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METHODS OF SYNTHESIS OF POLYPHENYL HYDROCARBONS

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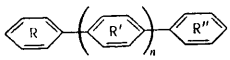
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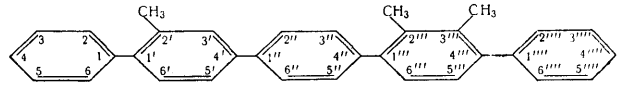
INTRODUCTION

The term polyphenyls is used for compounds whose molecules consist of a chain of substituted or unsubstituted phenyl and phenylene units.



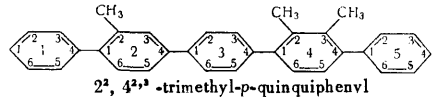
Each inner, phenylene, link of the molecule carries two aromatic residues in the *ortho*-, *meta*-, or *para*-position to one another; hence the existence of *ortho*-, *meta*-, and *para*-polyphenyls as well as mixed ones. The nomenclature is based on the use of latin numerical prefixes to give the number of aromatic nuclei in the molecule (e.g. terphenyl, quaterphenyl), the type of the polyphenyl also being indicated. The carbon atoms in each ring are numbered from the one linked to the preceding nucleus. In the "leading" phenyl radical the numbering starts either at the carbon linked to another nucleus or the one in the *para* -position to it. In the former case the rings are designated by primes, the position of the substituent being indicated by numerals. In the latter case the numeral denotes the ring containing the substituent and the numerical superscript the position of the substituent in the ring. Both methods are illustrated below:

1.



2′, 2″, 3‴-trimethyl-*p*-quinquiphenyl

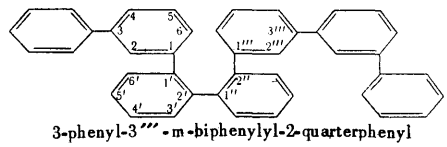
2.



$2^2, 4^{2,3}$-trimethyl-*p*-quinquiphenyl

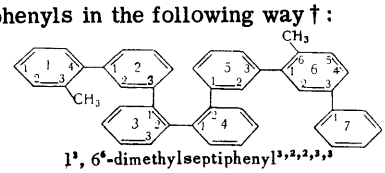
The second method is more convenient for compounds with a large number of rings[1].

Mixed polyphenyls are named by taking a part of the polycyclic chain with the same relative positions of the units and considering it as the main one, e.g.



3-phenyl-3‴-*m*-biphenylyl-2-quarterphenyl

We suggest an extension of the numeral method to mixed polyphenyls in the following way†:



$1^3, 6^6$-dimethylseptiphenyl$^{1^3,2^2,2^3,3^3}$,

the superscript numerals following the name indicating the points of attachment of subsequent rings, starting from the second one.

The interaction of non-condensed aromatic rings gives rise to a characteristic electronic structure of the polyphenyl chain and gives these compounds their specific properties which justify their classification as a separate group of compounds. Biphenyl is the first representative of the group of linear aromatic polycyclic hydrocarbons, just as the fused-ring analogue, naphthalene, is the first member of condensed aromatic hydrocarbons.

† The nomenclature based on the use of primes which has been more widely employed is adhered to in this review.

The ever growing interest in the polyphenyls is associated with their properties and the problems connected with the chemistry and physics of these compounds (thermal stability, conductivity, optical isomerism, the mechanism of radical reactions, scintillation activity, etc.). However, the synthesis of some polyphenyls of a given structure is quite difficult; so far the interesting and in many ways unique *p*-polyphenyls containing more than 7 rings in the molecule have not been prepared. The present review is limited to the published data on the synthesis of this class of hydrocarbons as a whole; it does not extend to the preparation of branched polycyclic chain compounds. A number of surveys[2-5] have already been published on individual problems in polyphenyl synthesis.

I. SYNTHESES WITH LENGTHENING OF THE POLYPHENYL CHAIN

1. Pyrolysis

The pyrolysis of benzene has long attracted the attention of investigators, starting with Berthelot[6]. When its vapour is passed through a heated iron, porcelain, or quartz tube the main reaction product is biphenyl as well as a mixture of products of further condensation (isomeric terphenyls, triphenylene, and others[7]), carbon, hydrocarbon gases, and hydrogen. The process depends on heterogeneous catalysis. The material of the reactor[8,9] and its surface area[10] affect the yield of biphenyl. Thus at 825°, a quartz surface has a constant specific activity and the rate of reaction rises in direct proportion to the increase in surface. Migration of atoms or groups at the catalyst surface is characteristic of catalytic reactions since their migration as a result of the thermal movement of the intermediate complexes with the catalyst is energetically more advantageous than migration resulting from their own thermal movements. This accounts for the extensive recrystallisation of the glass surface within the reaction zone which has been observed[10] under these conditions, whereas in an atmosphere of nitrogen no such changes occurred even at higher temperatures. Kinetic studies[11] also suggested heterogeneous catalysis.

The range of catalysts which can be used is wide and includes pumice[12-14], alkali and alkaline-earth metal oxides and carbonates[15,16], oxides of Mo, Mg, Ba, Ca, Ce, Sr, Ti, Zr, Th, W, Mn, Cr, U, Al, V, and Be coated with graphite, zincates, vanadates, chromates, molybdates, aluminates and tungstates[17,18], K_2CO_3, ThO_2 and CoO on pumice[19], Nichrome wire[20,21], refractory clay and porcelain[9,22], activated charcoal[13], and others. The macroporosity of the catalyst[23] has been found to affect the course of reaction. Porous and non-porous catalysts behave differently presumably because of the difference in the area of catalytic surface and in the concentration of hydrogen. A rise in the latter shifts the equilibrium towards benzene[24,25]. Moreover, carbonisation occurs more intensively on porous catalysts and this lowers the yield of biphenyl calculated on the basis of the reacted benzene. The course of this side reaction is also determined by the chemical nature of the catalyst and the material of the apparatus wall[10]. In order to diminish carbonisation, it is recommended that the walls of iron and steel reactors be coated with Se, CoS, $K_2Cr_2(SO_4)_4$, $NiCl_2$, CuS, As, Si, Sb, $SbCl_3$, Sn, Sb_2S_3, Mo, MoS_x, P_2S_5, As_2S_5, SnS_x, ZnS, FeS, Zn, P[62,27], or a film of carbide[28]; addition of 0.1% of sulphur or sulphur-containing compounds to the benzene is also recommended[29].

Much research into the pyrolysis of benzene has led to industrial methods of preparation of biphenyl[9] and terphenyl[30-32]. For example, benzene vapour is passed through a heated inert liquid (Pb, NaCl, $CaCl_2$, etc.)[33,34] which sometimes contains partially oxidised organic compounds such as alcohols, ethers, esters or ketones[35]. The procedure is usually repeated twice, at 600°–650° and 750°–800°[9,36]. A method which can be easily carried out using apparatus for petroleum pyrolysis has been described[9]. Materials which serve for fettling chemical installations act as catalysts. The best yields (approximately 30% per cycle) have been obtained with refractory clay and porcelain at 750°–800°. Reaction under pressure[9,12,37-39] can be used to increase the yield of biphenyl and lower the reaction temperature; this can be brought down to 625°–695° if a pressure of 10–60 atm is used in steel tubes; the conversion of benzene per cycle reaches 20%[37,38].

Both laboratory and industrial apparatus for the preparation of biphenyl is quite simple and has been described repeatedly[9,20,36,40-43].

The thermal conversions of polyphenyl hydrocarbons have not been studied as extensively as the pyrolysis of benzene. The equilibrium constants of the reactions

$$2C_6H_6 \rightleftarrows C_6H_5C_6H_5 + H_2 ,$$

$$C_6H_5C_6H_5 + C_6H_6 \rightleftarrows C_6H_5C_6H_4C_6H_5 + H_2 ,$$

and of more profound condensations at 845°–920° have been found to be of the same order[25,24]. Pyrolysis of a mixture of biphenyl and benzene at 650°–950° gives a mixture of polyphenyls[44]. Terphenyl can be converted into biphenyl and benzene by heating in an atmosphere of hydrogen[45]. Thermal decomposition of *p*-terphenyl in a sealed tube has been studied in more detail[46]; at 279°–390° it only occurs to the extent of 3% over a period of 10 days, at 460° it amounts to 74%, and at 475° there is a further 2–3-fold increase in the rate of pyrolysis. The reaction products consist of H_2, gaseous hydrocarbons, biphenyl (10–20%), and higher polyphenyls (50–60%). The latter include *p*-quater-, and *p*-sexiphenyl, 3-phenyl-*p*-terphenyl, 3,4'--bis-(*p*-biphenylyl)biphenyl, 3-phenyl-*p*-quaterphenyl, and 4,4"-diphenyl-*m*-terphenyl. Pyrolysis of an equimolar mixture of biphenyl and terphenyl (480°, 2 days) gives 30.6% of biphenyl, 17.3% of *p*-terphenyl, 5% of *m*-quater- and *m*-quinqui-phenyl, 4% of 4-phenyl-*m*-quaterphenyl, 8% of 4-phenyl-*m*-terphenyl, 5% of 3-phenyl-*p*-quaterphenyl, and 30% of higher polymers including 4,4"--diphenyl-*m*-terphenyl. Thus polyphenyl hydrocarbons tend to condense together largely in the *meta*-position.

Reactions closely related to those considered above include the catalytic condensation of acetylene at 550°–725° yielding a mixture of products containing biphenyl[47-49], oxidation of benzene in the vapour phase giving biphenyl as a side product[50-52], and preparation of polyphenyls from benzene in an electric discharge[53-56].

The high-temperature transformations of alkylbenzenes are more complex than of benzene itself and yield a mixture of products with very small amounts of polyphenyls[57-59].

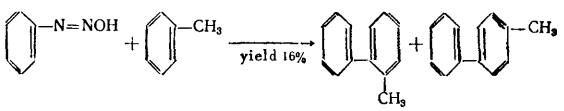
2. Preparation of Polyphenyls from Aromatic Amines

a) The Gomberg reaction. This method was proposed in 1924[60] and consists of two stages: (1) diazotisation of the aromatic amine in an aqueous medium and

(2) arylation of the aromatic hydrocarbon:

$$ArNH_2 \xrightarrow[HCl]{NaNO_2} ArN_2{}^+Cl^- \xrightarrow[NaOH]{Ar'H} ArAr'.$$

Arylation is carried out either in neutral or alkaline medium. In the former case 15–40% alkali is added gradually to a mixture of the diazonium salt solution and the hydrocarbon, in the latter the solution of the diazonium salt is added to a mixture of the aromatic hydrocarbon with a sufficient amount of dilute alkali. The reaction is usually carried out at 0°–10° but in the neutral medium it is successful even at temperatures up to 30°[61]. The choice of the method of arylation does not appear to be critical[61,62] although the second variant has been recommended[63] when the amine contains electron-donating substituents such as CH_3. The use of hydrocarbons melting above 30° raises difficulties in the choice of solvent. For example, benzenediazoniumhydroxide and biphenyl in chloroform (40°, 10 h) yielded only a small amount of *p*-terphenyl[61] since the solvent proved to be not entirely inert with respect to the diazonium compounds. This method is characterised by: (1) a low yield of polyphenyl hydrocarbons (10–25%); (2) the formation of a mixture of isomers during arylation of substituted hydrocarbons:



(the *m*-isomer was not isolated in the example cited[63] but it was almost certainly present); and (3) side reactions involving reduction of the diazo group and formation of a high-boiling tar including azo compounds and linear polyphenyls. For example, when benzene reacts with diazotised *p*-toluidine isomeric 4-methylquaterphenyls[64] are formed in addition to the main product, and when it reacts with diazotised mesitidine, 5,7-dimethylindazole and 3-mesitylenazo-5,7-dimethylindazole[65] are formed. Other alkaline agents were tried instead of NaOH in an attempt to reduce tar formation and increase the yield of polyaryl compounds. The yield of biphenyl increases by 5–10% when $Mg(OH)_2$ and $Ca(OH)_2$ are used[2] but is lowered somewhat with CH_3COONa[66]. Salts added to the reaction mixture only raise the yield in isolated cases[61,67].

