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Syntheses of Tetracarboxylic Acids

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A systematic and general account of the literature data on the methods of synthesising tetracarboxylic acids capable of forming internal cyclic dianhydrides is given for the first time in the present review. These products have found extensive applications as starting materials for the synthesis of heterocyclic polymers, dyes, plasticisers, hardening agents for epoxy-resins, etc. Particular attention has been devoted to methods of synthesising aromatic tetracarboxylic acids and also products of greatest practical importance.
The bibliography includes 214 references

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I. INTRODUCTION

Only 10–15 years ago tetracarboxylic acids did not have practical applications although many of them had been isolated from the oxidation products of organic compounds or in the identification of diene systems by the Diels–Alder reaction. However, the situation changed radically when it became known that tetracarboxylic acids and their functional derivatives can be used as starting materials for the synthesis of thermostable products [polyimides [1] and poly(aroylenebisbenzimidazoles) [2]], plasticisers, antioxidants [3], hardening agents for epoxy-resins [4], etc. In addition, aroyleneimidazole dyes have again roused interest in recent years [5]. A systematic and general account of data on the methods of synthesising tetracarboxylic acids has therefore become necessary.

The present review deals with the methods of synthesis of only those tetracarboxylic acids whose derivatives are capable of intramolecular cyclisation. This limitation was imposed because in the main fields of their application—the synthesis of polymers and dyes—tetracarboxylic acids enter into a reaction with amines and the products of this reaction are subjected to intramolecular dehydration with formation of cyclic structures. Here it is noteworthy that the size of the ring formed corresponds to the size of the anhydride of the initial acid. Subsequently the term "tetracarboxylic acid" will be applied only to acids capable of forming five-, six-, and seven-membered internal cyclic dianhydrides.

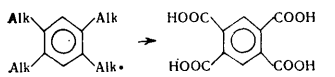
Among the numerous method of synthesising carboxylic acids [6], the following have found application in the preparation of the compounds in which we are interested: oxidation of organic compounds, cycloaddition reactions, condensation of dicarboxylic acids and their derivatives, and malonic ester syntheses. In addition there are several non-general methods, specific to the given tetracarboxylic acid.

II. OXIDATION OF ORGANIC COMPOUNDS

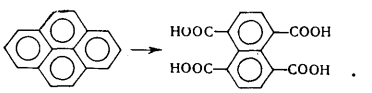
Hitherto the oxidation of organic compounds has been essentially the only method of synthesising tetracarboxylic acids having extensive practical applications. This is because oxidation reactions are particularly suitable for the synthesis of aromatic tetracarboxylic acids on the basis of which polymers with the most valuable properties have been obtained. The method of oxidation has already been applied on an industrial scale, although the range of products manufactured is fairly narrow.

The method can be clearly divided into three types in terms of the compound undergoing oxidation.

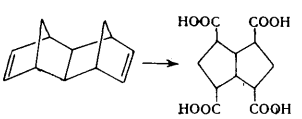
A. Oxidation of side chains in aromatic hydrocarbons, for example:



B. Oxidation of the rings of polynuclear aromatic compounds, for example:



C. Oxidative cleavage of olefins, for example:



The same reagents are used in laboratory practice for all three types of reactions: nitric acid, permanganates, chromates, dichromates, ozone, peroxides, and hypochlorites. Therefore initially we shall briefly characterise the scope and mechanism of the action of each of these substances.

The oxidation of hydrocarbons to acids is a multistage process and proceeds as a rule according to the following scheme: hydrocarbon → alcohol → aldehyde (ketone) → carboxylic acid. The slowest stage is the oxidation of the C–H or C–C bonds, while the subsequent stages take place with increasing ease: the alcohol is oxidised more readily than the hydrocarbon and the aldehyde more readily than the alcohol [7].

All organic compounds can be oxidised by hot nitric acid which need not necessarily be very concentrated for this purpose. This reagent is particularly active in the vapour phase [6]. The oxidation proceeds via a homolytic mechanism and includes stages involving the formation and decomposition of nitro-compounds, nitrates, and nitrites [7]. Chain reactions take place at some of the stages and nitro-compounds and nitrates do not accumulate in the course of the reaction. However, the contamination of the final product by nitrogen-containing compounds is one of the principal disadvantages of oxidation with nitric acid.

Chromic acid, chromates, dichromates, and chromyl chloride are more selective than nitric acid. They are capable of oxidising only activated C–H bonds in allyl and benzyl groups, at tertiary carbon atoms, and carbon atoms adjoining a heteroatom [7]. The reaction is usually carried out in dilute sulphuric acid solutions but aqueous solutions of alkali and glacial acetic acid can be employed.

The oxidation by chromates of the side chains in aromatic hydrocarbons and of alcohols and aldehydes constitutes a heterolytic process including a stage in which a new C–O–Cr linkage is formed. In the oxidation of alcohols by chromic acid, the first stage is rapid and reversible esterification and the rate of the overall process is limited by that of the stage of the concerted decomposition of the ester [8].

The oxidation of olefins involves a direct electrophilic attack on the π electrons of the C–C bond by one of the oxygen atoms of the reagent. The reaction is more difficult than with alcohols, so that the oxidation takes place only in acid media. Chromates attack aromatic compounds at the carbon atom with the highest electron density, for example they oxidise anthracene to anthraquinone [9].

Permanganates are very powerful reagents capable of oxidising in neutral, alkaline, and acid aqueous media and also in organic solvents—acetone or pyridine. In contrast to chromates, the oxidation of benzyl C–H bonds by permanganate involves a hydride transfer stage [7], for example:

$$MnO_4^- + H-\overset{|}{\underset{|}{C}}-O^- \rightarrow \overset{|}{\underset{|}{C}}=O + (HMnO_4)^{3-} .$$

This reaction is catalysed by both acids and bases, but alkaline solutions are not used for extensive oxidation, since the process is complicated by the Cannizzaro reaction in the aldehyde formation stage.

When acted upon by permanganates in a neutral or acid medium, olefins initially give rise to acyloins, which are then rapidly oxidised until the attainment of more advanced stages [7,8]. A disadvantage of this reagent is the necessity to separate the reaction products from the manganese dioxide precipitate.

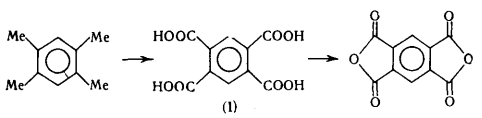
Ozone is used to oxidise condensed polynuclear hydrocarbons and for the oxidative cleavage of olefins. In the synthesis of acids, ozonides are decomposed by peroxides, peracids, oxygen, activated ozone, metal salts, etc. [10] In contrast to NO_2^+ or chromates, which attack the most nucleophilic carbon atom of the polynuclear compound, ozone is a test reagent for the most reactive double bond [11]. Thus pyrene is oxidised by ozone to biphenyl-2,2',6,6'-tetracarboxylic acid, while nitric acid and permanganate oxidise it to naphthalene-1,4,5,8-tetracarboxylic acid [12].

Hypochlorites and peroxides are effective reagents for the oxidation of polynuclear quinones to carboxylic acids. Initially one usually oxidises aromatic hydrocarbon by nitric acid, chromate, and permanganate to quinones and the latter are then treated with hypochlorite or hydrogen peroxide, which leads to acids in almost quantitative yields [13].

All the oxidation reactions enumerated above make it possible to obtain acids in yields reaching 90–95% and the oxidation methods have been fairly thoroughly developed and to some extent standardised.

1. Oxidation of Side Chains of Aromatic Hydrocarbons

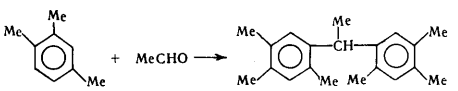
Since 1851 when Erdmann [14] obtained for the first time benzene-1,2,4,5-tetracarboxylic (pyromellitic) acid (I) (PMA) and its anhydride by oxidising durene with nitric acid, PMA has been for about 100 years virtually the only readily available aromatic tetracarboxylic acid obtained by this procedure. However, this method of synthesising tetracarboxylic acids (primarily PMA) has acquired practical importance only recently as a result of the development and improvement of the oxidation technology and methods of synthesising and purifying the initial alkylbenzenes:



(I)

The principal difficulty in the synthesis of PMA is that the initial 1,2,4,5-tetramethylbenzene (durene) is very difficult to free from isomers. In this connection three procedures have been outlined for the preparation of pure PMA: by developing methods of synthesising pure durene, by obtaining PMA from sources other than durene, and by devising methods for the separation of PMA from isomeric acids and for its purification.

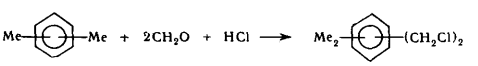
Pure durene is obtained by the hydrocracking of 1,1-dipseudocumenylethane (II), which is obtained by treating pseudocumene with acetaldehyde (yield 96%, purity 99.1%): [15-17]



(II)

The direct oxidation of (II) or durene obtained by the hydrocracking of (II) leads to pure PMA.

The greatest success was achieved by the second procedure in the chloromethylation of crude xylene [18]:



(III)

Di(chloromethyl)xylene isomers are readily separated by simple crystallisation. The pure 1,2,4,5-isomer is chlorinated further to the tetrachloro-derivative and then oxidised. This method was modified somewhat recently [19,20]: 4,5-di(hydroxymethyl)-1,2-dimethylbenzene, obtained by treating (III) with alkali, is oxidised. In both cases the reaction product is very pure PMA.

There are also methods of synthesising PMA from 1,2,4,5-R_n–$(HOOC)_{4-n}C_6H_2$, where R is a small alkyl

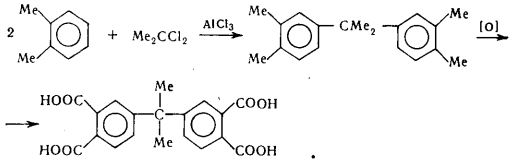
group and $n = 1-4$,[21] 2,5-di-isopropyl-1,4-dimethylbenzene obtained by propylating *p*-xylene or pseudocumene in the presence of Al_2O_3 and BF_3,[22] and also many other alkylbenzenes[17]. So far these methods have not acquired practical importance.

