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Mono- and Bis-α-diketones and Related Polymers

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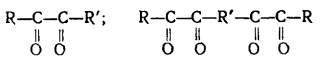
Published information on the methods of preparation and the reactions of mono- and bis-α-diketone is reviewed. Special attention is paid to use of the latter to obtain heat-resistant and thermostable polymers, in particular polyphenylquinoxalines. A list of 201 references is included.

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I. INTRODUCTION

The past decade has witnessed appreciable heightening of interest in mono- and bis-α-dicarbonyl compounds of general types



(where R and R′ represent aliphatic or aromatic groups), which are finding ever wider application in organic synthesis in virtue of their high reactivity. Such compounds provide a basis for obtaining aliphatic, aromatic, and heterocyclic products, whether of low or high molecular weight, possessing several valuable properties. Previous reviews[1-3] have paid insufficient attention to methods for the preparation of α-diketones, and have completely disregarded their chemical reactions and practical application. The present Review aims to fill this gap, paying special attention to methods of preparation that have already found or may find application in obtaining bis-α-dicarbonyl compounds, and also to the use of the latter in the synthesis of thermostable high polymers. Although compounds containing α-diketone groupings are mainly considered, methods of obtaining α-keto-aldehydes and polymers based on them are also included.

II. METHODS OF PREPARATION OF α-DIKETONES

Existing methods for preparing α-diketones can be separated into the following main groups—(1) oxidation of acyloins, (2) oxidation of α-methylene-carbonyl compounds, (3) oxidation of compounds containing carbon–carbon multiple bonds, and (4) other methods.

1. Oxidation of Acyloins

The first observations indicating that benzoin could be oxidised by nitric acid to benzil were made more than a century ago by Zinin[4]. Since then the reaction conditions and the oxidising agents have been varied. The most widely used oxidants have been copper(II) salts, applied in the presence of regenerating agents (air, ammonium nitrate): e.g.[5]

$$RCH(OH)COR' + 2\,Cu(OAc)_2 \rightarrow RCOCOR' + 2\,CuOAc + 2\,AcOH\ ,$$
$$2\,CuOAc + NH_4NO_3 + AcOH \rightarrow 2\,Cu(OAc)_2 + NH_4NO_2 + H_2O\ ,$$
$$NH_4NO_2 \xrightarrow{H^+} N_2 + 2H_2O\ .$$

Acetic acid not only acts as solvent but also favours decomposition of the ammonium nitrite formed in the regeneration of copper(II). The yield of α-diketones is often nearly theoretical. This reaction is specific to acyloins, for benzaldehyde, benzhydrol, and mandelic acid are not oxidised under these conditions[5].

Table 1. Characteristics of α-diketones from acyloins.

α-Diketone	Yield, %	M.p., °C	Ref.
(*a*) Oxidation by Cu^{II} sulphate in pyridine			
Benzil	86-97	94.5	6
o-Methoxybenzil	60	71-72	7
p-Methoxybenzil	68	64-65	7
o-Ethoxybenzil	60	101-102	7
oo′-Diethoxybenzil	50	157-158	7
pp′-Diphenylbenzil	95	141-142	8,9
(*b*) Oxidation by Cu^{II} acetate in acetic acid*			
Hexane-3,4-dione	70	32-35 (10)	10
2,7-Dimethyloctane-4,5-dione	70	67-70 (12)	11
Cyclodecane-1,2-dione	89	104-106 (10)	12
Cyclononane-1,2-dione	67-72	80-82 (3)	13
(*c*) Oxidation by Cu^{II} salts with NH_4NO_3 in acetic acid			
Benzil	100	95	5
pp′-Dimethoxybenzil	97	132	5
2,2′,3,3′-Tetramethoxybenzil	98	146	5
2,2′-Furil	91	165	5
oo′-Dichlorobenzil	55	132	14
Diphenanthr-9-yl diketone	90	283	15
Phenyl thien-2-yl diketone	93	59-69	16
p-Dimethylaminophenyl pyrid-3-yl diketone	40	132-133	17
p-Hydroxyphenyl pyrid-3-yl diketone	66	178	17

*Boiling points given (*p*, mmHg).

