183. *Decomposition Reactions of the Aromatic Diazo-compounds. Part VI. Reactions of Benzenediazonium Chloride with Metals.*

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A systematic study has been made of the influence of 38 elements on the decomposition of benzenediazonium chloride in suspension in acetone kept neutral with chalk. The results are reviewed theoretically. In general, elements of metallic character yield metallic chlorides. Both gold and palladium are reactive, though metals like chromium and aluminium, which have oxide films, are practically inert. Aromatic compounds are formed by Hg, Sn, As, Sb, S, Se, and Te, but not by Au, Tl, Ge, Pb, Bi, Mg, or other metals. It is concluded that the free aryl radicals produced in this decomposition will only react with metals when stable covalent organometallic products can be formed.

From arsenic there has been obtained a new organometallic compound, which is believed to be *triphenylarsine phenoxyhydroxide*, $AsPh_3(OPh)(OH)$, and is not an arsonium salt.

Diphenyl is a secondary reaction product, of which the yield can be increased by adding benzene to the reaction mixture. By substituting naphthalene for added benzene, both α- and β-phenylnaphthalenes can be obtained. The theoretical significance of this reaction, which affords a method of synthesis of unsymmetrically substituted diaryls, is discussed.

Chlorobenzene is another minor reaction product, which becomes a major product when copper is the metal used. The Gattermann reaction of diazo-compounds can therefore occur in acetone solution, and it seems to be a process in which copper plays a unique part.

Investigations (J., 1937, 2007; 1938, 843, 1077) of the reactions between neutral acetone suspensions of diazonium chlorides and certain chemical elements, such as mercury, antimony, and tellurium, have indicated that the mechanism of the decomposition is non-ionic, involving (i) isomerisation of the diazonium salt to the covalent diazo-chloride, $(PhN_2)^+Cl^- \longrightarrow Ph{\cdot}N{:}NCl$, followed by (ii) decomposition of the latter to nitrogen and neutral radicals, $Ph{\cdot}N{:}NCl \longrightarrow Ph{\cdot} + N_2 + Cl{\cdot}$, and (iii) subsequent reactions of these radicals with vicinal atoms and molecules.

Since free neutral radicals possess an unpaired electron, whereas all normal covalent molecules contain completed shells, or at least completed pairs, of electrons, the initial reactions between radicals and molecules must be substitutions, which start chain processes that lead to an eventual disproportionation, with some formation of an unsaturated compound and some polymerisation.

The primary reaction between a free radical and an atom is, in contrast, an addition process, *e.g.*,

$$(a)\ \mathrm{Ph}\cdot + \cdot\mathrm{Hg}\cdot + \cdot\mathrm{Cl} \longrightarrow \mathrm{Ph}\!:\!\mathrm{Hg}\!:\!\mathrm{Cl}$$

$$(b)\ 2\mathrm{Ph}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Se}}}\cdot \longrightarrow \mathrm{Ph}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Se}}}:\mathrm{Ph}$$

for the electrons in atoms, of other than zero valency, tend *not* to pair with one another, but to occupy different orbitals, keeping their spins parallel. Consequently, stable bonding pairs of electrons can be formed by union of the odd electrons of free radicals with the unpaired electrons of the atom.

Only when it is in the form of a monatomic vapour, however, can one be certain that

TABLE I.

Reactions between Elements and Benzenediazonium Chloride in Acetone.