Polyphenyls can be obtained without an alkaline agent[68]. Biphenyl is formed when trifluoroacetic acid, or its salt, is added to a mixture of an aqueous solution of phenyldiazonium chloride and benzene; the yield drops if the aqueous phase is diluted. The same result is achieved if the amine is diazotised in an aqueous solution of trifluoro- and trichloroacetic or perfluorobutyric acids, and is then mixed with benzene. Solid diazonium salts of perhalogeno carboxylic acids can also be used. The authors suggest that the diazotised amines exist in ionic and covalent forms in equilibrium, the latter reacting with the aromatic hydrocarbon.

b) Synthesis through *N*-nitrosoanilides. Diazonium acetates can also react with aromatic hydrocarbons, since sodium acetate can replace NaOH. Sodium diazotates can react with a mixture of acyl chloride and an aromatic compound to give biaryls[69]:

$$ArN{=}NONa \xrightarrow[NaCl]{RCOC-} ArN{=}NOCOR \xrightarrow{Ar'H} ArAr' + N_2 + RCOOH.$$

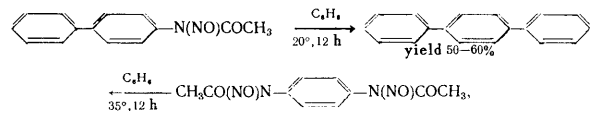
N-nitroso-*N*-arylacetamides, which are tautomers of diazonium acetates were used as arylating agents by Bamberger[70]:

$$ArN(NO)COCH_3 \rightleftarrows ArN{=}NOCOCH_3.$$

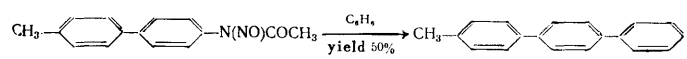
Subsequently they found preparative application.

N-Acetylarylamines are nitrosated in glacial acetic acid and acetic anhydride using nitrogen oxides ($NO + NO_2$)[71] or nitrosyl chloride in the presence of fused acetate and a small amount of P_2O_5[72]. Alkyl nitrites and sodium nitrite in trifluoroacetic acid anhydride can also be used[68]. Other *N*-acylamines can be employed instead of *N*-acetylamines[71,73]. *N*-acetyl-*N*-nitrosoarylamines dissolve in aromatic hydrocarbons and react with them completely in 12–48 h at room temperature. The reaction is more vigorous at an elevated temperature but the yield of biaryl usually falls[70,74]. Therefore temperatures of 35°–60° are only used with sufficiently stable nitroso compounds[1,71,73,75]. The yield is usually higher than in the Gomberg reaction (20–70%); it decreases to some extent when large quantities of reagents are employed since tar is formed in greater amounts[62,74].

As in the Gomberg reaction there are usually several routes towards the desired polyphenyl and the choice falls on that which avoids the formation of a mixture of isomers[76–79]. For example, *m*- and *p*-terphenyl can be prepared from *N*-nitroso-*N*-acetylaminobiphenyls and from *N*, *N*'-dinitroso-*N*, *N*'-diacetylphenylenediamines[72,73,80,81],

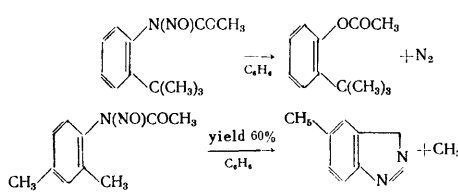


but only biphenylamines are suitable for the preparation of unsymmetrical 2- and 4-methyl-*p*-terphenyl[75]:



When the second component is a substituted aromatic hydrocarbon, a mixture of all the possible isomers is formed. Since the alkylbenzene molecule has two *o*- and *m*- and one *p*-position the "normal" ratio of the isomers should be 2 : 2 : 1. The reaction product of *N*-nitrosoacetanilide with toluene consists of 62% *o*-, 20% *m*-, and 18% *p*-methylbiphenyl[76]. The methyl group in the toluene molecule thus relatively activates the *o*- and deactivates the *m*--position for arylation (*o*-, *p*-directing group). The ratio of the *o*- and *m*-isomers alters when cumene and t-butylbenzene are used. The isopropylbiphenyl obtained contains 26% *o*-, 53% *m*-, and 21% *p*-substituted isomers, the t-butylbiphenyl contains 15, 63, and 22% (approximately) of the isomers respectively. The decrease in *o*-substitution is presumably due to steric hindrance. The *m*-directing effect of the isopropyl and t-butyl groups, with a constant amount of the *p*-isomer, may be explained by the predominance of the induction effect over the mesomeric effect.

However, not all *N*-nitroso-*N*-acetylarylamines react with aromatic hydrocarbons. Thus, *N*-nitroso-*o*-t-butylacetanilide in benzene yields principally *o*-t-butylphenyl acetate[76] and *N*-nitroso-2,4-dimethylacetanilide gives 5-methylindazole[77].



c) Direct synthesis from diazonium salts. Dry diazonium salts react with excess aromatic hydrocar-

bon on heating [82]. Benzenediazonium chloride decomposes in a mixture of benzene, acetone, and chalk (for neutralisation) to give up to 25% of biphenyl [83]:

$$2C_6H_5N_2Cl + 2C_6H_6 + CaCO_3 \rightarrow 2C_6H_5C_6H_5 + 2N_2 + CaCl_2 + H_2O + CO_2.$$

The reaction can be carried out at room temperature by adding zinc dust to the reaction mixture and the double salt of diazonium chloride with $ZnCl_2$ can be used. $AlCl_3$ serves as a good catalyst at higher temperatures [82,84].

Stabilised diazonium salts in ether react also with arylmagnesium halides [85,86]:

$$ArN_2Cl \cdot 0.5ZnCl_2 + Ar'MgBr \rightarrow ArAr' + MgClBr + 0.5ZnCl_2 + N_2.$$

In some cases biaryls can be derived from the aryl groups of the initial salt only. The Gatterman reaction which involves the decomposition of diazonium salts in the presence of powdered copper,

$$ArN_2X \xrightarrow[Cu]{} ArX + N_2$$

gives biaryls in an alcoholic medium [87]. The greater the amount of alcohol, the greater the formation of linear polyphenyls with a large number of rings in the chain. Under these conditions benzenediazonium sulphate yields 16.8% of biphenyl, ~ 7.8% of *p*-terphenyl, 5.5% of quaterphenyl, and 0.8% of *p*-quinquiphenyl [88]. When alcohol is replaced by anhydrous formic acid (diazotisation in acetic acid) the yield of biphenyl is 10.3% and of *p*-polyphenyls 24.8% [89]. Biphenyl has been prepared in 50% yield by the action of copper powder on benzenediazonium sulphate in acetic anhydride [90]. A small amount of biphenyl (up to 5%) has been isolated on decomposition of a suspension of benzenediazonium chloride in acetone in the presence of various elements, including Ag, Au, Cd, Sn, Pb, Ni, Bi, B, and others [83], and on reduction of stabilised diazonium salts with organomagnesium compounds, for example $C_6H_5N_2Cl \cdot 0.5\,ZnCl_2$ with ethylmagnesium bromide [91].

d) Other methods. A small amount of biphenyl is formed when phenylazotriphenylmethane undergoes thermal decomposition in benzene [92]. Since the solvent takes part in the reaction, toluene yields a mixture of isomeric methylbiphenyls [93]. This is a theoretically interesting reaction but unsuitable for preparative use since only one of the phenyl groups of the initial compound (22 wt. %) enters the biaryl molecule if the formation of $(C_6H_5)_4C$ is disregarded:

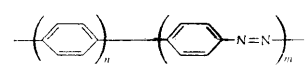
$$C_6H_5N{=}NC(C_6H_5)_3 \xrightarrow{ArH} C_6H_5Ar + (C_6H_5)_3CH + N_2\,[+ \text{small quantity of } (C_6H_5)_4C].$$

This objection applies equally to the use of triazens ($RN{=}N{-}NR'R''$). When a 4% solution of diazoaminobenzene in cumene is heated for 40 h at 160° the products include, among other substances, isopropylbiphenyls [94]:

$$C_6H_5N{=}NNHC_6H_5 \xrightarrow{C_6H_4CH(CH_3)_2} C_6H_5C_6H_4CH(CH_3)_2 + (C_6H_5)_2NH +$$
$$+ C_6H_5NH_2 + (CH_3)_2\underset{\displaystyle C_6H_5}{\overset{\displaystyle C_6H_5}{\underset{|}{\overset{|}{C}}}}{-}\underset{\displaystyle C_6H_5}{\overset{\displaystyle C_6H_5}{\underset{|}{\overset{|}{C}}}}(CH_3)_2 + N_2.$$

Isomeric substituted biphenyls are formed from 1-phenyl-3,3-dimethyltriazen in alkyl benzenes with yields of 18–22% [76] and in practically the same ratios as in the phenylation of *N*-nitrosoacetanilide. 1-*o*-Tolyl-3,3-dimethyltriazen in boiling benzene and acetic acid yields 9% of 2-methylbiphenyl and 21% of indazole [95].

