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RECENT PROGRESS IN THE SYNTHESIS OF MONOCYCLIC AND POLYCYCLIC AROMATIC HYDROCARBONS

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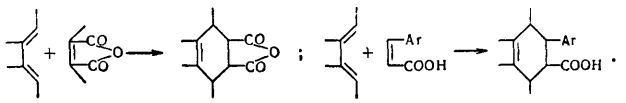
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1. INTRODUCTION

Tetrahydrophthalic acids and their anhydrides, as well as tetrahydrobenzoic acids, are readily accessible compounds, being obtained by diene synthesis from conjugated diene hydrocarbons with maleic anhydride, its homologues and cyclic analogues, and hence with cinnamic acids:

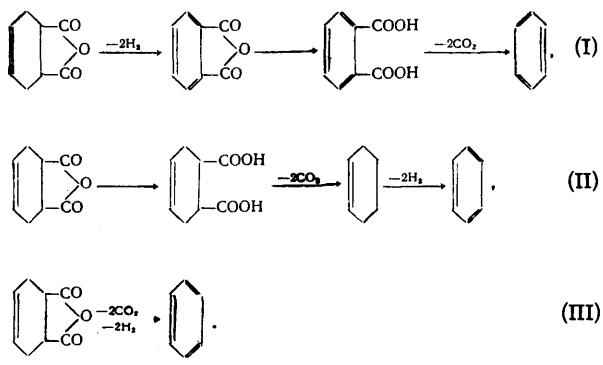


The chemical and physical properties of tetrahydrophthalic acids of various structures have been reviewed by Buckles[1], who examined methods for their preparation, reactions involving addition at the double bond, reactions of the carboxyl groups, oxidative reactions, and also reactions involving isomerisation and dehydrogenation.

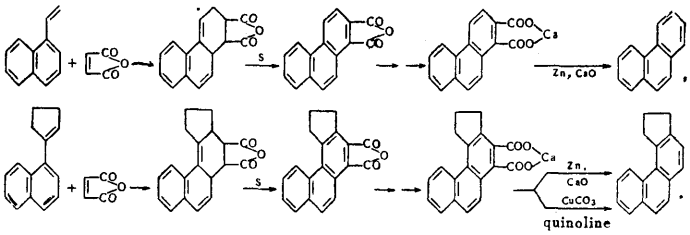
The present review surveys the conversion of 1,2,3,6-tetrahydrophthalic (cyclohex-4-ene-1,2-dicarboxylic) acids and their anhydrides and also of 1,2,5,6-tetrahydrobenzoic (cyclohex-3-enecarboxylic) acids into aromatic hydrocarbons.

2. AROMATISATION OF ADDUCTS OF DIENE SYNTHESIS — TETRAHYDROPHTHALIC ACIDS AND THEIR ANHYDRIDES — BY DECARBOXYLATION AND DEHYDROGENATION

Aromatisation of the adducts from diene synthesis is usually accomplished in three successive stages: (I) tetrahydrophthalic anhydride is dehydrogenated, the resulting aromatic anhydride is converted into the acid or a salt, and the product then subjected to decarboxylation; alternatively (II) the initial tetrahydrophthalic anhydride is first converted into tetrahydrophthalic acid or a salt thereof, a hydroaromatic hydrocarbon (or a mixture of isomeric hydrocarbons) is obtained by decarboxylation, and then the hydrocarbon is dehydrogenated to an aromatic hydrocarbon; or finally (III) the adducts undergo simultaneous decarboxylation and dehydrogenation:



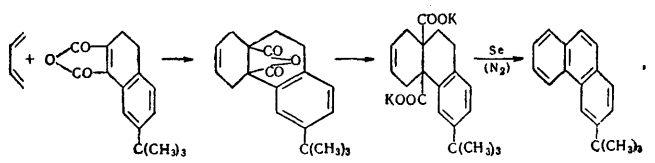
Thus the first reaction sequence (I) has been used for the synthesis of phenanthrene and 3,4-cyclopentenophenanthrene[2]:



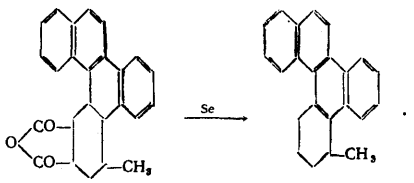
Decarboxylation of calcium phenanthrene-1,2-dicarboxylate by heating with copper carbonate in quinoline gave, instead of phenanthrene, a substance of undetermined structure.

Dehydrogenation of Adduct from Diene Synthesis

Dehydrogenation of adducts by heating with sulphur has been described by other workers too[3-5]. Some adducts are resistant to heating with sulphur (for example 1,2,3,4-tetrahydro-1,2-dimethylphenanthrene-3,4-dicarboxylic anhydride), but are readily dehydrogenated by selenium[4]. When adducts are heated with selenium, however, dehydrogenation may be accompanied, depending on their structure, by decarboxylation, for example[6]:

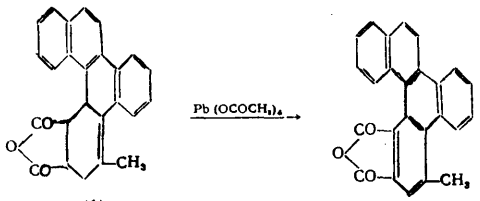


or else decarboxylation alone may take place[7]:



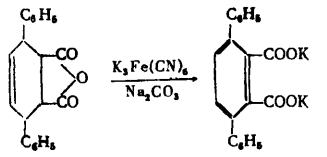
(A)

Tetrahydrophthalic acids and their anhydrides can be dehydrogenated in other ways. Thus the anhydride (A), which on being heated with selenium was decarboxylated and converted into methylcyclohexenochrysene, was not decarboxylated but dehydrogenated on being heated with lead tetraacetate[7]:



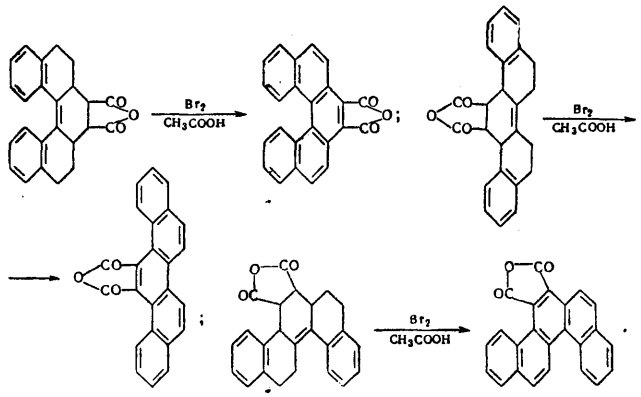
(A)

1',2',3',4'-Tetrahydro-*p*-terphenyl-2',3'-dicarboxylic anhydride was converted into a salt of 3,6-diphenylphthalic (*p*-terphenyl-2',3'-dicarboxylic) acid by heating with potassium ferricyanide† (in sodium carbonate solution)[8]:

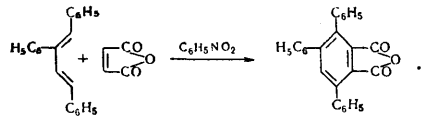


This same anhydride was dehydrogenated by heating in nitrobenzene[10].

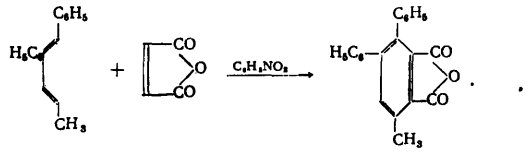
The partial dehydrogenation of fused hydroaromatic anhydrides by heating them with bromine in acetic acid has been described[11]:



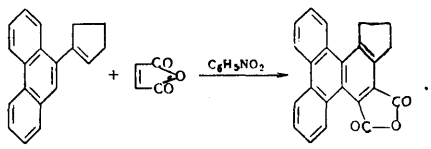
Diene synthesis in nitrobenzene yields aromatic anhydrides directly. Thus when 1,2,4-triphenylbuta-1,3-diene was heated with maleic anhydride in nitrobenzene, only 3,4,6-triphenylphthalic anhydride was isolated[12]:



1,2-Diphenylpenta-1,3-diene and maleic anhydride under these conditions yielded 3-methyl-5,6-diphenylphthalic anhydride[12]:

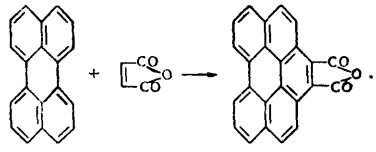


Diene synthesis with 9-cyclopentenylphenanthrene and maleic anhydride in nitrobenzene took place in an analogous manner[12]:

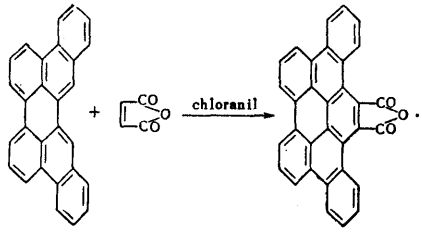


† The action of this reagent on tetrahydrofluoranthenedicarboxylic acid produced decarboxylation as well as dehydrogenation, with the formation of fluoranthene[9] (see p. 577).

Many multifused aromatic hydrocarbons (perylene[13], ovalene[14], 2,3:4,5-dibenzocoronene[15]), which do not give adducts with maleic anhydride when heated in inert solvents, form adducts of aromatic structure on being heated in nitrobenzene, for example:



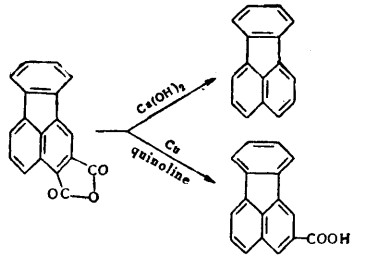
Anhydrides of aromatic structure can be obtained also by heating the components of diene synthesis in the presence of chloranil[16-20]:



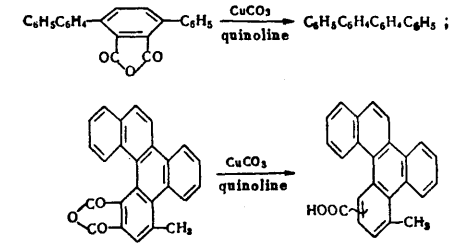
Decarboxylation of Aromatic Dicarboxylic Acids, Salts, and Anhydrides Obtained by Dehydrogenation of Adducts of Diene Synthesis

Such decarboxylation has been carried out in various ways — by dry distillation with zinc dust in the presence of calcium oxide[2], by heating with copper powder in the presence of sodium carbonate and calcium oxide[21] or barium oxide[4,11] or hydroxide[5], by heating with calcium hydroxide[22,23], or by prolonged heating with caustic potash in an autoclave[20], dry distillation with soda lime[8,13-15,17-19], or boiling in quinoline with copper[11,15-18,21] or copper carbonate[3,7].

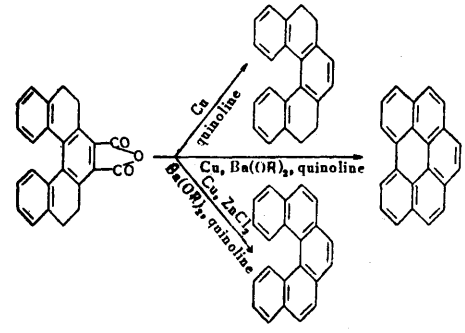
Decarboxylation is most often effected by dry distillation with soda lime and boiling with copper powder in quinoline. The reaction can go in different ways depending on the structure of the initial compound and on the reagent employed. Heating fluoranthene-3,4-dicarboxylic anhydride with calcium hydroxide at red heat, for example, gives a 50% yield of fluoranthene; when the same anhydride is boiled with copper bronze in quinoline, only partial decarboxylation occurs, the reaction product being fluoranthene-3-carboxylic acid[22]:



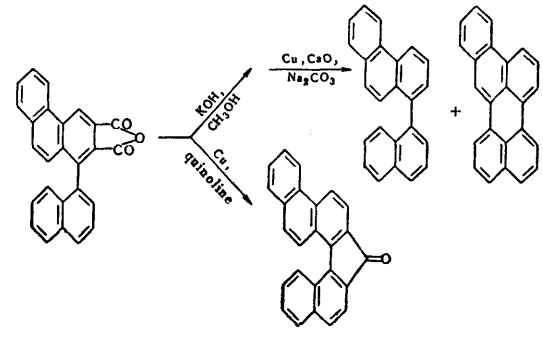
3-*p*-Biphenylyl-6-phenylphthalic anhydride on being heated with copper carbonate in quinoline was converted into a 31% yield of quaterphenyl[3]; whereas when an aromatic anhydride having a fused polycyclic system was heated under these conditions, only partial decarboxylation took place, the product of the reaction being the corresponding monocarboxylic acid[7]:



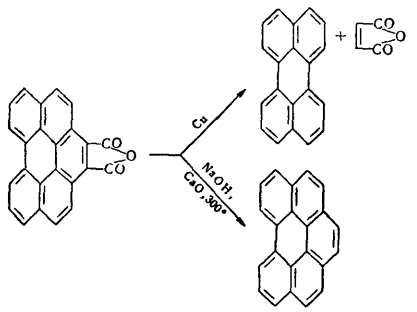
1,2,7,8-Tetrahydro-3,4:5,6-dibenzophenanthrene-9,10-dicarboxylic anhydride on decarboxylation by heating with copper in quinoline gave the tetrahydro-3,4:5,6-dibenzophenanthrene; when this anydride was heated under the same conditions but with the addition of barium hydroxide, decarboxylation was accompanied by dehydrogenation and pyrocondensation with the formation of 1,12-benzoperylene; when barium hydroxide and zinc chloride were added to the reaction mixture, the anhydride underwent decarboxylation and dehydrogenation, but in this case 3,4:5,6-dibenzophenanthrene was isolated as the final product of the reaction[11]:



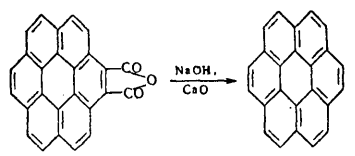
The anhydride of 1-1′-naphthylphenanthrene-2,3-dicarboxylic acid can also undergo decarboxylation in various ways[21] depending on the conditions and the reagents used:



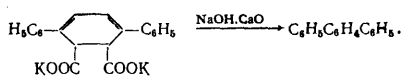
The adduct of perylene and maleic anhydride on being heated with copper powder in a vacuum underwent breakdown, the original perylene being re-formed[13]:



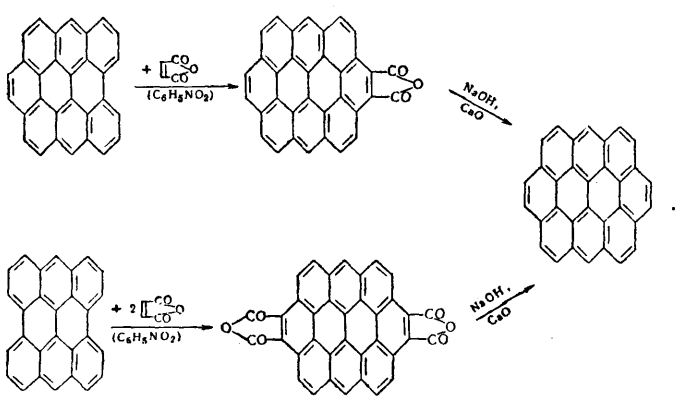
Coronene-1,2-dicarboxylic anhydride was decarboxylated to only an insignificant extent on being heated with copper in quinoline; successful decarboxylation of this anhydride to coronene (as also of the maleic anhydride adduct of perylene to benzoperylene[13]) was accomplished by heating with soda lime (in a current of nitrogen at 400°)[18]:



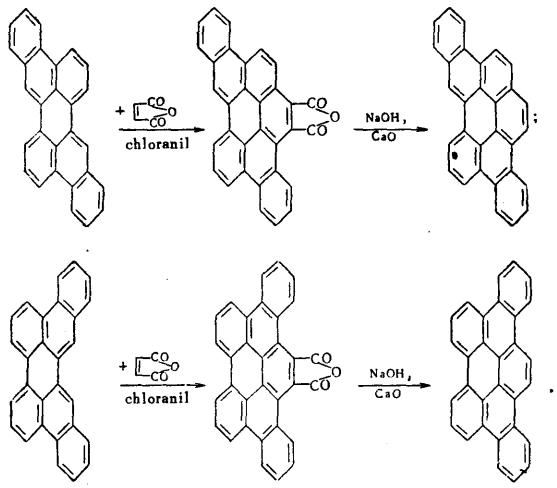
When soda lime is used as decarboxylating agent, reaction usually occurs in only one way, with formation of the corresponding aromatic hydrocarbons (in higher yields than when copper in quinoline is used). Thus a good yield of *p*-terphenyl has been obtained by distilling potassium 3,6-diphenylphthalate with soda lime[8]:



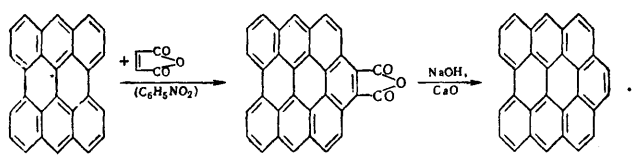
Decarboxylation with soda lime of dehydrogenated adducts of diene synthesis has been used to obtain many fused polycyclic aromatic hydrocarbons. Clar synthesised ovalene by distilling with soda lime (at atmospheric pressure and 400°) the adduct of 1,14-benzobisanthene and maleic anhydride or the adduct of bisanthene with two molecules of maleic anhydride[14]:



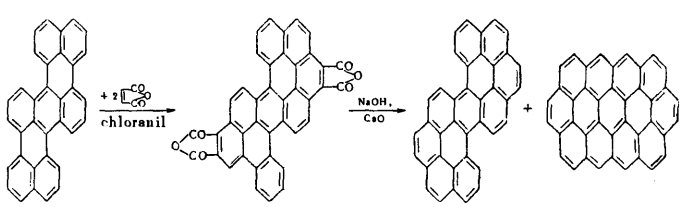
Analogous reactions have been used to convert 2,3:8,9-dibenzoperylene into 1,12:2,3:8,9-tribenzoperylene[14], and 2,3:10,11-dibenzoperylene into 1,12:2,3:10,11-tribenzoperylene[19]:



2,3:4,5-Dibenzocoronene has been obtained by heating 2,3:4,5-dibenzocoronene-9,10-dicarboxylic anhydride with soda lime at 500° (in a vacuum) in a current of hydrogen[15]:



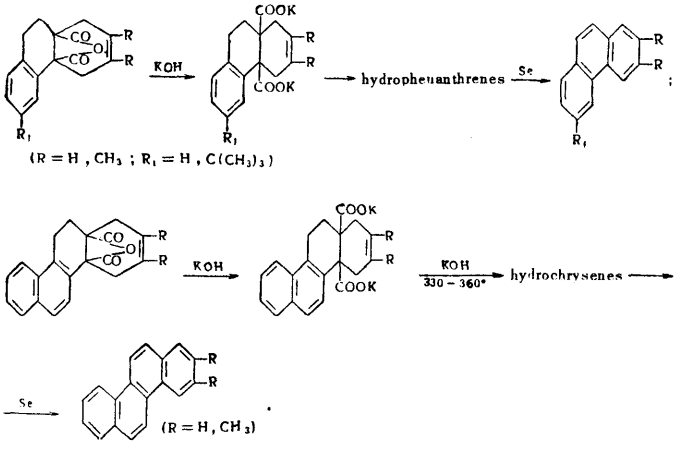
When the dianhydride resulting from the interaction of di-1,8-naphthyleneanthracene (tetrabenzopentacene) and maleic anhydride in the presence of chloranil is heated with soda lime (under the conditions described for the preparation of coronene[18]), formation of the normal reaction product, dinaphthoperopyrene, is accompanied by that of yet another polycyclic aromatic hydrocarbon ["circumanthracene" (Ed. of Translation)][17]:



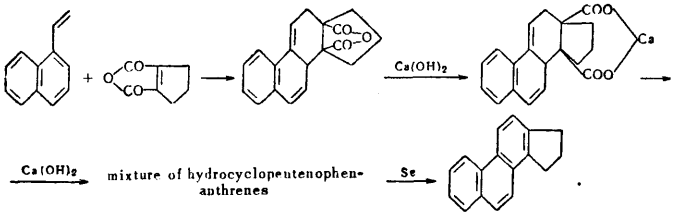
From the published results above it can be concluded that the conversion of adducts of diene synthesis into aromatic hydrocarbons by dehydrogenation followed by decarboxylation has been accomplished by many workers using various techniques and various dehydrogenating and decarboxylating agents. But methods which have been used successfully for the aromatisation of some adducts prove unsuitable for other adducts, sometimes of similar structure, and therefore the reactions which have been described (and the reagents employed in them) are not of general validity.

In the work of Fieser[6,24-26], Sen-Gupta[27-29], and their coworkers, and also in the work of other investigators[30], conversion of adducts of diene synthesis into aromatic hydrocarbons has been achieved by dehydrogenation and

decarboxylation in a different sequence: the initial adducts (or acids and salts obtained from them) were subjected first to decarboxylation and then to a subsequent dehydrogenation. This route (II) (p. 571) would have advantages over the first series of reactions (I), as it might be employed for the synthesis of hydroaromatic hydrocarbons. However, dibasic hydroaromatic acids or their anhydrides on decarboxylation usually yield a mixture of isomeric hydroaromatic hydrocarbons. Thus decarboxylation‡ of the potassium salts of dibasic acids of the hexahydrochrysene or hexahydrophenanthrene series (by heating them with excess of caustic potash) yields a mixture of hydrochrysenes or of tetra- and hexa-hydrophenanthrenes respectively[6,24-26].



When the calcium salts of dibasic acids obtained from adducts of various diene hydrocarbons with cyclopent-1--ene-1,2-dicarboxylic anhydride were distilled with calcium hydroxide, a mixture of hydroaromatic hydrocarbons was also formed, dehydrogenation of which gave the corresponding individual fused aromatic hydrocarbons containing the indane system, for example[27-29]:

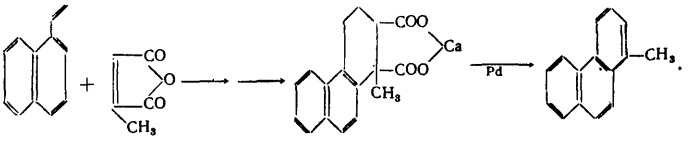


Thus the method is not suitable for the synthesis of individual hydroaromatic hydrocarbons of this structure: furthermore, subsequent dehydrogenation of hydroaromatic hydrocarbons is sometimes accompanied by cyclisation, aromatisation, or dealkylation. Hence the aromatisation of diene adducts by decarboxylation followed by dehydrogenation is of only limited application.

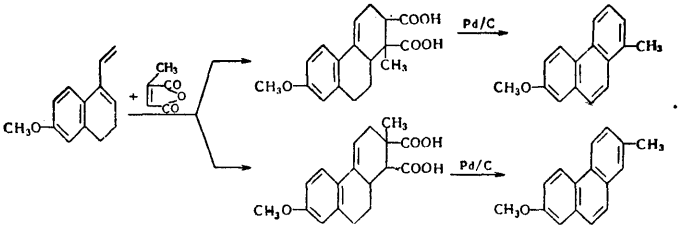
Depending on their structure, some diene adducts can be converted into aromatic hydrocarbons by simultaneous decarboxylation and dehydrogenation (III) (p. 571). Such a reaction is effected by the action of catalysts, such as platinum and palladium blacks[31], palladium on carbon[32-42], and others[30,43-48].

‡ Decarboxylation was accompanied by partial dehydrogenation and decarbonylation, and also elimination of potassium formate and oxalate[25].

