.*—The action of hydrogen peroxide on the corresponding nitrile afforded this *amide* (in very low yield) as an oil which partly solidified, but decomposed on attempted distillation; it separated from benzene–light petroleum as a waxy solid, m. p. 50—53° (Found : C, 65·1; H, 6·4; N, 8·8. $C_9H_{11}O_2N$ requires C, 65·4; H, 6·6; N, 8·5%). Its reaction with hypobromite was not investigated.

The low b.p. of the *ortho*-amine (IV), compared with that of the *meta*- and the *para*-isomer, probably indicates appreciable intramolecular hydrogen bonding.

o-Phenoxymethylaniline was prepared as Thiele and Dimroth (*loc. cit.*) describe.

o-*Methoxymethyl*-NN-*dimethylaniline* (XIII).—(*a*) A solution of methyl NN-dimethyl-anthranilate (64 g.) in ether (100 c.c.) was reduced with lithium aluminium hydride (7·5 g.) in ether (220 c.c.) in the standard way, the solution being finally hydrolysed with aqueous Rochelle salt. Distillation gave o-*dimethylaminobenzyl alcohol* as a very pale yellow oil, b. p. 123—124°/11 mm. (Found : N, 9·4. $C_9H_{13}ON$ requires N, 9·2%) : 48 g., 89%. A solution in methyl iodide, when boiled under reflux for 15 hr., gave the *methiodide*, m. p. 131°, after crystallisation from methanol–ether (Found : C, 40·8; H, 5·7; N, 4·7. $C_{10}H_{16}ONI$ requires C, 40·9; H, 5·4; N, 4·7%); this salt gave the corresponding *methopicrate*, yellow crystals, m. p. 147—148°, from ethanol (Found : C, 48·5; H, 4·7; N, 14·5. $C_{16}H_{18}O_8N_4$ requires C, 48·7; H, 4·5; N, 14·2%).

(*b*) A solution of thionyl chloride (8 g., 1 mol.) in benzene (20 c.c.) was added during 30 min. to a stirred, chilled solution of the above alcohol (10 g.) in benzene (40 c.c.). The complete chilled solution was stirred for 1 hr. and then boiled under reflux for 1 hr., cooled, treated slowly with a solution obtained from sodium (4 g., 2·2 equivs.) and methanol (120 c.c.), and boiled again for 4 hr. The solution was concentrated, diluted with water, and extracted with ether, which on distillation gave the *aniline* (XIII) as a mobile liquid, b. p. 106—108°/13 mm. (7·8 g., 75%) (Found : N, 8·7. $C_{10}H_{15}ON$ requires N, 8·4%). It gave a *picrate*, yellow crystals, m. p. 133—134°, from ethanol (Found : C, 48·7; H, 4·7; N, 14·0. $C_{10}H_{15}ON,C_6H_3O_7N_3$ requires C, 48·7; H, 4·5; N, 14·2%).

p-*Methoxymethyl*-NN-*dimethylaniline.*—*p*-Dimethylaminobenzyl alcohol was prepared in low yield by the lithium aluminium reduction of the corresponding aldehyde (cf. Nystrom and Brown, *J. Amer. Chem. Soc.*, 1948, **70**, 3738); unlike its *ortho*-isomer, it decomposed extensively on distillation, and much 4 : 4'-bisdimethylaminodiphenylmethane was always formed during its preparation. It could not be methylated with methyl sulphate. The alcohol was therefore treated with thionyl chloride as above; sulphur dioxide was removed under reduced pressure from the chilled solution, and this was treated at the b. p. with sodium methoxide (4·5 mols.), giving p-*methoxymethyl*-NN-*dimethylaniline*, b. p. 133—136°/15 mm. (65%) (Found : N, 8·6. $C_{10}H_{15}ON$ requires N, 8·4%). It readily gave a *methiodide*, m. p. 184—185° (effervescence), from methanol–ether (Found : C, 43·1; H, 6·1; N, 4·6. $C_{11}H_8ONI$ requires C, 43·1; H, 5·8; N, 4·5%), and a *methopicrate*, yellow needles, m. p. 131—132° (from ethanol) (Found : C, 50·2; H, 4·9; N, 13·9. $C_{17}H_{10}O_8N_4$ requires C, 50·0; H, 4·9; N, 13·7%).

