173. *The Introduction of the* MgBr *Group into Anisole and Phenetole.*

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In the hope of preparing di-2-thienyl disulphide and thence thiophen-2-thiol, 2-thienylmagnesium bromide was heated with sulphur in presence of phenetole as a high-boiling solvent. The desired product was not obtained, but a thiol was finally isolated which, with chloroacetic acid, gave a compound having the composition $EtO{\cdot}C_6H_4{\cdot}S{\cdot}CH_2{\cdot}CO_2H$. The MgBr group having apparently entered the phenetole nucleus with elimination of thiophen, the course of the reaction was studied.

When phenetole was boiled with ethylmagnesium bromide and then treated with ether and mercuric bromide, *o*-phenetylmercury bromide, $EtO{\cdot}C_6H_4{\cdot}HgBr$, was obtained, and converted into di-*o*-phenetylmercury, $Hg(C_6H_4{\cdot}OEt)_2$. Similarly, anisole with ethylmagnesium bromide or *n*-propylmagnesium bromide gave *o*-anisylmercury bromide, characterised as the corresponding iodide and chloride, and as di-*o*-anisylmercury. No *p*-compounds were isolated. Phenetole does not react appreciably with sulphur at its boiling point, nor is anisole or phenetole mercurated by boiling ethereal mercuric chloride or bromide. Interaction of ethylmagnesium bromide and boiling dimethylaniline, followed by treatment with carbon dioxide, gave dimethylanthranilic acid. *p*-Dimethylaminobenzoic acid, obtained by other workers under more drastic conditions, was not detected. The formation of *o*-derivatives in these experiments is possibly facilitated by formation of co-ordination compounds between the Grignard reagent and the phenol ether or dimethylaniline.

For the purposes of another investigation it was proposed to synthesise 2-thienylthiolacetic acid, $C_4H_3S{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, from thiophen-2-thiol (Biedermann, *Ber.*, 1886, **19**, 1616), chloroacetic acid, and sodium hydroxide. Phenylthiolacetic acid is readily prepared by the analogous method (Ramberg, *Z. physikal. Chem.*, 1900, **34**, 562).

Biedermann obtained only 0·5 g. of the thiol from 30 g. of thiophen-2-sulphonyl chloride and V. Meyer also isolated only small quantities as a by-product during the large-scale synthesis of thiophen from sodium succinate and phosphorus trisulphide (*Ber.*, 1887, **20**, 1756). A more promising method appeared to be that of Taboury (*Bull. Soc. chim.*, 1903, **29**, 761), who found that sulphur reacts with phenyl- and α-naphthyl-magnesium bromides at 0°, giving on acidification the corresponding thiols and disulphides. One of us and Harrison (*J. Inst. Pet. Tech.*, 1935, **21**, 153) obtained di-2-thienyl sulphide, $(C_4H_3S)_2S$, from sulphur and 2-thienylmagnesium bromide, but were unable to obtain a thiol or disulphide.

The present authors modified this procedure by carrying out the reaction in boiling phenetole, but could not obtain a homogeneous product, much polysulphide being produced. The mixture on reduction yielded a thiol; this with chloroacetic acid gave a product which was not a thiophen derivative but a *phenetylthiolacetic acid*, $EtO{\cdot}C_6H_4{\cdot}S{\cdot}CH_2{\cdot}CO_2H$. This was not due to formation of a phenetylthiol by direct union of the phenetole with sulphur, since this can be almost quantitatively recovered from boiling phenetole. The MgBr group would therefore appear to have entered the nucleus, the resulting phenetylmagnesium bromide then reacting with sulphur according to the Taboury reaction :

$$EtO{\cdot}C_6H_4{\cdot}H + C_4H_3S{\cdot}MgBr = EtO{\cdot}C_6H_4{\cdot}MgBr + C_4H_4S$$

Confirmation of this view was afforded by addition of mercuric bromide and ether to the product obtained from ethylmagnesium bromide and boiling phenetole; *o*-phenetylmercury bromide, $EtO{\cdot}C_6H_4{\cdot}HgBr$ (Michaelis, *Ber.*, 1894, **27**, 261), was readily isolated. This is in accordance with the general behaviour of Grignard reagents to mercuric halides (Hilpert and Grüttner, *Ber.*, 1913, **46**, 1686; 1915, **48**, 906). No other mercury derivative was detected. Potassium iodide in alcohol converted this into di-*o*-phenetylmercury (see p. 895).