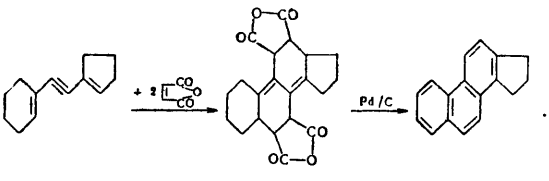
Thus the calcium salt of the dicarboxylic acid obtained by hydrolysis of the adduct of 1-vinylnaphthalene and methylmaleic (citraconoyl) anhydride has been converted into 1-methylphenanthrene by heating with palladium black in a current of nitrogen at 310°:[31]



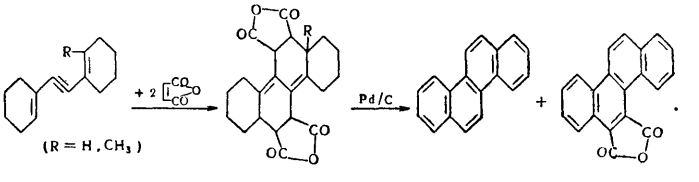
3,4-Dihydro-6-methoxy-1-vinylnaphthalene on reaction with methylmaleic anhydride forms a mixture of isomeric (*"ortho"* and *"meta"*) adducts, the structures of which were proved by heating them each with palladium on charcoal (in a current of nitrogen at 300°–315° or 320°), when they were converted respectively into 7-methoxy-1(and 2)-methylphenanthrene[32,37]:



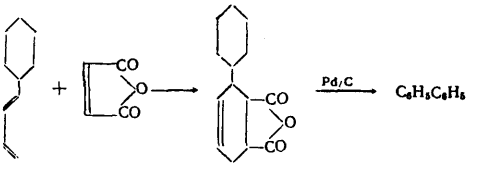
Butz and his coworkers subjected to aromatisation the dianhydride of steradiene-6,7,11,12-tetracarboxylic acid — the adduct of cyclohexenylcyclopentenylacetylene with two molecules of maleic anhydride — by heating it to 340°–390° with palladium on carbon (in the presence or absence of calcium hydroxide), with the aim of preparing 1,2-cyclopentenophenanthrene[33,34]:



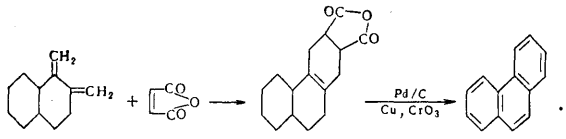
The structurally analogous dianhydride of tetradecahydrochrysene-5,6,11,12-tetracarboxylic acid on being heated under the same conditions was converted only into an insignificant yield of chrysene[35]:



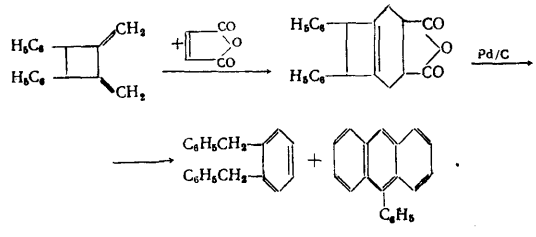
The adduct of cyclohexylbuta-1,3-diene and maleic anhydride has been converted into biphenyl by heating its benzene solution in the presence of 10% palladium on carbon in an atmosphere of nitrogen at 300° for 7 h:[36]



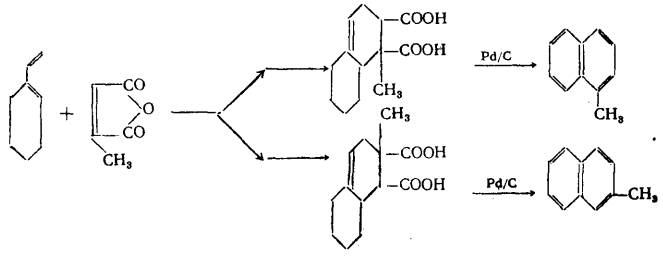
The structure of 1,2-dimethylenedecalin has been proved by converting its adduct with maleic anhydride into phenanthrene (in 67% yield) by heating it in the presence of 10% palladium on carbon and a copper–chromium oxide catalyst at 275° for $3\frac{1}{2}$ h:[45]



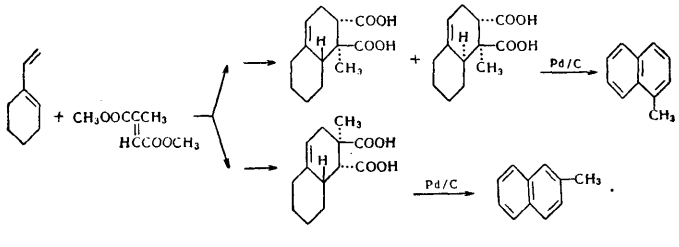
It is interesting that the vacuum distillation of the adduct of 1,2-dimethylene-3,4-diphenylcyclobutane with maleic anhydride in the presence of a mixed catalyst (10% palladium on carbon together with barium oxide) gives a mixture of two hydrocarbons, *o*-dibenzylbenzene and its dehydrogenation product, 9-phenylanthracene[49]:



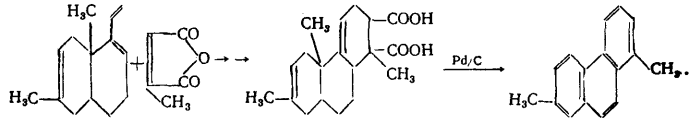
In a study of the condensation products formed by 1-vinylcyclohexene with methylmaleic anhydride, Nazarov converted the isomeric acids obtained by hydrolysis of the *"ortho"* and *"meta"* adducts into methylnaphthalenes. Aromatisation was effected by heating benzene solutions of the acids in the presence of 10% palladium on carbon in an autoclave at 360°–370° for 18 h:[39]



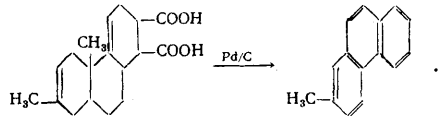
Under the same conditions isomeric methylnaphthalenes were obtained from acids, themselves obtained by hydrolysing diene adducts of 1-vinylcyclohexene with dimethyl mesaconate[40]:



When the dicarboxylic acid obtained by hydrolysis of the adduct of *cis*-3,4,5,8,9,10-hexahydro-6,9-dimethyl-1-vinylnaphthalene with methylmaleic anhydride is heated over 5% palladium on carbon in an autoclave (1 h at 140°–150° and 2 h at 340°–350°), decarboxylation and dehydrogenation are accompanied by partial demethylation, the methyl group in the ring-fusion position being split off with the formation of 1,7-dimethylphenanthrene[41]:

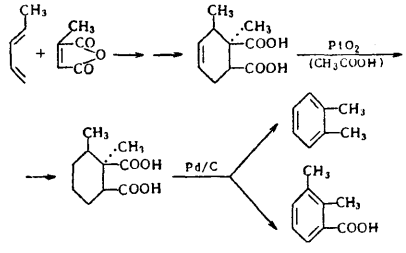


Similar demethylation took place in the aromatisation of 7,13-dimethyl-$\Delta^{4,6}$-decahydrophenanthrene-1,2-dicarboxylic acid. This acid, which has a similar structure to the above, was converted into 2-methylphenanthrene on heating over 10% palladium on carbon under more severe conditions (370° for 11 h), but the yield was only 4%[38]:

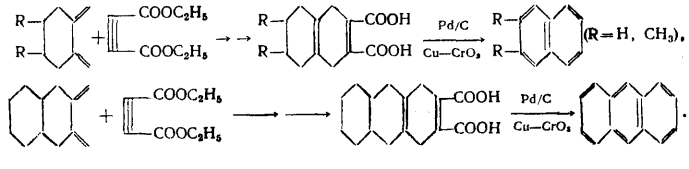


Thus this method for the aromatisation of the adducts of diene synthesis in the presence of catalysts also is not of general application, often giving low yields of aromatic hydrocarbons and being accompanied by side-reactions, including dealkylation.

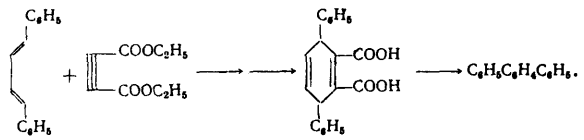
Aromatisation with decarboxylation over palladium on carbon is characteristic not only of tetrahydrophthalic acids (or their anhydrides), several hexa- and di-hydrophthalic acids undergoing a similar reaction. For example, hexahydro-2,3-dimethylphthalic acid, obtained by hydrogenation of the adduct of *trans*-pentadiene with methylmaleic anhydride, was converted into *o*-xylene by heating with 10% palladium on carbon in a sealed tube at 320° for 24 h; heating under the same conditions for 16 h produced only partial decarboxylation with the formation of 2,3-dimethylbenzoic acid[42]:



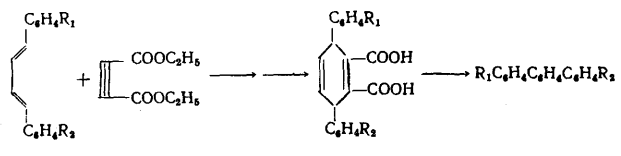
Several substituted dihydrophthalic acids (obtained by hydrolysis of the adducts of dienes with acetylenedicarboxylic ester) have been converted by heating them with palladium on carbon in the presence of a copper–chromium oxide catalyst[43,44,50]:



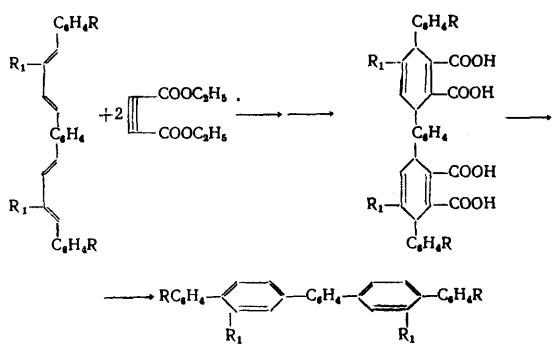
An interesting reaction is the oxidative decarboxylation of dihydrophthalic acids. Lohaus converted 3,6-dihydro--3,6-diphenylphthalic acid (from the adduct of 1,4-diphenylbutadiene with acetylenedicarboxylic ester) into the theoretical yield of *p*-terphenyl by heating it with $K_3Fe(CN)_6$ in alkaline solution[48]:



McDonald and Campbell used the Lohaus method (without isolating the products of diene synthesis from the reaction mixture) to obtain high yields of polyphenyls: *p*-terphenyl (in 60% yield), 4-methyl-*p*-terphenyl (70%), 4,4″-dimethyl-*p*-terphenyl (42%), quinquephenyl (52%), and 4,4‴- and 2′,3‴-dimethylquinquephenyl[47]:

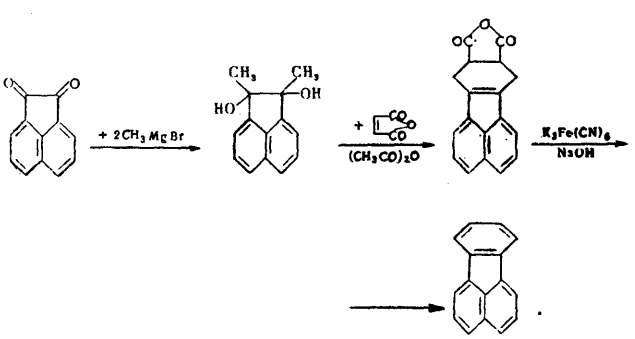


($R_1=R_2=H$, CH_3; $R_1=H$, $R_2=CH_3$).

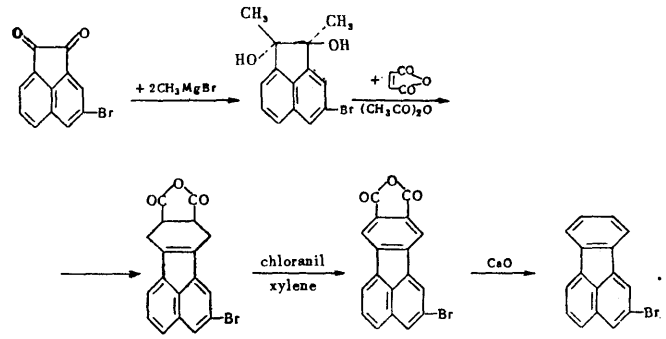


($R=R_1=H$; $R_1=H$, $R=CH_3$; $R=H$; $R_1=CH_3$).