The possibility of isolating PMA from a mixture of isomeric acids is due to the fact that benzene-1,2,3,4-tetracarboxylic (mellophanic) acid isomerises to PMA at 330–340°C. For example, by refluxing a mixture of PMA and mellophanic acid in trichlorobenzene, one obtains fairly pure PMA.[23]

There are also methods whereby PMA obtained by oxidation with nitric acid can be freed from nitrogen-containing impurities by partition chromatography at 100 to 110°C (purity 98%),[24] by passing heated air or an inert gas through the acid melt at 300°C (purity 98.6%),[23] and by treatment with reducing agents—acetaldehyde, formaldehyde, and hydroquinone—at 200–210°C and a pressure of 45–70 atm.[25] The PMA dianhydride is purified by recrystallisation from a dioxan–acetic anhydride mixture[26] and via complexes with dimethylformamide (DMF)[27] or chlorine-containing aromatic compounds[28].

Apart from PMA, a number of other aromatic tetracarboxylic acids obtained by the oxidation of side chains have been known since the beginning of this century. These compounds were synthesised by the usual method for the oxidation or demonstration of the structures of alkyl derivatives of aromatic compounds or were obtained as intermediates. Thus mellophanic acid was obtained by oxidising the corresponding tetramethyl- and tetraethylbenzenes with permanganate[29]; biphenyl-3,3′,4,4′-tetracarboxylic acid was synthesised by oxidising 3,3′-dimethylbiphenyl-4,4′-dicarboxylic acid[30]; the oxidation of 2,3,6,7-tetramethylanthraquinone yielded anthraquinone-2,3,6,7-tetracarboxylic acid and its reduction gave anthracene-2,3,6,7-tetracarboxylic acid; pyridine-2,3,5,6-tetracarboxylic acid was obtained from 3,5-dicarboxy-2,6-dimethylpyridine[32]; benzoquinonetetracarboxylic acid was synthesised from durene via dinitropyromellitic and diaminopyromellitic acids[33]. The oxidation method has been used for the specific synthesis of products of practical value only since the appearance of new applications of tetracarboxylic acids.

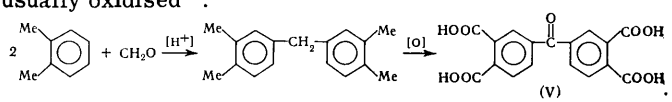
A method for the oxidation of 2,2,-di-(*o*-xylyl)propane, obtained by the Friedel–Crafts reaction between *o*-xylene and 2,2-dichloropropane, to 2,2,-di-(3,4-dicarboxyphenyl)-propane (IV) was patented as early as 1955:[34]



(IV)

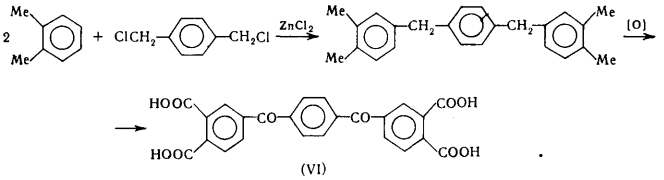
This procedure was subsequently extended to other alkylenediphthalic acids[35].

Several methods of synthesising the initial alkyl derivatives were developed in order to obtain benzophenon-3,3′,4,4′-tetracarboxylic acid (V). Di-(*o*-xylyl)methane is usually oxidised[36]:



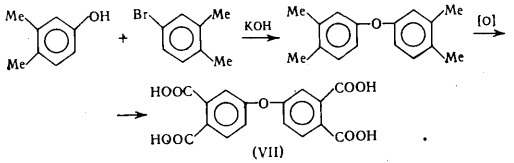
(V)

Di-(*o*-xylyl)ethane and other 1,1-di-(*o*-xylyl)alkanes[37], di-(*o*-xylyl)ethylene[38], and di-(*o*-xylyl) ketone obtained by the Friedel–Crafts reaction between *o*-xylene and phosgene[39], have also been used. The last method has been employed to synthesise a tetracarboxylic acid with two keto-groups (VI):[40]



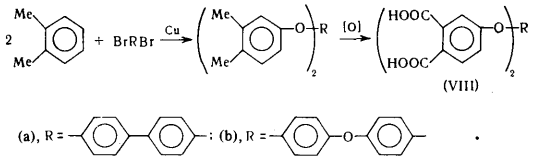
(VI)

By oxidising the products of the reaction of 3,4-dimethylphenol with 4-bromo-*o*-xylene in the presence of alkali, di-(3,4-dicarboxyphenyl) ether (VII) was obtained[35]:



(VII)

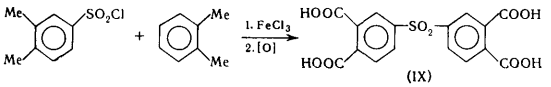
The acids (VIIIa) and (VIIIb) were obtained in low yields by a similar procedure[41]:



(VIII)

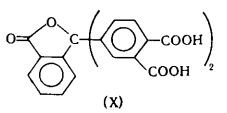
(a), R = ; (b), R =

Di-(3,4-dicarboxyphenyl) sulphone (IX) is formed by oxidising the corresponding tetramethyl derivative[42], which is obtained either by the reaction of thionyl chloride with *o*-xylene in the presence of aluminium chloride[43] or by the reaction of *o*-xylenesulphonyl chloride with *o*-xylene[44]:



(IX)

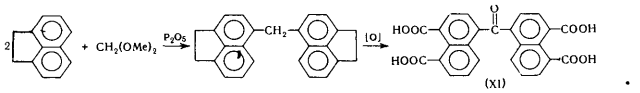
Korshak and coworkers[45] developed a procedure for the synthesis of the tetracarboxylic acid (X) by oxidising 3,3-di(3,4-dimethylphenyl)phthalide with permanganate in pyridine and then in water:



(X)

Yet another version of the side chain oxidation method involves the use of acenaphthene derivatives as starting materials. Thus the oxidation of 3,4-dicarboxyacenaphthene by nitrogen oxides and treatment of the resulting intermediate acenaphthenequinone with hypochlorite or hydrogen peroxide yielded naphthalene-1,2,4,5-tetracarboxylic acid[46,47].

The synthesis of the very interesting dianhydride of the tetracarboxylic acid (XI), involving the oxidation of bisacenaphthenyl derivatives, has been developed[48]:



(XI)

Compound (XI) is also obtained by the oxidation of diacenaphthenyl ketone synthesised by the Friedel–Crafts reaction between acenaphthene and phosgene. The

method of oxidising side chains is also suitable for the preparation of acids containing organic groups combined with various elements. The oxidation of phenyldi-(3,4-xylyl)-phosphine yielded di-(3,4-dicarboxyphenyl)phenylphosphine oxide used in the synthesis of polyimides [49], and treatment of dixylylcarboranes with CrO_3 leads to the corresponding tetracarboxylic acid in a yield of about 50% in the oxidation stage [50].

The method has been used industrially to synthesise pyromellitic dianhydride by the liquid-phase (with nitric acid) and vapour-phase oxidation of the side chains of tetra-alkylbenzenes. It is noteworthy that the principal characteristics of the oxidation of durene and other tetra-alkyl derivatives of aromatic hydrocarbons are analogous to those of the thoroughly investigated mechanism of the oxidation of *o*-xylene to phthalic anhydride [51].

The oxidation of durene with nitric acid leads to PMA in high yields, but the product contains a large amount of impurities which are difficult to separate, mainly nitro-compounds [52]. The use of nitric acid requires the application of expensive corrosion-resistant apparatus, which, together with the cost of pure durene makes this process relatively uneconomical. At present the liquid-phase oxidation of durene is hardly used to synthesis PMA. However, nitric acid is employed to oxidise chloromethylated xylenes to PMA intended for the synthesis of polyimides. In this case there is a possibility of obtaining high-purity PMA without the need for additional operations [20,53].

The industrial methods for the preparation of PMA dianhydride on the largest scale involves the catalytic vapour-phase oxidation of durene and other tetra-alkylbenzenes by atmospheric oxygen [54-57]. Vanadium pentoxide is the active component of the catalyst. The process is carried out by a continuous process and the yield of products in one cycle is 60% (90%) with respect to the alkylbenzene consumed [58,59]. There is also a method involving the almost complete oxidation of durene to PMA dianhydride in one cycle with 98% purity (the principal impurity is PMA). [60]

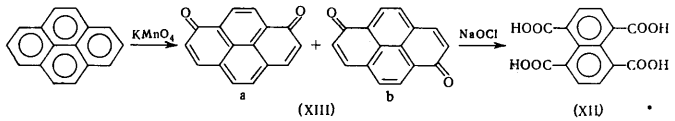
The main advantage of the vapour-phase oxidation method is the simplicity of the apparatus required for this process. The reaction is carried out in apparatus and with catalysts employed for the vapour-phase oxidation of *o*-xylene, which permits cheap large-scale manufacture of PMA. The cost of PMA obtained by the vapour-phase oxidation is lower by a factor of 3–5 than that of the product synthesised by oxidation with nitric acid [60].

The examples quoted illustrate fairly completely the scope of the method of oxidation of side chains of aromatic compounds, which is at present the principal method for the synthesis of aromatic tetracarboxylic acids. In all cases the yield of acids in the oxidation stage approaches 90%. However, we have consistently drawn attention to the synthesis of substances undergoing oxidation. The simpler and more reliable the oxidation stage the more complex are the methods of synthesising and purifying the initial alkyl derivatives. As a rule, the yield of acids barely exceeds 50% when account is taken of the synthesis of the initial compound, and the key starting materials—pure *o*-xylene and particularly durene—are at present fairly expensive.

2. Oxidation of the Rings of Polynuclear Aromatic Compounds

A typical example of the oxidation of condensed aromatic compounds is the treatment of graphite with hot nitric acid, which leads to a mixture of mono- and polycarboxybenzenes. The oxidation of graphitised charcoal has been suggested for the synthesis of aromatic acids [61,62]. However, this method lacks practical importance owing to the complexity of the isolation of the individual compounds, although there is a procedure for the separation of acids by fractionating the esterification products [63].