Action of Grignard Reagents on the Aniline (IV).—In all the following preparations, unless otherwise stated, the aniline (IV) was slowly added with stirring to the Grignard reagent, prepared from the organic halide (4 mols.), each in ethereal solution. The complete mixture was then boiled under reflux for 2 hr., cooled, and hydrolysed with aqueous ammonium chloride, and the

product was isolated from the ether by distillation, or by evaporation of the solvent followed by steam-distillation of the amine and its conversion into the hydrochloride.

(i) Phenylmagnesium bromide, on the addition of the amine (IV), gave initially a white deposit (with brisk ebullition of the ether), which rapidly redissolved and ultimately furnished *o*-benzylaniline, b. p. 172—176°/11 mm., m. p. 54—55° [from light petroleum (b. p. 60—80°)] (63%). Carré (*Compt. rend.*, 1909, **148**, 102) gives b. p. 172—173°/12 mm., m. p. 52°. It gave a hydrochloride, m. p. 176—177°, from ethanol–ether, an acetyl derivative, m. p. 125—126°, from aqueous ethanol, and a benzoyl derivative, m. p. 113—114° from ethanol (Found : C, 83·6; H, 5·6; N, 4·8. Calc. for $C_{20}H_{17}ON$: C, 83·6; H, 6·0; N, 4·8%). Fischer and Schütte (*Ber.*, 1893, **26**, 3086) give m. p. 175° and 135° for the hydrochloride and acetyl compound respectively, while Fischer and Schmidt (*Ber.*, 1894, **27**, 2786) give m. p. 107° and 116° for the acetyl and benzoyl derivative respectively.

(ii) *n*-Propylmagnesium bromide gave *o*-*n*-butylaniline, isolated as its hydrochloride, m. p. 139—140°, from dilute hydrochloric acid (Found : N, 7·9. Calc. for $C_{10}H_{15}N,HCl$: N, 7·6%), and the *benzoyl* derivative, m. p. 116—117°, from light petroleum (b. p. 80—100°) (Found : C, 80·3; H, 7·3; N, 5·5. $C_{17}H_{19}ON$ requires C, 80·6; H, 7·5; N, 5·5%). Read and Mullin (*J. Amer. Chem. Soc.*, 1928, **50**, 1763) give m. p. 137° for the hydrochloride.

(iii) *iso*Propylmagnesium bromide gave o-iso*butylaniline* (XXVII; R = NH$_2$) (72%), b. p. 110—111°/13 mm., having a sweet, rather sickly odour (Found : N, 9·3. $C_{10}H_{15}N$ requires N, 9·4%). It gave an *acetyl* derivative, m. p. 98°, from aqueous ethanol (Found : N, 7·4. $C_{12}H_{17}ON$ requires N, 7·3%), and a *benzoyl* derivative, m. p. 126—127°, from light petroleum (b. p. 80—100°) (Found : C, 80·5; H, 7·1; N, 5·7. $C_{17}H_{19}ON$ requires C, 80·6; H, 7·5; N, 5·5%); a mixture with the *n*-butyl isomer had m. p. 111—117°.

A solution of o-iso*butylaniline* (4·7 g.) in 10% sulphuric acid (50 c.c.) was diazotised at 0° by sodium nitrite (2·2 g.) in water (5 c.c.) and then poured into saturated aqueous potassium iodide (12 g.). When nitrogen evolution subsided, the solution was heated at 100° for 1 hr., mixed with sodium hydrogen sulphite (0·5 g.), and steam-distilled. The distillate, when extracted with ether, gave o-iso*butyliodobenzene* (XXVII; R = I), a pale yellow liquid (4·6 g., 57%), b. p. 112—115°/11 mm. (Found : C, 45·4; H, 4·7. $C_{10}H_{13}I$ requires C, 46·1; H, 5·0%).