Table 1 gives some data on α-diketones obtained by oxidising acyloins with salts of bivalent copper[5-17]. Salts of tervalent iron can also be used for this purpose[10,18-20].

2. Oxidation of α-Methylene-carbonyl Compounds

In 1932 Riley et al.[21] first showed that selenium dioxide is a specific reagent for oxidising a methylene-carbonyl group to dicarbonyl. Since then the dioxide has been widely used for obtaining α-dicarbonyl compounds from aliphatic or aliphatic–aromatic aldehydes and ketones under mild conditions. In contrast to chromic acid, potassium permanganate, and other reagents that oxidise primarily the carbonyl group, selenium dioxide acts on a methyl or methylene group attached to various activating groups—alkene, alkyne, aldehyde, ketone, carboxyl, ester, amide, anhydride, nitrile, or an aromatic ring—where the degree of activation varies within wide limits[22-28]. Oxidation can be accomplished either in the absence of a solvent or in various organic solvents not oxidised by selenium dioxide—in alcohol, acetic anhydride or acid, or dioxan[29].

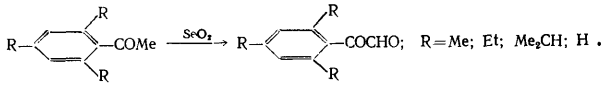
Oxidation occurs most simply with carbonyl compounds RCH_2COR' having one active position, when high yields of α-dicarbonyl products are obtained. For example, acetaldehyde gives a 90% yield of glyoxal[21,29]:

$$CH_3CHO \xrightarrow{SeO_2} CHOCHO .$$

Propionaldehyde and butyraldehyde form methyl- and ethyl-glyoxal respectively; phenylacetaldehyde is converted into phenylglyoxal; etc.[29] The rate of oxidation of aliphatic aldehydes decreases with increase in their molecular weight[30]. α-Keto-aldehydes or α-diketones are the main products of the oxidation of ketones by selenium dioxide[21,22,30-46]. Thus acetone is converted into methylglyoxal in 60% yield[21], and acetophenone into phenylglyoxal in 50% yield[21,47]. α-Diketones are obtained in high yields when various substituted benzyl phenyl ketones are oxidised with selenium dioxide; for example, deoxybenzoin and its derivatives containing various unoxidisable substituents in the ring are converted into theoretical yields of benzils[29,48]:

$$ArCCH_2Ar' \xrightarrow[96-100\%]{SeO_2} Ar{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}Ar' .$$

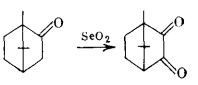
Here the methylene group is doubly activated, and the steric conditions do not favour secondary aldol condensation. 2,4,6-Trialkylacetophenones are oxidised without steric hindrance to the corresponding glyoxals[49-51]:



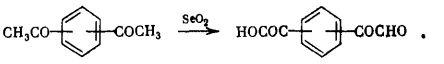
It is interesting that a higher yield of phenylglyoxal is obtained by the oxidation of acetophenone than by that of phenylacetaldehyde, which is probably due to the liability of the latter to undergo aldol condensation[3]. The oxidation of ω-bromoacetophenone in methanol gives an 80% yield of methyl phenylglyoxylate[52]:

$$PhCOCH_2Br \xrightarrow[MeOH]{SeO_2} PhC(O)C(O)OMe .$$

Non-aromatic systems, having only one position open to attack, give high yields of α-diketones when oxidised. For example, camphor is converted into camphorquinone in 90% yield[53], and α-santene forms the corresponding dione in quantitative yield[55]. Several bicyclic compounds containing a methylene-carbonyl grouping also give α-diketones[53,56]:



Nor does the presence of two equivalent α-methylene-carbonyl functions in the molecule present special difficulties in oxidation. Thus *p*- and *m*-diacetylbenzene are oxidised to the corresponding diglyoxals[57,58]:

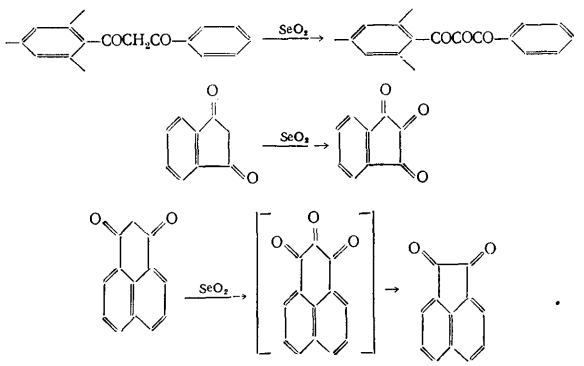


This reaction formed the basis for the later development of general methods for preparing diglyoxals of type $CHOCOArCOCHO.2H_2O$ [59-64] (Table 2) and bis-α-diketones of general formula $Ar'COCOArCOCOAr'$ [65-80] (Table 3, No. 1–9 and 15–25).

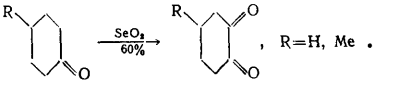
Table 2. Aromatic bisglyoxals[59-64].

No.	Compound	M.p., °C (decomp.)
1	HOCOC–C6H4–COCOH·2H2O	162—164
2	HOCOC–C6H4–C6H4–COCOH·2H2O	162—166
3	HOCOH–(C6H4)3–COCOH·2H2O	211—214
4	HOCOC–C6H4–O–C6H4–COCOH·2H2O	141—143
5	HOCOC–(C6H4–O–)2C6H4–COCOH·2H2O	157—160
6	HOCOC–(C6H4–O–)3C6H4–COCOH·2H2O	154—156.5
7	(H2O·HOCOC–C6H4–O–C6H4–)x	178—180
8	HOCOC–C6H4–SO2–C6H4–COCOH·2H2O	138—139
9	HOCOH–C6H4–S–C6H4–COCOH·2H2O	100—100.5
10	HOCOC–C6H3–COCOH·2H2O	110—111

Several systems containing β-diketone groups can be oxidised to 1,2,3-triones[54,56]:

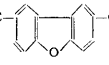
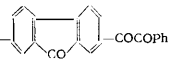
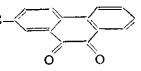
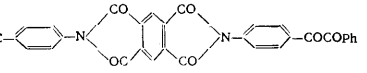
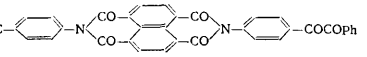
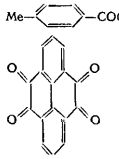
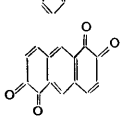


Oxidation by means of selenium dioxide presents no difficulties also with symmetrical systems containing two equivalent groups separated by an activating centre. For example, cyclohexanone and 4-methylcyclohexanone are oxidised to cyclohexane-1,2-dione and 4-methylcyclohexane-1,2-dione respectively[21,81]:



1,2-Diones are formed more slowly from cyclopentanone and cycloheptanone than from cyclohexanones, and cyclooctanone does not give diones at all[42]. Alicyclic ketones

Table 3. Aromatic bis-α-diketones.