The most important reaction of this method is the oxidation of pyrene to naphthalene-1,4,5,8-tetracarboxylic acid (XII). When pyrene is oxidised by permanganate or dichromates, 1,8- and 1,6-pyrenequinones (XIIIa) and (XIIIb) are formed initially and are then oxidised by hypochlorite in an alkaline medium to (XII): [64-66]

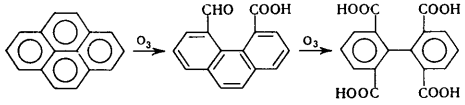


(XIII) (XII)

The method of synthesising (XII) from 1,3,6,8-tetrachloropyrene formed in high yields by the chlorination of pyrene in tetrachloroethane, is convenient. Treatment of the chloro-derivative with concentrated nitric acid or oleum leads to di-*peri*-naphthindandione, which is oxidised by nitric acid, manganese dioxide in sulphuric acid, or hypochlorite to (XII). [67,68]

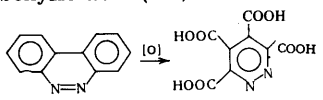
Derivatives of (XII) containing SO_3H, OH, OR, NO_2, and NH_2 groups in the ring, formed on oxidising substituted 5,6-dicarboxyacenaphthenes, are also available [69].

On ozonolysis, pyrene absorbs two moles of ozone, biphenyl-2,2',6,6'-tetracarboxylic acid (XIV) being formed in 60% yield after the decomposition of the ozonides [12,70]:



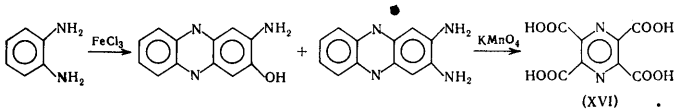
(XIV)

The ring oxidation method is very useful for the synthesis of heteroaromatic acids, since rings free from electronegative heteroatoms are more readily oxidised in polynuclear compounds. Thus the oxidation of phenazone by an alkaline solution of permanganate leads to pyridazinetetracarboxylic acid (XV): [71]



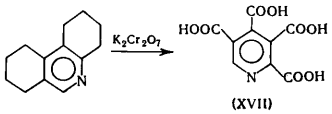
(XV)

Pyrazinetetracarboxylic acid (XVI) is formed via the mechanism [72]:



(XVI)

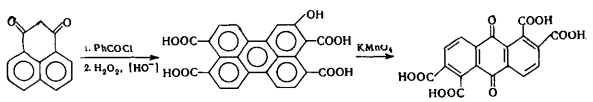
The oxidation of phenanthridine, obtained by treating cyclohexanone with formaldehyde, ammonium acetate, and ammonium hydroxide, resulted in the synthesis of pyridine-2,3,4,5-tetracarboxylic acid (XVII): [73]



(XVII)

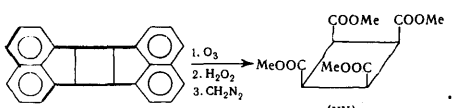
In order to illustrate the scope of this method, one may mention the synthesis of biphenyl-2,3,5,6-tetracarboxylic acid by oxidising 1-phenylnaphthalene-2,3-dicarboxylic

acid[74] and the synthesis of hydroxyperylenetetracarboxylic acid (XVIII) and anthraquinone-1,2,5,6-tetracarboxylic acid (XIX):[75]



(XVIII) (XIX)

The synthesis of an aliphatic tetracarboxylic acid by the ozonolysis of β-heptacyclene—an acenaphthene dimer—constitutes an interesting example. The decomposition of the ozonide with hydrogen peroxide and treatment with diazomethane lead to the ester (XX):[76]

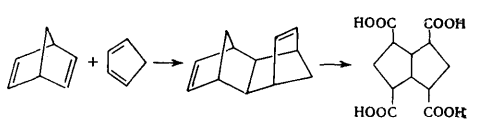


(XX)

The method of oxidation of polynuclear aromatic compounds has all the advantages and disadvantages of the side chain oxidation method discussed above. The method is of greatest value for the synthesis of naphthalene-1,4,5,8-tetracarboxylic acid—one of the cheapest and most readily available tetracarboxylic acids.

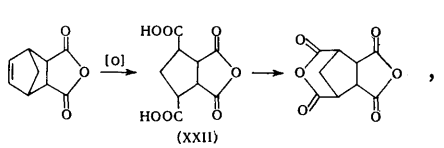
3. Oxidative Cleavage of Olefins

A classical example of the synthesis of tetracarboxylic acids by oxidative cleavage of olefins is provided by the synthesis of bicyclo[3,3,0]octane-2,4,6,8-tetracarboxylic acid (XXI) from hexahydro-1,4,5,8-*exo*,*endo*-dimethanonaphthalene[77,78]:

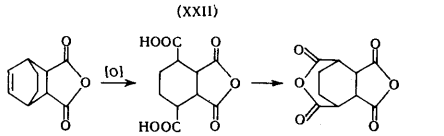


(XXI)

Diels–Alder adducts of maleic anhydride and cyclic dienes, for example cyclohexa-1,3-diene and cyclopenta-1,3-diene, are used as the compounds oxidised in other cases. After oxidation, a mixture of the stereoisomeric tetracarboxylic acid (XXII) and (XXIII) is formed[79]:



(XXII)



(XXIII)

The oxidation is carried out with nitric acid and permanganate, but best results have been obtained by the ozonolysis of the adducts followed by treatment with peracetic acid[80].

It is noteworthy that *endo*-methylenetetrahydrophthalic acids have recently become readily available, since a method has been devised for their synthesis by treating with maleic anhydride the C_5-fraction from the cracking of light petroleum.

The range of tetracarboxylic acids which can be readily obtained by the oxidative cleavage of double bonds is limited to the products enumerated above. Although the preparative aspect of the method is simple and the overall yield of products is close to 90%, their structures preclude their employment in the applications of tetracarboxylic acids known at present.

III. CYCLOADDITION REACTIONS

Cycloaddition reactions are understood as electrocyclisation processes involving polyenes in which new σ bonds are formed as a result of the opening of the π bonds in the groups added. Such reactions include processes involving the formation of at least two σ bonds, i.e. $2\pi \rightarrow 2\sigma$, $3\pi \rightarrow 3\sigma$, and $4\pi \rightarrow 4\sigma$ reactions. Only the most common $2\pi \rightarrow 2\sigma$ reactions have found application in the synthesis of tetracarboxylic acids. Such processes are observed in 2 + 2, 4 + 2 (the Diels–Alder reaction), 4 + 4, and 6 + 4 cycloadditions.

According to Woodward–Hoffmann rules[82-84], the mode of the concerted single-stage electrocyclisation reactions and also the stereochemistry of the adducts formed are determined by the symmetry of the π orbitals involved and formed in the reaction. This type of cycloaddition is possible only when the molecular orbitals involved in the reaction are correlated, without an energy barrier, with the molecular orbitals of the reaction product. For thermal reactions proceeding via the molecular ground state, the symmetry of the highest occupied π orbital is of decisive importance and in photochemical reactions involving excited states the mode of reaction depends on the symmetry of the lowest unfilled orbital. Since the symmetries of these orbitals are different, it follows that, when a given type of cycloaddition is allowed in the thermal reaction, it is forbidden in photochemical electrocyclisation processes.

According to the selection rules, $2\pi \rightarrow 3\sigma$ processes are thermally allowed for systems in which the number of π electrons involved in the reaction is $4n + 2$ and photochemical reactions are allowed for systems in which the number of π electrons is $4n$.

This conclusion is of fundamental importance for cycloaddition reactions, since it determines both the structure of the product formed and its stability. One may conclude that photo-adducts are thermally stable, since, in accordance with the principle of microscopic reversibility, their thermal dissociation is a forbidden process.

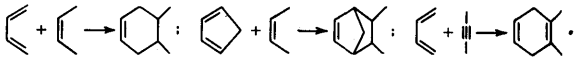
The characteristics of electrocyclisation reactions discovered by Woodward and Hoffmann constitute, in particular, a theoretical justification of Alder's empirical rules[85] for 4 + 2 cycloadditions and are confirmed by very extensive experimental data.

The two most common types of cycloadditions—thermal 4 + 2 and photochemical 2 + 2 processes—as well as their combinations have found the widest applications in the synthesis of tetracarboxylic acids and their functional derivatives.

1. The Diels–Alder Reactions (4 + 2 Cycloaddition Reactions)

The Diels–Alder reaction or diene synthesis involves the addition of olefins or acetylenes (dienophiles) to the

1,4-positions of *cis*-1,3-dienes with formation of unsaturated six-membered cyclic compounds (adducts):



Electron-donating substituents in the diene and particularly electron-accepting substituents in the dienophile facilitate the addition and the latter factor is responsible for the extensive scope of this method in the synthesis of carboxylic acids. Indeed the carboxy-group and its functional derivatives exhibit a powerful electron-accepting effect and $\alpha\beta$-unsaturated acids are active dienophiles. The interaction of compounds containing two diene systems, or compounds capable of their formation, with $\alpha\beta$-unsaturated $\alpha\beta$-dicarboxy-derivatives constitutes a direct method for the synthesis of tetracarboxylic acids and the use of maleic anhydride—one of the most powerful dienophiles—leads directly to the anhydrides.

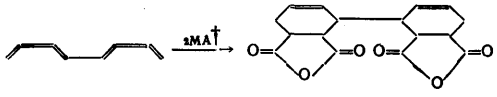
The Diels–Alder reaction can be carried out on a preparative scale without difficulty—by simple mixing of the components, frequently in an inert solvent—and heating to moderate temperatures leads to adducts, as a rule in high yields.

There is no need to discuss the principal characteristics and mechanism of the diene synthesis, since these problems have been considered in many monographs [85-87] and reviews [88,89]. We shall mention only one very important factor: the Diels–Alder reaction is a reversible process and elevated temperatures favour the dissociation of the adducts into the initial components (the retrodiene synthesis).

However, there are several procedures whereby one can synthesise adducts incapable of the retrodiene synthesis or requiring for dissociation temperatures at which single carbon–carbon bonds are ruptured.