Polyphenyl hydrocarbons are not infrequently formed by the deamination of arylamines. Sodium benzenediazoate is reduced by alcohol giving 50% of benzene and 25% of biphenyl [96]. When deamination is effected with hypophosphorous acid, biphenyl (9.1%) and *p*-terphenyl (2.6%) are formed as by-products [97]. It is interesting that when the bisdiazonium compound from benzidine is treated with activated copper or an ammoniacal solution of cuprous oxide to obtain a macromolecular product, only the nitrogen-containing polymer of the following structure [98–100] can be obtained:



3. Arylation with Aromatic Acid Peroxides. Mechanism of Arylation

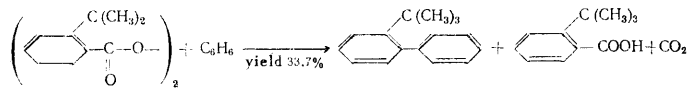
The main products of the reaction between benzoyl peroxide and boiling benzene are biphenyl and benzoic acid [101]. Peroxides of monosubstituted acids yield only monosubstituted biphenyls. The main reaction can thus be represented by the equation

$$(ArCOO)_2 + Ar'H \rightarrow ArAr' + ArCOOH + CO_2.$$

In practice, however, the reaction is much more complex. Gelissen and Hermans [101] isolated not only biphenyl (yield 26%) and benzoic acid, but also an appreciable amount of *p*-quaterphenyl, phenyl benzoate, and *p*-terphenyl. If the reaction is carried out at 78° and an initial concentration of the peroxide equal to 2–10%, the composition of the reaction products corresponds to the following stoichiometric equation [102]:

$$1.00\,(C_6H_5COO)_2 + 0.98C_6H_6 \rightarrow 1.19CO_2 + 0.42C_6H_5COOH + 0.04C_6H_5C_6H_4COOH +$$
$$+ 0.40C_6H_5C_6H_5 + 0.06C_6H_5COOC_6H_5 + 0.01C_6H_5C_6H_4C_6H_5 + 0.025C_6H_5C_6H_4C_6H_4C_6H_5 +$$
$$+ 0.05\,(C_6H_5COO)_2O + 0.05H_2O + 0.06C_6H_5C_6H_5C_6H_5C_6H_5\ (\text{"quinhydrone type" structure}) + \text{high-boiling residue (composition } 0.50\ C_6H_5,$$
$$0.40\ C_6H_4,\ 0.15\ C_6H_5COO).$$

The choice of reagents for the synthesis is governed by the same considerations as those discussed for the other methods of arylation. For example, individual t-butylpolyphenyls can be prepared using substituted peroxides but not t-butylbenzene [79].



A mixture of isomers is always formed when substituted hydrocarbons are used, e.g. fused biphenyl treated with benzoyl peroxide for 13 h at 78° gives 64% of isomeric terphenyls [103]. In reactions of this type the quantitative proportions of the isomers are independent of the reagents used (peroxide, *N*-nitrosoacetanilide, etc.) and reflect the directing effect of the substituent [76]. Comparison of the rate of phenylation of the substituted hydrocarbon with that of benzene indicates the effect of the substituent on the reactivity. The benzoyl peroxide reaction is particularly convenient for this [102]. The relative rates are measured by the "competitive substitution" method [104]. The peroxide is decomposed in an excess of an equimolar mixture of

benzene and the hydrocarbon in question (usually at 80°); the excess must be sufficient to prevent a substantial change in the molar composition of the mixture as a result of the different rate of disappearance of the components. This gives

$$K_H^R = \frac{\text{rate constant for } C_6H_5R \text{ phenylation}}{\text{rate constant for } C_6H_6 \text{ phenylation}} = \frac{\text{amount of } C_6H_5C_6H_4R}{\text{amount of } C_6H_5C_6H_5}.$$

The two separate characteristics of the substituent effect (isomer ratio and K_H^R) can be combined into one, expressed by the partial-rate factors. These are the factors (F) which relate the rate of substitution at a given carbon atom to that at a benzene carbon atom. The rate of substitution in an alkylbenzene equals the sum of the rates of substitution at the two *ortho*-, two *meta*-, and one *para*--positions:

$$V = 2V_o + 2V_m + V_p.$$

The rate of reaction at each benzene carbon atom is taken to be unity and the total rate therefore equals 6. Hence for C_6H_5R

$$6K_H^R = 2F_o + 2F_m + F_p$$

and

$$F_p = \frac{6K_H^R c}{100}, \quad F_m = \frac{3K_H^R b}{100}, \quad F_o = \frac{3K_H^R a}{100},$$

where a, b, and c represent the percentage content of the isomer in the mixture. If R = C_6H_5 the number of these positions in the hydrocarbon doubles and therefore

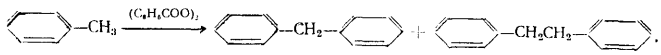
$$F_p = \frac{3K_H^{C_6H_5}c}{100}, \quad F_m = {}^3/_2\,\frac{K_H^{C_6H_5}b}{100} \text{ and } F_o = {}^3/_2\,\frac{K_H^{C_6H_5}a}{100}.$$

Data from various sources are summarised in the Table.

The effect of the substituent on the rate of hydrocarbon phenylation.

R	K_H^R	Amounts of isomers, %			F_o	F_m	F_p	References
		o	*m*	*p*				
CH_3	1.9	62—70.8	16.7—25	12.4—17	3.5—4.0	1.0—1.2	1.4—1.9	76,77,105, 106
C_2H_5	1.2	50	25	25	1.8	0.9	1.8	77,106
$(CH_3)_2CH$	0.87	10—29	50—60	21—30	0.3—0,8	1.3—1.6	1.1—1.6	106,76,77
$(CH_3)_3C$	0.87	17—24	49—62	22—27	0.5—0,6	1.3—1.6	1.1—1.4	76,77,79
C_6H_5	4.0	48.5	23	28.5	2.9	1.4	3.4	107
1,2-CH_3,CH_3		63		37				77
1,4-$(CH_3)_2C$, $(CH_3)_3C$	0.63		100				0.95	79

These results indicate that arylation reactions using both peroxides and nitrogen-containing compounds are homolytic[62,77,108] (for a detailed account see ref. 109). Substituents like the nitro group in this case activate the ring and direct the incoming aryl group to the *o*- and *p*--positions, unlike the situation in electrophilic-substitution reactions. The differences in the reactivity of the *o*-, *m*- and *p*-positions are relatively small (Table), whereas in heterolytic substitutions these differences are considerably greater, since the position of entry is controlled by the charge of the species and polarity of the substituted aromatic ring. Further evidence for a homolytic mechanism comes from the appearance of such side products as polyphenyls and compounds formed by the action of the attacking agent on the side chains of the hydrocarbon undergoing arylation[76,77,106]:



In general, homolytic reactions can occur in several ways[110]: (1) the radicals generated enter the bulk of the reaction mixture and give an intermediate complex with the substrate; chain reactions are also possible with splitting off of the peripheral atom by the radical (radical transfer) $-R\cdot + X:Z \rightarrow R{\cdot}X:Z$; $R\cdot + X:Z \rightarrow R:Z + X\cdot$; (2) the initial reagents form an intermediate complex $R:S + X:Z \rightarrow R:SX:Z$; (3) the compound K:S, being solvated, decomposes into radicals which recombine without entering the bulk of the solvent, a process similar to that occurring on the surface of finely-divided metals[111].

A free-radical mechanism has been postulated for arylation[62,92], suggested by the following evidence: (a) the ability of arylating agents to undergo spontaneous decomposition in the absence of the second component; (b) the constant rate of monomolecular breakdown of benzenediazonium acetate in various solvents (in fact the velocity constants are not identical but are of the same order of magnitude[62,74]: in benzene $K_{20°} = 0.00461$, in *m*-xylene 0.00466, in toluene 0.00344, in mesitylene 0.00507, in carbon tetrachloride 0.00405, and so on); (c) the independence of the ratio of the isomeric polyphenyls obtained of the phenylating agent and consequently of the reaction temperature which is governed by the choice of the agent. Nonetheless, this mechanism is not the only possible one[112]. Work with labelled atoms[110,111] has shown that whereas free phenyl radicals do arise in the decomposition of benzoyl peroxide, a cryptoradical mechanism must underlie arylation with *N*-nitrosoacetanilide. On testing for free radicals by their exchange with benzene, it was found that in the case of benzoyl peroxide some of the "primary" radicals are converted into benzene:

$$\dot{C}_6H_5 \cdot \xrightarrow{C_6H_6} \dot{C}_6H_6 + C_6H_5\cdot,$$

and the radicals formed from the solvent can be trapped by mercury acetate:

$$C_6H_5\cdot \xrightarrow{\dot{C}_6H_6} C_6H_5 + \dot{C}_6H_5, \qquad \dot{C}_6H_5\cdot \xrightarrow{(CH_3COO)_2Hg} \dot{C}_6H_5HgOCOCH_3.$$

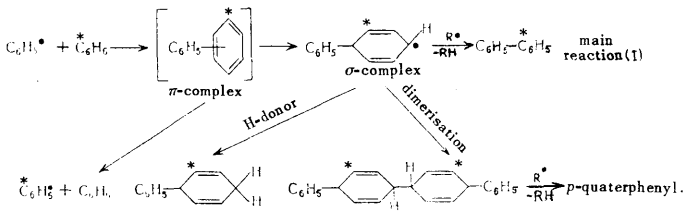
No transfer of radicals was discovered in the case of *N*--nitrosoacetanilide:

$$\dot{C}_6H_5N{=}NOCOCH_3 + C_6H_6 \rightarrow \dot{C}_6H_5C_6H_5 + N_2 + CH_3COOH$$

$$C_6H_5N{=}NOCOCH_3 \xrightarrow[\dot{C}_6H_6]{Hg} C_6H_5HgOCOCH_3 + N_2.$$

Thus arylation with benzoyl peroxide consists of the following sequence of events: breakdown into radicals, combination of a radical with the hydrocarbon molecule, and splitting off of a hydrogen atom by another radical[113,114]. During the attachment of the radical a π-complex, which is probably formed first, is either converted into a σ-complex or undergoes another internal rearrangement[110]. Isolation of 1,4-dihydrobiphenyl and 1',4',1'',4''-tetrahydro-*p*--quaterphenyl[115] from the reaction products and the carbon isotope evidence suggests the following scheme for the

course of the reaction[116]:



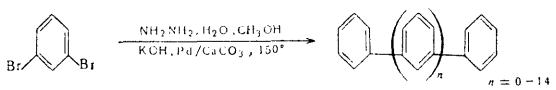
p-Terphenyl is probably formed from biphenyl in a way similar to reaction (I)[116,117].

4. Preparation of Polyphenyls from Aryl Halides

(*a*) Reduction using a palladium catalyst. Aryl halides can be reduced by a 4–6% solution of alkali in methanol using a $Pd/CaCO_3$ catalyst at temperatures up to 135°–150°[118,119]. Bromobenzene treated in this way gives 35% of biphenyl[120]. The yield rises to 50.4% when methanol is diluted with water and to 75% when hydrazine hydrate is added[118,119].

The formation of biaryls depends primarily on the specific properties of the catalyst, the choice of the reducing agent and the presence of an adequate amount of strong alkali. When the catalyst is poisoned by small amounts of nickel or copper salts, which do not affect the parallel reduction of bromobenzene to benzene, the yield of biphenyl drops to 5% or less. No biphenyl is formed when nickel, platinum and copper catalysts, or even palladium on a polyvinyl alcohol carrier, are used. Methanol cannot be replaced as a reducing agent by ethanol or isopropyl alcohol, presumably because of differences in the ease of their dehydrogenation and the action of the condensation products of the resulting aldehyde or ketone on the catalyst. In the presence of hydrazine, to which is ascribed the role of an aldehyde-binding agent, ethanol and dioxane as well as methanol can be employed[119].