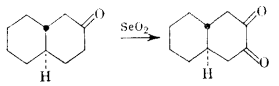
No.	Compound	M.p., °C	Ref.
1	2	3	4
1	PhOCOC-$(CH_2)_6$-COCOPh	63—64	71,72
2	PhOCOC-C$_6$H$_4$-COCOPh	98—99.5	66,72,74
3	PhOCOC-C$_6$H$_4$-COCOPh	123—124.5	66,67, 72,88
4	PhCCOC-C$_6$H$_4$-C$_6$H$_4$-COCOPh	205—206	68,72, 73,76
5	PhOCOC-C$_6$H$_4$-CH_2-C$_6$H$_4$-COCOPh	144—144.5	72,73,88
6	PhOCOC-C$_6$H$_4$-O-C$_6$H$_4$-COCOPh	107—108.0	68,72, 73,76
7	PhOCOC-C$_6$H$_4$-CO-C$_6$H$_4$-COCOPh	128—130	72,76
8	PhOCOC-C$_6$H$_4$-S-C$_6$H$_4$-COCOPh	90—91.6	72,73
9	PhOCOC-C$_6$H$_4$-SO_2-C$_6$H$_4$-COCOPh	164—166	72
10	PhOCOC--COCOPh	193—194	76
11	PhOCOC--COCOPh	239—241	76,77
12	PhOCOC-	230—232	76
13	PhOCOC--COCOPh	365—367	70
14	PhOCOC--COCOPh	358—360	106
15	Et-C$_6$H$_4$-COCO-C$_6$H$_4$-COCO-C$_6$H$_4$-Et	53.5—54.5	75
16	MeO-C$_6$H$_4$-COCO-C$_6$H$_4$-COCO-C$_6$H$_4$-OMe	116.5—117.5	75
17	PhO-C$_6$H$_4$-COCO-C$_6$H$_4$-COCO-C$_6$H$_4$-OPh	131.5—132.5	75
18	Ph-C$_6$H$_4$-COCO-C$_6$H$_4$-COCO-C$_6$H$_4$-Ph	136—137.5	75
19	CN-C$_6$H$_4$-O-C$_6$H$_4$-OCOC-C$_6$H$_4$-COCO-C$_6$H$_4$-O-C$_6$H$_4$-CN	139.5—141.5	75
20	OH-C$_6$H$_4$-COCO-C$_6$H$_4$-COCO-C$_6$H$_4$-OH	204—205	75
21	Br-C$_6$H$_4$-COCO-C$_6$H$_4$-COCO-C$_6$H$_4$-Br	192—193	75
22	CN-C$_6$H$_4$-COCO-C$_6$H$_4$-O-C$_6$H$_4$-COCO-C$_6$H$_4$-CN	194—196	75
23	MeCOCO-C$_6$H$_4$-O-C$_6$H$_4$-COCOMe	80.5—81.5	75
24	Ph-(-O-C$_6$H$_4$-)$_2$-COCO-C$_6$H$_4$-COCO-(-C$_6$H$_4$-O-)$_2$-Ph	170—172	157
25	Ph-(-O-C$_6$H$_4$-)$_3$-COCO-C$_6$H$_4$-COCO-(-C$_6$H$_4$-O-)$_3$-Ph	153—154.5	157
26	Me-C$_6$H$_4$-COCO-C$_6$H$_4$-COCO-C$_6$H$_4$-Me	167—168	99
27		365—370	107
28		305—306	108,109

(cyclohexanone and the isomeric methylcyclohexanones) are oxidised by selenium dioxide more rapidly than are aromatic and aliphatic ketones containing the same number of carbon atoms. 4-Methylcyclohexanone is oxidised most rapidly, and the 2-methyl isomer the most slowly[42,81].

It is often observed that only one of two or more oxidisable groups is predominantly oxidised. Thus the doubly activated methylene group in pentane-2,4-dione is oxidised to give a 29% yield of the final product, which indicates the simultaneous occurrence of side-reactions:

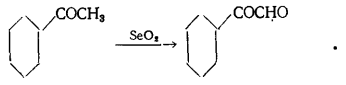
$$CH_3COCH_2COCH_2 \xrightarrow{SeO_2} CH_3COCOCOCH_3 .$$

trans-2-Decalone (which enolises at the 3 position) forms the 2,3-dione in 60–65% yield[46]:



3-Keto-steroids are oxidised by selenium dioxide to the corresponding 2,3-diones[46].