Element.	Conditions of reaction.	Reaction products.						Comments.
		Metallic chloride.	$CH_2Cl\cdot COMe$.	C_6H_6.	Ph·Ph.	PhCl.	Organo-metallic compounds.	
Cu	Brisk in cold	?	+	—	(+)	60%	—	Action possibly catalytic.
Ag	Slow in cold	AgCl	+	+	5%	+	—	
Au	Slow in cold	$AuCl_3$	+	+	3%	1%	—	
Mg	Not in cold	$(MgCl_2)$	—	+	?	(+)	—	Also mesityl oxide and phorone.
Zn	Very brisk at 0°	$ZnCl_2$	0	+	—	0	—	
Cd	Not in cold	$(CdCl_2)$	+	+	2%	+	—	
Hg	Slow in cold	HgCl; $HgCl_2$	+				HgPhCl	See J., 1937, 2007.
Al	Not in cold	$(AlCl_3)$	+	+	2%	1%	—	
In	Not in cold	$(InCl_3)$	+	+	+	?	—	
B, Ce, Tl	No action		+	+	+		—	
C, Si, Ti, Ge, Zr, Th	No action		+	+	+		—	Ferrosilicon also inactive.
Sn	Slow in cold	$SnCl_2$	+	+	4%	(+)	$SnPh_2Cl_2$	Cf. Nesmejanow *et al.*, *Ber.*, 1935, **68**, 1877.
Pb	Slow in cold	$PbCl_2$	+	+	3%	+	—(?)	
As	Not in cold	$AsCl_3$; $AsCl_5$	+	(+)			$Ph_3As{<}^{OPh}_{OH}$	See p. 867.
Sb	Brisk at 0°	$SbCl_3$	+	—			$SbPh_3Cl_2$	See J., 1938, 843.
Bi	Not in cold	$BiCl_3$	+	+	3%		—	
P (red), V, Ta	No action						—	
S	Not in cold		+				Ph_2S; Ph_2S_2	See J., 1938, 1077.
Se (black)	Not in cold		+				Ph_2Se	
Te	Brisk in cold	+	+				$TePh_2Cl_2$	
Cr, W	No action		+	+	+	+	—	
Mo	Not in cold	$(?MoCl_5)$	+	+	+		—	
Mn	Brisk in cold	$MnCl_2$	+	+	2%	3%	—	
Fe	Brisk in cold	$FeCl_2$	—	+	1%	20%	—	
Co	Not in cold	$CoCl_2$	+	+	2%	1%	—	
Ni	Slow in cold	$NiCl_2$	+	+	4%	2%	—	
Pd	Not in cold	$(PdCl_2)$	+	+	+		—	
Pt	No action						—	

Note.—The metallic salts indicated in parentheses, *e.g.*, $(PdCl_2)$, were identified as reaction products, though formed in traces only. Organic reaction products marked + were identified in each case, but the yield was not estimated.

any element possesses the electronic configuration characteristic of its free atoms. The polyatomic forms of many elements, which exist as gases, solvent molecules, and as non-conducting crystals (*e.g.*, carbon as diamond), do not possess unpaired electrons and so would not be expected to react easily with free radicals (Part V; J., 1938, 1077). All these elements are, in fact, inert towards benzenediazonium chloride. In metallic crystals, however, the electrons are not all arranged in stable pairs but can easily act as individual entities, and, indeed, one finds that most metals are paramagnetic just as are the free radicals. Hence, one may differentiate between the metallic and the non-metallic character of any chemical element by investigating its reactivity towards free radicals, and for this purpose benzenediazonium chloride in acetone suspension is quite a good diagnostic reagent, since the substitution reactions between the benzenediazonium chloride and the acetone:

$$\mathrm{Ph\cdot + CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow Ph{\cdot}H + {\cdot}CH_2{\cdot}CO{\cdot}CH_3} \quad . \quad . \quad . \quad . \quad (A)$$

$$\mathrm{Cl\cdot + CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow Cl{\cdot}CH_2{\cdot}CO{\cdot}CH_3 + H\cdot} \quad . \quad . \quad . \quad . \quad (B)$$

occur in preference to any other substitution processes necessitating the fission of a stable electron pair belonging to the element under investigation.

The reactions between a neutral suspension of benzenediazonium chloride in acetone containing chalk and 38 elements are summarised in Table I. All easily accessible elements, other than those which react with acetone, have been investigated, and it will be seen that, in general, one can correlate reactivity with metallic character, particularly when one remembers that some metallic elements, such as chromium, are invariably coated with resistant oxide films and so would be immune from attack.