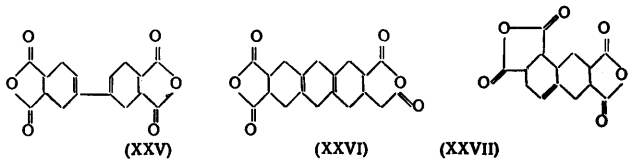
The first of these is based on the fact that the greater the energy gain on conversion of the initial compounds into the adducts the higher the temperature at which the adduct undergoes the retrodiene synthesis. Hence follows the practically important conclusion that open-chain bisdiene adducts should decompose at fairly high temperatures. Indeed acyclic bisdienes are involved in cycloaddition in a thermodynamically unstable conformation with pairs of cisoid double bonds, and their adducts are substituted cyclohexene structures with minimal Baeyer strain.

This conclusion has been confirmed experimentally. Octa-1,3,5,7-tetraene forms with maleic anhydride an adduct (XXIV) in almost quantitative yield, having a decomposition temperature in excess of 280°C: [90]



(XXIV)

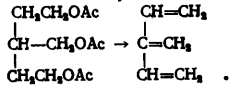
The dianhydrides (XXV)–(XXVII) also melt without decomposition at temperatures comparable to the melting points of their aromatic analogues [91-93]:



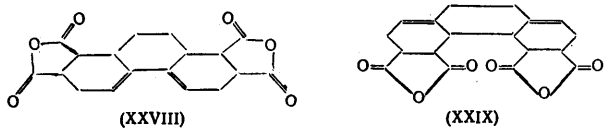
(XXV) (XXVI) (XXVII)

† In the formulae MA denotes maleic anhydride.

The starting compounds for the synthesis of these bisadducts are tri- and tetra-enes obtained by a general method—the pyrolysis of acetyl derivatives of tri- and tetra-hydric alcohols at 550°, for example:



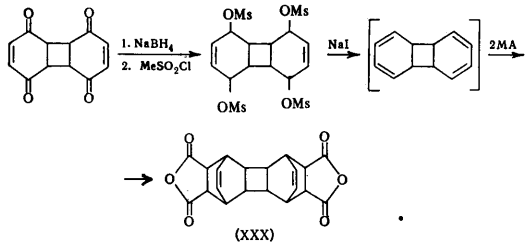
Thermal isomerisation of cyclodeca-1,2,6,7-tetraene yielded 2,3-divinylcyclohexa-1,3-diene, which combined with two molecules of maleic anhydride to form the dianhydride (XXVIII). [94] In the presence of an excess of the dienophile, compound (XXVIII) forms a trianhydride:



(XXVIII) (XXIX)

Similarly 1,4-divinylcyclohexa-1,3-diene (obtained from 1,4-diethynylcyclohexane-1,4-diol) yields the dianhydride (XXIX). [95]

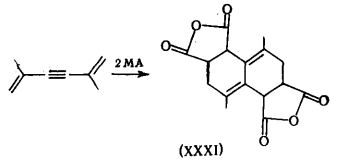
Sometimes the difference between the thermodynamic stabilities of the diene and the adduct is so great that even with cyclic bisdienes the equilibrium in the diene synthesis reaction is completely displaced to the right. Thus the tetramethylsulphonate of the reduced photo-dimer of *p*-benzoquinone yields the dianhydride (XXX) on treatment with sodium iodide in the presence of maleic anhydride, but the corresponding bisdiene cannot be isolated [96]:



(XXX)

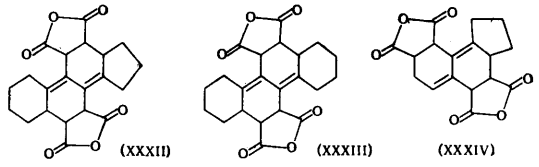
Compound (XIX) does not melt up to 360°C and sublimes without decomposition at 250°.

There is a method of synthesising dianhydrides involving the addition of two molecules of the dienophile to substituted 1,5-dien-3-ynes [97]. For example, 2,5-dimethylhexa-1,5-dien-3-yne yields the dianhydride of hexahydronaphthalenetetracarboxylic acid (XXXI): [98]



(XXXI)

Dienynes in which one or both double bonds are in cyclic systems are also reactive in this reaction. Thus cyclohex-1-en-ylcyclopent-1-enylacetylene, di(cyclohex-1-enyl)acetylene, and cyclopent-1-enylisopropenylacetylene form with two molecules of maleic anhydride the bisadducts (XXXII)–(XXXIV) [99-101] having decomposition temperatures in excess of 260°C:

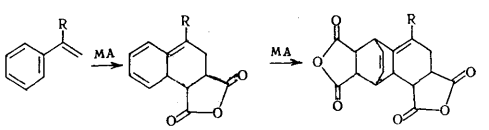


(XXXII) (XXXIII) (XXXIV)

The addition of dienophiles to 1,5-diene-3-ynes differs from the reactions of bisdienes enumerated above by the fact that in this case the adduct is formed with simultaneous addition of two dienophile molecules to the diene, i.e. via a trimolecular reaction.

In assessing the method of synthesis of dianhydrides involving open-chain bisdienes, one should note that it suffers from a fundamental deficiency—the difficulty of obtaining the starting compounds. The achievement of a high thermal stability of the bisadducts requires in this instance thermodynamically unstable bisdienes, i.e. the very principle of the method is responsible for the difficulty of synthesising the initial compounds on a preparative scale. As a rule, acyclic bisdienes are obtained by multistage procedures with very low yields of the final products. For example, in the pyrolysis of acetates, the yield of bisdienes does not exceed 5–15% and dienynes are obtained in a yield of 10–30%.

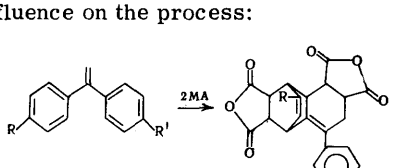
The method of synthesising the dianhydrides by the Wagner–Jauregg reaction [102], in which substituted styrenes or 1,1-diarylethylenes are employed as the bisdienes, is free from this disadvantage. In the first stage, a molecule of maleic anhydride is added to a system including an exocyclic double bond and the π electrons of the α- and β-carbon atoms of the aromatic ring with formation of the adduct (XXXV). The addition of a second molecule of the dienophile to the newly formed diene system leads to the dianhydride (XXXVI): [103]



(XXXV) (XXXVI)

Although, owing to its tendency towards polymerisation, styrene itself gives low yields of adducts by this reaction [104], its α-substituted analogues form adducts in yields of 90%, particularly in the presence of polymerisation inhibitors. Many dianhydrides having the general formula (XXXVI) with R = alkyl, halogen, phenyl, naphthyl, etc., melting at 220–300°C, have been synthesised by this method [103,105,106]. β-substituted styrenes do not form bisadducts as a rule [106].

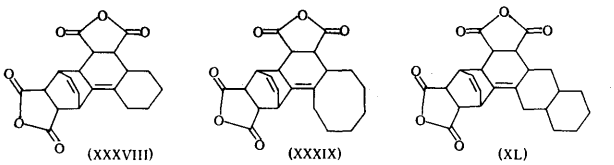
The efficiency of cycloaddition is appreciably influenced by the electronic nature of the substituents in the *para*-position of the aromatic ring. It has been shown [107] that electron-donating substituents, particularly the methoxy-group, facilitate the reaction, while electron-accepting substituents frequently make the reaction impossible, as has been observed also in other Diels–Alder reactions. Substituents in the *meta*-position hardly affect the course of the reaction, and *ortho*-derivatives are usually inactive owing to the steric hindrance to the planarity of the system. Substituents in the aromatic ring of 1,1-diarylethylenes not involved in the diene synthesis have a similar influence on the process:



(XXXVII)

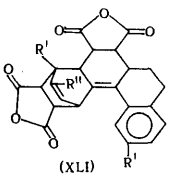
Thus the yield of the dianhydrides (XXXVII) varies from 22% for the difluoro-derivatives to 90% for the di-t-butyl analogue, while the melting point varies in the opposite sense: from 350° to 240°C respectively.

Arylcyclenes—compounds with a double bond in a partly hydrogenated ring—are also reactive in the Wagner-Jauregg reaction [108,109]. For example cyclohex-1-enylbenzene, cyclo-oct-1-enylbenzene, and 2-phenyl-Δ^2-octahydronaphthalene form the adducts (XXXVIII)–(XL) respectively in high yields:



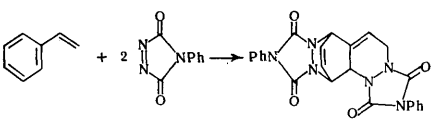
(XXXVIII) (XXXIX) (XL)

A number of substituted dianhydrides (XLI) based on 1-phenyl-3,4-dihydronaphthalene, where R, R′, and R″ are combinations of H, CH_3, C_6H_5, Cl, and OCH_3 groups, with melting points up to 300°C, have also been synthesised [108].



(XLI)

The use of a more powerful dienophile—4-phenyl-1,2,4-triazoline-3,5-dione—made it possible to obtain the bisadduct (XLII) by the reaction with styrene [110]:



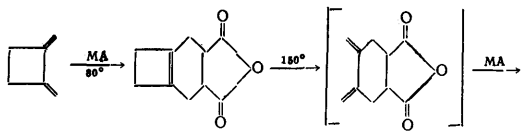
(XLII)

Since all the dianhydrides obtained by the Wagner-Jauregg reaction have a sterically strained tricyclic structure, they split off smoothly one dienophile molecule above the melting point. However, the melting points of the bisadducts reach 350°C and the decomposition temperatures are comparable to the temperatures at which carbon–carbon single bonds are ruptured, which, together with the ready availability of the initial compounds and the high yield of the desired products, suggests that the method is of practical value.

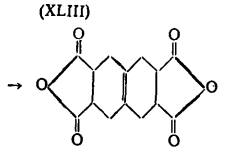
All the procedures for the application of the 1,4-addition reaction in the synthesis of tetracarboxylic acids enumerated above involve a reversible adduct formation stage. On the other hand, there is a fundamentally different type of Diels–Alder reaction in which, simultaneously with the addition of the dienophile to the diene, the adduct undergoes irreversible changes, in relation to the initial diene, associated with the rupture of chemical bonds.