Under comparable conditions the oxidation of α-methyl groups by selenium dioxide is more vigorous than that of α-methylene. Thus cyclohexyl methyl ketone gives a 59% yield of cyclohexylglyoxal:



More butane-1,2-dione than butane-2,3-dione is formed by the oxidation of butan-2-one[21]:

$$CH_3COCH_2CH_3 \xrightarrow{SeO_2} \underset{(17\%)}{CH_3CH_2COCHO} + \underset{(1\%)}{CH_3COCOCH_3} .$$

The reason for such behaviour is still obscure. It may be supposed that steric factors play an important part, as well as secondary processes involving further oxidation, polymerisation, etc. of the products. The rates of oxidation of aldehydes and ketones by selenium dioxide depend on their structure and the reaction conditions. The rate falls with increase in the molecular weight of aldehydes and of straight-chain alkyl methyl, dialkyl, and alkyl phenyl ketones, as well as in the presence of secondary and tertiary groups in the α-position with respect to the carbonyl[82]. Alkyl methyl ketones are oxidised more rapidly than are straight-chain aldehydes containing the same number of carbon atoms[30]. Ketones of general formula $C_6H_5[CH_2]_nCOCH_3$ with n and even number are oxidised more slowly by selenium dioxide than are ketones containing an odd number of methylene groups[3]. The nature of the substituent influences the rate of oxidation of substituted acetophenones: thus the rate constants for oxidation by selenium dioxide of the compounds $RC_6H_4COCH_3$ in 75% acetic acid decrease according as R represents[3]

$$p\text{-I} > p\text{-M} > \text{H} > p\text{-MO} > p\text{-Cl} > p\text{-Br} > m\text{-NO}_2 .$$

The rate constant of the oxidation of ketones by selenium dioxide depends also on the solvent: it is lower in alcohols than in acetic acid, which is related to the formation of complexes between ketones and alcohols. The oxidation of ketones by selenium dioxide is catalysed by acids[3].

MECHANISM OF OXIDATION BY SELENIUM DIOXIDE

Although the oxidation of aldehydes and ketones by selenium dioxide has been the subject of many detailed studies, its mechanism cannot be regarded as fully established.

The first kinetic data on this reaction in 75% acetic acid, obtained from gravimetric determinations of the precipitate of colloidal selenium, were published by

Mel'nikov et al.[3] These workers stablished the second order, and noted that the reaction was controlled by enolisation of the ketonic group by means of a hydrogen atom from the α-carbon atom, since ketones incapable of enolisation are not oxidised by selenium dioxide.

Later Duke[83] suggested the third order for this reaction, regarding formation of an intermediate reactive complex as the rate-determining stage:

$$RCOCH_2R' + SeO_2 - H^+ \xrightarrow{\text{slow}} \left[\begin{array}{l} R-C(=O)-CH_2R' \\ \quad \rightarrow SeO(OH) \end{array}\right]^+ .$$

The most careful investigation was made by Corey and Schaefer[29], although doubt was cast on their results by Waters et al.[84] Deoxybenzoin was chosen for investigation, having only one possible oxidisable position and forming benzil in theoretical yield:

$$PhCOCH_2Ph \xrightarrow{SeO_2} PhCOCOPh + Se + H_2O.$$

The introduction of various substituents into the aryl groups revealed their electronic influence on the oxidation. Kinetic measurements were made by titrating the unchanged selenous acid in 70% acetic acid over a wide range of substrate and selenium dioxide concentrations. The results indicated the third order in conformity with the equation

$$-d[SeO_2]/dt = k[SeO_2] \cdot [PhCOCH_2Ph] \cdot [H^+] .$$

Electron-donating groups in the benzyl component and electron-accepting substituents in the benzoyl group increased the reaction velocity. The easier oxidation of benzyl methyl ketone than of acetone indicated that the course of the reaction was not affected by steric hindrance at the carbonyl group. On the other hand, steric hindrance at the α-methylene group explains why the rate of oxidation of phenyl 2,4,6-trimethylbenzyl ketone is around 10% of that of benzyl methyl ketone. Benzoin is not an intermediate product, since it is oxidised at one-twentieth of the rate of oxidation of deoxybenzoin. The reaction is initiated by bases (alkali-metal acetates), is insensitive to radical initiators and inhibitors, and hence cannot be described in terms of a radical-chain mechanism.