This method has been used for the synthesis of higher polyphenyls[119]. *p*-Dibromobenzene treated in an autoclave at 150° yields 21% of biphenyl, 14% of *p*-terphenyl, 10% of *p*-quaterphenyl, 2% of *p*-quinquiphenyl, 0.7% of *p*-sexiphenyl, and 0.2% of *p*-septiphenyl. *m*-Dibromobenzene gives an 86% yield of *m*-linked hydrocarbons containing up to 16 aromatic rings in the molecule:



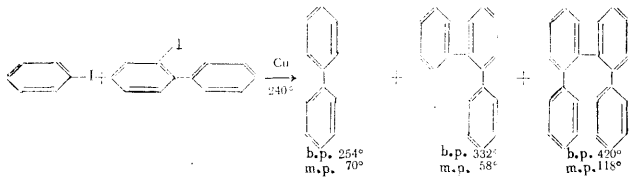
The mechanism of the reaction has not been adequately investigated. Formation and recombination of radicals on the catalyst surface has been postulated[120].

(*b*) The Ullmann reaction. This consists of removing the halogen from two molecules of aryl halide using copper, and is one of the most useful methods for the preparation of polyphenyl hydrocarbons[1,81,118,121–144]:

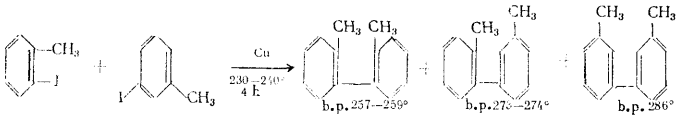
$$ArX + Ar'X' + Cu \rightarrow ArAr' + CuXX'.$$

The reaction is carried out at 200°–330°, depending on the reactivity of ArX (X is usually I), in a sealed tube[121] or autoclave[137] if necessary. The use of a solvent prevents local overheating and in some cases enhances the yield of the biaryl. For example, the yield of 3,3'-dimethylbiphenyl from *m*-iodotoluene is 55% in boiling dimethylformamide (72 h)[122], whereas without solvent (205°–240°, 3 h) it is only 35%[121]. If the initial compounds have substituents in the 2,6-positions, the yield of biaryl drops owing to steric hindrance; the yield of dixylyl from 2,6-dimethyliodobenzene at 240°–265° is only 21%[125] and that of bimesityl does not exceed 12.5%[121,126].

The preparation of unsymmetrical polyphenyl hydrocarbons by this method is further complicated by the formation of a mixture of three products. This problem is rendered easier if the reaction gives a mixture of polyphenyls with a different number of rings[130]:



Otherwise the separation of the hydrocarbons is extremely difficult. For example, 3 bitolyls were obtained from a mixture of *o*- and *m*-iodotoluene[137]:



Only the 2,2'-isomer could be separated satisfactorily by distillation. Two other fractions contained a mixture of 2,3'- and 3,3'-bitolyl which were only separated after oxidation to biphenyldicarboxylic acids. The use of disubstituted aryl halides opens up interesting possibilities. The reaction between 4,4-diiodobiphenyl and 4-iodobiphenyl yields 24.4% of *p*-sexiphenyl[143]; 3,3'-dimethyl-4,4'-diiodobiphenyl in α-methylnaphthalene gives higher polyaryls with molecular weights of 1000–300 000 but probably with a branched structure[141,142].

Attempts to replace copper by other metals (Mg, Zn, Fe, Ag) proved unsuccessful[121], although silver is effective in the synthesis of certain polycyclic hydrocarbons[89,123,143], e.g. *p*-sexiphenyl from 4-iodo-*p*-terphenyl at 330°[123]. With copper the reaction is sluggish at 300° and only specially activated copper yields a small amount of the desired product[143].

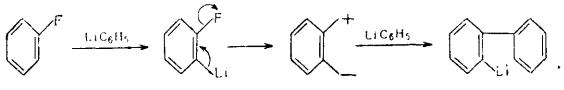
The mechanism of the Ullmann reaction has not yet been fully clarified. A free-radical mechanism has been postulated on the basis that, when ethyl benzoate is added to the reaction mixture of iodobenzene with copper, the products include esters of 2- and 4-biphenylcarboxylic acids[145]. The absence of characteristic polymeric side products and a number of other facts[3] suggest recombination of radicals on the surface of the finely divided metal or an activated-complex stage in the reaction, without generation of kinetically independent species. The possibility of intermediate organocopper compounds is also not excluded.

(*c*) The Wurtz-Fittig reaction. Although aryl halide condensation with the help of alkali metals has been known for nearly 100 years[146,147], this method has been applied to relatively few polyphenyl hydrocarbons. Probably, the use of aryl dihalides yields the most interesting results[148–152]. Polycondensation of dichlorobenzene using sodium or a liquid sodium-potassium alloy (KNa_2) gives a

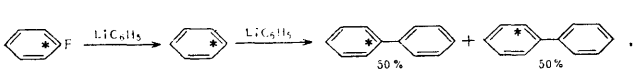
polymeric product, so-called "polyphenyl" [151,152]. The alloy is introduced gradually into a boiling solution of *p*-dichlorobenzene in dioxane; after prolonged heating the polymer is isolated with an 80% yield, of which approximately 90% is soluble in benzene. The molecular weight of this soluble polyphenyl is of the order of 2700–2800 (±500); it contains 4.9 ± 0.9 chlorine atoms per mole, so that the molecule consists on average of 34 benzene rings some of which appear to have a quinonoid structure. The rings are presumed to be joined together in the *p*-position [151] and the molecular chain is probably branched [141]. "Polyphenyl" is highly thermostable but friable. Its friability and the rigidity of the polymer chain preclude its practical use [153,154].

A methylated polymer has also been obtained [141,142], by condensation of 3,3'-dimethyl-4,4'-diiodobiphenyl with sodium in toluene; the reaction product is partially soluble in benzene and has a branched-chain molecule.

The Wurtz-Fittig-synthesis consists of two stages: (1) formation of an arylsodium and (2) its reaction with more arylhalide [155]. The second stage is accompanied by the formation of a number of side products [156–158] such as *o*- and *p*-terphenyl, triphenylene, and hydrocarbon tar [130,157,159]. The arylsodium is presumably formed by ArBr reacting successively with two neighbouring sodium atoms with the appearance of radicals on the metal surface [156,160]. This type of reaction was investigated with phenylithium [156,161] and it was unexpectedly found that the most reactive compound was fluorobenzene despite the well-known inertness of the fluorine atom in it. Under identical conditions it yielded 8 times as much biphenyl as did iodobenzene. The intermediate product – 2-lithiumbiphenyl – was isolated with the help of benzophenone. The inductive effect of the strongly electronegative fluorine apparently enhances the mobility of the hydrogen atom in the *o*-position of the initial aryl halide which is replaced by lithium. This substitution by the considerably more electropositive lithium leads to splitting off of the fluoride anion and formation of benzyne which then condenses with the second molecule of phenyllithium:



The nature of the bonds formed in the benzyne ring has not been established precisely. Work with labelled atoms [162] has shown that 50% of the phenyllithium molecules enter the position formerly occupied by fluorine and 50% the positions *ortho* to it. This suggests the formation of a new π-electron cloud in the plane of the benzene ring.



Data on benzyne have been considered in detail [163].

(*d*) The Grignard synthesis. As already mentioned, Ullmann's attempt to use magnesium for the preparation of biphenyl failed. The Grignard reagent prepared beforehand might have been supposed to react with aryl halide, but boiling phenylmagnesium bromide with iodo- or bromobenzene in ether, toluene, or without solvent (140°–180°) only gave a very low yield of biphenyl (10–13%) [164,165]; the yield could be raised a little by carrying out the reaction at 150°–200° in an autoclave [166]. Preparative methods of obtaining polyphenyls from organomagnesium compounds only became possible with the use of certain metal halides. One of these consists in oxidation of ArMgX, usually in boiling ether, with stoichiometric amounts of salts such as $CuCl_2$ [124,126,134,167–170], AgBr [171,172], $MoCl_5$ [173], $CoCl_2$ [167], $CrCl_3$ [168,169], and others [174]:

$$2ArMgBr + 2CuCl_2 \rightarrow ArAr + Cu_2Cl_2 + 2MgBrCl\,.$$

Preliminary preparation of the Grignard reagent is not always necessary and sometimes even undesirable; for example, biphenyl-4-ylmagnesium bromide gives a 52% yield of *p*-quaterphenyl whereas boiling a mixture of 4-bromobiphenyl with magnesium and $CuCl_2$ in ether gives a 63% yield [124]. The oxidation reaction occurs in two stages [175,176]:

$$ArMgX + MX \rightarrow ArM + MgX_2,$$
$$2ArM \xrightarrow{(O_2)} ArAr + 2M \quad (M_2O).$$

The reaction between phenylmagnesium iodide and CuI at 0° in an atmosphere of nitrogen yields phenylcopper [175] which, on decomposition (20°), atmospheric oxidation, and other transformations, gives biphenyl. Phenylsilver prepared from phenylmagnesium bromide and AgBr at -18° behaves similarly [175,176]. An interesting phenomenon was demonstrated by using copper sulphate as the oxidising agent [168]. Owing to its extremely low solubility in ether, it reacts with phenylmagnesium iodide with great difficulty; however, when iodobenzene is added to the reaction mixture, biphenyl is formed smoothly according to the equation

$$4C_6H_5MgI + 2C_6H_5I + 2CuSO_4 \rightarrow$$
$$\rightarrow 3C_6H_5C_6H_5 + 2MgSO_4 + 2MgI_2 + Cu_2I_2.$$

Thus half of the initial phenylmagnesium iodide is oxidised not by the metal salt but by iodobenzene. Preparation of polyphenyls by oxidation of ArMgX with halogen-containing compounds in the presence of small amounts of metal salts was discovered independently of the above observation, during a search for catalysts of the reaction

$$ArMgX + ArX \rightarrow ArAr + MgX_2.$$

It was found [165] that an excess of bromobenzene boiled in ether for 11 h with magnesium and $FeCl_3$ (4 mole %) gave a quantitative yield of biphenyl. The yield was 65% when $CuCl_2$ catalyst was used. The reaction was later investigated in detail [177] and a mechanism was postulated for it [178]. In the presence of 2.5–7 mole % $CoCl_2$ and 0.74–0.88 mole of bromobenzene 83–86% of phenylmagnesium bromide is converted to biphenyl. The molecule of the latter does not contain phenyl groups from the free bromobenzene which can be successfully replaced by alkyl and other aryl halides [177,179,180]. In accordance with this *p*-tolylmagnesium bromide and bromobenzene with $CoCl_2$ yield 95% 4,4'-dimethylbiphenyl [177].