The organic reaction products, other than organometallic compounds, result from the reaction between benzenediazonium chloride and acetone. Although this reaction does not occur spontaneously at temperatures under 50° it can be initiated at room temperature, or even lower, by the addition of many metals and is strongly exothermic. The metals are evidently general catalysts for this decomposition, even such inert elements as gold and palladium being effective agents, though much less potent than metals which occupy higher places in the electrochemical series. This general catalytic action of metals must be regarded as a catalysis of the decomposition of the non-ionic diazo-chloride, $\mathrm{Ph{\cdot}N{:}NCl}$, and not as a decomposition of the diazonium kation $(\mathrm{PhN_2})^+$, for reactions of the latter would be capable of occurrence in aqueous solutions, in which circumstances copper seems to be the unique catalyst (Gattermann's reaction, see below). It is possible that metals may catalyse the non-ionic decomposition by acting as electron donors, and a reaction of the type

$$\mathrm{Ph{\cdot}N{:}NCl + M\cdot \longrightarrow Ph\cdot + N_2 + M^+Cl^-}$$

may occur, bringing about the liberation of a free aryl radical.

Production of Diaryls.—Small quantities of diphenyl are invariably formed in this reaction, but in no case is more than about 5% of the diazonium chloride converted into this product. In accordance with the conclusions of Grieve and Hey (J., 1934, 1797; 1938, 108; cf. *Chem. Rev.*, 1937, **21**, 169), the diphenyl can be regarded as the product of a secondary reaction between the primary product, benzene, and the phenyl radical, since it is formed even when the added metal takes no part in the decomposition. The evidence of Grieve and Hey, indicating that phenyl radicals always react with vicinal solvent molecules in these non-ionic decompositions of diazo-compounds, is supported by the fact that the yield of diphenyl is less than 5% when benzenediazonium chloride decomposes in acetone alone. When a solvent mixture of acetone and benzene is used, the reaction

$$\mathrm{Ph\cdot + C_6H_6 \longrightarrow C_6H_5{\cdot}C_6H_5 + H\cdot}$$

becomes more prominent, and a yield of diphenyl of up to 25% of the weight of the benzenediazonium chloride used can be obtained. The diphenyl can be produced either by heating benzenediazonium chloride in the mixed solvent, or by adding zinc dust and allowing the decomposition to proceed at room temperature. Moreover, the zinc chloride double salts of diazonium compounds can be employed.

The decomposition of aryldiazonium chlorides in mixed solvents, or in solutions of aromatic compounds in acetone, is thus available as a method of preparation of unsymmetrically substituted diaryls. With the assistance of Mr. W. E. Hanby, it has been shown that a mixture of both α- and β-phenylnaphthalene is formed when benzenediazonium chloride, or its zinc chloride double salt, is decomposed in a solution of naphthalene in acetone by cautiously adding zinc dust. This decomposition can be controlled more easily than that of Möhlau and Berger (*Ber.*, 1893, **26**, 1196, 1994), who used no solvent, and may be found to be of more general utility than that of Grieve and Hey (J., 1938, 112), who used carbon tetrachloride as a solvent for naphthalene in their analogous studies of the decomposition of diazo-hydroxides, but found that the carbon tetrachloride brought about some replacement of the diazo-group by chlorine. The simultaneous production of the two isomeric phenylnaphthalenes is again evidence that the reaction is non-ionic and not affected by the normal polar directive influences.

Production of Organo-metallic Compounds.—Two more elements—arsenic and tin—have now been found to yield aryl derivatives when allowed to react with benzenediazonium chloride under acetone.