For example, 1,2-dimethylcyclobutane, obtained by the dimerisation of allene, gives the adduct (XLIII) in 94% yield on refluxing with maleic anhydride in benzene. When the temperature is raised to 150°C, a bond in the cyclobutane ring of (XLIII) is cleaved with formation of a diene

system the addition of a dienophile to which gives rise to the dianhydride (XLIV):[111]

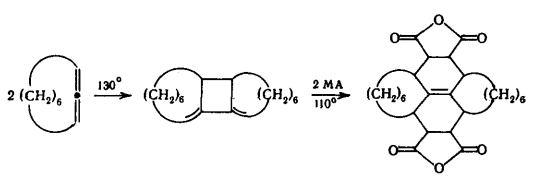


(XLIII)



(XLIV)

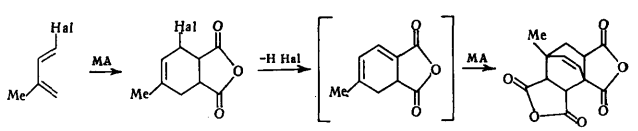
A similar procedure has been used[94] to synthesise the dianhydride (XLV), which melts without decomposition above 300°C:



(XLV)

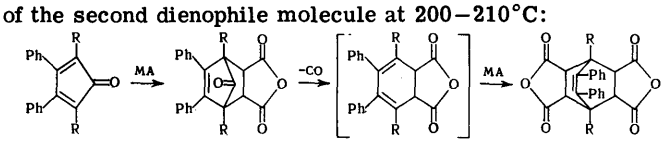
However, irreversible Diels–Alder reactions are usually accompanied by the abstraction of volatile substances from the intermediate.

A method has been suggested[112] for the synthesis of the adduct (XLVI) using 1-halogeno-3-methylbuta-1,3-dienes (obtained from ethynyldimethylmethanol) as the bisdienes. Compound (XLVI) is obtained in an exothermic reaction with liberation of the hydrogen halide:



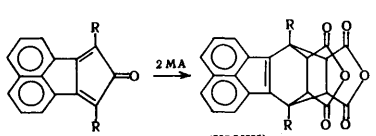
(XLVI)

Reactions are also known in which carbon monoxide is split off from the intermediate adduct. These reactions involve the use of cyclopentadienones (cyclones) as the dienes. 3,4-Diphenylcyclones, formed on dehydration of anhydroacetone benzils, are the most suitable for this purpose. The bisadducts (XLVII, R and R′ = H or alkyl) are formed in quantiative yields[113–116]. The decarbonylation is as a rule carried out with the simultaneous addition of the second dienophile molecule at 200–210°C:



(XLVII)

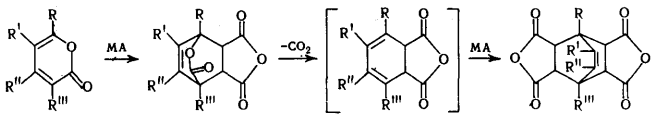
Condensed cyclones react similarly; for example an acecyclone yields the dianhydride (XLVIII, R = methyl or n-hexyl)[117]:



(XLVIII)

Dianhydrides of a similar type are also formed when α-pyrones or coumalins, the adducts of which split off a carbon dioxide molecule, are employed as the bisdienes[118].

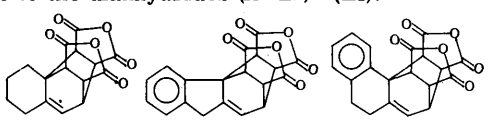
The reaction proceeds via the mechanism



(XLVII)

The synthesis of a whole series of alkyl- and phenyl-substituted derivatives (XLVII) has been described by Shusherina and coworkers[119,120]. The preparation of the perchloro-1,4-diphenyl derivative of (XLVII) and also the continuous method for the synthesis of the dianhydride of bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic acid (XLVII, all R = H) in 99% yield have been patented[121–123].

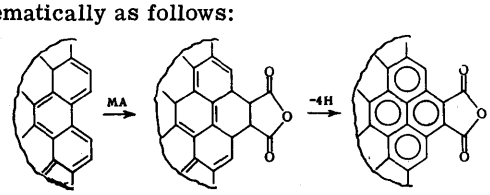
Dianhydrides with decomposition temperatures in excess of 300°C, obtained on the basis of condensed coumalins, are also known. Thus 5,6-dicyclohexano- and 5,6-indeno-α-pyrones and 7,8-benzo-5,6-dihydrocoumarin give rise to the dianhydrides (XLIX)–(LI):[124]



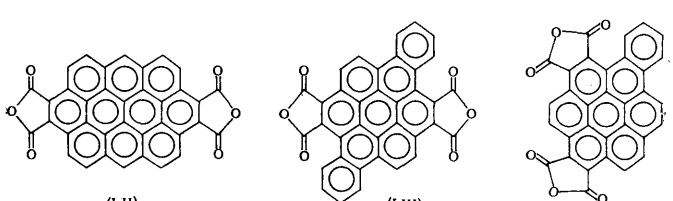
(XLIX) (L) (LI)

Adducts of type (XLVII) decompose above the melting point with liberation of maleic anhydride, i.e. reactions of this type are not strictly speaking irreversible. However, the dissociation reaction occurs at 320–350°C and is accompanied by the decomposition of the product by other mechanisms too.

Clar[125] developed a method for the synthesis of dianhydrides involving the addition of maleic anhydride to polycyclic aromatic structures with simultaneous dehydration of the adducts formed. The method can be represented schematically as follows:



The dehydrogenation is carried out either with chloranil added to the melt of the components or by refluxing the substances to be added in an active solvent—nitrobenzene. Dianhydrides based on bisanthene, 2,3:8,9-dibenzoperylene, 1,2:4,5-dibenzopyrene, 1,2:4,5:8,9-tribenzopyrene, and di-*peri*-naphthyleneanthracene have been obtained by this method—for example the dianhydrides (LII)–(LIV):[126–129]



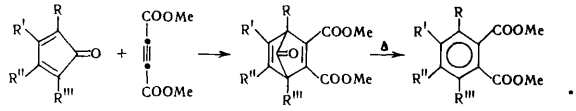
(LII) (LIII) (LIV)

This method is so far of purely theoretical importance, since the initial bisdienes are very difficult to obtain and most of them are very active carcinogens.

All the methods of preparation of tetracarboxylic acids by the Diels–Alder reaction known hitherto lead to products with hydroaromatic or bicyclic structures. On the

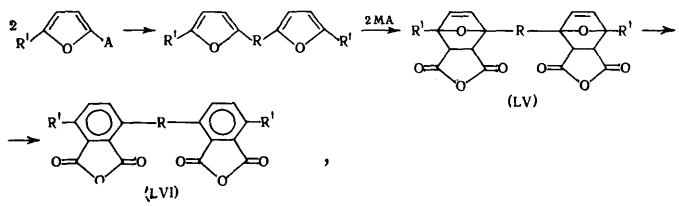
other hand, aromatic acids are necessary for the main applications of tetracarboxylic acids—the synthesis of thermostable polymers and dyes.

Certain types of monoadducts obtained in the 1,4-cycloaddition reaction propagated by thermal or chemical factors are known [85] to undergo a rearrangement into aromatic structures. For example, the adducts of dimethyl acetylenedicarboxylate and cyclones split off a carbon monoxide molecule on heating and form phthalic acid esters:

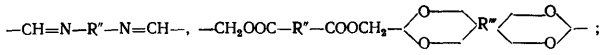


Adducts of coumalins with acetylenes, of furans with maleic anhydride, and certain others are also capable of aromatisation.

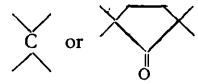
The authors of the present review [130-136] developed a method for the synthesis of tetracarboxylic acids the main idea of which involves the aromatisation of the adducts of maleic anhydride with bisfuran compounds via the general mechanism



where A is a functional group or a hydrogen atom, R = arylene,



R′ = aryl (for example phenyl) or a hydrogen atom,
R″ = arylene (*p*-phenylene, *pp*′-diphenylene, and others),

and R‴ =  .

The use of bisfuran compounds in these reactions has many advantages. Firstly, the furan ring is a fairly reactive diene in reactions with maleic anhydride and forms stable adducts in yields of 90–95%. Secondly, the synthesis of compounds containing two furan rings can be readily achieved with a high yield when readily available and cheap functional derivatives of furan are employed: furfural, furfuryl alcohol, furancarboxylic acids, etc.

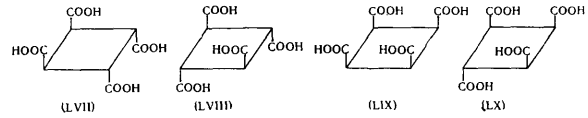
Bisfuran compounds have been obtained by the decomposition of diazonium salts in furan, by the reaction of furfural with aromatic amines or tetramethoxy-derivatives, for example pentaerythritol, and by the reaction of furfuryl alcohol with aromatic dicarboxylic acid esters.

The reactions of bisfuran with maleic anhydride occur at a temperature as low as 25°C and compound (LV) is formed in a quantitative yield. The aromatisation of (LV) to (LVI) takes place in concentrated sulphuric acid at temperatures below 0°C, in polyphophoric acid at 25 to 50°C, or when acted upon by gaseous hydrogen chloride or by hydrogen bromide in glacial acetic acid.

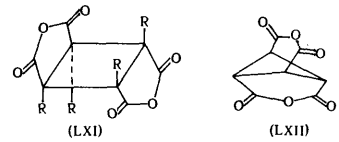
The use of α-phenylfuran or 5-phenylfurfural in the above reactions makes it possible to obtain tetracarboxylic acids with phenyl substituents in the ring of the phthalic acid group.