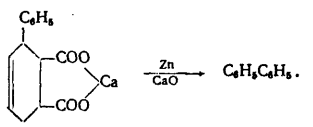
The substituted 1,2,3,6-tetrahydrophthalic anhydride formed by reaction of maleic anhydride with the *trans*-diol, itself obtained from acenaphthenequinone and methylmagnesium iodide, also underwent oxidative decarboxylation on being heated with alkaline $K_3Fe(CN)_6$ solution, and was converted into fluoranthene (in 50% yield)[9]:



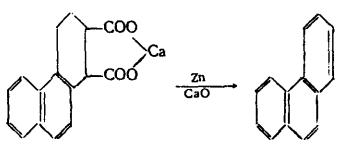
This reaction probably represents only a particular case, since the same workers employed a different scheme to prepare substituted fluoranthenes (7,10-dimethylfluoranthene, 1-bromofluoranthene, 7,8-benzofluoranthene, and 2,5-di-*p*-tolyl-8,9-benzofluoranthene), although these compounds were obtained by them in considerably smaller yields (12–25%[9,23]), for example:



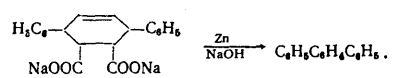
Several cases have been reported of the simultaneous decarboxylation and dehydrogenation of tetrahydrophthalate salts in the presence of zinc dust. Dry distillation of calcium 3-phenyltetrahydrophthalate with zinc dust and calcium oxide gave biphenyl[46]:



The same reaction has been used to convert calcium tetrahydrophenanthrene-1,2-dicarboxylate into phenanthrene[2]:

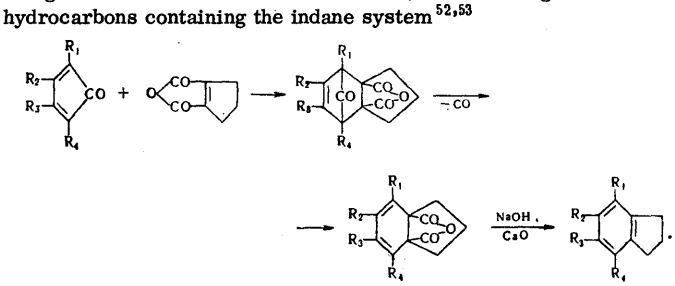


Distillation of sodium 3,6-diphenylhexahydrophthalate with zinc dust and caustic soda gave *p*-terphenyl[46]:

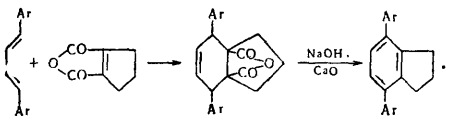


Diene adducts in which the anhydride group is combined with tertiary carbon atoms are also able to undergo simultaneous decarboxylation and dehydrogenation on being heated with soda lime in a vacuum. Thus the adducts of dienes with cyclopent-1-ene-1,2-dicarboxylic anhydride§

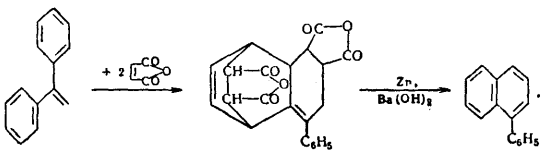
§ Cyclopent-1-ene-1,2-dicarboxylic anhydride gives with tetrasubstituted cyclopentadienones adducts which, on being heated in tetralin, readily split off the *endo*-carbonyl group, being converted into dihydroindanedicarboxylic anhydrides; these last compounds are in turn decarboxylated and simultaneously dehydrogenated on being heated with soda lime in a vacuum, also forming aromatic hydrocarbons containing the indane system[52,53]



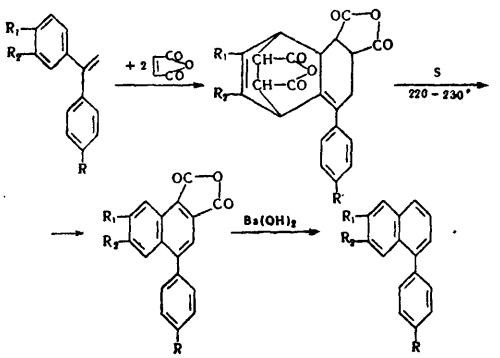
have been converted into aromatic hydrocarbons containing an indane group[51]:



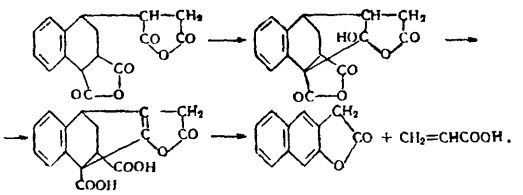
Apart from the usual products of diene synthesis — 1,2,3,6-tetrahydrophthalic anhydrides — the products obtained by reaction of dienes with two molecules of maleic anhydride can also be converted into aromatic hydrocarbons. Thus Wagner-Jauregg obtained 1-phenylnaphthalene by distilling with zinc dust or barium hydroxide the adduct of 1,1-diphenylethylene with two molecules of maleic anhydride[54]:



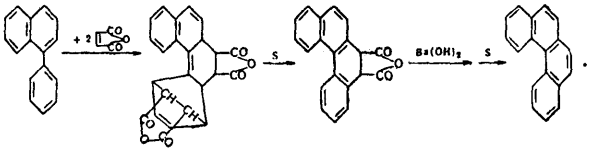
When these "double" adducts¶ are heated with sulphur, they split off one of the maleic anhydride molecules and, being dehydrogenated, are converted into anhydrides of arylnaphthalenedicarboxylic acids; the latter have in turn been converted into their barium salts, which on decarboxylation by heating with copper bronze are converted into 1-arylnaphthalenes (in yields of 22–90%)[55,56]:



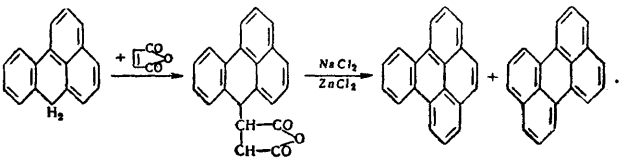
¶ Aromatic and hydroaromatic hydrocarbons of the "styrene" type on reaction with maleic anhydride may form "double" adducts of different structure (of the Schmitz–Josten type), which on dry distillation split off acrylic acid and are converted into lactones of hydroxynaphthylacetic acid[57,58]



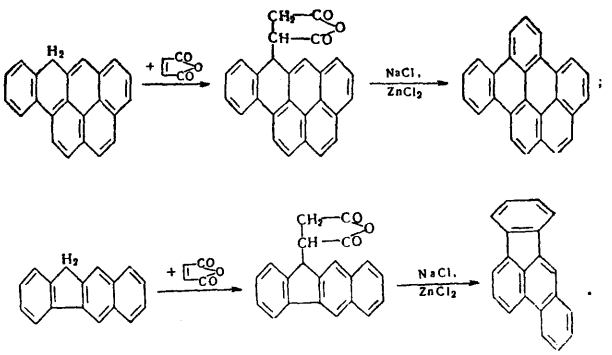
3,4-Benzophenanthrene has been obtained by a similar series of reactions[59]:



To obtain fused aromatic hydrocarbons of complicated structure, Clar used addition products of non-benzenoid fused polycyclic hydrocarbons with maleic anhydride. These compounds, which are substituted succinic anhydrides, undergo aromatisation on being melted with sodium chloride and zinc chloride, with the elimination of carbon dioxide and water. Mesobenzanthrene has been converted by this method into 1,2-benzopyrene (contaminated with perylene)[60]:

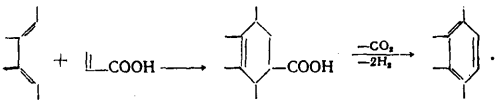


Similar schemes have been used to obtain 1,2:4,5-dibenzopyrene[60], 1,12:10,11-dibenzoperylene[61], and 2,3-benzofluoranthene[61], for example:

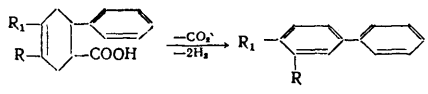


It is evident from the published results which have been quoted that only tetra(and hexa- and di)-hydrogenated *phthalic acids* and their anhydrides — the adducts of dienes with maleic anhydride, its homologues and cyclic analogues — have been converted into polycyclic aromatic hydrocarbons by successive or simultaneous decarboxylation and dehydrogenation.

The present reviewer has shown that *tetrahydrobenzoic acids* — the adducts of dienes with acrylic, cinnamic, and *p*-phenylcinnamic acids — can also be converted into aromatic hydrocarbons by simultaneous decarboxylation and dehydrogenation without the use of any chemical reagents or catalysts. This thermal aromatisation of tetrahydrobenzoic acids is achieved simply by heating in an autoclave; adducts with acrylic acid (at 500°) have given benzene and alkylbenzenes[62]:

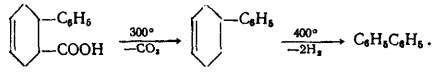


Adducts of dienes with cinnamic acid have been decarboxylated and dehydrogenated by heating them in an autoclave to 400°, hydrocarbons of the biphenyl series being formed[63]:

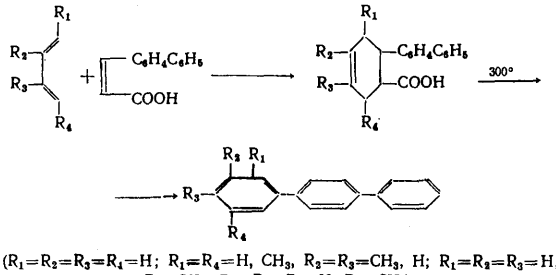


(R=R$_1$=H, CH$_3$; R=H, R$_1$=CH$_3$).

Separate experiments established that the first stage in the reaction is decarboxylation with the formation of cyclohexenes, which are then dehydrogenated. Thus when 1,2,3,6-tetrahydro-2-phenylbenzoic acid (the adduct of butadiene and cinnamic acid) was heated in an autoclave at 300°, it was merely decarboxylated with the formation of cyclohex-3-enylbenzene; when the latter was heated in an autoclave to 400° (*i.e.* under conditions for the aromatisation of 2-phenyltetrahydrobenzoic acids), it was readily dehydrogenated to biphenyl[63]:



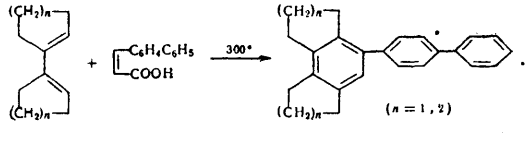
Adducts of *p*-phenylcinnamic acid already split off hydrogen and carbon dioxide at 300°, being converted into *p*-terphenyl and its homologues[64]:



(R$_1$=R$_2$=R$_3$=R$_4$=H; R$_1$=R$_4$=H, CH$_3$, R$_2$=R$_3$=CH$_3$, H; R$_1$=R$_2$=R$_3$=H, R$_4$=CH$_3$; R$_1$=R$_2$=R$_4$=H, R$_3$=CH$_3$).

Hydrocarbons of the benzene, biphenyl, and *p*-terphenyl series can also be obtained in a single stage, by directly heating under the above conditions the original components of the diene synthesis (diene hydrocarbons with acrylic, cinnamic, and *p*-phenylcinnamic acids respectively); yields of the hydrocarbons are increased if the initial reaction mixture is first heated in an autoclave under the optimum conditions for obtaining the given adduct, and then at 500°, 400°, or 300° respectively[62-64].

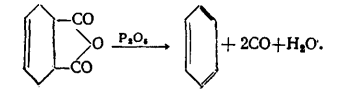
Dicyclic hydrocarbon ring assemblies — 1,1′-bi(cyclohexenyl) and 1,1′-bi(cyclopentenyl) — yielded by the same reaction *polycyclic hydrocarbons containing the* p-*terphenyl system* (2,3 : 4,5-dicyclohexeno-*p*-terphenyl and 2,3 : 4,5-dicyclopenteno-*p*-terphenyl)[65]:



3. AROMATISATION OF ADDUCTS OF DIENE SYNTHESIS — TETRAHYDROPHTHALIC ACIDS, THEIR ANHYDRIDES, AND TETRAHYDROBENZOIC ACIDS — BY DECARBONYLATION AND DEHYDRATION

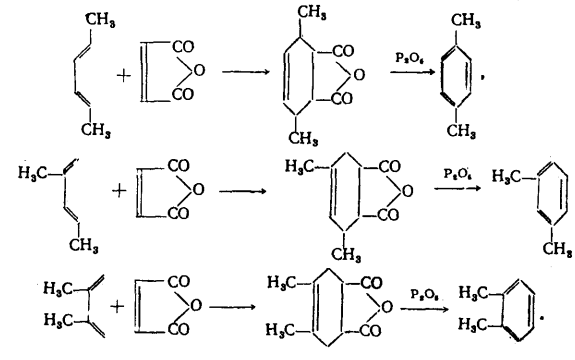
In all the methods described above, the conversion of 1,2,3,6-tetrahydrophthalic anhydrides (or acids) into aromatic hydrocarbons has been accomplished by successive or simultaneous decarboxylation and dehydrogenation.

A fundamentally different route for the aromatisation of such anhydrides is reaction with phosphorus pentoxide, involving the simultaneous elimination of carbon monoxide and water:

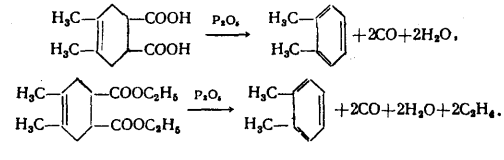


This reaction, discovered in 1953[66], is now a general method for preparing aromatic hydrocarbons of various classes — alkylbenzenes, biphenyls, polyphenyls, and fused aromatic and hydroaromatic hydrocarbons (tetralins, indanes, fluorenes, phenanthrenes, octahydrophenanthrenes, and chrysenes).