The following scheme is proposed for this process:

$$ArMgX + CoCl_2 \rightleftharpoons ArCoCl + MgClX,$$
$$2ArCoCl \rightleftharpoons ArAr + 2CoCl.$$

The halogenated derivative reacts with cobalt subhalide regenerating the salt of the divalent metal and forming a radical:

$$CoCl\cdot + RX \rightarrow CoClX + R\cdot\,.$$

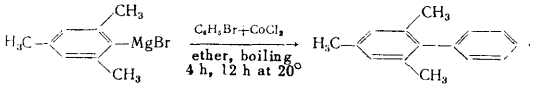
The side products arise through further transformations of this radical. Thus when C_4H_9MgBr reacts with C_6H_5Br and $CoCl_2$ the products include 44% of C_6H_6, 3% of $C_6H_5C_6H_5$, and 11% of other polyphenyls [179].

$$xC_6H_5 \rightarrow C_6H_6 + C_6H_5C_6H_5 + C_6H_5C_6H_4C_6H_5 + (C_6H_5C_6H_4)_2 + \ldots$$

If the oxidising agent is an alkyl halide, however, no

high-boiling polyphenyls are formed. In the absence of RX the cobalt subhalide can be disproportionate and be oxidised by atmospheric oxygen.

In spite of Kharasch's scheme an unsymmetrical product can be formed in this reaction as well, presumably because of the radical mechanism of arylcobalt chloride decomposition. For example, phenylmesitylene has been prepared (yield 18.4%) from mesitylmagensium bromide and a four--fold excess of bromobenzene[167]:

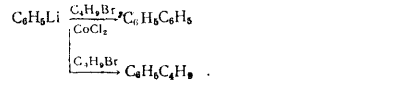


Nickel chloride, ferrous chloride, and other substances can also be used as catalysts[177,181]. The Grignard reaction proved to be of little value for the preparation of methylated polyphenyl from 4,4'-diiodo-3,3'-dimethylbiphenyl and 2,5--dibromotoluene[182]. Khorschak[183,184] discovered and studied the preparation of polyphenyls from arylmagnesium halides and hexachloroethane without addition of salts:

$$2ArMgX + C_2Cl_6 \rightarrow ArAr + MgXCl + C_2Cl_4.$$

This method gave a 35% yield of biphenyl from phenylmagnesium bromide at 22°. Thanks to the intermediate formation of radicals, a solution of the Grignard reagent initiates styrene polymerisation more energetically in the presence of hexachloroethane.

(*e*) Preparation of polyphenyls from other organometallic compounds. Certain other organometallic compounds behave similarly to the Grignard reagents; for example, phenyllithium is oxidised by butyl bromide in the presence of $CoCl_2$ giving a 67% yield of biphenyl, whereas in the absence of the salt the usual Wurtz-Fittig synthesis takes place[180]:



2,2'-Dilithiobiphenyl in the presence of $TiCl_4$, $CuCl_2$, $MnCl_2$, $FeCl_2$, or $CoCl_2$ forms a mixture of aromatic hydrocarbons including biphenyl (up to 79%), *o*-quaterphenyl (up to 38%), *o*-sexiphenyl (up to 8%), and *o*-octaphenyl (up to 1.4%)[185].

When phenylaluminium diiodide is heated with bromobenzene in benzene it is converted to biphenyl (97.7%)[186].

$$2C_6H_5AlI_2 \xrightarrow[1\ h]{245°-255°} C_6H_5C_6H_5 + 2AlI_2,$$

$$AlI_2 + C_6H_5Br \rightarrow C_6H_5\cdot + AlI_2Br.$$

As in Kharashch's experiments, *p*-terphenyl, *p*-quaterphenyl, and *p*-quinquiphenyl are isolated. When bromobenzene is replaced by *p*-chloro- or *p*-bromotoluene, no methylbiphenyls are formed, biphenyl remaining the main reaction product (yield up to 30%).

Oxygen can also be used for the oxidation of organometallic compounds of polyphenyls. Phenyl and *p*-biphenyllithium in ether are oxidised to biphenyl (yield 65%) and *p*-quaterphenyl (yield 85%) respectively[187]:

$$4ArLi + O_2 \rightarrow 2ArAr + 2Li_2O.$$

When phenyllithium and triphenylindium are oxidised with oxygen in benzene they give phenyl (17–26%) and 20–25% of biphenyl[188,189]

Thermal decomposition of triphenylthallium[190,191] and tetraphenylchromium iodide[192] and catalytic decomposition of diphenylmercury and tetraphenyllead, in the presence of Pd and other metals[193,194] leads to the formation of biphenyl. Biaryls are also produced by photochemical reactions[195-198] and some complex reactions such as those of arylsodium or lithium with N_2O[199], arylmagnesium halides with nitroaromatic[200] and azoxy compounds[201] or with iodoaryl dichlorides[202]. They are formed also as side products, sometimes in considerable amounts, in the course of many organometallic syntheses[203-208].

5. Preparation by Elimination of Sulphur and Selenium

Biaryls are obtained by removal of sulphur from thioethers, disulphides, and thiophenols and their esters by Raney nickel or the Sabatier nickel catalyst at sufficiently high temperatures[209]:

$$Ar_2S \xrightarrow{Ni} ArAr$$

Heating is continued for 15 h in a sealed tube, either in the presence of benzene or without it. An appreciable amount of biphenyl already forms at 180°. Diphenyl disulphide, which at 140° is converted to the extent of 84–87% into diphenyl sulphide, at 180° gives 54% and at 220° 65–85% of biphenyl. If the initial compound contains two different aryl radicals, or if a mixture of two substances is taken, three hydrocarbons are formed simultaneously:

$$ArSAr' \xrightarrow{Ni} ArAr + ArAr' + Ar'Ar'$$

In some cases *p*-terphenyl (up to 6% of the theoretical amount) can be isolated from the tarry reaction products.

The nickel catalyst is first degassed at 200°. The small amount of H_2 which remains takes part in the side reaction

$$Ar_2S \xrightarrow[Ni]{H_2} ArH,$$

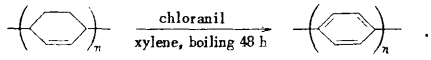
without affecting the course of the main process: the yield of biaryls is not diminished when the catalyst is degassed at 500° and is practically H_2-free. Reduced iron catalysts used for purification of industrial gases react with diphenyl sulphide at 350° also giving chiefly biphenyl[210].

Organic selenium-containing compounds behave similarly to the sulphur-containing ones. Whereas at 140° (14.5 h) diphenyl diselenide gives, with degassed Raney nickel, 21.5% of diphenyl selenide and 31% of biphenyl, at 180° 72% of biphenyl is formed in 8 h[211]. Di(*o*-methylphenyl)selenide is converted into 2,2'-dimethyl biphenyl in 52% yield.

II. SYNTHESIS WITHOUT ALTERATION OF THE CYCLIC CARBON SKELETON (DEHYDROGENATION)

Dehydrogenation of polycyclic hydroaromatic compounds is used for two purposes: (1) for the synthesis of polyphenyl hydrocarbons of a given structure and (2) for the determination of the structure of unknown hydroaromatic compounds. Dehydrogenation is effected either by the use of hydrogen acceptors or catalytically. The reaction conditions depend on the choice of dehydrogenating agent and the structure of the initial compound. The most widely used acceptors are tetrachlorobenzoquinone, sulphur, and selenium. Tetrachlorobenzonequinone (chloranil) is often preferred since it is effective at a relatively low temperature. Benzonquinone itself is a much less active dehydrogenating agent[212].

When an excess of chloranil is used in boiling xylene (140°–145°), dehydrogenation to aromatic compounds occurs within 4–48 h. Saturated cyclic hydrocarbons are not dehydrogenated under these conditions [213]. The reaction evidently follows a radical mechanism [213]. This method has been used for the synthesis of a number of two to six-ring polyphenyls from hydrocarbons containing, in the polycyclic chain, cyclohexane, cyclohexadiene, and aromatic units [1,167,212,214–218]. It is noteworthy that the best conversion of poly-1,3-cyclohexadiene to polyphenyl also occurs when chloranil is used [219]



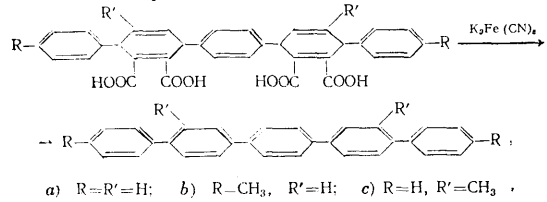
Dehydrogenation with sulphur usually occurs within 1.5–5 h at 180°–250°. Longer heating is sometimes necessary [80,220]. A solvent is used in some cases (quinoline) [80,221]. Substituted arylcyclohexenes [80,134,220,222–226], and less frequently cyclic alcohols and hydrocarbons, of varying degrees of unsaturation [223,227–229] undergo aromatisation. An interesting observation made during the synthesis of dimethylbiphenyls [133] is that a mixture of sulphur and palladised charcoal is more effective than either component individually: the reaction is more rapid and takes place at a lower temperature (190°–200°). Dehydrogenation with sulphur is sometimes complicated by the migration of a mobile alkyl group: attempts to obtain 3- and 4-t-butylbiphenyl failed though migration of the t-butyl group and formation of a mixture of isomers [76].

Selenium is often used for the preparation of polyphenyls especially from aryl substituted cyclohexanes [230–238]. Dehydrogenation occurs at 320°–370°. Other dehydrogenating agents are only used in isolated cases, e.g. bromine at 160° [237,238], diphenyl disulphide at 250°–260° [239], and *N*-bromosuccinimide in carbon tetrachloride [240].

The most frequently used catalyst is probably palladium on activated charcoal. It has been used for the synthesis of polyphenyl hydrocarbons containing up to 8 aromatic rings [77,133,241–249]; Pd/Al_2O_3 [250,251], Pt/C [230,252], Pt/Al_2O_3 [253], Cr_2O_3/Al_2O_3 [254–257], and reduced nickel chromite [258] are also suitable.

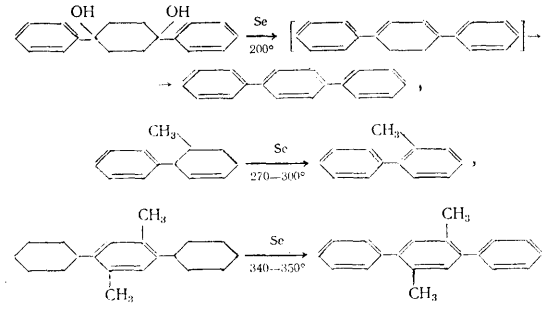
Some general comments can be made on the variation of the conditions necessary for the dehydrogenation of polycyclic hydroaromatic compounds with their structure.

1. As expected, the greater the number of double bonds in the initial molecule, the easier its transformation into an aromatic system. Therefore aryl-substituted cyclohexadienes show the greatest tendency to dehydrogenation. 1,3-Dipehnylcyclohexa-1,3-diene undergoes autooxidation on standing [242], its *p*-isomer loses hydrogen on distillation [225], and phenylcyclohexadiene hydrogenated with palladised charcoal at 20° forms, through irreversible catalysis, a mixture of biphenyl and phenylcyclohexane [259]. If the diene ring contains carboxyl groups, as in the case of 3,6-diphenyl-3,6-dihydrophthalic acid [260] or of tetracarboxylic acids of tetrahydro-*p*-quinquiphenyls [261], simultaneous oxidation and decarboxylation occur on gentle heating with potassium ferricyanide solution:

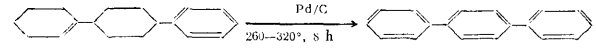


a) R=R'=H; *b*) R=CH_3, R'=H; *c*) R=H, R'=CH_3.