(i) Arsenic powder does not react in the cold, but, upon heating, derivatives of triphenylarsine are formed which indicate that triphenylarsine dichloride, Ph_3AsCl_2, is the probable primary reaction product. By evaporating the acetone solution, which results from this decomposition, and then extracting the residue with hot water, there can be isolated a colourless crystalline solid of m. p. 129°, which appears to be *triphenylarsine phenoxyhydroxide*, $Ph_3As(OPh)(OH)$, since on treatment with hydrogen sulphide in warm alcoholic solution it gradually reacts to give, in quantitative yields, triphenylarsine sulphide, Ph_3AsS, and phenol. The substance, however, yields a neutral, non-conducting solution in aqueous alcohol which does not react with metallic salts, including ferric chloride, or with chloroplatinic acid. It is evident, therefore, that it is not an arsonium hydroxide, $(Ph_3As{\cdot}OPh)^+(OH)^-$, or phenoxide, $(Ph_3As{\cdot}OH)^+(OPh)^-$ but a compound in which the arsenic atom possesses more than an octet of valency electrons, as indicated above.

In contrast to both arsenic and antimony, bismuth did not yield an organometallic derivative, although bismuth chloride was formed. This may well be due to the lower stability of the organic bismuthines. A sample of vanadium metal, which readily dissolved in dilute hydrochloric acid, did not even react with the benzenediazonium chloride.

(ii) Tin powder reacts slowly with benzenediazonium chloride in the cold, and a little diphenyltin dichloride, $SnPh_2Cl_2$, is formed. This observation is in accord with that of Nesmejanow, Kozeschkow, and Klimowa (*Ber.*, 1935, **68**, 1877; *J. Gen. Chem. Russia*, 1936, **6**, 167; see, A., 1936, *A*, 1004), who decomposed suspensions, in acetone or ethyl acetate, of the stannic chloride double salts of diazonium chlorides by means of various metals, including tin, and obtained thereby small yields of a number of diaryltin dichlorides. By using the corresponding plumbous and plumbic double chlorides, Nesmejanow and his colleagues (*loc. cit.*, 1935; *J. Gen. Chem. Russia*, 1936, **6**, 172; see A., 1936, *A*, 837) also obtained traces of lead aryls of the types $PbAr_3Cl$ and $PbAr_2Cl_2$, but did not use metallic lead to bring about these decompositions. No indications of the formation of lead aryls have been obtained in the course of the present work, but it is possible that the reaction occurred to give traces of material too minute for detection.

Germanium and silicon, which have aryl derivatives analogous to those of tin, were both inert to benzenediazonium chloride, and this inactivity may be ascribed to the fact that both these elements form crystals with the covalent diamond structure. No silicon derivatives were formed when a sample of ferrosilicon, which readily gave silicon hydrides when treated with acid, was used. The inertness of the other elements of Group IV is in accord with their general chemical inactivity.

The inertness of the metals of Group III is rather surprising, for these possess an odd number of electrons in their atomic structures. One can ascribe the relative inactivity of aluminium to oxide-film formation, but the complete inertness of cerium is more difficult to explain, since the specimen used reacted readily with cold water. Indium had about the same degree of reactivity as aluminium, but thallium again was inert. Very stable organo-thallic compounds may easily be prepared by other methods, and it was expected that this metal would resemble gold, mercury, or lead. Attempts to prepare organometallic compounds by the direct addition of aryl radicals to the thallous ion of thallium carbonate and to the plumbous ion of lead carbonate were also unsuccessful.

The sharply contrasting reactivity of the Group I metals is best illustrated by the element gold, which reacts slowly with benzenediazonium chloride at room temperature, and gives auric chloride. An unsuccessful search was made for phenylauric chlorides of the types described by Kharasch and Isbell (*J. Amer. Chem. Soc.*, 1931, **53**, 3053). The formation of phenylgold, or of the phenyl derivatives of copper and silver which have been described by Gilman and Straley (*Rec. Trav. chim.*, 1936, **55**, 821), would not be anticipated in this reaction, for these compounds are almost certainly substances of ionic nature, *e.g.*, Cu^+Ph^-, and so would not be formed readily by a reaction involving neutral radicals.