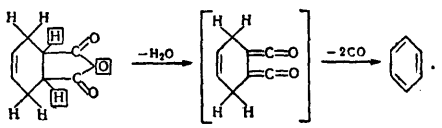
The aromatisation of 1,2,3,6-tetrahydrophthalic anhydrides by means of phosphorus pentoxide is distinguished by its experimental simplicity (a mixture of the anhydride and the pentoxide is heated in a Wurtz flask, and the resulting hydrocarbon is distilled off), it gives high yields (40–90%), and permits the preparation of aromatic hydrocarbons having substituents in definite positions, uncontaminated by isomeric hydrocarbons. Thus the maleic anhydride adducts of the isomeric alkadienes C_6H_{10} (hexa-2,4-diene, 2-methylpenta-1,3-diene, and 2,3-dimethylbuta-1,3-diene) gave on aromatisation over phosphorus pentoxide the *isomeric xylenes*[66]:



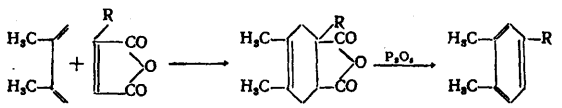
Not only the anhydrides but the tetrahydrophthalic acids themselves and their esters undergo similar cleavage under the influence of phosphorus pentoxide, losing water and carbon monoxide (and in the case of esters also eliminating ethylene) and being converted into aromatic hydrocarbons. Thus *o*-xylene has been obtained from 4,5-dimethyltetrahydrophthalic acid and its ethyl ester[67]:



It might be supposed that the first stage in the reaction between phosphorus pentoxide and tetrahydrophthalic anhydrides is dehydration with the intermediate formation of the corresponding diketens, which then undergo decarbonylation with simultaneous intracyclic redistribution of hydrogen and formation of a stable aromatic ring:

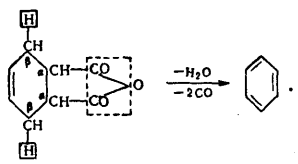


For aromatisation to take place via the intermediate formation of diketens, it is necessary that hydrogen atoms should be present in position 1, *i.e.* in the α position with respect to the carboxyl groups; reaction should not have taken place with tetrahydrophthalic anhydrides having an alkyl group in one of these positions. It was found, however, that in this case the reaction took place normally, with the formation of aromatic hydrocarbons: adducts of 2,3-dimethylbuta-1,3-diene with alkylmaleic anhydrides gave 1,2,4-trialkylbenzenes (1,2,4-trimethylbenzene, ethyldimethylbenzene, and butyldimethylbenzene)[67,68]:

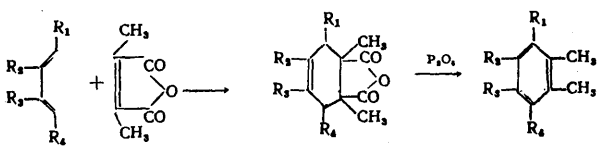


(R=CH_3, C_2H_5, C_4H_9).

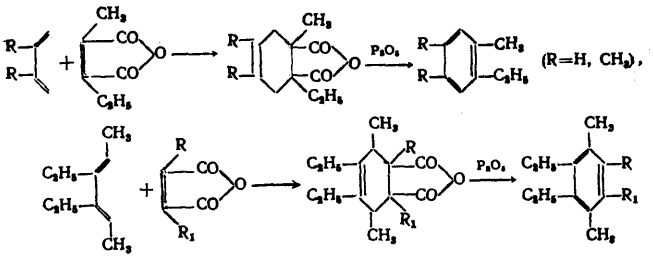
From this it was concluded that the formation of aromatic hydrocarbons by the reaction of tetrahydrophthalic anhydrides with phosphorus pentoxide is due to simultaneous dehydration (involving hydrogen atoms in the β positions with respect to the carboxyl groups) and decarbonylation, and does not involve the intermediate formation of diketens[67]:



Adducts of dienes with dialkylmaleic anhydrides can also undergo aromatisation in the presence of phosphorus pentoxide. This method has been used to synthesise tetramethylbenzenes (using dimethylmaleic anhydride as the initial dienophil)[69], ethyltoluene and ethyltrimethylbenzene (using ethylmethylmaleic anhydride as dienophil)[70], and also diethylpolymethylbenzenes (using 3,4-diethylhexa-2,4-diene as a suitable diene, and maleic anhydride and its homologues as dienophils)[71,72]:

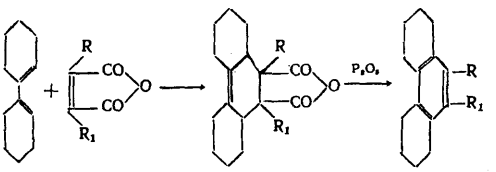


(R_1=R_4=H, CH_3; R_2=R_3=CH_3, H; R_1=R_2=H, R_3=R_4=CH_3).



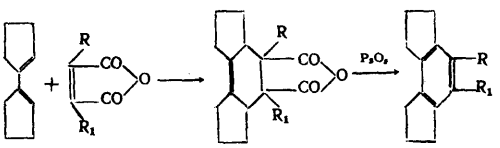
(R=R_1=H,CH_3; R=H_1, R_1=CH_3).

The aromatisation of tetrahydrophthalic anhydrides in the presence of phosphorus pentoxide has also been used to obtain tricyclic hydroaromatic hydrocarbons of fused structure. The initial diene hydrocarbons were the bi(cycloalkenyls): 1,1′-bi(cyclohexenyl), 1,1′-bi(cyclopentenyl), and 1-(cyclopent-1-enyl)cyclohexene[73,74]. With 1,1′-bi(cyclohexenyl) as initial diene hydrocarbon, and maleic and alkylmaleic anhydrides as dienophils, octahydrophenanthrene and its homologues have been prepared[73]:



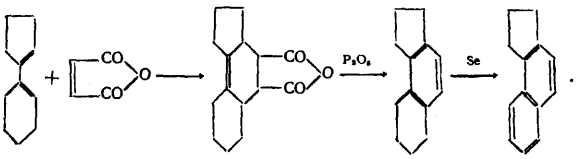
(R=R_1=H, CH_3; R=H, R_1=CH_3).

1,2,3,6,7,8-Hexahydro-as-*indacene* and its homologues have been obtained from adducts of 1,1′-bi(cyclopentenyl) with maleic, methylmaleic, and dimethylmaleic anhydrides[73]:

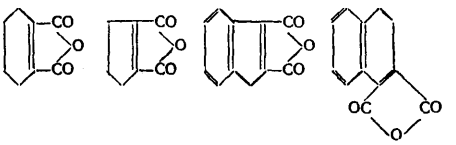


(R=R_1=H, CH_3; R=H, R_1=CH_3).

The adduct of 1-(cyclopent-1-enyl)cyclohexene with maleic anhydride has been converted by reaction with phosphorus pentoxide into 4,5-cyclohexenoindane, which was then dehydrogenated to 1,2-cyclopentenonaphthalene by heating with selenium[74]:

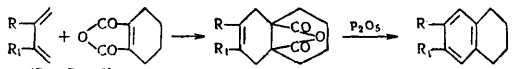


In the synthesis of *hydroaromatic polycyclic hydrocarbons* the dienophils used were cyclic analogues of maleic anhydride — the 1,2-dicarboxylic anhydrides of cyclohexene, cyclopentene, indene, and 3,4-dihydronaphthalene:



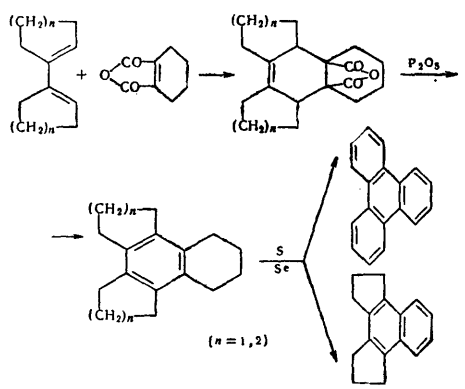
The products resulting from reaction of adducts of these dienophils with phosphorus pentoxide were polycyclic aromatic hydrocarbons — tetralins, indanes, fluorenes, and 9,10-dihydrophenanthrenes. Their formation also involved elimination of carbon monoxide and water, and in all cases it was only the six-membered ring containing a double bond which became aromatic.

The adducts of butadiene and its homologues (isoprene and 2,3-dimethylbuta-1,3-diene) with *cyclohex*-1-*ene*-1,2-*dicarboxylic anhydride* on being heated with phosphorus pentoxide gave tetralin[75] and alkyltetralins[76]:



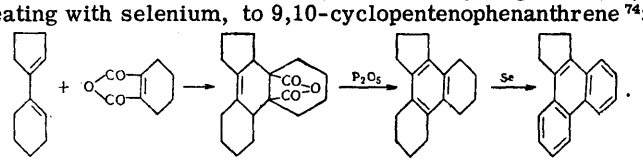
(R = R$_1$ = H, CH$_3$; R = H, R$_1$ = CH$_3$).

Aromatisation by means of phosphorus pentoxide of adducts of cyclohex-1-ene-1,2-dicarboxylic anhydride with dicyclic diene hydrocarbons — 1,1′-bi(cyclohexenyl) and 1,1′-bi(cyclopentenyl) — yielded *hydroaromatic fused polycyclic hydrocarbons containing a tetralin ring system* (1–12-dodecahydrotriphenylene and dicyclopentenocyclohexenobenzene), which were then dehydrogenated (by heating with sulphur or selenium) to triphenylene and 1,2:3,4-dicyclopentenonaphthalene[75]:

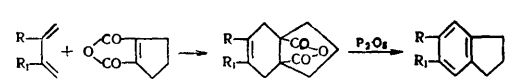


(n = 1, 2)

The use of 1-(cyclopent-1-enyl)cyclohexene as initial diene component enabled a polycyclic aromatic hydrocarbon containing the indane ring system (dicyclohexenocyclopentenobenzene) to be obtained; it was dehydrogenated, by heating with selenium, to 9,10-cyclopentenophenanthrene[74]:

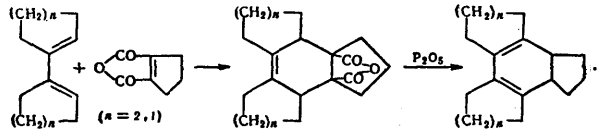


Adducts of another cyclic analogue of maleic anhydride — *cyclopent*-1-*ene*-1,2-*dicarboxylic anhydride* — have been converted, by heating with phosphorus pentoxide, into *indane* and *its homologues*, as well as into *polycyclic hydrocarbons containing the indane system* — 4,5:6,7-dicyclohexenoindane† and 4,5:6,7-dicyclopentenoindane (tricyclopentenobenzene)[77]:



(R = R$_1$ = H, CH$_3$; R = CH$_3$, R = H).

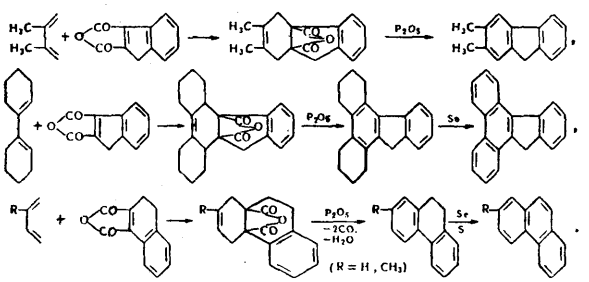
† As mentioned in the previous paragraph, this hydrocarbon has also been obtained by using phosphorus pentoxide in a different way[74].



(n = 2, 1)

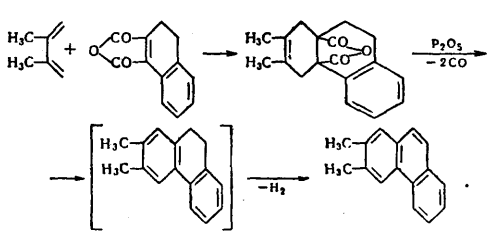
Thus aromatisation in the presence of phosphorus pentoxide can be used to convert adducts of diene hydrocarbons with cyclic analogues of maleic anhydride into high yields (44–84%) of dicyclic and also — with bi(cycloalkenyls) as dienes — polycyclic hydroaromatic hydrocarbons, which can then be dehydrogenated in the usual way to the corresponding aromatic hydrocarbons.