The reaction was then extended to anisole, ethylmagnesium bromide being used; after treatment with mercuric bromide as before, the only product was *o*-anisylmercury bromide, m. p. 186—187°. This compound is described by Michaelis (*loc. cit.*, p. 257) as having m. p. 183°. With potassium iodide and alcohol it gave *o*-anisylmercury iodide which with sodium iodide in acetone yielded di-*o*-anisylmercury. (When an alkali iodide reacts with an arylmercury halide, either an arylmercury iodide, or diarylmercury and sodium mercury iodide are produced: $2RHgX + 2NaI = R_2Hg + HgI_2 + 2NaX$. Compare Steinkopf, *Annalen*, 1917, **413**, 310.) The di-*o*-anisylmercury so obtained was converted by mercuric chloride into *o*-anisylmercury chloride (Whitmore and Middleton, *loc. cit.*).

o-Anisylmercury bromide (m. p. 186—187°) was also prepared from *n*-propylmagnesium bromide and boiling anisole, followed by treatment with ethereal mercuric bromide. It was shown in separate experiments that phenetole and anisole are not mercurated by boiling ethereal solutions of mercuric chloride or bromide.

These results indicate that substitution of the MgBr group for a hydrogen atom in anisole or phenetole under the conditions of these experiments occurs exclusively in the *o*-position (see p. 896).

This conclusion has been confirmed in the case of anisole by Dr. E. Rothstein, who has submitted the products from two separate experiments (with ethylmagnesium bromide) to a careful fractional crystallisation. Only *o*-anisylmercury bromide and some ethylmercury bromide could be isolated.

The recorded m. p. of *p*-anisylmercury bromide, 187°, seemed open to suspicion, as *p*-anisylmercury chloride melts at 239° (Michaelis and Rabinerson, *Ber.*, 1890, **23**, 2344) and an inspection of the m. p.'s of several corresponding organo-mercury chlorides and bromides shows that these lie fairly close together and often differ by less than 10°. Differences of over 50° do not occur.

The point was of importance, since, if *p*-anisylmercury bromide melts at 187°, it might appear that substitution of MgBr in the anisole nucleus had taken place in the *p*-position. In view of the transformations to which the reaction product was submitted (see above), and of the *o*-substitution observed in phenetole, this would seem highly improbable. Nevertheless, a further study was made of the *o*- and *p*-anisylmercury bromides.

p-Anisylmagnesium bromide with mercuric chloride and bromide gave *p*-anisylmercury chloride, m. p. 237—238°, and *p*-anisylmercury bromide, m. p. 241—242°, respectively.

Similarly *o*-anisylmagnesium bromide gave *o*-anisylmercury bromide, m. p. 186°, identical in m. p. and mixed m. p. with the product obtained from anisole and ethyl- or *n*-propyl-magnesium bromide. We have also prepared *o*- and *p*-anisylmercury bromides by the method of Nesmejanow (*Ber.*, 1929, **62**, 1010), confirming these results. Michaelis was therefore in error in stating that *p*-anisylmercury bromide melts at 187°. The correct figure is 241—242°.

o- and p-*Anisyldiazoniummercury bromides*, $MeO{\cdot}C_6H_4N_2{\cdot}HgBr_3$ and $(MeO{\cdot}C_6H_4N_2)_2HgBr_4$, have not previously been described.