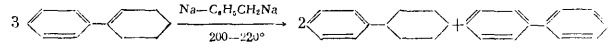
The increasing difficulty of dehydrogenation with increasing saturation can be traced in several examples. Whereas 1,4-diphenylcyclohexane-1,4-diol gives *p*-terphenyl with selenium at 200° [262], 2-phenyl-Δ^3-tetrahydrotoluene is not converted to 2-methylbiphenyl below 270°–300° [263], and 1,4-dimethyl-2,5-dicyclohexylbenzene only undergoes aromatisation at 340°–350° [264]:



Diarylcyclohexadienes are converted smoothly into polyphenyls when palladium in boiling cymene (177°) is used [242,244–247]; however, when *p*-terphenyl is prepared from 1-phenyl-4-(cyclohexen-1'-yl)cyclohexane heating has to be continued for 8 h at 260°–320° [248]:

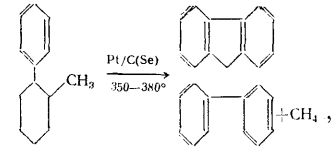


The role of a double bond conjugated with the phenyl ring is clearly seen on comparison of the dehydrogenation of 1-phenylcyclohexene and phenylcyclohexane. The former is converted to biphenyl to the extent of 52% in 4 h using chloranil [212], whereas the latter gives only 13% of the product after 16 h heating with a larger amount of the reagent [213]. In the presence of sodium–benzylsodium catalyst, 1-phenylcyclohezene disproportionates almost quantitatively at 200°–220° [265]:



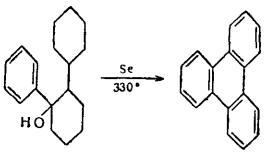
but the phenylcyclohexane so obtained requires a higher temperature (above 240°) for dehydrogenation.

2. The presence of a substituent in the position *ortho* to the internuclear bond may lead to undesirable side reactions and requires particular care in the choice of experimental conditions. Thus 1-methyl-2-phenylcyclohexane treated with 20% platinised charcoal at 350°–380° or dehydrogenated with selenium gives fluorene as the main product; simultaneously elimination of the methyl group leads to the formation of some biphenyl [251]:

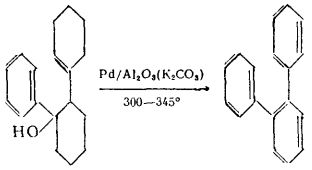


When 3-*p*-tolyl-3-menthene is heated with sulphur at 220°–230°, 3,4'-dimethyl-6-isopropylbiphenyl is formed with an 85% yield [220]. If the temperature is raised by 100°, however, considerable amounts of 2,6,9,9-tetramethylfluorene and 2,6,9-trimethylphenanthrene are formed. Similar condensations may occur in the case of a cyclic substituent. Dehydrogenation of 1-phenyl-2-cyclohexylcyclohexanol with selenium gives the triphenylene con-

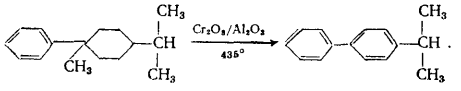
densed system[234]:



However, aromatisation of one of the isomeric 1-phenyl-2-(cyclohexen-1'-yl)cyclohexanols-1 (m.p. 58°–59°) using a Pd/Al_2O_3 catalyst pre-boiled with a 5% solution of K_2CO_3 gives *o*-terphenyl (yield 63%)[250]:

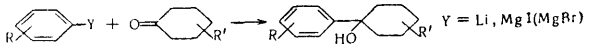


3. In some cases dehydrogenation may be accompanied by elimination or migration of alkyl and alkenyl substituents. 1,4-Diphenyl-5-vinylcyclohex-1-ene is converted to *p*-terphenyl (yield 86.5%) over 30% Pd/C at 320°[241]. An example of the migration of an alkyl group on dehydrogenation with sulphur has been mentioned above. In the case of an alkyl-aryl *gem*-substitution an alkyl group is usually eliminated[230,253,255,256] and this has served as a basis for a patented method of preparation of 4-alkylbiphenyls by dehydrogenation of 1-alkyl-1-phenyl-4-alkylcyclohexanes[256]:

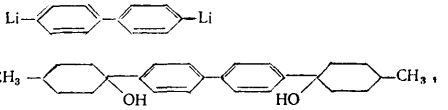


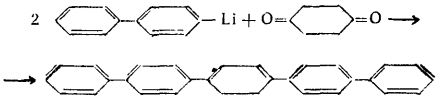
4. In isolated instances polyphenyl hydrocarbons can be prepared from derivatives of hydroaromatic hydrocarbons; when 4-bromo-4'-cyclohexylbiphenyl is dehydrogenated with selenium, the bromine atom is replaced by a hydrogen atom and *p*-terphenyl is formed[238].

Dehydrogenation is the final stage in the synthesis of polyphenyl hydrocarbons and the polycyclic chain molecule must be first constructed. Some methods of obtaining the initial hydroaromatic compound consist in linking separate cyclic molecules, others involve cyclisation and formation of new rings. Rings can be linked by the following methods: organometallic synthesis of the Grignard type, cycloalkylation of aromatic compounds, reduction of cyclic ketones to pinacols, and polymerisation of cycloolefines or cyclodienes. The first method is the most general, the number of rings being increased by interaction of cyclohexanes with aryllithium or arylmagnesium halide:



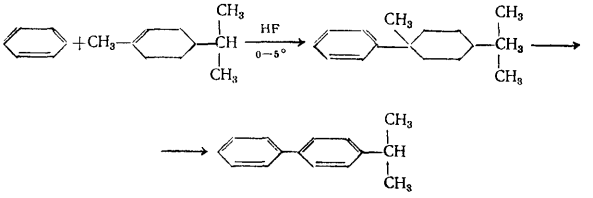
The use of dilithiobiphenyl[218], cyclohexane-1,4-dione[187], and bicyclohexyl-4,4'-dione makes it possible to lengthen the cyclic chain in two directions at once:



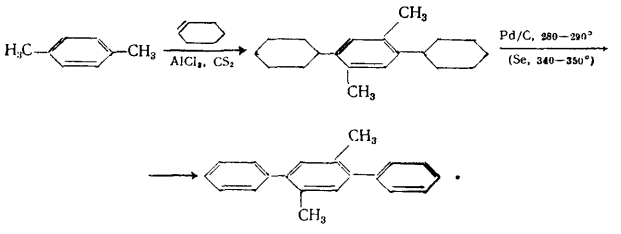


The wide scope of this method is demonstrated by the synthesis of a whole range of *m*-diarylbenzenes based on 3-ethoxycyclohex-2-en-1-one[242,244–247]

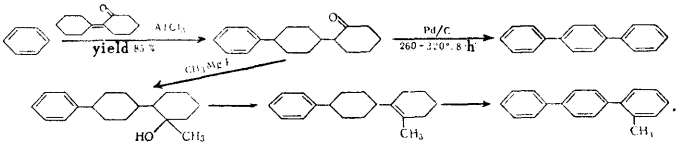
Cycloalkylation has been used repeatedly for the preparation of intermediate products in the synthesis of *p*-polyphenyl hydrocarbons[73,231,232,237,248,256,264,266]. Dihydroterpenes or dihydroterpene alcohols in the presence of HF have been recommended for the alkylation of benzene to yield 4-alkylbiphenyls[256]:



Alkylation of *p*-xylene with cyclohexene in the presence of $AlCl_3$ gives 2',5'-dimethyl-*p*-terphenyl[264]:

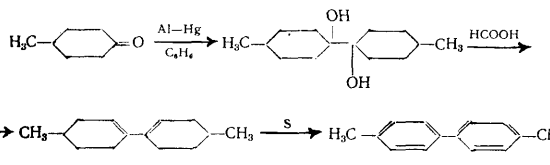


Condensation of benzene with cyclohexyl bromide has been used for the preparation of *p*-terphenyl[237]. The use of cyclohexylidenecyclohexanone for the synthesis of *p*-terphenyls is of interest[248]:



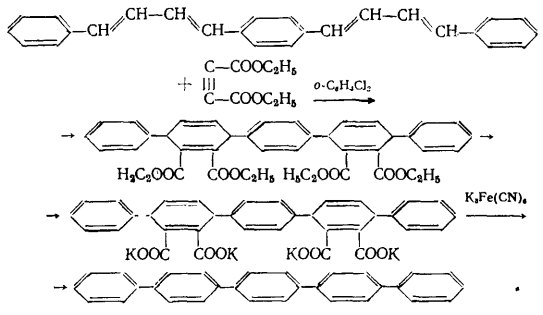
In some cases successful alkylation is achieved by the cyclohexyl ester of *p*-toluenesulphonic acid[266].

Much has been published on the cycloalkylation reaction, usually in connection with the use of dehydrogenation to prove the structure of the products obtained. Only in isolated cases are these products important as starting materials for polyphenyl synthesis. The same applies to polymerisation of unsaturated cyclic compounds[219,258]. The reduction of cyclohexanones to pinacols has been used successfully for the preparation of symmetrical biphenyls[228]:

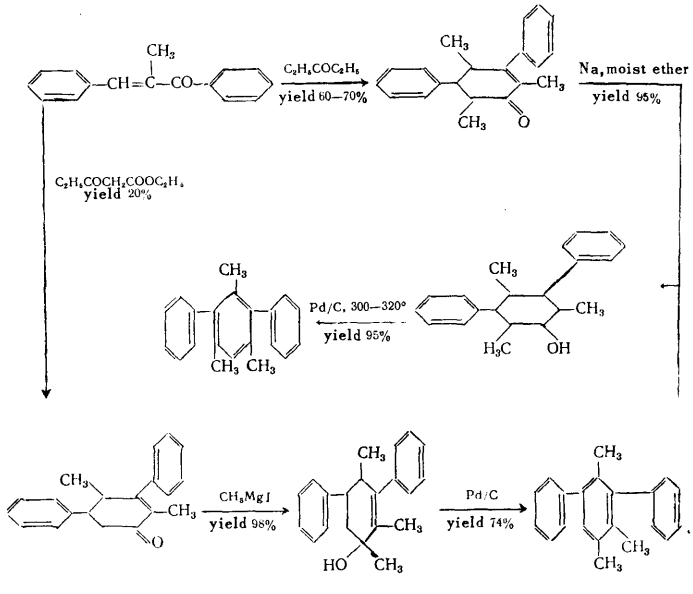


Any other type of construction of a polynuclear chain is based primarily on the diene synthesis and the Michael reaction in which new rings are formed by cocyclisation of the aliphatic parts of the initial molecules to form a contin-

uous chain with the already existing rings. The diene synthesis is very convenient for the preparation of polyphenyl hydrocarbons, but sometimes difficulties are encountered due to the relative unavailability of the starting materials; various polyphenyls have been synthesised by this method up to and including quinquiphenyls [241,249,260,261,263,267], *p*-quinquiphenyl, for example, being prepared as follows:

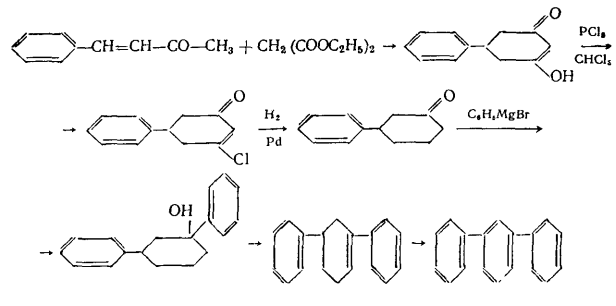


The Michael condensation has been used for the preparation of isomeric trimethyl-*m*-terphenyls [249]:

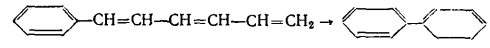


Condensation of *α*-benzylidene-*α'*-phenylacetone with malonic ester gives compounds of the *p*-terphenyl group [235].