2. 2 + 2 Photocycloaddition Reactions

Until recently the application of the 2 + 2 photoaddition method for the synthesis of tetracarboxylic acids was restricted to the dimerisation of dimethyl fumarate and maleic anhydride and of their substituted analogues to form cyclobutane-1,2,3,4-tetracarboxylic acids. Among the four isomers of this acid, (LVII)–(LX), the first three are capable of forming the dianhydride and by virtue of this method all are known:

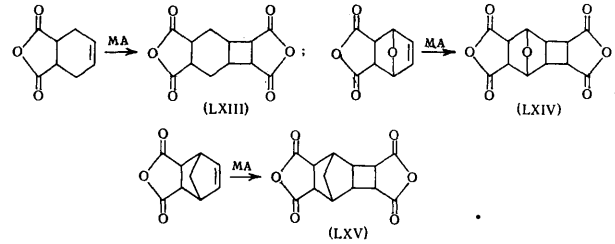


Irradiation at 253 nm of dimethyl fumarate in the solid phase, usually in the presence of a sensitiser, leads to the tetramethyl ester of (LVII) in the course of 7–8 days, which isomerises at 300°C to the thermodynamically more stable ester of (LVIII). [137] The hydrolysis of the esters and subsequent dehydration lead to the corresponding dianhydrides (LXI) and (LXII). [138] The dianhydride of the acid (LIX) was obtained by the ozonolysis of the acenaphthene dimer [76]. Irradiation of maleic anhydride under the same conditions leads directly [139] to compound (LXI, R = H):



The method is applicable also to methyl-, dimethyl-, and diphenyl-maleic anhydrides [139,140]. In this case, the reaction proceeds more readily. Dimethylmaleic anhydride dimerises to compound (LXI, R = CH_3) in 60% yield over a period of 6 h and the dimer (LXI, R = C_6H_5) is formed in a quantitative yield when the monomer is merely exposed to sunlight.

The scope of the 2 + 2 cycloaddition method was greatly extended recently in relation to the formation of dianhydrides [141]. The sensitised addition of maleic anhydride to tetrahydrophthalic anhydride and its 1,4-*endo*-*exo*- and 1,4-*endo*-methano-derivatives leads to the dianhydrides (LXIII)–(LXV):



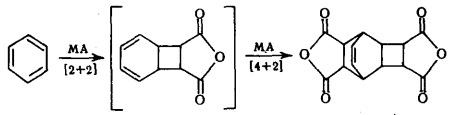
This method is particularly valuable because the initial compounds are very readily available—they are adducts obtained in the Diels–Alder reaction between maleic anhydride on the one hand and butadiene, furan, and cyclopentadiene on the other. Thus there is a possibility of using for the synthesis of dianhydrides a whole class of compounds—maleic anhydride monoadducts. The yield of compounds (LXIII)–(LXV) reaches 30–35%. [142]

The high thermal stability of the 2 + 2 photocycloaddition adducts is striking, this incidentally being in full agreement with theoretical postulates. Thus the dimer

of diphenylmaleic anhydride melts without decomposition at 325°C, the dianhydride of tetramethylcyclobutanetetracarboxylic acid decomposes above 350°C, and the adduct (LXIV) has a very high decomposition temperature for non-aromatic compounds (410°C, on fusion).

3. Successive 2 + 2 and 4 + 2 Cycloaddition Reactions

Irradiation of maleic anhydride solutions in benzene leads to the formation of a 2:1 adduct which has the structure of the dianhydride of tricyclo[4,2,2,$0^{2,5}$]dec-7-ene-3,4,9,10-tetracarboxylic acid (LXVI) according to chemical and physical data [143-145]. Since thermal 2 + 2 addition reactions are forbidden on symmetry grounds and benzene does not react with maleic anhydride in the dark even under very severe conditions, a process mechanism involving successive 2 + 2 and 4 + 2 cycloadditions was proposed [144]:



(LXVI)

It has been shown [144,146] that maleic anhydride and benzene form a charge-transfer complex absorbing in the range 230–280 nm, where the photochemical reaction takes place. Irradiation in the non-sensitised process activates the charge-transfer complex and not the species to be added, the activated intermediate being insensitive to oxygen, since it is in a singlet state [147]. Cycloaddition sensitised by aromatic ketones, for example benzophenone, involves energy transfer from benzophenone in the triplet state to the charge-transfer complex. The sensitised mechanism of the intermolecular energy transfer is more effective, although the sensitiser inhibits the reaction involving the non-sensitised addition mechanism. Acetone also behaves as a sensitiser and in addition plays the role of an active solvent [148].

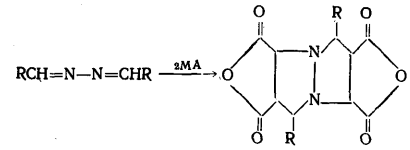
Apart from maleic anhydride, maleimide and its n-alkyl derivatives are capable of reacting with benzene. Among the *N*-aryl derivatives only those are involved in the reaction where the substituent at the nitrogen atom is not coplanar with the remainder of the molecule, for example the benzyl, *o*-tolyl, and 2,6-xylyl derivatives [149].

Many mono- and poly-substituted benzenes, naphthalene, and biphenylene have been employed as the aromatic component. In this group of compounds only monoalkyl- (methyl, ethyl, isopropyl, t-butyl, and C_3–C_{13} n-alkyl) and monohalogeno-benzenes, *o*- and *p*-xylenes, and biphenyl proved to be reactive [150-152]. All the substituents lower the rate of sensitised addition of maleic anhydride and the yield of products. If the rate of reaction of benzene is adopted as unity, then the rates are 0.5 for toluene, 0.25 for t-butylbenzene and chlorobenzene, 0.12 for biphenyl, 0.15 for *o*-xylene, and 0.08 for *p*-xylene [152].

From the practical point of view, the adduct of benzene and maleic anhydride is of greatest interest: it is obtained in the highest yield (70%) and has the highest melting point (350°C).

4. 1,3-Cycloaddition Reactions

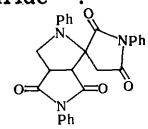
In view of the small number of examples of the application of this method for the synthesis of tetracarboxylic acids, we did not devote a separate section to reactions of this type, although the principle and mechanism of the 1,3-cycloaddition process are very different from those of the reaction discussed above. Haring and Wagner-Jauregg [153] showed that azines react with maleic anhydride via a 1,3-addition mechanism with formation of the dianhydrides (LXVII), in which R = H, phenyl, 2-furyl, *p*-chlorophenyl, *p*-methoxyphenyl, etc.:



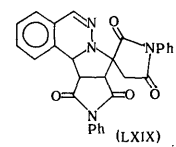
(LXVII)

When bismaleimides are employed instead of maleic anhydride, the azines can form polyimides [154].

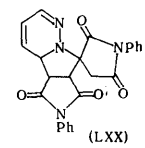
Schiff bases are also reactive in dipolar addition reactions with many maleic acid derivatives. Benzylidenemethylamine reacts with *N*-phenylmaleimide to form the spiroadduct (LXVIII) [155] via an intermediate azomethinylide [156]. Similarly phthalazine and pyridazine form the 1:2 adducts (LXIX) and (LXX) with maleimide in very high yields [157], although previously a structure with condensed rings was proposed for the adduct of pyrazine and maleic anhydride [158]:



(LXVIII)

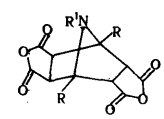


(LXIX)



(LXX)

Functional derivatives of tetracarboxylic acid (LXXI) with R = phenyl or *p*-methoxyphenyl and R′ = H or methyl were also obtained by the reaction of maleic anhydride or maleimides with azlactones or mesoionic azlactones—2,4-diphenyl-5-oxazolone, *N*-(*p*-methoxybenzyl)phenylglycine, and anhydro-5-hydroxy-3-methyl-2,4-diphenyloxazolium hydroxide [159]. The reaction is carried out by 1,4-cycloaddition methods and the products are obtained in an almost quantitative yield.



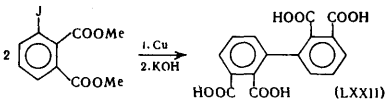
(LXXI)

IV. CONDENSATION OF DICARBOXYLIC ACIDS AND THEIR DERIVATIVES

The methods of synthesising tetracarboxylic acids discussed in this section cannot strictly speaking be combined in a general group, since they involve the employment of a very great variety of reactions. However, in view of the general idea underlying these reactions—the employment of chemical transformations of dicarboxylic acids for the preparation of tetracarboxy-derivatives—we separated these procedures from section V below.

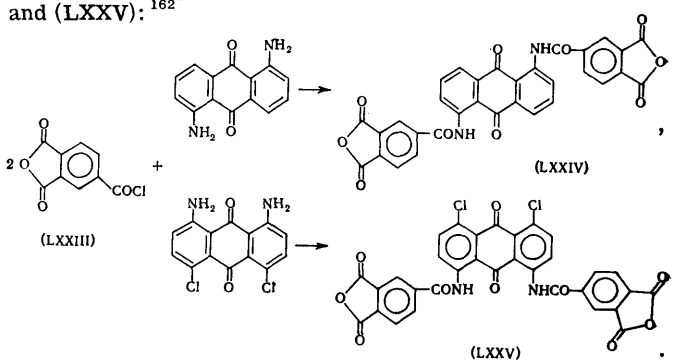
Reactions involving substituted phthalic acids are most often used for the synthesis of tetracarboxylic acids. Thus, when dimethyl 2-iodoisophthalate is heated at 240 to 250°C in the presence of powdered copper, tetramethyl biphenyl-2,2′,6,6′-tetracarboxylate is obtained [160]. The tetraester of biphenyl-2,2′,3,3′-tetracarboxylic acid was synthesised similarly from dimethyl 3-iodophthalate, the

free acid (LXXII) being produced by the hydrolysis of the ester[161]:



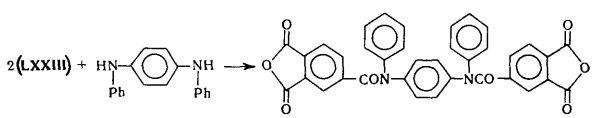
(LXXII)

Many tetracarboxylic acids specially designed for the synthesis of polymers have been obtained from trimellitic acid and its functional derivatives. The reaction of the chloride of the 1,2-anhydride of trimellitic acid (LXXIII) with 1,5-diaminoanthraquinone and 1,8-diamino-4,5-dichloroanthraquinone yielded the dianhydrides (LXXIV) and (LXXV):[162]



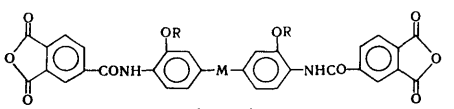
(LXXIII) (LXXIV) (LXXV)

The similar reaction of (LXXIII) with *NN'*-diphenyl-*p*-phenylenediamine leads to the dianhydride (LXXVI):[163]



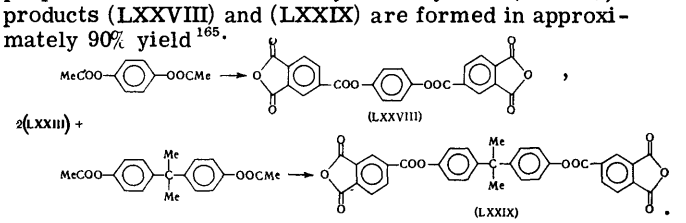
(LXXVI)

Seven dianhydrides with the general formula (LXXVII), in which R = alkyl and M = oxygen atom or a single bond, were obtained by the reaction of (LXXIII) with the hydrochlorides of di-(3-alkoxy-4-aminophenyl) ethers or 3,3'-dialkoxybenzidines[164]:



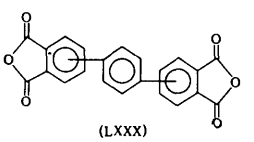
(LXXVII)

When *p*-diacetoxybenzene and 2,2-di-(*p*-acetoxyphenyl)-propane are transesterified by the anhydride (LXXIII), the products (LXXVIII) and (LXXIX) are formed in approximately 90% yield[165].