The fact that boiling phenetole and anisole react with alkylmagnesium halides was first observed by Grignard (*Compt. rend.*, 1910, **151**, 322), who obtained phenol on acidification of the reaction product. Simonis and Remmert (*Ber.*, 1914, **47**, 269), on heating methylmagnesium iodide with anisole, obtained ethane and (on acidification) phenol: $Ph{\cdot}OMe + MgMeI = Ph{\cdot}O{\cdot}MgI + Me{\cdot}Me$. Phenetole similarly gave phenol and a gaseous product, stated to be propane. Späth (*Ber.*, 1914, **47**, 766), however, showed this gas to be a mixture of hydrocarbons. Grignard and Ritz (*Bull. Soc. chim.*, 1936, **3**, 1181) made a comprehensive study of this type of reaction. The gases were always mixtures, phenetole and methylmagnesium iodide giving ethane, ethylene, and propane and with ethylmagnesium iodide, ethane, ethylene, and butane. Magnesium iodide was also found to react with anisole according to the equation $Ph{\cdot}OMe + MgI_2 = Ph{\cdot}O{\cdot}MgI + MeI$.

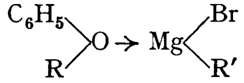
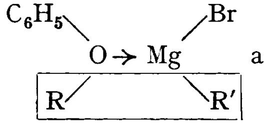
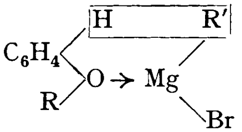
Similar results are recorded by Späth (*Monatsh.*, 1914, **35**, 319), who also examined benzyl alkyl ethers, *e.g.*, $CH_2Ph{\cdot}OEt + MgMeI = EtO{\cdot}MgI + CH_2Ph{\cdot}Me$. This reaction is analogous to that of the Grignard reagent on acetals (Tschitschibabin, *Ber.*, 1904, **37**, 186).

In none of this earlier work is any mention made of the entry of an MgX group into the aromatic nucleus. As the products of reaction were always decomposed by water or dilute acid, any anisyl- or phenetyl-magnesium bromide formed would be reconverted into the phenol ether and so escape detection.

Furthermore, under the conditions of our experiments this reaction occurs to a relatively small extent. With phenetole the yield of organo-mercury bromide was 24%, but with anisole only 3 and 9—11%, calculated on the magnesium, was obtained from *n*-propyl bromide and ethyl bromide respectively.

Interaction with alkylmagnesium bromide has, however, been shown to effect the introduction of MgBr into the methylene group of indene, *cyclo*pentadiene, and fluorene (Grignard and Courtot, *Compt. rend.*, 1911, **152**, 272, 1493; 1914, **158**, 1763; Courtot, *Ann. Chim.*, 1915, **4**, 76) and into the 2-position in thionaphthen (Weissgerber and Krüber, *Ber.*, 1920, **53**, 1557).

Sodium behaves similarly with these hydrocarbons and also with thionaphthen (Schönberg, Petersen, and Kaltschmitt, *Ber.*, 1933, **66**, 234).

In the experiments here described the exclusive *o*-substitution may be connected with the formation of the complex  $\mathrm{(C_6H_5)(R)O \rightarrow Mg(Br)(R')}$ which has been shown to break down in two ways,  and  The first is that established by Grignard, Späth and others (*loc. cit.*). The second type of decomposition, described in this communication, might favour *o*-substitution.