The iodo-compound (4·5 g.) readily formed a Grignard reagent, which was added to an excess of solid powdered carbon dioxide and allowed to attain room temperature. The ethereal residue was extracted with 10% aqueous sodium hydroxide, which when boiled (charcoal), filtered, cooled, and acidified gave o-iso*butylbenzoic acid* (XXVII; R = CO$_2$H), m. p. 64—65° (from water) (Found : C, 74·5; H, 8·1. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·9%) : 0·9 g., 30%.

(iv) 2-Phenylethylmagnesium bromide gave o-3-*phenylpropylaniline*, b. p. 131—135°/0·2 mm. (Found : N, 6·7. $C_{15}H_{17}N$ requires N, 6·6%) (77%), which formed a *hydrochloride*, m. p. 198—200° (decomp.), from ethanol (Found ; C, 73·0; H, 7·4; N, 5·9. $C_{15}H_{17}N,HCl$ requires C, 72·7; H, 7·2; N, 5·6%), and a *benzoyl* derivative, m. p. 90—91°, from light petroleum (b. p. 80—100°) (Found : C, 83·7; H, 6·5; N, 4·3. $C_{22}H_{21}ON$ requires C, 83·8; H, 6·6; N, 4·4%).

(v) Benzylmagnesium chloride gave o-2-*phenylethylaniline* (80%), b. p. 193—197°/19 mm., 186—188°/11 mm. Ruggli and Staub (*Helv. Chim. Acta*, 1937, **20**, 37) give b. p. 173—183°/11 mm., m. p. 33°, solidification being long delayed. To confirm its identity, a solution of the amine (1 g.) in concentrated hydrochloric acid (5 c.c.) and water (10 c.c.) was diazotised at 0°, stirred at 0° for 30 min., filtered, treated with 50% aqueous hypophosphorous acid (10 c.c.), and set aside at 0° for 24 hr. The crystalline precipitate of dibenzyl (0·6 g., 65%), when crystallised from ethanol, had m. p. and mixed m. p. 52—53°.

The amine gave a hydrochloride, m. p. 178—179°, an acetyl derivative, m. p. 115—116°, and a benzoyl derivative, m. p. 159—160° (Found : C, 83·8; H, 6·4; N, 4·6. Calc. for $C_{21}H_{19}ON$: C, 83·7; H, 6·3; N, 4·6%). Ruggli and Staub (*loc. cit.*) give m. p.s 198°, 117°, and 166° respectively.

(vi) 1-Naphthylmagnesium bromide gave much brown resin and 1-*o*-aminobenzylnaphthalene, isolated initially as the *hydrochloride* (52%), needles, m. p. 195—196° (decomp.) (from water) (Found : C, 75·3; H, 5·9; N, 5·5. $C_{17}H_{15}N,HCl$ requires C, 75·7; H, 5·9; N, 5·2%), which furnished the amine, m. p. 100—101°, from aqueous ethanol (Found : N, 6·0. Calc. for $C_{17}H_{15}N$: N, 6·0%). Badger (*J.*, 1951, 351) gives m. p. 101—102°.

(vii) 2-Naphthylmagnesium bromide also gave much resin and 2-o-*aminobenzylnaphthalene* (XXIV), isolated initially as the *hydrochloride* (33%), m. p. 187—188° (decomp.) from ethanol–ether (Found : C, 75·0; H, 5·7; N, 5·1. $C_{17}H_{15}N,HCl$ requires C, 75·7; H, 5·9; N, 5·2%) which gave the amine (XXIV) as a brown syrup, b. p. 204—206°/0·2 mm., m. p. 62—63° (from ethanol) (Found : N, 6·0. $C_{17}H_{15}N$ requires N, 6·0%). The amine gave a *benzoyl* derivative,

m. p. 160—161°, from ethanol (Found : C, 85·0; H, 5·8; N, 4·3. $C_{24}H_{19}ON$ requires C, 85·4; H, 5·6; N, 4·1%). The amine, when de-aminated as above, gave 2-benzylnaphthalene, m. p. 53·5—54·5° (from ethanol); Barrett and Linstead (*J.*, 1936, 611) give m. p. 55—56°.