Only two types of reactions with metals are to be expected of neutral radicals: (*a*) the metal may form a covalent molecule by direct addition, *e.g.*,

$$\mathrm{Ph}\cdot + \cdot\mathrm{Hg}\cdot + \cdot\mathrm{Cl}\!:\longrightarrow \mathrm{Ph}\!:\!\mathrm{Hg}\!:\!\mathrm{Cl}\!:$$

or (*b*) it may act as an electron donor and be converted into a stable kation, *e.g.*,

$$\mathrm{Ag}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow \mathrm{Ag}^+(:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:)^-$$

but the formation of an organic anion by reaction (*b*), *e.g.*,

$$\mathrm{Ag}\cdot + \mathrm{Ph}\cdot \longrightarrow \mathrm{Ag}^+(\mathrm{Ph}\!:)^-$$

is not a reaction which gives stable products of low energy content. Even in the triphenylmethyl series, in which the anion may be stabilised by resonance, the reactions of the latter type, *e.g.*,

$$\mathrm{Na}\cdot + \cdot\mathrm{CPh_3} \longrightarrow \mathrm{Na}^+(:\mathrm{CPh_3})^-$$

are reversible (compare Bent, *J. Amer. Chem. Soc.*, 1930, **52**, 1499; 1931, **53**, 1789). For this reason fewer types of organometallic compounds can be prepared by the action of free radicals on metals than by means of the Grignard reagent, which will react even with metallic salts just as if it were itself an ionic compound, *e.g.*, $Ph^-Mg^{++}Br^-$. In exact accordance with this view, it has been found that when benzenediazonium chloride decomposes in the presence of metallic magnesium there is no formation of the Grignard reagent, MgPhCl, or of any of its possible reaction products with the acetone, *e.g.*, phenyldimethylcarbinol. The production of both mesityl oxide and phorone, instead of chloroacetone, may be ascribed either to the formation of $CH_3\cdot CO\cdot CH_2\cdot MgCl$ from the chloroacetone, or to a dehydration of the acetone brought about by magnesium chloride in a corresponding manner to the dehydration brought about by calcium chloride.

The Gattermann Reaction.—Chlorobenzene is invariably one of the minor reaction products of the decomposition of benzenediazonium chloride in acetone, and is a major product when the mixture is not kept neutral with chalk (J., 1937, 2011). One may therefore ascribe its formation, in the absence of a metal, to the secondary reactions

$$\mathrm{Ph}\cdot + \mathrm{HCl} \longrightarrow \mathrm{Ph\cdot Cl} + \mathrm{H}\cdot \text{ (in acid solution)}$$

and

$$\mathrm{Ph}\cdot + \mathrm{CH_2Cl\cdot CO\cdot CH_3} \longrightarrow \mathrm{Ph\cdot Cl} + \cdot\mathrm{CH_2\cdot CO\cdot CH_3} \text{ (in neutral solution)}$$

rather than to a direct combination of the phenyl and chloride radicals. Hantzsch (*Ber.*, 1900, **33**, 2534) has recorded that chlorobenzene may be obtained in up to 60% yield when benzenediazonium chloride is decomposed in very concentrated aqueous solution, or in concentrated hydrochloric acid, but that the yield falls off rapidly as the solution is diluted. This action again may be represented by the first of the equations above, which will only be possible when the probability of collision between a phenyl radical and an un-ionised hydrogen chloride molecule is high.

In dilute aqueous solution, copper is the only effective metallic catalyst for replacing the diazo-group by chlorine, bromine, or pseudo-halogens (Gattermann, *Ber.*, 1890, **23**, 1218), and even in acetone suspension its effect is outstanding, as Table II shows.

TABLE II.

Yields of Chlorobenzene from Decomposition of Benzenediazonium Chloride in Acetone.