On the basis of the above results the following mechanism was suggested[29] for the oxidation of deoxybenzoin by selenium dioxide:

$$ArCOCH_2Ar' + HSeO_3^+ + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{OSeO_2H}{ArC(=CHAr')} + H_2O + H_3O^+ \rightarrow$$

$$\rightarrow ArCO-\underset{OSeOH}{CH}-Ar' \rightarrow ArCOCOAr' .$$

This is analogous to acid-catalysed enolisation, and has closely similar Hammett constants. According to the above mechanism unsymmetrical ketones should be oxidised on the side on which they are enolised in an acid. Thus *trans*-2-decalone will be enolised and oxidised at the 3 position. However, there are exceptions: as remarked earlier, the oxidation of ethyl methyl ketone yields 17% of ethylglyoxal and only 1% of biacetyl, although enolisation should take place at the methylene group[21]. The low yield of butane-2,3-dione can be attributed to its degradation by secondary reactions after it has been formed. The selenous ester of the enol may be assumed to rearrange more rapidly than biacetyl is formed from it.

Since benzoin is not an intermediate product in the oxidation of deoxybenzoin, it may be concluded that the formation of benzil is more rapid than is solvolysis of the intermediate product to benzoin. This conclusion is not entirely consistent with results obtained by Schaefer and Horvath[85] in a study of the behaviour of analogous intermediate products in the oxidation of alkenes. However, the difference can be attributed to the circumstance that, whereas solvolysis of intermediate products in the oxidation of alkenes yields resonance-stabilised cations, solvolysis of intermediate products in the oxidation of deoxybenzoins is always accompanied by the appearance of a positive charge on the carbon atom adjacent to the positive end of the carbonyl dipole. The α-hydrogen atom is then acidic owing to the contiguity of the carbonyl, and is more liable to direct abstraction under the influence of bases:

$$Ar-\underset{H}{\underset{|}{C}}(-\underset{O}{\underset{\|}{C}}-Ar')(-O-Se-OH) \longrightarrow ArCOCOAr' + H_2O + Se .$$

Formation of the selenous ester of the enol was regarded[29] as the rate-determining stage. An attempt was made to use the suggested mechanism to explain the formation from certain ketonic systems of $\alpha\beta$-unsaturated compounds instead of the expected α-diketones, as well as the greater rapidity of the oxidation of aldehydes and ketones than of the aldol condensation, but the latter is still not entirely clear.

3. Oxidation of Compounds containing Carbon–Carbon Multiple Bonds

Compounds of transition metals, because of their stability and adequate selectivity towards different functional groups and also unsaturated bonds, occupy an important place among the oxidising agents used in organic chemistry[86]. The principal oxidant used for a triple bond C≡C is potassium permanganate in neutral or weakly acid medium, when the main undegraded products of the oxidation of alkynes are α-diketones and $\alpha\beta$-unsaturated alcohols[87]. The oxidation of acetylenic bonds by potassium permanganate has recently been successfully applied to the preparation of bis-α-diketones, previously obtained by oxidising the corresponding deoxybenzoins with selenium dioxide (Table 3, No. 3–7 and 10–12):[76,88,89]

$$Ph{\equiv}C-Ar-C{\equiv}CPh \xrightarrow{KMnO_4} PhC(=O)-C(=O)-Ar-C(=O)-C(=O)-Ph$$