(viii) Mesitylmagnesium bromide (Barnes, *Org. Synth.*, 1941, **21**, 77) gave *o*-aminobenzyl-mesitylene (XXV), isolated as the *hydrochloride* (84%), hygroscopic needles, m. p. 208° (decomp.), from ethanol–ether (Found : C, 72·9; H, 7·8; N, 6·0. $C_{16}H_{19}N,HCl$ requires C, 73·4; H, 7·7; N, 5·3%), which gave the *amine*, m. p. 89—89·5° (from ethanol) (Found : C, 85·0; H, 8·4; N, 6·3. $C_{16}H_{19}N$ requires C, 85·3; H, 8·5; N, 6·2%).

(ix) *o*-Bromobenzylmagnesium bromide, prepared as described by Beeby and Mann (*J.*, 1951, 411), gave 2-amino-2′-bromodibenzyl (XXVI; R = NH_2), isolated as the *hydrochloride*, m. p. 179—180°, from ethanol–ether (Found : N, 4·9. $C_{14}H_{14}NBr,HCl$ requires N, 4·7%) (68%), which gave the *amine*, a yellow oil, b. p. 156—160°/0·2 mm., m. p. 50—51° (Found : N, 5·2. $C_{14}H_{14}NBr$ requires N, 5·0%). The amine gave an *acetyl* derivative, crystals, m. p. 157—158°, from ethanol (Found : C, 60·3; H, 5·1; N, 4·6; $C_{16}H_{16}ONBr$ requires C, 60·3; H, 5·0; N, 4·4%), and a *benzoyl* derivative, needles, m. p. 156—157°, from ethanol (Found : C, 66·0; H, 4·3; N, 3·8. $C_{21}H_{18}ONBr$ requires C, 66·3; H, 4·7; N, 3·6%).

The amine, when diazotised in dilute sulphuric acid and then poured into potassium iodide solution, furnished 2-*bromo*-2′-*iododibenzyl* (XXVI; R = I), m. p. 84—85° (from ethanol) (Found : C, 43·4; H, 3·5. $C_{14}H_{12}BrI$ requires C, 43·4; H, 3·1%).

Reduction of o-*Methoxymethylaniline* (IV).—A solution of the amine (IV) (0·5 g.) in ether (10 c.c.) was added to a stirred suspension of lithium aluminium hydride (0·25 g.) in ether (10 c.c.), which was then boiled for 30 min.; working up in the normal way gave a residue which on benzoylation furnished *N*-benzoyl-*o*-toluidine, m. p. 140—141° (alone and mixed) (from ethanol), and a red resinous by-product in small amount.

Action of isoPropylmagnesium *Bromide on* o-*Phenoxymethylaniline.*—This reaction, per-formed as with (IV), also gave *o*-*iso*butylaniline, b. p. 109—112°/11 mm. (43%) (acetyl deriv-ative, m. p. 98°, alone and mixed with previous sample), and a reddish-orange resinous residue.

Action of Grignard Reagents on p-*Methoxymethylaniline.*—(i) *iso*Propylmagnesium bromide gave a product which on distillation furnished *p*-*iso*butylaniline (62%), having an unpleasant odour and b. p. 122—126°/15 mm. (Found : N, 9·6. Calc. for $C_{10}H_{15}N$: N, 9·4%), a hard reddish resin remaining undistilled. The amine was characterised as the acetyl derivative, leaflets, m. p. 130—131°, from aqueous ethanol (Found : C, 75·6; H, 8·9; N, 7·0. Calc. for $C_{12}H_{17}ON$: C, 75·3; H, 8·9; N, 7·3%), and the benzoyl derivative, needles, m. p. 127—128°, from ethanol (Found : C, 80·5; H, 7·5; N, 5·5. Calc. for $C_{17}H_{19}ON$: C, 80·6; H, 7·5; N, 5·5%); Hickinbottom and Preston (*J.*, 1930, 1566) give m. p. 127—128° for the acetyl deriv-ative and Zalesskaya (*J. Gen. Chem. U.S.S.R.*, 1947, **17**, 489) gives m. p. 131—131·5° and 129° for the acetyl and benzoyl derivative respectively.