As similar addition products are probably formed in the case of the dialkylanilines, the interaction of ethylmagnesium bromide with boiling dimethylaniline was investigated. Treatment of the product with carbon dioxide at the ordinary temperature gave dimethylanthranilic acid. *p*-Dimethylaminobenzoic acid was not isolated, although this compound was obtained in several experiments by Houben and Freund (*Ber.*, 1909, **42**, 4815) from magnesium, methyl iodide, and boiling dimethylaniline, followed by heating in carbon dioxide, in some cases, under pressure. In two cases methylanthranilic acid was suspected by these authors but not isolated. Using monoethylaniline, ethyl iodide, and magnesium at the boiling point, and treating the product with carbon dioxide under pressure, they obtained *p*-diethylaminobenzoic acid and monoethylanthranilic acid. The formation of the latter compound was presumably due to the isomerisation of $C_6H_5{\cdot}NEt{\cdot}MgBr$ or of $C_6H_5{\cdot}NEt{\cdot}CO{\cdot}O{\cdot}MgBr$, a reaction entirely different from that occurring with diethylaniline.

These results form an interesting parallel to those of Morton and Hechenbleikner (*J. Amer. Chem. Soc.*, 1936, **58**, 2599). By heating *n*-amyl chloride and sodium with ligroin and (i) anisole and (ii) dimethylaniline, and treating the product with carbon dioxide, they obtained *o*-methoxybenzoic and dimethylanthranilic acids in minimum yields of 20 and 18%: $MeO{\cdot}C_6H_5 + NaC_5H_{11} \longrightarrow C_5H_{12} + MeO{\cdot}C_6H_4Na$. No mention of the *p*-isomers is made. Substitution by Na and by MgBr would appear, therefore, to take a similar course in anisole and dimethylaniline as well as in the compounds enumerated above.

Apparently the only other recorded instance of exclusive *o*-substitution in anisole and phenetole is their nitration by means of benzoyl nitrate (Francis, *Ber.*, 1906, **39**, 3801).

Although the results here described were obtained with ethyl- and *n*-propyl-magnesium bromides, it is suggested that hot anisole and phenetole should not be used as solvents for methylmagnesium iodide in the determination of active hydrogen by the Zerewitinoff reaction.

EXPERIMENTAL.

2-Thienylmagnesium Bromide and Phenetole.—A solution of magnesium (1·5 g.) and 2-bromothiophen (10 g.) in ether (100 c.c.) was prepared in an atmosphere of nitrogen, sulphur (4 g.) and phenetole (30 c.c.) added, and the stirring and slow nitrogen stream continued overnight. The ether was then removed, and the residue heated at 200—205° for 6 hours in nitrogen, cooled in ice and salt, acidified with hydrochloric acid (some hydrogen sulphide being evolved), and extracted with ether. The combined extracts were shaken with aqueous sodium hydroxide, and the ethereal layer (A) separated from the alkaline solution (B). Removal of ether from (A) and distillation of the phenetole in steam left a dark oil (3 c.c., A_1), which appeared to be a polysulphide.

Acidification of (B) yielded an oil containing a thiol, most of which formed a tar on distillation, but a few drops came over at 70°/18 mm. This and the residue were re-united and mixed with A_1, and the whole reduced with zinc dust and dilute hydrochloric acid, distilled in steam, and extracted with ether. The yellow oil so obtained was separated from a few white crystals, m. p. 215—216° (too small in amount for further examination), and distilled at the ordinary pressure, about 0·5 c.c. being collected from 160—200°. This unpromising material contained a thiol, recognised by its odour and reaction with mercury salts. In the belief that it might contain the desired thiophen-2-thiol it was dissolved in sodium hydroxide solution (10 c.c.), mixed with chloroacetic acid (0·5 g.) in water (1 c.c.), warmed, and left overnight. The precipitated sodium salt was washed with ether and acidified. On cooling, an acid separated, m. p. 64—65° after recrystallisation from hot water. It was free from halogen, gave no indophenin reaction, and depressed the m. p. of phenylthiolacetic acid, m. p. 61—62° (the desired 2-thienylthiolacetic acid was not available) (Found: C, 56·0; H, 5·6; S, 14·7. $C_2H_5{\cdot}O{\cdot}C_6H_4{\cdot}S{\cdot}CH_2{\cdot}CO_2H$ requires C, 56·6; H, 5·7; S, 15·1%).