Metal catalyst	Ti	V	Mn	Fe	Co	Ni	Cu	Zn
Chlorobenzene, %	+ trace +		3	20	1	2	60	0

It is uncertain whether the metallic copper is itself attacked by the diazonium chloride. No cupric salts are formed, but cuprous chloride may be a reaction product. Unfortunately, one cannot place any reliance upon attempts to establish the presence of cuprous chloride by extracting the reaction product with hydrochloric acid or with ammonia, for both these reagents attack copper powder to some extent. Hantzsch and Blagden (*Ber.*, 1900, **33**, 2544) have suggested that the Gattermann reaction is purely catalytic, and the present work does not controvert this view. It may be suggested tentatively that the Gattermann reaction, which takes place so well in dilute aqueous solution, is a reaction of the diazonium salt and not of the covalent diazo-chloride, for it most certainly has no generic relationship to any of the non-polar decompositions of benzenediazonium chloride, which occur under acetone in the presence of other metals.

EXPERIMENTAL.

All decompositions were carried out as described in Part II (J., 1937, 2012), standard quantities of 20 g. of benzenediazonium chloride, 15 g. of dry precipitated chalk, 150 c.c. of acetone, and 20 g. of clean powdered metal, except with the rarer elements, being used. Chloroacetone and benzene were identified as previously described, and chlorobenzene, when present in traces only, was identified by treating the mother-liquors of the nitrated benzene fraction with aniline and warming, whereupon a few mg. of 2 : 4-dinitrodiphenylamine gradually crystallised. The residue from the removal of the acetone and benzene was distilled in steam, diphenyl and further traces of chlorobenzene separating. The percentage yields listed for these products are those of purified specimens. Metallic chlorides were frequently present in the aqueous residues from the steam distillations, and, in other listed cases, could be extracted from the excess of chalk by washing with water or dilute acid. Blank tests were always conducted to ascertain that the metal itself was not affected by the method adopted for the separation of its chloride.

Elements known to form covalent organometallic compounds were examined in greater detail, the residues from the evaporation of the filtered acetone solutions, and also the solid residue containing the chalk, being, in each case, extracted with a series of solvents in which possible reaction products were known to dissolve. When only tarry material resulted, this was burnt, and the ash, if any, was tested for the presence of the element under investigation. When magnesium was used, the acetone filtrate set to a jelly on treatment with water. After decomposition with acid, this was extracted with ether, dried, and fractionated. There were obtained mesityl oxide (5 g.), b. p. 130° (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 200°; α-semicarbazone, m. p. 164°), and phorone, b. p. 190—210°, which solidified on standing. No chloroacetone was formed.

Reaction with Arsenic.—The acetone solution from the arsenic reaction was evaporated, and the residue extracted with water. The aqueous solution, after filtration from tar, was saturated with hydrogen sulphide; the precipitate was collected and extracted with hot alcohol, leaving arsenious sulphide and sulphur. From the alcoholic solution triphenylarsine sulphide, m. p. 164°, separated out (cf. *Nature*, 1938, **142**, 1077) (Found : *C, 63·8; *H, 4·7; As, 22·3. Calc. : C, 63·9; H, 4·5; As, 22·25%).

Triphenylarsine hydroxychloride, which is water-soluble, may therefore be present in the aqueous solution. It would be formed by the immediate hydrolysis of any triphenylarsine dichloride (compare Michaelis, *Annalen*, 1902, **321**, 141).

When the extraction of the acetone residue was carried out with hot, very dilute, alcohol, a white solid crystallised on cooling, having m. p. 129° after crystallisation from dilute alcohol and then benzene : yield variable = 3—7 g. from 40 g. of benzenediazonium chloride. Analyses correspond to *triphenylarsine phenoxyhydroxide*, $Ph_3As(OPh)(OH)$ [Found : *C, 69·4, 69·6; *H, 5·1, 5·0; *As, 18·05; *M* (ebullioscopic in benzene, by method of Menzies and Wright, *J. Amer. Chem. Soc.*, 1921, **43**, 2314), 415 ± 16. $C_{24}H_{21}O_2As$ requires C, 69·2; H, 5·1; As, 18·0%; *M*, 416]. The solution of the product in dilute alcohol was neutral, did not conduct electricity,