Formation of hydroaromatic ketones as intermediates permits further lengthening of the chain by means of organometallic reagents; this forms the basis of a method for the preparation of *m*-terphenyl [80]:



Another method of forming a bicyclic molecule consists of cyclisation of 1-phenylhexa-1,3,5-triene over Al_2O_3 at 350° [259]:



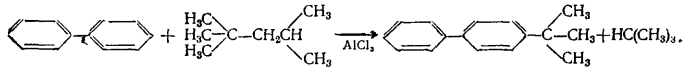
III. SYNTHESES WITHOUT ALTERATION OF THE AROMATIC CARBON SKELETON

1. Alkylation

The alkylation of biphenyl is the cheapest method for the preparation of many potentially useful industrial compounds [254,268-273]. Biphenyl reacts with olefines and alkyl halides in the presence of $AlCl_3$ usually giving a misture of mono-, di-, and sometimes even trialkylbiphenyls [268,269,274,275]. 2,4,4-Trimethylpent-2-ene taken in equimolar proportion at 70°–75° gives a 32.5% yield of alkyl derivatives with 52.6% mono-, 29.9% di-, and 17.5% tris-2,4,4-trimethylpent-2-yl-biphenyls [269]. Condensation with n-hexyl bromide in hexane yields mono- and di-hexylbiphenyls with an overall yield of 80% [275].

When biphenyl is alkylated with but-2-ene in the presence of $BF_3 . H_3PO_4$ catalyst in the molar ratio biphenyl : but-2-ene : catalyst = 1–4 : 1 : 0.2–0.3 at 50–100°, the main products are monobutylbiphenyls [276]. Their yield is 58–60% and they constitute 92% of the alkylate. Above 70° but-2-ene undergoes isomerisation and the product is therefore a mixture of *p*-*s*- and *p*-t-butylbiphenyl whose relative amounts depend on the reaction conditions.

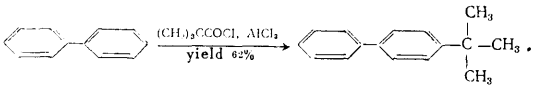
Biphenyl can also be alkylated by the saturated hydrocarbon 2,2,4-trimethylpentane in the presence of $AlCl_3$ to give mono-t-butylphenyls from which the *p*-isomer can be isolated by freezing out in 27% yield [277]:



When alcohols, in excess, act on biphenyl in the presence of H_3PO_4 catalyst with heating for 10–20 h [278], the main products are *p*-monoalkylbiphenyls (yield up to 60%). The optimum temperature is determined by the structure of the alcohol; it is 120°–125° for pentanols and 90°–110° for butanols. The rate of reaction increases from normal to tertiary alcohols. When iso-alcohols are used, isomerisation leads to the formation of t-alkylbiphenyls. When BF_3 catalyst is used, the reaction takes places in two stages [273,279]: (1) a molecular compound $2ROH . BF_3$ is formed when the cooled alcohol is saturated with boron fluoride, and (2) biphenyl is alkylated by the $2ROH . BF_3$ complex at 162°–170°. Under normal pressure, monosubstitution in the *p*-position predominates, but at 25–30 atm the amount of *p*,*p'*-dialkyl derivatives increases up to 46–50%. The total yield of alkylbiphenyls is 80–98%. Longer heating and a larger excess of alcohol are necessary when $BF_3 . H_3PO_4$ is used, but the yield does not exceed 65%. The authors postulate intermediate formation of unsaturated hydrocarbons, or of carbonium ions directly, e.g. by dissociation of the molecular compound of a normal alcohol with BF_3.

Interesting examples of alkylation are the preparation of ethylbiphenyls by heating biphenyl and diethylbenzene with $AlCl_3$ at 80°–110° [281] and the formation of *p*-t-butylbiphenyl in attempted acylation of biphenyl with trimethylacetyl

chloride[282]:



2. Preparation by way of Aliphatic-Aromatic Ketones

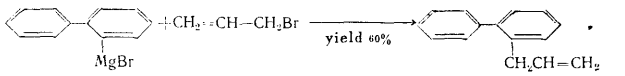
Alkyl substituted polyphenyls can be prepared by reduction of aliphatic-aromatic ketones, e.g. *p*-alkylbiphenyls containing up to 18 carbon atoms in the side chain[64,281,283-287], 4-alkyl-*m*-terphenyls[288], and 4-butyl-*o*-terphenyl[289]. The reduction is effected by the Clemmensen method with zinc amalgam and hydrochloric acid[281,284,286,287,289], hydrazine hydrate and alkali[288], hydroxylamine and metalic potassium[285], or with hydriodic acid[283]. Sometimes it is desirable or even necessary to obtain first the corresponding carbinol, dehydration of which also permits the synthesis of polyphenyl hydrocarbons with an unsaturated side chain[281,290]. For example, when 2',2'-diacetylbiphenyl is reduced by the Clemmensen method, the product is anomalous[290] and the diactyl compound is therefore first converted with lithium aluminiumhydride to the glycol, which is then dehydrated to 2,2'-divinylbiphenyl which, in turn, is hydrogenated to 2,2'-diethylbiphenyl.

When aliphatic-aromatic ketones react with Grignard reagents, tertiary alcohols and polyphenyls with branched side chains are formed. This method has been suggested for the preparation of *p*-isopropenyl-[219-293] and *p,p'*-diisopropenylbiphenyl[294] used as monomers for polymer syntheses. Similarly, (1-butyloctadecyl)biphenyl has been prepared from stearoylbiphenyl and butylmagnesium chloride[287]. The alcohols and glycols are dehydrated by the usual methods taking into account the tendency of the olefines formed to polymerise[271,281,287,291-298].

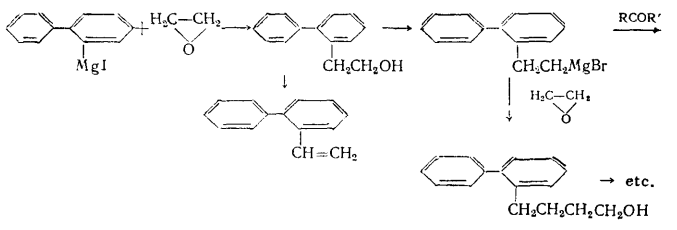
3. Grignard Synthesis from Polyphenyl Halides

The reactions of polyphenylmagnesium halides with aliphatic aldehydes and ketones give a variety of alkyl- and alkenyl-polyphenyls, in particular alkylbiphenyls[76,254,257,281,291-293,299-302]. This method has been used for the preparation of *o*-substituted biphenyls with large unsaturated substituents[300,301], which it would be difficult or impossible to prepare by any other method.

If the carbonyl compound is replaced by an allyl halide, it is possible to introduce a double bond into the β-position of the side chain[302]:



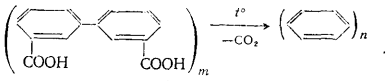
Ethylene oxide provides further possibilities[302]:



Moreover, organometallic compounds undergo direct alkylation: the reaction between CH_3HSO_4 and 4-lithio-*p*-terphenyl gives a 67% yield of 4-methyl-*p*-terphenyl[222], and biphenyl-2-yl magnesium iodide and diethyl sulphate give 42% of 2-ethylbiphenyl[254].

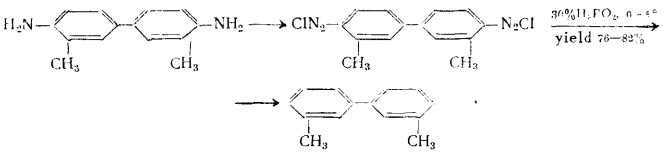
4. Preparation by Elimination of Functional Groups

Polyphenyl hydrocarbons can be prepared by decarboxylation of aromatic acids; *o*-terphenyl is formed on dry distillation of the silver salt of *o*-terphenyl-2-carboxylic acid[135]. The anhydride of *p*-quaterphenyl-2',3'-dicarboxylic acid gives a hydrocarbon when heated with basic copper carbonate in quinoline[267]. The polymer obtained by deamination of 4,4'-diaminobiphenyl-3,3'-dicarboxylic acid at an elevated temperature is, apparently, converted to polyphenyl[98-100]:

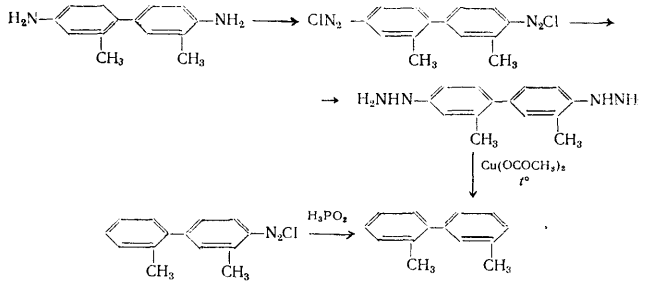


Fission of various carbonyl compounds has been used for the preparation of 3',6'-dimethyl-[303] and unsubstituted *o*-terphenyl[218].

The hydroxyl and methoxy groups can be removed by distillation with zinc dust[304-306]. Another way of converting phenols into hydrocarbons is by reduction of the corresponding phosphates[307]: diethyl-*p*-biphenyl phosphate is reduced by alkali metal in liquid ammonia to biphenyl with a yield of 75–80%. Deamination is also achieved by the usual methods[308]: diazotised *o*-tolidine is reduced by 30% hypophosphorous acid to 3,3'-dimethylbiphenyl[309]:



2,3'-Dimethylbenzidine is first converted to the corresponding hydrazine derivative which is oxidised by distillation with copper acetate to 2,3'-dimethylbiphenyl[137]. The latter can also be prepared from hypophosphorous acid and 4-amino-2',3-dimethylbiphenyl[310]:

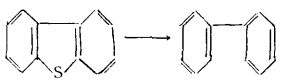


The diazonium salt of 4-amino-*p*-terphenyl forms *p*-terphenyl when reduced by sodium stannite in an alkaline medium[311]. Benzidine yields biphenyl when it is diazotised and treated either with Cu_2O in $H_2SO_4-CH_3COOH$[312], or with hypophosphorous acid, or boiling ethyl alcohol[308] (yield 23–80%).