(I) *Ethylmagnesium Bromide and Phenetole.*—Magnesium (2 g.) and ethyl bromide (9 g.) were dissolved in ether (120 c.c.), phenetole (25 g.) added, the ether removed, and the residue heated at about 200° for 5 hours under reflux, some white fumes being observed during the first hour. The residue was then treated with ether and mercuric bromide (20 g.) in portions, the mixture boiled for 30 minutes, the ether removed, and water added. The residue was washed with hot water and extracted with acetone, which yielded 8 g. of a solid, m. p. 112—115°. This was twice recrystallised from aqueous acetone, once from benzene and once from aqueous alcohol. On each occasion the m. p. was 118° (Found: Hg, 50·3. Calc. for C_8H_9OBrHg: Hg, 50·0%). *o*-Phenetylmercury bromide melts at 121° (Michaelis, *loc. cit.*).

1 G. was boiled with potassium iodide (3 g.) in alcohol (50 c.c.) for 1 hour and diluted with water, giving an oil (0·3 g.) which solidified below 0°, m. p. 75—77°. Three recrystallisations from alcohol gave a halogen-free product, m. p. 82—83°. This is the m. p. recorded by Dimroth (*Ber.*, 1899, **32**, 758) for di-*o*-phenetylmercury, whereas Whitmore and Middleton (*J. Amer. Chem. Soc.*, 1923, **45**, 1753) give m. p. 81°. The values given by Michaelis (*loc. cit.*) for the m. p.'s of *p*-phenetylmercury bromide and di-*p*-phenetylmercury are 241·5° and 135°.

The aqueous filtrate from the crude *o*-phenetylmercury bromide contained the excess of phenetole and phenol.

(II) n-*Propylmagnesium Bromide and Anisole.*—The procedure was as described in (I), the quantities being: magnesium (2 g.), *n*-propyl bromide (11 g.), ether (100 c.c.), anisole (20 g.). After heating at 180—190° for 4 hours, gas being evolved, ether and mercuric bromide (20 g.) were added. Extraction with water, followed by alcohol, left some mercurous bromide and yielded 1 g. of *o*-anisylmercury bromide as a white solid, m. p. 186—187°, which was unaltered by two further crystallisations from aqueous acetone (Found: Hg, 52·3. Calc. for C_7H_7OBrHg: Hg, 51·8%).

The formation of phenol was demonstrated by conversion into tribromophenol, m. p. 95—96°. Yield, 24 g. This represented 87% of the weight (27·5 g.) to be expected if the whole of the propylmagnesium bromide had been used in demethylation (see p. 895).

(III) *Ethylmagnesium Bromide and Anisole.*—Quantities: Ethyl bromide (55 g.), magnesium (11·7 g.), ether (400 c.c.), anisole (140 g.). After removal of the ether the residue was heated at 180° for over 8 hours. Ether was again added, and the mixture divided into two parts, to one of which (C) was added mercuric chloride (30 g.) and to the other (D) mercuric bromide (40 g.), after which the mixtures were refluxed for an hour. Treatment with cold and then boiling water, followed by extraction with acetone–benzene, gave 7 g. of a solid which after three crystallisations from the same mixture melted at 186—186·5° alone and in admixture with the product, m. p. 186—187°, obtained from (D) below or with authentic *o*-anisylmercury bromide (see p. 898).

The pure product from (C) was therefore *o*-anisylmercury bromide; the crude product probably contained some chloride.

From (D) 11 g. of *o*-anisylmercury bromide, m. p. 186—187°, were similarly obtained. Two recrystallisations from acetone–benzene did not alter the m. p.

Mixed m. p.'s of (C) with ethylmercury chloride and ethylmercury bromide (m. p.'s 191—192° and 190°), obtained as below, both showed depressions to 170—175°.