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* Analyses by Dr. G. Weiler, Oxford.

and gave no reactions with salts of heavy metals, including ferric chloride, or with chloroplatinic acid. The product (6·0 g.) was refluxed in methyl alcohol, and hydrogen sulphide was passed in for an hour. Crystalline triphenylarsine sulphide gradually separated. After further refluxing, the solution was diluted and the precipitate collected and weighed [4·9 g. = theoretical quantity for $Ph_3As(OPh)(OH) + H_2S = Ph_3AsS + PhOH + H_2O$]. Pure phenol was extracted from the residual solution, distilled (1·0 g. of pure distillate, b. p. 180°), and identified by conversion into phenyl benzoate, m. p. and mixed m. p. 69—70°.

Reaction with Tin.—The acetone solution from this reaction was evaporated, the residue extracted with light petroleum (b. p. 60—80°), this extract evaporated, and the residue from it again extracted with light petroleum (b. p. 40—60°) and again evaporated. The resulting pale yellow solution was diluted with methyl alcohol and treated with ammonia, whereupon a white infusible precipitate of diphenyltin dihydroxide formed (0·3 g., dried), leaving in solution diphenyl and some ammonium chloride. Qualitative tests established that the infusible precipitate was an organic tin compound, soluble in hydrochloric acid with regeneration of an oily petroleum-soluble product (compare Nesmejanow *et al.*, *loc. cit.*).

Production of Diaryls.—(i) 20 G. of benzenediazonium chloride and 15 g. of chalk were warmed in a mixture of 50 c.c. of acetone and 100 c.c. of benzene, and finally refluxed for 1 hour. After cooling, the liquid was filtered, the excess of solvents removed, and the residue distilled in steam. The solid product was recrystallised from methyl alcohol and gave 4·6 g. of diphenyl, m. p. and mixed m. p. 70°.

(ii) To a similar cold mixture were added slowly, with cooling, 10 g. of zinc dust; a vigorous reaction occurred, and the reaction mixture, which contained no chloroacetone, yielded 5·0 g. of diphenyl.

(iii) (With W. E. Hanby.) The zinc chloride double salt of benzenediazonium chloride, from 20 g. aniline, was stirred with 15 g. of chalk in a mixture of 50 c.c. of acetone and 200 c.c. of benzene, and zinc dust (10 g.) was added in small portions. The reaction was completed by warming, and the diphenyl (6 g.) separated as before. When double this quantity of benzene was added, the yield of diphenyl was considerably reduced (3·3 g.).

(iv) 20 G. of benzenediazonium chloride were suspended in a solution of 100 g. of naphthalene in 150 c.c. of acetone, and 10 g. of zinc dust were gradually added. The vigorous reaction was completed by refluxing, and the mixture was then filtered and fractionated. The portion of b. p. 300—330° (6 g.), which had a blue fluorescence, was collected separately. On cooling, part solidified. This solid was separated, recrystallised repeatedly from methyl alcohol, and yielded eventually pure β-phenylnaphthalene, m. p. 101—102°. The residual liquid portion was oxidised with chromic acid in glacial acetic acid solution and yielded *o*-benzoylbenzoic acid, m. p. and mixed m. p. 93—94° (hydrated), 127° (anhydrous). This establishes the presence of α-phenylnaphthalene (compare Grieve and Hey, J., 1938, 108).

The yield of phenylnaphthalenes was slightly less when the zinc chloride double salt was used, but the reaction was less violent. Substitution of zinc shavings for zinc dust lowered the yield considerably.

(v) 31 G. of β-naphthylamine were diazotised in aqueous solution, the double zinc diazonium chloride was precipitated, washed with acetone, and then decomposed with zinc dust in a mixture of 50 c.c. of acetone and 200 c.c. of benzene. There were obtained 0·8 g. of pure β-phenylnaphthalene of the same m. p. and mixed m. p. as the previous specimen.

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