A study has been made of the reaction with phosphorus pentoxide of adducts of diene hydrocarbons with dienophils of more complicated structure (*indene*-1,2-*dicarboxylic* and 3,4-*dihydronaphthalene*-1,2-*dicarboxylic anhydrides*). Under the influence of phosphorus pentoxide (at 160°–300°) these adducts, like those of cyclohex-1-ene-1,2-dicarboxylic and cyclopent-1-ene-1,2-dicarboxylic anhydrides, underwent aromatisation, eliminating carbon monoxide and water and being converted into fluorenes[78] and 9,10-dihydrophenanthrene[79] respectively:



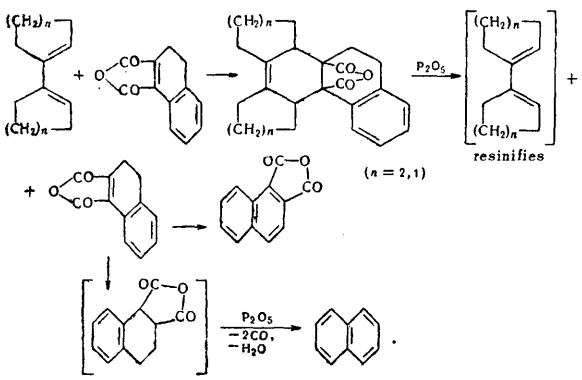
(R = H, CH$_3$)

In the case of one of the adducts of 3,4-dihydronaphthalene-1,2-dicarboxylic anhydride, it was shown that heating the reaction mixture with phosphorus pentoxide to 350° for several hours resulted in the appearance of a secondary reaction, dehydrogenation of the normal reaction product (a homologue of dihydrophenanthrene). Thus when the adduct from 2,3-dimethylbuta-1,3-diene was heated with phosphorus pentoxide at 320°–350° for 6 h, instead of the expected 9,10-dihydro-2,3-dimethylphenanthrene, only its dehydrogenation product, 2,3-dimethylphenanthrene, was isolated[79]:



Adducts of the same dienophil with dicyclic diene hydrocarbons proved most resistant to the action of phosphorus pentoxide: their decomposition was carried out at 300°–400° for 10 h, but neither 1,2:3,4-bi(cyclohexeno)- nor 1,2:3,4-bi(cyclopenteno)-9,10-dihydrophenanthrene (nor the corresponding phenanthrenes) were found among the reaction products, both adducts giving only naphthalene-1,2-dicarboxylic anhydride and naphthalene. The formation of these substances can be explained by decomposition of the

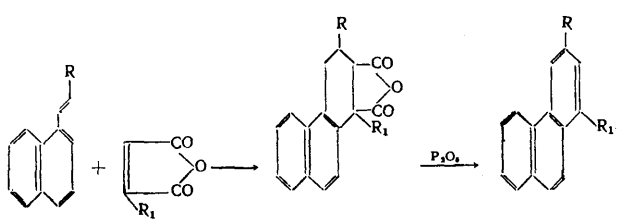
adducts at the high temperatures (300°–400°) into the original diene (which resinifies under the influence of the phosphorus pentoxide) and the dienophil, 3,4-dihydronaphthalene-1,2-dicarboxylic anhydride; the latter is converted (by a type of irreversible catalysis) into a mixture of naphthalene-1,2-dicarboxylic anhydride, which does not change further and is among the final products of the reaction, and 1,2,3,4-tetrahydronaphthalene-1,2-dicarboxylic anhydride, which in the presence of the phosphorus pentoxide undergoes the usual aromatisation, splitting off carbon monoxide and water and being converted into naphthalene (second reaction product)[79]:



Thus adducts of dicyclic diene hydrocarbons with 3,4-dihydronaphthalene-1,2-dicarboxylic anhydride, in contrast to adducts of these dienes with the other cyclic dienophils studied, undergo breakdown on being heated with phosphorus pentoxide.

Depending on the structure of the diene adducts, their reaction with phosphorus pentoxide may not yield dihydrogenated derivatives of aromatic hydrocarbons but the fused aromatic hydrocarbons — phenanthrenes and chrysenes — directly (in one stage).

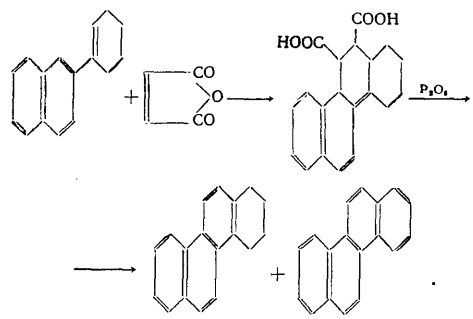
The initial diene components used in the preparation of hydrocarbons of the *phenanthrene* series were 1-vinylnaphthalene and 1-propenylnaphthalene, the adducts‡ of which with the simplest dienophils — maleic and methylmaleic anhydrides — were made to react with phosphorus pentoxide[80]:



(R=R$_1$=H, CH$_3$; R=H, CH$_3$, R$_1$=CH$_3$, H).

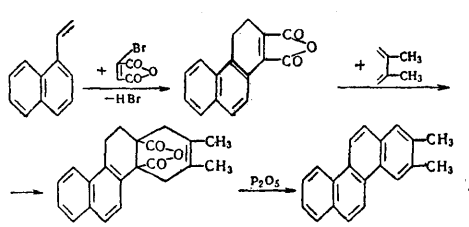
The formation only of 1-methylphenanthrene (from the adduct of 1-vinylnaphthalene) and 1,3-dimethylphenanthrene (from the 1-propenylnaphthalene adduct), not mixed with isomeric hydrocarbons having a different orientation of the methyl groups, provides in addition a proof of the *"ortho"* structure of the adducts of these dienes with such unsymmetrical dienophils as methylmaleic anhydride.

The synthesis of *chrysene* from 2-cyclohexenylnaphthalene was accomplished in a similar manner to that of phenanthrenes from adducts of 1-vinyl- and 1-propenyl--naphthalene. 4b,5,6,6a,7,8,9,10-Octahydrochrysene-5,6--dicarboxylic acid, obtained by hydrolysing the adduct of 2-cyclohexenylnaphthalene with maleic anhydride, was heated with phosphorus pentoxide. Decarbonylation and dehydration of the acid by the phosphorus pentoxide took place only on gradual and prolonged heating (from 210° to 350° during 6–7 h), 1,2,3,4-tetrahydrochrysene being formed; a small amount of chrysene was also isolated from the reaction products, its formation being due to simultaneous dehydrogenation[81]:



The synthesis of *homologues of chrysene* by the same method necessitated the use either of homologues of 2-cyclohexenylnaphthalene as the initial diene component, or of homologues of maleic anhydride as the dienophil. However, these last homologues do not react even with 2-cyclohexenylnaphthalene itself, and therefore chrysene homologues were obtained by a synthesis involving a larger number of stages but from more readily available components.

2,3-Dimethylchrysene was synthesised by the reaction of phosphorus pentoxide with 1,4,4a,11,12,12a-hexahydro--2,3-dimethylchrysene-4a,12a-dicarboxylic anhydride, which was obtained by a two-stage diene synthesis: reaction of 1-vinylnaphthalene with bromomaleic anhydride gave 3,4-dihydrophenanthrene-1,2-dicarboxylic anhydride, and the latter then entered into a diene synthesis with 2,3-dimethylbuta-1,3-diene in the presence of picric acid and phenothiazine[81]:

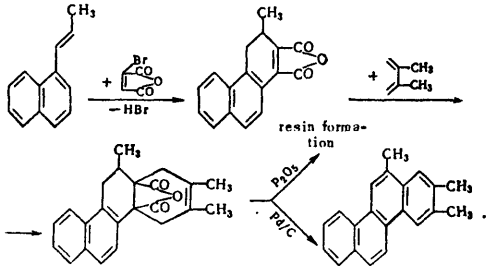


The tetrahydro-2,3-dimethylchrysene formed as an intermediate was immediately and completely dehydrogenated

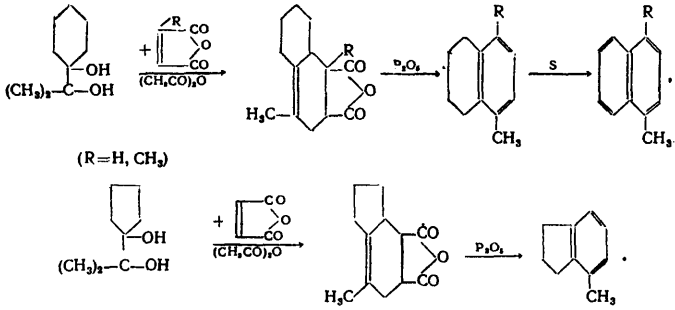
‡ Adducts of 1-vinylnaphthalene and its homologues with some dienophils are unstable: in acid medium or on prolonged heating they isomerise readily into a more stable isomer, with migration of the double bond into the naphthalene ring. Under the conditions of diene synthesis employed[80] all the adducts obtained were anhydrides of 1,2,3,4-tetrahydrophenanthrene-1,2-decarboxylic acid.

under the conditions of the reaction (whereas tetrahydrochrysene was only partly dehydrogenated).

2,3,12-Trimethylchrysene could not be synthesised in a similar manner using 1-propenylnaphthalene as the initial diene: when the 1,4,4a,11,12,12a-hexahydro-2,3,12-trimethylchrysene-4a,12a-dicarboxylic anhydride obtained by a similar two-stage diene synthesis was heated with phosphorus pentoxide, it resinified, and only on being heated with palladium on carbon to 330°–340° could it be converted into 2,3,12-trimethylchrysene[81]:



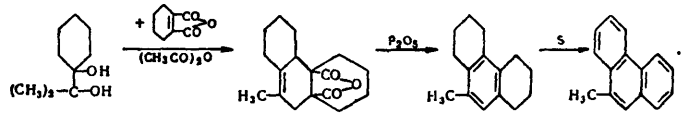
It is evident from the above that the initial dienes used in the synthesis of dicyclic and polycyclic aromatic hydrocarbons have included alkadienes, bi(cycloalkenyls), alkenylnaphthalenes, and alkenylcycloalkenes. Alkadienes and alkenylcycloalkenes are in many cases obtained by dehydration of the corresponding pinacols. In the synthesis of several *tetralin and indane hydrocarbons*, the adducts for aromatisation with phosphorus pentoxide have been obtained in a single stage, by heating unsymmetrical pinacols with maleic or methylmaleic anhydride in acetic anhydride[82]:



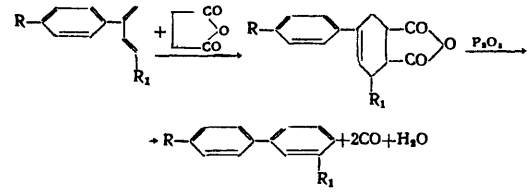
The 5,8-dimethyltetralin and the 1,4-dimethylnaphthalene obtained from it were uncontaminated with the isomeric hydrocarbons 5,7-dimethyltetralin and 1,3-dimethylnaphthalene respectively, which could have been formed if the initial anhydride had been contaminated with a small quantity of the isomeric *"meta"* adduct, the anhydride of Δ^4-octahydro-2,4-dimethylnaphthalene-1,2-dicarboxylic acid.

The use of pinacols enables the stage of preparing the diene hydrocarbons to be avoided, the latter often being unstable and polymerising readily under the conditions of diene synthesis; the above method for obtaining several homologues of tetralin and indane is simpler than the method described earlier (p. 581).

The preparation of aromatic hydrocarbons from adducts in which the diene component is a pinacol has been applied also to the synthesis of methylphenanthrenes. Thus 9-methylphenanthrene has been obtained from the adduct of the mixed pinacol of acetone and cyclohexanone with 3,4,5,6-tetrahydrophthalic anhydride[80]:

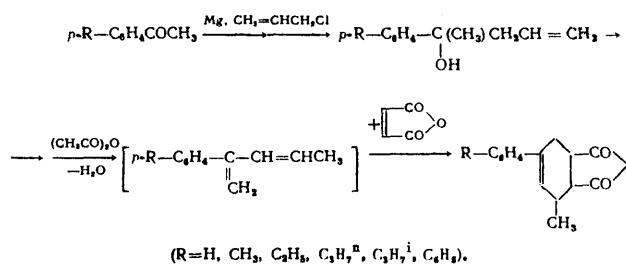


The aromatisation of diene adducts in the presence of phosphorus pentoxide can be employed for the synthesis not only of fused dicyclic and polycyclic aromatic-hydrocarbons but also of non-fused hydrocarbons — *biphenyls* and p-*terphenyls*. Thus 4-aryltetrahydrophthalic anhydrides, in which the aryl substituent is remote from the anhydride group (the behaviour of the 2- and 3-aryl anhydrides, in which the aryl substituent is located closer to the anhydride group, will be considered below), behave in a similar manner to alkyltetrahydrophthalic anhydrides on being heated with phosphorus pentoxide, simultaneous decarbonylation and dehydration yielding aromatic hydrocarbons of these series[83,84]:



R=R₁=H; R₁=CH₃; R=H, CH₃, C₂H₅, C₃H₇ⁿ, C₃H₇ⁱ, C₆H₅).