There are also isolated examples of dehalogenation[81], elimination of selenium[313], elimination of silicon-containing groups[314], etc.

5. Preparation from Heterocyclic Compounds

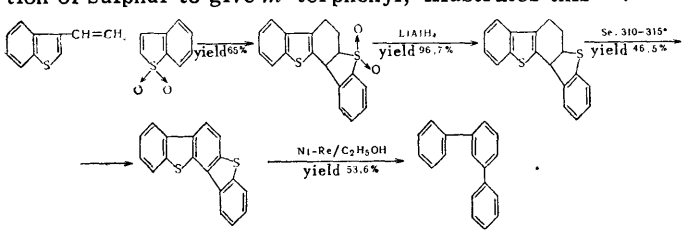
The molecules of some heterocyclic compounds with five-membered rings contain polyphenyl hydrocarbon skeletons. Dibenzothiophene can be regarded as biphenyl with a sulphur bridge in the 2,2'-position; on treatment with Raney nickel in boiling alcohol, an atom of sulphur is replaced by 2 atoms of hydrogen and biphenyl is formed in 97.5% yield[315]:



Dibenzoselenophene under these conditions gives a low yield of biphenyl but if the reaction is carried out in 10–20% solution of alcohol in benzene with nickel (approximately 20 times the weight of the sample), the yield rises to 87%[313]. Dibenzoselenophene oxide and dichloride give 72% biphenyl.

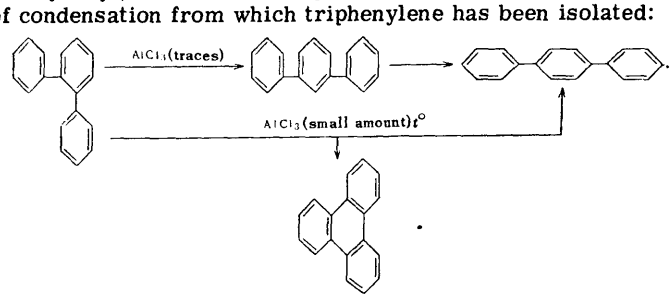
When dibenzothiophene is boiled with lithium (molar ratio 1 : 2.2) in dioxane, 30.5% is converted to biphenyl[316]. Dibenzofuran gives only *o*-hydroxybiphenyl when treated with lithium.

Elimination of sulphur by nickel may be accompanied by replacement of functional groups in the initial compound by hydrogen. Simultaneous dehalogenation causes 2-bromodibenzothiophene to yield approximately 35% of biphenyl[316]. An interesting series of conversions, which includes the preparation of a heterocyclic compound followed by elimination of sulphur to give *m*-terphenyl, illustrates this[317]:



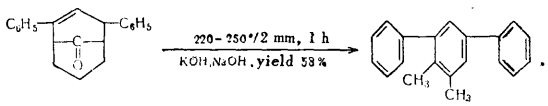
IV. SYNTHESES WITH ISOMERISATION AND FISSION OF THE CYCLIC CARBON SKELETON

These reactions are used only in exceptional cases. *o*-Terphenyl undergoes isomerisation under the influence of traces of $AlCl_3$[218], forming first *m*-terphenyl which then gradually changes to the *p*-isomer. Further reactions occur simultaneously and become more important the higher the temperature and the larger the amount of $AlCl_3$. The main product of heating with molten $AlCl_3$–NaCl at 130° is *p*-terphenyl, but at 200° the predominant products are those of condensation from which triphenylene has been isolated:

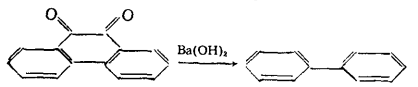


No triphenylene is formed on pyrolysis of *o*-terphenyl without $AlCl_3$.

Examples of ring fission of cyclic molecules are the preparation of 4,5'-dimethyl-*m*-terphenyl by heating 2,4-diphenylbicyclo[3,3,1]-non-2-en-9-one with a mixture of NaOH and KOH in vacuo[318],



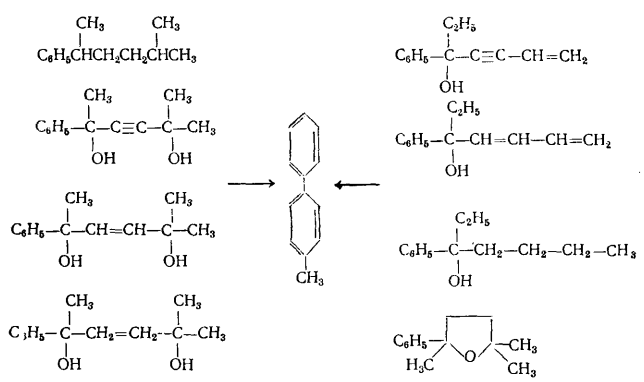
and the preparation of biphenyl by thermal fission of phenanthrenequinone with $Ba(OH)_2$[319].



Biphenyls can also be formed by catalytic dehydrogenation of bicyclic compounds containing a seven-membered ring[320,321].

V. SYNTHESES WITH FORMATION OF INDIVIDUAL UNITS OF THE POLYPHENYL CHAIN (DEHYDROCYCLISATION)

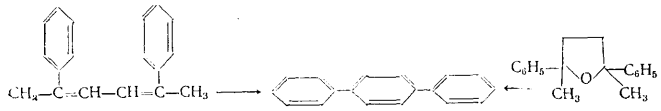
The side chain of aliphatic aromatic compounds which contains not less than 6 carbon atoms can be cyclised on a chromium-aluminium catalyst into a further aromatic ring which is not condensed with the already existing rings in the initial molecule[322–326]. This process can be applied to oxygen containing compounds (glycols, tetrahydrofurans, alcohols) as well as to hydrocarbons. The water which is split out during the reaction does not hinder the aromatisation.



The best yield of 4-methylbiphenyl from the various substances shown above using an $MgO/Cr_2O_3/Al_2O_3$ (2 : 18 : 80) catalyst is obtained with 2,2,5-trimethyl-5-phenyltetrahydrofuran (550°, 0.36 kg of catalyst per litre per hour)[322]. Under other conditions (HF or H_2SO_4) the latter is cyclised to a mixture of 1,2,4-trimethylnaphthalene and 1,1,4-trimethyl-1,2,3,4-tetrahydronaphthalene[327].

Terphenyls can be synthesised from diaryl-substituted compounds with sufficiently long aliphatic side chains[328,329]: 2,5-diphenyl-hexa-2,4-diene and 2,5-dimethyl-2,5-diphenyltetrahydrofuran undergo aromatisation at 530° with the

same catalyst to give *p*-terphenyl in 45–50% yield:



The limits of application of catalytic dehydrocyclisation to polyphenyl synthesis are at present difficult to establish as the reactions cited are among the first examples reported. When higher paraffins and olefines, or alkylbenzenes with shorter side chains, undergo this reaction, the products consist of condensed systems. The reaction has been studied in greater detail in these cases.

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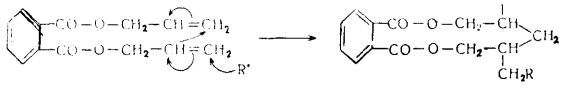
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POLYMERISATION OF UNCONJUGATED DIENES

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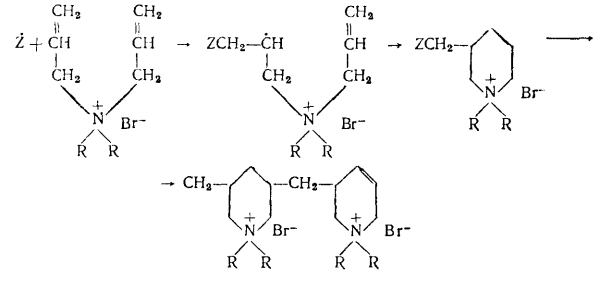
Ring closure during the polymerisation of compounds containing isolated double bonds was first proposed by Simpson[1] to explain the structure of the soluble poly(diallyl *o*-phthalate), obtained at low degree of polymerisation. A year later Howard[2] demonstrated the "intramolecular cross-linking" of some of this ester, during peroxide-induced polymerisation, giving an eleven-membered ring, and possibly some of the ten- and twelve-membered ring compounds:



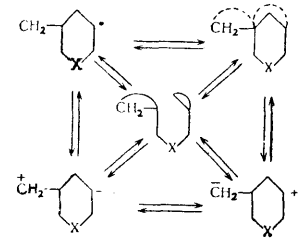
Later, Simpson and Holt[3,4] investigated the polymerisation, under the same conditions, of the diallyl and di-β-methylallyl esters of oxalic, malonic, succinic, glutaric, adipic, azelaic, sebacic, carbonic, and the three phthalic acids.

Polymers from such esters have recently been shown to be typical of many polymers from compounds containing two isolated double bonds, being abnormally soluble in organic solvents and showing little unsaturation. Many such polymers turn into equally soluble transparent plastics at high temperature and pressure.

Butler and his coworkers[5-13] investigated the free-radical polymerisation of many allyl and methylallyl derivatives of quaternary ammonium salts, with the initial purpose of making strongly basic ion-exchange resins. Monoallyl derivatives did not polymerise at all, tri- and tetraallyl derivatives gave insoluble three-dimensional polymers, but the polymers from diallyl derivatives dissolved readily in water and ethanol[10-12]. This refuted the general assumption that polymers from monomers with one double bond are relatively soluble, while those from monomers with two or more double bonds are sparingly soluble or insoluble[15]. The effects of the initiator type and concentration, the nature of the anion, the amount of solvent, and the presence of oxygen, etc., on the polymerisation of compounds containing two double bonds, and the hydrogenation of polymers, were also studied[5-14]. Molecular-weight determination was complicated by the polyelectrolyte nature of the polymers. Butler and Angelo[11] found that polymerisation is most efficient if initiated by 2–3 wt.% of t-butyl peroxide or an azo compound, and continued for 48 h at about 60°. They concluded that free radicals initiate polymerisation of the diallyl derivatives to soluble products of relatively low molecular weight and a low degree of unsaturation, the mechanism they suggested involves radical chain propagation by a succession of intra- and intermolecular steps. Methylene and 3,5-disubstituted piperidinium groups alternate in the saturated, unbranched chain of the product, five- and six-membered rings being preferentially formed:



Butler[14] explained the strong tendency of 1,6-dienes to polymerise, in comparison with compounds containing only one double bond, in terms of mesomerism:



In order to establish the structures of the polymers, Butler et al.[13] investigated the degradation products of poly(diallylammonium bromide) and poly(diallyldimethylammonium bromide):