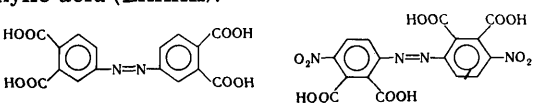
(LXXVIII) (LXXIX)

The reaction of *p*-di(chlorosulpho)benzene with phthalic anhydride has been patented as a method of synthesising a mixture of isomeric dianhydrides of terphenyltetracarboxylic acids (LXXX):[166]



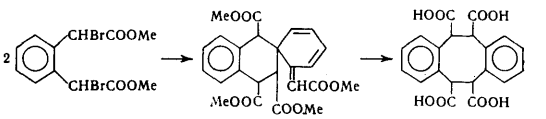
(LXXX)

The reduction of nitrophthalic acids constitutes a very convenient method of synthesising azobisphthalic acids. When *p*-nitrophthalic acid is treated with aluminium powder in an alkaline solution, azobenzene-3,3',4,4'-tetracarboxylic acid (LXXXI) is formed[167]. 3,6-Dinitrophthalic is reduced by glucose in the presence of sodium thiosulphate to 6,6'-dinitroazobenzene-2,2',3,3'-tetracarboxylic acid (LXXXII):[168]



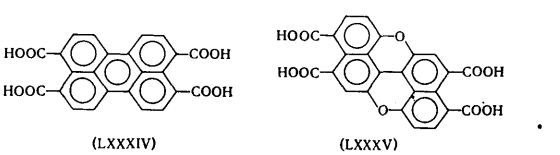
(LXXXI) (LXXXII)

On treatment with sodium iodide in DMF and further heating in boiling xylene, the ester of *o*-phenylenedi-(bromoacetic) acid gives rise to the acid (LXXXIII) after hydrolysis[169]:



(LXXXIII)

Only two examples of the dimerisation of the functional derivatives of naphthalic acid are known, but these reactions lead to very valuable products. By fusing the imide of naphthalic acid with alkalies in the presence of oxygen and subsequent hydrolysis with sulphuric acid, perylene-3,4,9,10-tetracarboxylic acid (LXXXIV) was obtained[170,171] and dehydrogenation of 3-hydroxynaphthalic anhydride in boiling nitrobenzene in the presence of copper(II) chloride yields the dianhydride of perixanthenoxanthene-3,4,8,10-tetracarboxylic acid (LXXXV).[172]



(LXXXIV) (LXXXV)

Certain reactions employed in the dimerisation method, particularly those involving trimellitic anhydride, have attracted attention by their flexibility: they make it possible to obtain many tetracarboxylic acids and their anhydrides with a wide variety of groups linking the anhydride rings. In certain cases this method permits a simplification of the synthesis of the acid.

Moreover its value lies in the fact that it allows one to synthesise compounds which cannot be prepared by other methods, for example azodiphthalic, perylenetetracarboxylic and perixanthenetetracarboxylic acids.

V. SYNTHESIS FROM DERIVATIVES OF ACIDS

Syntheses with malonic ester are very widely used to prepare aliphatic tetracarboxylic acids with both linear and cyclic structures. However, in this case the products are mainly compounds each of which contains two carboxy-groups at the same carbon atom, for example cyclohexane-1,1,3,3-tetracarboxylic acid. Such compounds are outside the scope of the present review.

There remain only a few examples of the synthesis of tetracarboxylic acids capable of forming stable dianhydrides and only the syntheses of ethanetetracarboxylic and ethylenetetracarboxylic acids constitute examples of the classical application of this method, while the preparation of other products involves additional decarboxylation, oxidation, etc. stages.

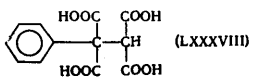
The interaction of bromo- and dibromo-malonic esters with sodium iodide leads to the tetraesters of ethanetetracarboxylic and ethylenetetracarboxylic acids from which the free acids (LXXXVI) and (LXXXVII) were isolated by hydrolysis [173]:

$$2\,CHBr(COOEt)_2 \xrightarrow{2NaI} (EtOOC)_2CHCH(COOEt)_2 \rightarrow (HOOC)_2CHCH(COOH)_2\ ,$$
(LXXXVI)

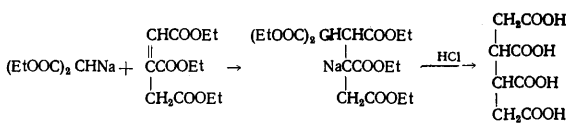
$$2\,CBr_2(COOEt)_2 \xrightarrow{2NaI} (EtOOC)_2C{=}C(COOEt)_2 \rightarrow (HOOC)_2C{=}C(COOH)_2\ .$$
(LXXXVII)

While treatment of compound (LXXXVI) with acetic anhydride leads smoothly to the dianhydride [174], the dianhydride of the acid (LXXXVII) is unstable and has not been isolated in a free state. However, being a powerful dienophile, it readily forms adducts with many dienes at the instant of its formation. Thus treatment of ethylenetetracarboxylic acid with acetyl chloride in the presence of 9,10-dimethoxyanthracene leads to the formation of its adduct with the dianhydride of the acid (LXXXVII). [89]

Treatment of (LXXXVII) with phenylmagnesium bromide yields phenylethane-1,1,2,2-tetracarboxylic acid (LXXXVIII): [175]

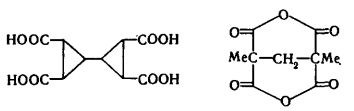

(LXXXVIII)

Butane-1,2,3,4-tetracarboxylic acid (LXXXIX) can be obtained by the reaction of sodiomalonic ester with aconitic acid ester [176,177]:


(LXXXIX)

The synthesis of dicyclopropyl-2,2',3,3'-tetracarboxylic acid (XC) also includes the decarboxylation stage [178]. The reaction of sodiomalonic ester and *trans,trans*-$CH_3OOCCCl{=}CHCH{=}CClCOOCH_3$ in methanol yields the hexamethyl ester of bicyclopropylhexacarboxylic acid, which gives rise to (XC) after hydrolysis and heating to 180°C.

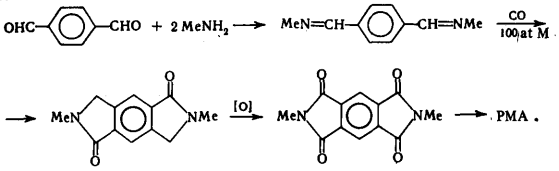
Pentane-1,2,4,5-tetracarboxylic and pentane-2,2,4,4-tetracarboxylic acids, (XCI) and (XCII), are also known. (XCI) has been obtained by the oxidation of the product of the reaction of malonic ester, methylene iodide, and sodium methoxide [179]. On treatment with diphenylketen, (XCII) is converted into the dianhydride (XCIII): [180]


(XC) (XCIII)

VI. SPECIFIC METHODS OF SYNTHESIS

In this section we shall consider methods of preparation of tetracarboxylic acids which are not general. However, all the examples described below satisfy one of three criteria: the method of preparation is specific, but the reaction product is of considerable interest; there is a prospect of further development of the method used at present to synthesise only one product; the method is used to synthesise many products, but the reaction mechanism has not been established.

The reactions involving the direct introduction of the carbonyl group constitute a familiar method of synthesising carboxylic acids, but it is applicable to the synthesis of only one tetracarboxy-compound—pyromellitic acid. A method of preparing pyromellitic acid by adding carbon monoxide to the Schiff base obtained from terephthalic aldehyde and methylamine and subsequent oxidation has been patented [181-183].

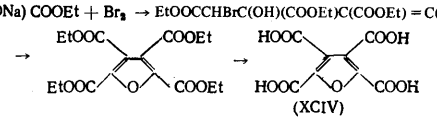


Pyromellitic acid is also formed in 35% yield on heating a mixture of sodium and potassium phthalates with calcium oxide and copper(II) chloride at a carbon dioxide pressure of 25 atm and 450°C. [184]

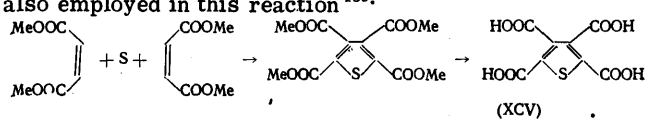
Of the tetracarboxylic acids which have already found practical applications, furan-, thiophen-, and dithiin-tetracarboxylic acids and the dianhydride of 1,2,5,6-bis-($\alpha\beta$-dicarboxypyrazino)anthraquinone were not described in the previous sections.