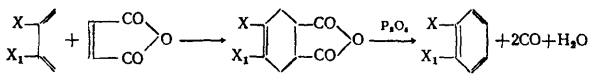
A general method for synthesising alkylbiphenyls having the unsymmetrical structure of 4′-alkyl-3-methylbiphenyls (R = Alk, $R_1 = CH_3$) involves the reaction of phosphorus pentoxide with adducts of 2-arylpenta-1,3-dienes and maleic anhydride. Here, too, there is no need to isolate the 2-arylpentadienes on formation from the corresponding unsaturated alcohols: it has proved possible to make maleic anhydride react (in the presence of acetic anhydride and potassium hydrogen sulphate) with unsaturated aromatic alcohols — allylarylmethylmethanols — which are readily obtained from *p*-alkylacetophenones, magnesium, and allyl chloride, and are dehydrated (with simultaneous migration of the double bond) in the process of diene synthesis itself[84]:



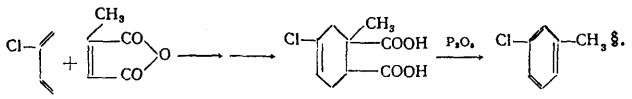
(R=H, CH₃, C₂H₅, C₃H₇ⁿ, C₃H₇ⁱ, C₆H₅).

Halogenated tetrahydrophthalic acids and their anhydrides — the adducts of halogenated dienes with maleic and

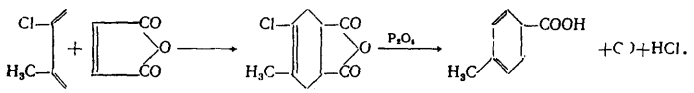
methylmaleic anhydrides — can also undergo decarbonylation and dehydration in the presence of phosphorus pentoxide[85]:



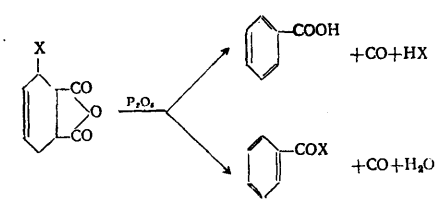
(X=Cl, Br, X_1=H; X=X_1=Cl).



Further study of the reaction of halogenated tetrahydrophthalic acids with phosphorus pentoxide gave unexpected results: 4-chloro-1,2,3,6-tetrahydro-5-methylphthalic anhydride (the adduct of methylchloroprene and maleic anhydride) yielded, instead of the expected *o*-chlorotoluene, *p*-toluic acid (with the elimination of hydrogen chloride and one molecule of carbon monoxide):



This type of anomalous reaction was found to be characteristic of other halogenated tetrahydrophthalic acids. For example, 3-chloro-1,2,3,6-tetrahydrophthalic anhydride (the adduct of butadiene and chloromaleic anhydride) and the corresponding 3-bromo derivative are converted into benzoic acid on reaction with phosphorus pentoxide; but in these two cases, in contrast to the preceding case, the corresponding benzoyl halides were also isolated from the reaction products:

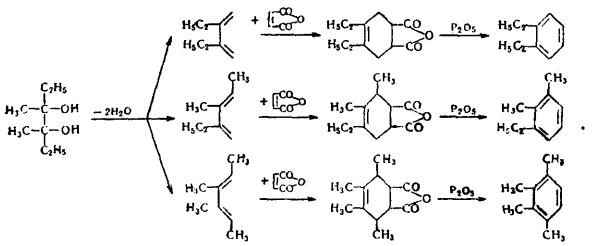


Thus if halogenated tetrahydrophthalic acids and their anhydrides readily split off hydrogen halide, their aromatisation under the influence of phosphorus pentoxide does not result in the formation of aryl halides.

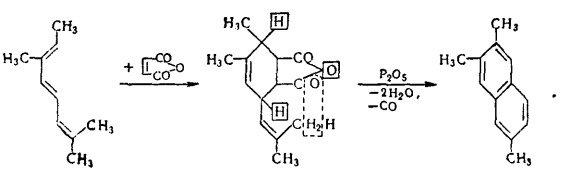
Thus the two consecutive reactions — diene synthesis using maleic anhydride, its homologues, and cyclic analogues as dienophils followed by aromatisation of the adducts by the action of phosphorus pentoxide — represent a convenient and fairly general route for the synthesis of mono-, di-, and poly-cyclic aromatic and hydroaromatic hydrocarbons of fused and non-fused structure, such as alkylbenzenes and their halogenated derivatives, tetralins, indanes, fluorenes, including polycyclic hydrocarbons containing the tetralin, indane, and fluorene systems, and also phenanthrenes and hydrophenanthrenes, chrysenes, biphenyls, and *p*-terphenyls.

The above survey shows that all the reactions undergone by adducts of diene synthesis (alkyl-, cycloalkenyl-, and some aryl-tetrahydrophthalic anhydrides) under the influence of phosphorus pentoxide consist in simultaneous decarbonylation and dehydration. This represents the *first type of aromatisation reaction* of adducts of diene synthesis[83].

Apart from preparative purposes, the aromatisation of diene adducts by means of phosphorus pentoxide can also be used to establish the structure of the original diene system. Thus this reaction has been employed by Kazanskii and his coworkers[91] to identify the individual components in the mixture of diene hydrocarbons obtained by the dehydration of 3,4-dimethylhexane-3,4-diol (the pinacol from ethyl methyl ketone):



In order to establish the structure of alloocimene, its maleic anhydride adduct was also subjected to aromatisation with phosphorus pentoxide: the product of the reaction was 2,3,6-trimethylnaphthalene, the formation of which was represented as follows[92]:

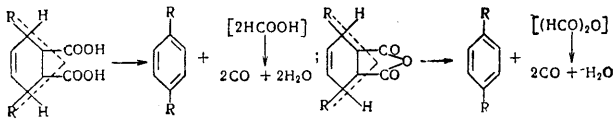


The reaction of diene adducts with phosphorus pentoxide — their conversion into easily identifiable aromatic hydrocarbons — is of value also for elucidating the spatial direction of diene synthesis with dienophils of unsymmetrical structure. This method has been used, for example, to demonstrate the *"ortho"* structure of the adducts of 1-vinyl- and 1-propenyl-naphthalene with methylmaleic anhydride[80], the preferential formation of the *"para"* adduct of this same dienophil with the mixed pinacol of cyclohexanone and acetone[82], and finally the preferential formation of the *"meta"* adduct in the reaction of chloroprene with methylmaleic anhydride in propionic acid[85].

Since the aromatisation of tetrahydrophthalic anhydrides under the influence of phosphorus pentoxide consists in decarbonylation accompanied by dehydration involving β-hydrogen atoms[67] (see p. 580), a formal analogy can probably be drawn between this reaction and the pyrolysis of xanthates, esters, and acetyl derivatives of amines, which also results in the formation of a double bond as a result of β-elimination[93,94]. In the last three reactions, however, a C–O or a C–N bond undergoes cleavage, whereas in the

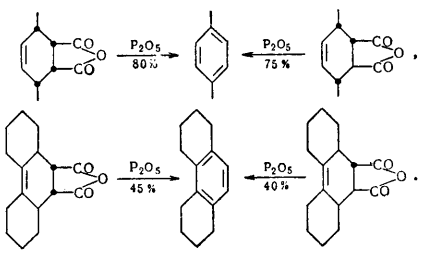
§ The infrared absorption spectrum showed that the resulting *m*-chlorotoluene was contaminated with the *para* isomer, but insufficient of the latter was present to be detected by chemical methods (for example, by oxidation). The preferential formation of the *"meta"* adduct in the reaction of chloroprene with methylmaleic anhydride is perhaps due to the fact that it was prepared by heating in propionic acid, whereas the *"para"* adducts of chloroprene described by other workers[86–90] were obtained by heating in non-polar solvents (benzene, toluene) or else in the absence of solvent.

aromatisation of tetrahydrophthalic anhydrides in the presence of phosphorus pentoxide it is a C–C bond which is broken, formic acid or its anhydride is split off, and decomposes into carbon monoxide and water:



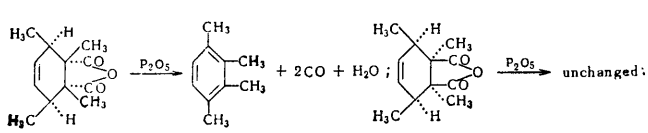
The above scheme gives grounds for assuming that the course of this reaction may depend on certain spatial factors — the mutual disposition of the β-hydrogen atoms which are to be eliminated and the anhydride grouping in the reactant tetrahydrophthalic anhydride molecule, or of the carboxyl groups in tetrahydrophthalic acids. Thus the reaction with phosphorus pentoxide, like several pyrolytic reactions[93,94], might prove stereospecific in the case of 3-alkyl- or 3,6-dialkyl-tetrahydrophthalic anhydrides, which can exist in different spatial conformations.

However, the stereoisomeric 1,2,3,6-tetrahydro-3,6-dimethylphthalic (*cis* and *trans*) anhydrides, and also the stereoisomeric (*cis* and *trans*) 3,4:5,6-dicyclohexeno--1,2,3,6-tetrahydrophthalic anhydrides, show identical behaviour with phosphorus pentoxide: on being heated to 150°–160° they are converted into the corresponding hydrocarbons (*p*-xylene and octahydrophenanthrene) in practically the same yield[95]:



The fact that in these cases the reaction with phosphorus pentoxide is unaffected by the spatial configuration of the adducts can, however, be explained by the possibility of interconversion of these stereoisomeric anhydrides, reaction with phosphorus pentoxide being preceded by isomerisation with preferential formation of the reactive configuration.

The stereoisomeric 1,2,3,6-tetrahydro-1,2,3,6-tetramethylphthalic anhydrides obtained by diene synthesis from hexa-2,4-diene and dimethylmaleic anhydride[95] and having *trans-cis-trans* and *cis-cis-cis* configurations (the *"exo"* and *"endo"* configurations respectively) react differently with phosphorus pentoxide: only one of these anhydrides, that possessing the *"exo"* configuration, undergoes aromatisation readily with conversion into 1,2,3,4-tetramethylbenzene[95], since in this particular case *cis*-elimination takes place (of β-hydrogen atoms and the anhydride group), which is the preferential direction in many pyrolytic processes[93,94]:

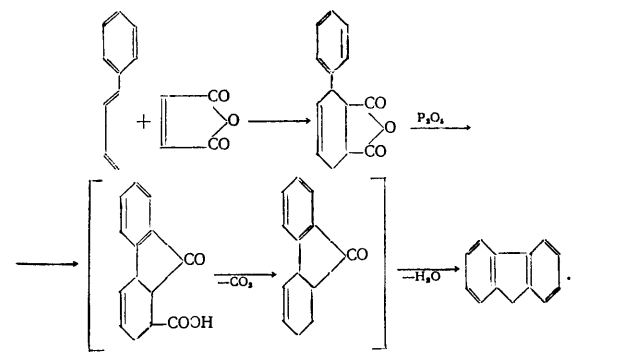


Thus the first type of reaction involving aromatisation of adducts of diene synthesis under the influence of phosphorus pentoxide can be employed not only for the purposes mentioned above (to synthesise aromatic hydrocarbons of various classes, establish the structure of the original dienes, and establish the structural direction of the diene synthesis), but in certain cases also to establish the spatial configuration of the diene adducts[95].

As has been reported above (see p. 583) aryltetrahydrophthalic anhydrides in which the aryl substituent is remote from the anhydride group undergo the first type of aromatisation in the presence of phosphorus pentoxide, carbon monoxide and water being split off with the formation of polyphenyls.

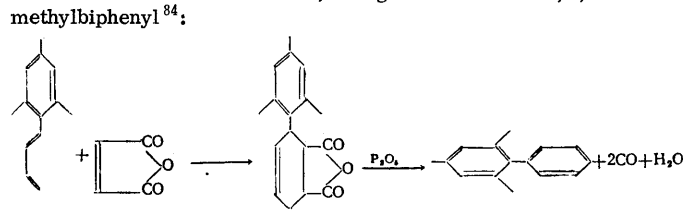
Aryltetrahydrophthalic anhydrides in which the aryl group occupies a different position can undergo aromatisation in a different way (without elimination of carbon monoxide) under the influence of phosphorus pentoxide, with the formation of hydrocarbons of the *fluorene series*.