(ii) Phenylmagnesium bromide similarly gave *p*-benzylaniline, b. p. 182—192° (44%), and a brown resinous residue. The amine was characterised as the *hydrochloride*, m. p. 210° (decomp.) (from ethanol–ether) (Found : C, 70·6; H, 6·6; N, 6·2; $C_{13}H_{13}N,HCl$ requires C, 71·0; H, 6·3; N, 6·2%), the *picrate*, m. p. 178—180° (decomp.) (from ethanol) (Found : C, 55·6; H, 4·3; N, 13·3. $C_{13}H_{13}N,C_6H_3O_7N_3$ requires C, 55·6; H, 3·9; N, 13·1%), the acetyl derivative, m. p. 125—126°, and the *benzoyl* derivative, needles, m. p. 159—160° (from ethanol) (Found : C, 83·5; H, 6·5; N, 4·9. $C_{20}H_{17}ON$ requires C, 83·6; H, 6·0; N, 4·8%). King (*J.*, 1920, **117**, 990) gives for the acetyl derivative m. p. 128—129° (corr.).

Action of Phenylmagnesium Bromide on p-*Methoxymethyl-*NN-*dimethylaniline* (XIV).—The reaction was carried out as described above, and distillation of the ethereal solution gave *p*-benzyl-*NN*-dimethylaniline (XVI) (84%), b. p. 194—198°/15 mm. (Found : N, 6·6. Calc. for $C_{15}H_{17}N$: N, 6·6%) and a crystalline residue of 2 : 6-*bisdimethylamino*-9 : 10-*dihydroanthracene* (XVII). The amine (XVI) readily gave a *methiodide*, m. p. 196—197°, from methanol–ether (Found : C, 54·3; H, 5·8; N, 4·3. $C_{16}H_{20}NI$ requires C, 54·3; H, 5·6; N, 3·9%), and a yellow *methopicrate*, m. p. 99—100° (Found : C, 58·0; H, 5·3; N, 12·3. $C_{22}H_{22}O_7N_4$ requires C, 58·1; H, 5·3; 12·3%). Singh (*J.*, 1925, **127**, 2448) gives b. p. 175°/2—3 mm. for (XVI).

The dihydroanthracene (XVII) gave crystals, m. p. 154—155°, from ethanol and then light petroleum (b. p. 80—100°) [Found : C, 81·2; H, 8·5; N, 10·5%; *M* (Rast), 290. $C_{18}H_{22}N_2$ requires C, 81·2; H, 8·3; N, 10·5%; *M*, 266].

Synthesis of the Diamine (XVII).—2 : 6-Bisdimethylaminoanthracene, m. p. 251° (1 g.), prepared by Albano's method (*loc. cit.*), was suspended in liquid ammonia (20 c.c.), to which sodium (0·2 g.) was added with vigorous stirring. After 1 hr., powdered ammonium nitrate (*ca.* 1 g.) was added and the ammonia allowed to evaporate. Extraction of the residue with cold

ethanol left a considerable residue of unchanged anthracene, but aqueous dilution of the extract precipitated the dihydroanthracene (XVII), colourless needles (from light petroleum), m. p. 153—154°, unchanged by admixture with the above product (Found: N, 10·5. Calc. for $C_{18}H_{22}N_2$: N, 10·5%). The low yield of (XVII) in this synthesis is due primarily to the very low solubility of the unhydrogenated anthracene in liquid ammonia.