Furantetracarboxylic acid (XCIV) is formed on ring closure in tetraethyl dioxalylsuccinate—synthesised by treating with bromine the *O*-sodio-derivative of diethyl malate [185,186]. It has been shown [187] that the aldol $C_2H_5OOCCHBrC(OH)(COOC_2H_5)C(COOC_2H_5){=}C(ONa)COOC_2H_5$ is formed as an intermediate, splitting off subsequently NaBr and water with formation of (XCIV):

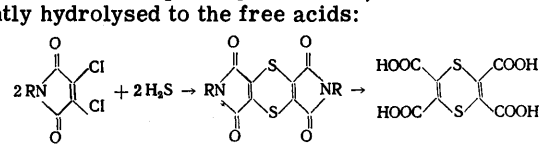
$$EtOOCCH{=}C(ONa)COOEt + Br_2 \rightarrow EtOOCCHBrC(OH)(COOEt)C(COOEt){=}C(ON_2)COOEt \rightarrow$$


(XCIV)

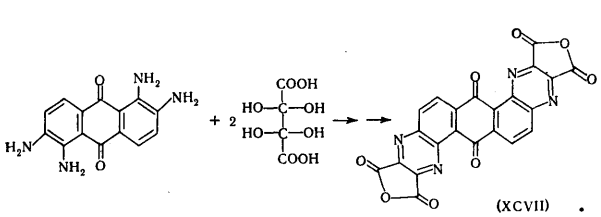
Thiophentetracarboxylic acid (XCV) was obtained initially by treating dimethyl acetylenedicarboxylate with sulphur [188] and later dimethylfumarate and maleate were also employed in this reaction [189].


(XCV)

Similar cyclisation reactions have been used to synthesise dithiintetracarboxylic acid (XCVI). [190] The interaction of dichloromaleimide with hydrogen sulphide or thiourea leads to the corresponding di-imides, which are subsequently hydrolysed to the free acids:

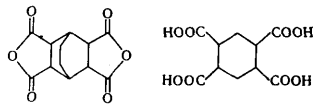

(XCVI)

The condensation of 1,2,5,6-tetra-aminoanthraquinone with dihydroxytartaric acid leads to 1,2,5,6-bis($\alpha\beta$-dicarboxypyrazino)anthraquinone, which cyclises to the anhydride (XCVII) on refluxing in acetic anhydride [191]:


(XCVII)

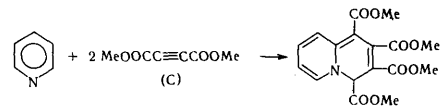
The dianhydride (XCVIII), which has a very high thermal stability, was obtained [192] by oxidising the adduct of dimethyl acetylenedicarboxylate and 7,8-diacetylbicyclo[4,2,0]octa-2,4-diene—the product of the intramolecular cyclisation of cyclo-octatetraene.

The Michael reaction has been used to synthesise a tetracarboxylic acid. The dehydrobromination product of trimethyl 1-bromopropane-1,1,2-tricarboxylate yields on treatment with sodium methoxide in methanol the hexamethyl ester of cyclohexane-1,1,2,4,4,5-hexacarboxylic acid, which is decarboxylated to cyclohexane-1,2,4,5-tetracarboxylic acid (XCIX) on refluxing with concentrated hydrochloric acid [193]:



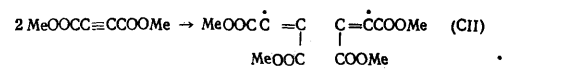
(XCVIII) (XCIX)

The adducts of pyridine with dimethyl acetylenedicarboxylate (C) [195,196] constitute a whole class of heteroaromatic tetracarboxylic acids, the first example of which was obtained by Diels [194]. Formally the reaction consists in the addition of two molecules of (C) to one molecule of pyridine with formation of the adduct (CI):



(C) (CI)

Diels proposed a mechanism for the process involving the formation of a dimer (C):



Next compound (CII) attacks the nitrogen atom of pyridine via the positively charged centres and the intermediate is cyclised. If this mechanism were confirmed, the reaction could be classified as an example of diene synthesis, albeit of an unusual type. However, compound (CII) has not been detected by either chemical or spectroscopic methods. It is only known that the reaction at 20°C gives rise to 9*H*-quinolizine, which on heating isomerises quantitatively to the thermodynamically more stable 4*H*-isomer.

Many tetracarboxy-compounds based on substituted pyridines as well as quinoline, isoquinoline, acridine, and phenanthridine have been synthesised by this method. The tetramethyl esters are normally hydrolysed to the free acids, but the preparation of the dianhydrides has not been described.

VII. PRINCIPAL APPLICATIONS OF TETRACARBOXYLIC ACIDS

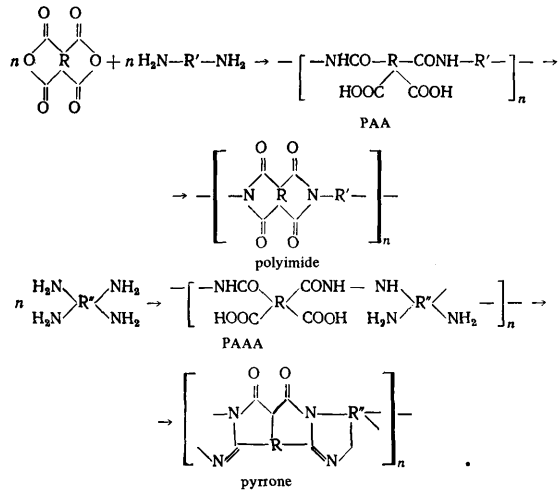
The first practical application of tetracarboxylic acids was discovered in the synthesis of dyes. The principal advances in this field are associated with the employment of the products of the condensation of naphthalene-1,4,5,8-tetracarboxylic acid and its substituted derivatives with aromatic *peri*- or *o*-diamines. The best known are Indanthren Bordeaux RR, Indanthren Brilliant Orange GR, and Indanthren Scarlet GG, which are respectively the *cis*- and *trans*-isomers of naphthoylenebisbenzimidazole and their mixture. These dyes are very stable, brillant, and have attractive tints [5].

Initially aroyleneimidazole dyes were used in vat-dying but in recent years they attracted considerable interest as disperse dyes for the dyeing of artificial fibres and Indanthren Scarlet GG and Indanthren Bordeaux RR were used to dye cotton.

Many dyes have been obtained on the basis of perylenetetracarboxylic acid (mainly di-imides) [197–199] and pyromellitic acid (benzoylenebisbenzimidazoles) [200].

The reactions of the dianhydrides of tetracarboxylic acids with diamines have been used to synthesise polyimides and the products of their reaction with *peri*-, *peri*- or *ortho*-, and *ortho*-tetramines are poly(aroylenebisbenzimidazoles) (pyrrones).

The polymers are formed via intermediate polyamidoacids (PAA) or polyaminoamidoacids (PAAA), which are then subjected to intramolecular cyclisation [1,2]:



The prepolymers (polyamidoacids, or polyaminoamidoacids), are made into articles by a two-stage method and are then subjected to solid-phase dehydration. In the one-stage method the mixture of components is heated to approximately 200°C in polyphosphoric acid or another solvent promoting dehydration, the intramolecular cyclisation processes being largely complete in the polymer isolated.

In the present review there is no need for a detailed analysis of the influence of the structure of the initial tetracarboxylic acid on the properties of the polymers, since these problems were discussed previously [1,2]. We shall only mention certain important characteristics.

The number of atoms in the anhydride rings of tetracarboxylic acids greatly influences the properties of the resulting polymers. This is due to the fact that the thermal stability and also many physicomechanical properties of polyimides and pyrrones are determined by the degree of completion of the intramolecular cyclisation processes. As stated above, in cyclisation the number of atoms in the resulting heterocycle is the same as in the initial dianhydride and therefore the degree of cyclisation in polymers based on six-membered dianhydrides, for example the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid, is higher and the resulting heterocycles are more stable than in the synthesis where five-membered dianhydrides, for example pyromellitic dianhydride, are employed [201–203].

The majority of polyimides and pyrrones have been obtained from aromatic dianhydrides and aromatic diamines or tetramines. Powerful intramolecular interactions,

which have a favourable effect on the thermal stability of the polymers but at the same time give rise to a poor solubility and absence of fluidity up to the decomposition temperature, are characteristics of such structures. It is fairly difficult and sometimes impossible to make such polymers into articles, so that usually one employs a two-stage method of synthesis with isolation of a soluble prepolymer, although this procedure suffers from a number of fundamental disadvantages [204]. On the other hand, it is known [204,205] that the introduction of bulky side groups into the polymer chain prevents close packing of the macromolecules and improves the solubility of the polymer. The employment of this procedure in the synthesis of polyimides and pyrrones, involving the use of the dianhydrides of aromatic tetracarboxylic acids containing phenyl, naphthyl, phthalide, fluorene, and other groups as substituents, permitted the synthesis of polymers capable of being made into articles when dissolved in organic solvents [206,207] without an appreciable decrease of their thermal stability.

Many methods of synthesising tetracarboxylic acids have been devised specially in order to obtain the starting compounds for the synthesis of polyimides and pyrrones. One may quote as examples the method for the preparation of adducts of maleic anhydride with caccyclones or coumalins [208], bisfuran derivatives [209], and benzene and its derivatives [210-212], the photoadducts with tetrahydrophthalic acids [3], and almost all the tetracarboxylic acids obtained by the oxidation of organic compounds and the condensation of dicarboxylic acids.

In the majority of studies dealing with the synthesis of new tetracarboxylic acids, it was stated that their dianhydrides were intended for the hardening of epoxy-resins and the preparation of plasticisers—the products of condensation with alcohols—in addition to the synthesis of polymers. However, few data have been quoted on the reactivity of the dianhydrides in these reactions and on the properties of the products.

Pyromellitic dianhydride is known [4] to be sparingly soluble in epoxy-resins and gel-formation takes place before complete dissolution of the dianhydride. On the other hand, a method has been discovered for the hardening of epoxides by the dianhydride of benzoquinonetetracarboxylic acid and its alkyl derivatives [213], whereby it is possible to raise the temperature of the onset of deformation to 288°C. The photoadducts of maleic anhydrides with ethylbenzene, cumene, and branched C_5–C_6 alkylbenzenes are highly compatible with epoxy-resins and the hardened products have very satisfactory mechanical properties, particularly at elevated temperatures [214].

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