Confirmation of the Formation of o-*Anisylmercury Bromide.*—(a) o-*Anisylmercury iodide.*

The *o*-anisylmercury bromide obtained in (III) (3·5 g.) was refluxed for 18 hours with potassium iodide (5 g.) in alcohol (50 c.c.). The mixture was then evaporated to half its bulk and water added. The precipitated solid (3·5 g.) had m. p. 165—166°, unchanged on recrystallisation from alcohol. *o*-Anisylmercury iodide melts at 165° and the *p*-compound at 227° (Michaelis, *Ber.*, 1894, **27**, 257).

(b) *Di-*o*-anisylmercury.*—*o*-Anisylmercury iodide (3·3 g.), sodium iodide (5 g.), and acetone (50 c.c.) were refluxed for 10 hours, and the solution concentrated to 25 c.c. and diluted with water. Below 0° a solid (1 g., m. p. 103—104°) was deposited; after two recrystallisations from alcohol this formed long needles, m. p. 108—108·5°. Michaelis (*loc. cit.*) and Whitmore and Middleton (*loc. cit.*) give m. p. 108°. The *p*-compound melts at 202° (Michaelis, *loc. cit.*).

(c) o-*Anisylmercury chloride.* Di-*o*-anisylmercury (0·2 g.) as obtained in (b) was boiled with mercuric chloride (0·5 g.) in alcohol for 30 minutes. Water precipitated a solid which, after washing with boiling water, melted at 176—177°. Recrystallisation from chloroform–ligroin gave a product, m. p. 177—178°. Michaelis (*loc. cit.*) gives m. p. 173—174°, but Whitmore and Middleton (*loc. cit.*) found m. p. 177—178° for *o*-anisylmercury chloride. Nesmejanow (*Ber.*, 1929, **62**, 1015) gives m. p. 180—181°.

Reaction of Ethylmagnesium Bromide and Anisole under Various Conditions.—An attempt was made to increase the formation of the intermediate *o*-anisylmagnesium bromide by using 55 g. of anisole instead of 140 g. as in the last experiment. After 1 hour's refluxing at 180° an explosion occurred.

When 140 g. of anisole were used and other ingredients as before, but heating for only 1½ hours, very little reaction occurred. Division into two parts (E and F), followed by addition of mercuric chloride and bromide, yielded in (E) ethylmercury chloride, mixed m. p. 191—192° with an authentic specimen of the same m. p. From (F) ethylmercury bromide was obtained, m. p. 190° (Marvel, Gauerke, and Hill, *J. Amer. Chem. Soc.*, 1925, **47**, 3009, give m. p. 193—195°), which depressed the m. p. of ethylmercury chloride to 160—162°.

In order to determine whether a higher temperature during the reaction between anisole and ethylmagnesium bromide would give rise to *p*-substitution, these substances, after being freed from ether, were heated in sealed tubes at 200° and 250° for 8 hours. The relative proportions were as in (D) on p. 897. Much gas was evolved when the tubes were opened. On addition of ether and mercury bromide no organo-mercury compound was formed. Distillation in steam gave an oil which appeared to contain phenol, bromophenols, and bromoanisoles.

o-*Anisylmercury Bromide and Bromine.*—The mercury compound was warmed with bromine water, giving 2 : 4 : 6-tribromoanisole, m. p., after crystallisation from alcohol, and mixed m. p. 85—88°.

o-*Anisylmercury Bromide from* o-*Anisidine.*—This preparation was analogous to that of the corresponding chloride (Nesmejanow, *Ber.*, 1929, **62**, 1015), employing method II (*ibid.*, p. 1012). Using *o*-anisidine (6·2 g.), ether (50 c.c.), mercuric bromide (18 g.), hydrobromic acid (*d* 1·49; 20 c.c.), and sodium nitrite (5 g.), we obtained the *diazonium mercuritribromide* as a red solid, which, after being washed with water, alcohol and ether, became greyish-white. Yield 20 g., m. p. 105—106°. It could be recrystallised from boiling water, giving a constant m. p. 117—118°, although much tar was formed (Found : N, 5·0. $CH_3{\cdot}O{\cdot}C_6H_4N_2{\cdot}HgBr_3$ requires N, 4·9%). The stability of this type of compound is remarkable. It readily couples, however, with an alkaline solution of β-naphthol.