Thus 1,2,3,6-tetrahydro-3-phenylphthalic anhydride (the adduct of 1-phenylbuta-1,3-diene and maleic anhydride), in which the phenyl substituent is next to the anhydride group¶, gave fluorene (in 21% yield) on reaction with phosphorus pentoxide. The reaction probably passes through intermediate stages involving intramolecular acylation of the benzene ring, resulting in formation of tetrahydrooxofluorenecarboxylic acid, which is then decarboxylated to tetrahydrofluorenone[96], the latter being converted into fluorene under the influence of the phosphorus pentoxide†:



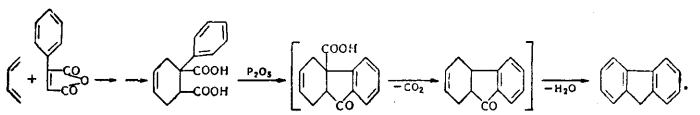
An analogous transformation is undergone by 1,2,3,6--tetrahydro-1-phenylphthalic acid, obtained from the

¶ It must be noted that 1,2,3,6-tetrahydro-3-mesitylphthalic anhydride — the adduct of 1-mesitylbuta-1,3-diene and maleic anhydride — in which the phenyl ring at the side of the anhydride group contains *ortho* substituents, underwent aromatisation under the conditions of reaction with phosphorus pentoxide by splitting off carbon monoxide and water, being converted into 2,4,6-trimethylbiphenyl[84]:



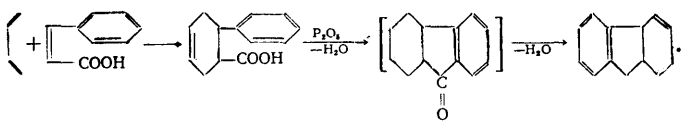
† Many published data support the possibility of each of the above reactions taking place in the presence of phosphorus pentoxide. Hydroaromatic ketones of different structures — with the ketone group inside or outside the ring and with the double bond in the γδ or the αβ position relative to the ketone group — are converted into aromatic hydrocarbons on being heated with phosphorus pentoxide, the yield depending on the structure of the original ketone[97,98].

adduct of butadiene and phenylmaleic anhydride (yield of biphenyl 50%)[83]:

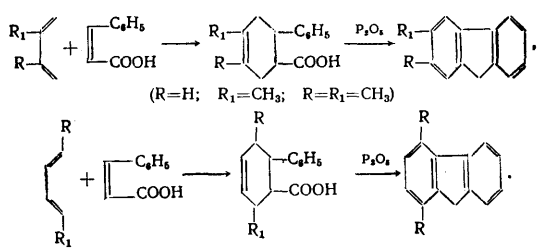


The conversion of aryltetrahydrophthalic acids and their anhydrides into fluorenes under the influence of phosphorus pentoxide has been termed the *second type of aromatisation reaction* of adducts of diene synthesis[83].

Since an intermediate stage in the above synthesis of fluorene from the adduct of butadiene and phenylmaleic anhydride is the splitting off of a carboxyl group from the adduct, this reaction was subsequently simplified by replacing the 2-phenyltetrahydrophthalic anhydride with 1,2,3,6-tetrahydro-2-phenylbenzoic acid, the adduct of butadiene and cinnamic acid. When this adduct was heated with phosphorus pentoxide, fluorene was obtained in higher yield (63%)[95,96]:

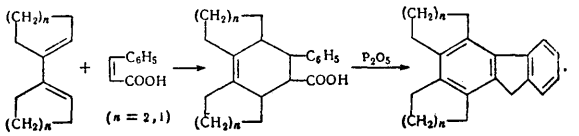


The adducts of cinnamic acid with isoprene, penta-1,3-diene, 2,3-dimethylbuta-1,3-diene, and hexa-2,4-diene yielded respectively 3-methylfluorene, 1-methylfluorene, 2,3-dimethylfluorene, and 1,4-dimethylfluorene[96,99]:



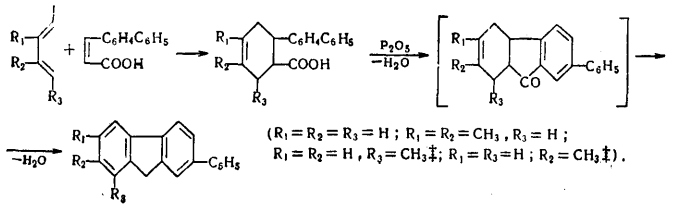
The preparation of 3-methylfluorene instead of the isomeric 2-methylfluorene from the adduct of isoprene and cinnamic acid, and also of 1-methylfluorene (not 4-methylfluorene) from the adduct of penta-1,3-diene and cinnamic acid, confirms the structure of these adducts as respectively 1,2,3,6-tetrahydro-4- and -6-methyl-2-phenylbenzoic acids.

The adducts of cinnamic acid with 1,1′-bi(cyclohexenyl) and 1,1′-bi(cyclopentyl) gave 1,2:3,4-dicyclohexenofluorene and 1,2:3,4-dicyclopentenofluorene[96]:

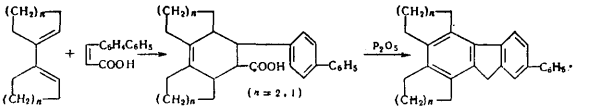


An advantage of this reaction for the preparation of fluorenes compared with those mentioned previously (see p. 581 and this page above) is that it makes use of more readily available dienes (alkylbutadienes instead of arylbutadienes) and a more accessible dienophil (cinnamic acid instead of indene-1,2-dicarboxylic or phenylmaleic anhydride).

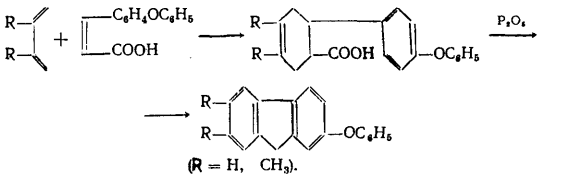
The reaction with phosphorus pentoxide has been carried out also with 2-aryltetrahydrobenzoic acids of more complicated structure, with *p*-biphenylyl as the aryl substituent (acids of this type have been obtained by diene synthesis using *p*-phenylcinnamic acid, which has proved an active dienophil)[100]:



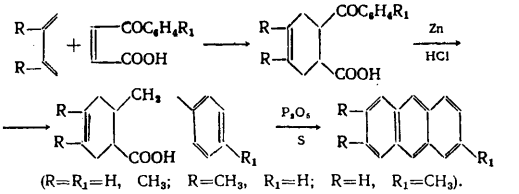
With *p*-phenylcinnamic acid as the initial dienophil, and the dicyclic diene hydrocarbons 1,1′-bi(cyclohexenyl) and 1,1′-bi(cyclopentenyl) as dienes, polycyclic aromatic hydrocarbons can be obtained containing the 2-phenylfluorene system — 2-phenyl-5,6:7,8-dicyclohexenofluorene and 2-phenyl-5,6:7,8-dicyclopentenofluorene respectively[65]:



Tetrahydro-2-phenoxybenzoic acids, the adducts of dienes with *p*-phenoxycinnamic acid, react in a similar manner with phosphorus pentoxide, being converted into 2-phenoxyfluorenes[101]:

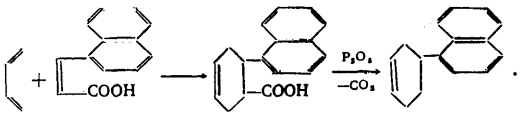


The second type of aromatisation is undergone also by 2-benzyl-1,2,3,6-tetrahydrobenzoic acids (obtained by reducing aroyltetrahydrobenzoic acids — the adducts of diene hydrocarbons and aroylacrylic acids — with amalgamated zinc in hydrochloric acid), which are converted into dihydroanthracenes, subsequent dehydrogenation of which (by heating with sulphur) yields anthracenes[102]. This synthesis of anthracenes could be simplified by carrying out the aromatisation of the benzyltetrahydrobenzoic acids by heating them with phosphorus pentoxide in the presence of sulphur, the dihydroanthracenes formed under these conditions being completely dehydrogenated to the corresponding anthracene hydrocarbons[102]:

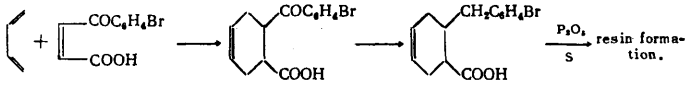


‡ The structure of these adducts (as "*ortho*" and "*meta*" adducts), obtained from unsymmetrical dienes and dienophil, was proved by converting them (by decarboxylation followed by dehydrogenation in the presence of platinum) into 3- and 4-methyl-*p*-terphenyls respectively.

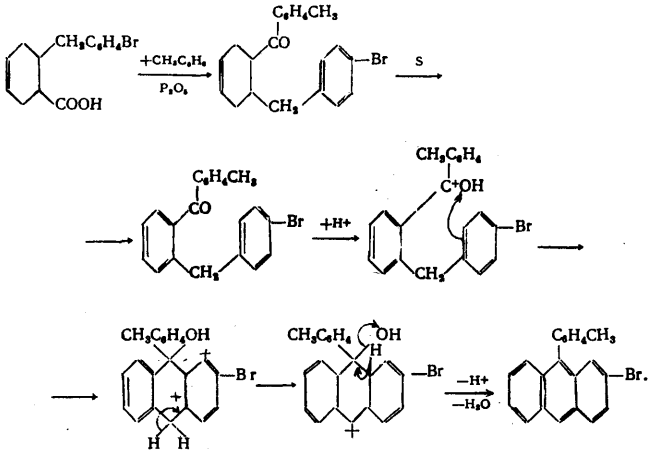
Different behaviour is shown by 1,2,3,6-tetrahydro-2-1'--naphthylbenzoic acid, obtained when 1'-naphthylacrylic acid is employed as dienophil. In this case carbox dioxide is split off on reaction with phosphorus pentoxide, with the formation of 1-cyclohex-3'-enylnaphthalene[103]:



Aromatisation of aryltetrahydrobenzoic acids by the second method is prevented by the presence of bromine atoms in the phenyl ring adjacent to the carboxyl group. Thus when 2-*p*-bromobenzyl-1,2,3,6-tetrahydrobenzoic acid (obtained by the reduction of *p*-bromobenzoyltetrahydrobenzoic acid, the adduct of butadiene and *p*-bromobenzoylacrylic acid) is heated with phosphorus pentoxide and sulphur, *i.e.* under conditions under which benzyltetrahydrobenzoic acids are converted into anthracenes, it is almost completely resinified[104]:



When this reaction was carried out in toluene, 2-bromo--9-tolylanthracene was obtained: under the influence of the phosphorus pentoxide, intermolecular acylation of the toluene by the *p*-bromobenzyltetrahydrobenzoic acid took place with the formation as intermediate of a hydroaromatic ketone, which then underwent dehydrogenation (under the influence of the sulphur) and cyclic dehydration (under the influence of the phosphorus pentoxide), being converted into the corresponding bromoanthracene[104]:



Fused aromatic and hydroaromatic hydrocarbons — tetralins, indanes, fluorenes, phenanthrenes, anthracenes, and also polycyclic hydrocarbons containing these systems — are chemically active compounds, capable of undergoing many chemical changes leading to substances having valuable physical properties and physiological activity.

Thus hydrocarbons of the tetralin series have been employed in the production of derivatives of 4-methyl-1,2--benzanthracenes, which are highly carcinogenic[105].

Indane can be used as an additive in high-grade motor fuel containing cycloalkenes and alkadienes as the principal ingredients[106]. Alkylindanes are used as starting materials in the synthesis of compounds possessing a musk odour[107-112]. The use of indanes in the synthesis of azulenes has been reported (in the photochemical reaction with diazomethane and diazoacetic ester)[113-117].

Several fused hydrocarbons containing the fluorene system are of interest for possible use as anti-cancer drugs. For example, 1,2:5,6-dibenzofluorenes are known to be biological antagonists of carcinogenic hydrocarbons such as 3-methylcholanthrene; these hydrocarbons suppress the growth of tumours grafted in mice[118]; 3,4-benzofluorenes exert an inhibiting action on mouse sarcoma[119].

1,7-Dimethylfluorene, the so-called "gibberene", is a product of the dehydrogenation of gibberellins (a most important group of plant-growth-promoting substances)[120].

Several hydrocarbons of the phenanthrene series are also physiologically active: they exert anti-malarial[121-123], oestrogenic[124-127], sedative[128,129], and carcinogenic[130-132] effects. Hydrocarbons containing a phenanthrene ring have been used in studying the conjugation of an exocyclic double bond with an aromatic ring[133-135], the stability of free radicals[136,137], and other phenomena[138]. In synthetic chemistry phenanthrene and its homologues serve as intermediates in the preparation of 1,2-cyclopentenophenanthrene[139-141], chrysene[142,143], triphenylene[144-146], and 1,2-benzanthracene[146,147].

Aromatic hydrocarbons of non-fused structure — biphenyls and *p*-terphenyls — are also of practical interest; during recent years, for example, *p*-terphenyl has acquired great value in the preparation of liquid and plastic phosphors for scintillation counters[148]. Anthracene also finds some application as a scintillator[149], and comparatively recently 9,10-diphenylanthracene has been shown to be a more effective scintillator than *p*-terphenyl[150].

Biphenyl and 4-isopropylbiphenyl have found application as high-temperature organic heat-transfer media[151]. Biphenyls together with various polyphenyls can be employed as moderators and coolants in atomic reactors[152].

Thus polycyclic aromatic hydrocarbons of the above classes are objects of theoretical studies[153] and have various practical applications[154]. It is therefore natural that considerable attention should be paid in the chemical literature to the search for new routes and methods for their synthesis, as is reflected in the present review.

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