The double salt was converted into *o*-anisylmercury bromide by boiling 9 g. with copper bronze (2 g.) in alcohol (70 c.c.), and filtering and concentrating the solution. A reddish solid separated, which was recrystallised from benzene (m. p. 178—180°) and twice from chloroform; it then melted at 186°, alone and in admixture with *o*-anisylmercury bromide, m. p. 186°, prepared from *o*-anisylmagnesium bromide (Found : C, 21·7; H, 2·2. Calc. : C, 21·7; H, 1·8%).

o-*Anisylmercury Bromide from the Grignard Reaction.*—A solution of magnesium (3 g.) and *o*-bromoanisole (25 g.) in ether (100 c.c.) was boiled with mercuric bromide (22 g.). After removal of ether and addition of water, the solid was washed with dilute hydrochloric acid and with boiling water, and extracted with chloroform. This deposited white crystals, m. p. 183—184°, rising to 186° (constant) on one further crystallisation.

p-*Anisylmercury Bromide from* p-*Anisidine.*—This was prepared by the method (I) described by Nesmejanow (*loc. cit.*, pp. 1013, 1015) for the *p*-phenetyl compound. Quantities : *p*-Anisidine (6 g.), hydrobromic acid (*d* 1·49; 70 c.c.), water (160 c.c.), sodium nitrite (4 g.). The diazonium salt was added to mercuric bromide (20 g.) in hydrobromic acid (*d* 1·49; 20 c.c.) and ice (20 g.). The diazonium double salt was washed with water, alcohol, and ether; m. p. 138—

139° [Found : Hg, 24·9; N, 7·6. Calc. for $(CH_3 \cdot O \cdot C_6H_4N_2)_2HgBr_4$: Hg, 25·4; N, 7·1%]. The composition is not analogous to that of the corresponding *o*-derivative (see p. 898), but Nesmejanow (*loc. cit.*, p. 1012) refers to the difference in composition of the diazonium mercury halides which is observed on slightly altering the conditions of preparation.

The double salt (10·5 g.) was warmed with copper bronze (2·5 g.) and alcohol (50 c.c.), left for 24 hours, and the alcohol evaporated. Extraction of the residue with acetone–benzene gave a deposit, m. p. 243—244°. It did not depress the m. p. 241—242° of a specimen obtained from *p*-bromoanisole (see below) (Found : C, 22·0; H, 2·1. Calc. : C, 21·7; H, 1·8%).

p-*Anisylmercury Bromide from* p-*Bromoanisole.*—Magnesium (3·8 g.) and *p*-bromoanisole (30 g.), dissolved in ether (100 c.c.), were treated with mercuric bromide (30 g.). After heating under reflux, the ether was removed, water added, and the solid washed with ether, boiled with water, and extracted with hot acetone–benzene. The deposit, crystallised four times from the same solvent, melted at 241—242°.

Action of Dimethylaniline on Ethylmagnesium Bromide.—A solution of ethyl bromide (9 g.) and magnesium (2 g.) in ether (120 c.c.) was treated with dimethylaniline (25 g.), and the ether removed. The residue was boiled under reflux for 5 hours and cooled, and, after addition of ether (200 c.c.), dry carbon dioxide was passed through, with stirring and cooling for about 2 hours. The product was dissolved in ammonium chloride solution and extracted twice with ether, and the aqueous layer acidified with acetic acid. There was no precipitate, indicating absence of *p*-dimethylaminobenzoic acid. The solution was then evaporated, and the residue extracted with boiling ether. The ether yielded dimethylanthranilic acid, m. p., after two crystallisations from ether, and mixed m. p. 70—71°.

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