(Ar = arylene). Potassium permanganate in acetic anhydride has been used to obtain α-diketones from cycloalkenes of the type[90]

$$(CH_2)_{10}\begin{array}{l} CH \\ \| \\ CH \end{array} \rightarrow (CH_2)_{10}\begin{array}{l} C=O \\ | \\ C=O \end{array} + (CH_2)_{10}\begin{array}{l} C=O \\ | \\ CHOAc \end{array} + (CH_2)_{10}\begin{array}{l} COOH \\ | \\ COOH \end{array} .$$

However, this method was unsuitable for the preparation of α-diketones from small rings (below cyclo-octene). The explanation proffered was that reaction takes place only when the carbonyl groups in the expected α-diketone are incapable of cisoid orientation. This oxidising system is advantageous because many organic compounds dissolve in acetic anhydride. In several cases, however, dimethoxyethane alone or added to acetic anhydride is recommended as solvent[90].

Numerous attempts have been made to use other oxidants, but convenient preparations of α-diketones have not resulted. Oxidation by organic peroxy-acids yields various products depending on the conditions and the acid

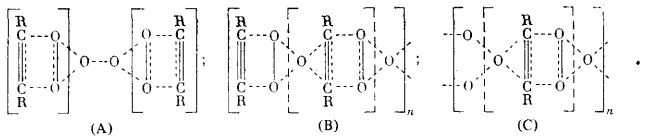
used[91]. Thus trifluoroperacetic acid converts diphenylacetylene into benzil and benzoic acid, the latter obviously a product of further oxidation of the benzil:

$$PhC{\equiv}CPh \xrightarrow[Na_2HPO_4,\ CH_2Cl_2]{2CF_3CO_3H} \underset{(76\%)}{PhCOCOPh} + \underset{(17\%)}{PhCOOH}\ .$$

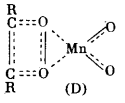
More highly oxidised products—finally a mixture of carboxylic acids or their esters—are obtained by the action of perbenzoic, peracetic, and trifluoroperacetic acids on penylacetylene, involving cleavage of the triple bond[92]. One reason suggested was the intermediate formation of [1,3-dioxabicyclo[1,1,0]butanes:]

$$R{-}C{\equiv}C{-}R' \rightarrow \left[R{-}C\begin{matrix}O\\ \diagup\ \diagdown\\ O\end{matrix}C{-}R'\right] \rightarrow \underset{O\ \ O}{RC{-}C{-}R'} + RCOOH + R'COOH\ .$$

Oxidation of a carbon–carbon triple bond has been accomplished by means of selenium dioxide in the presence of catalytic quantities of sulphuric acid[93], thallium trinitrate[94], ozone[95,96], tetracarbonylnickel in the presence of alkyl halides[97], bromosuccinimide in anhydrous dimethyl sulphoxide (e.g. No. 26 in Table 3), [98,99] oxides of nitrogen[100], and ruthenium tetraoxide[101]. In spite of good yields of α-diketones, however, these oxidants have not found wide application for preparative purposes.



Molecular aspects of mechanisms of the oxidation of acetylenic compounds to α-diketones by singlet oxygen, ozone, and potassium permanganate in neutral or weakly alkaline media have been discussed[102]. The oxidation is assumed to involve intermediate formation of dioxetans without the involvement of "ene", free-radical, or ionic processes, since traces of peroxides or products of an "ene" reaction are not detected when singlet oxygen is used. Ozonisation also involves formation and decomposition of a dioxetan as molecular intermediate transition complex (A), whose breakdown is accompanied by rapid evolution of singlet oxygen. The complex (A) may undergo rearrangement into the thermodynamically more stable complexes (B) and (C), which also decompose into monomeric ozonides and singlet oxygen. Oxidation by potassium permanganate (pH 7) involves intermediate formation of the complex



which then breaks down into the α-diketone, singlet oxygen, and manganese dioxide.

4. Other Methods of Preparation of α-Diketones

To complete the account mention must be made of a few other methods of obtaining α-diketones, which have not become widely used. Thus they can be obtained from monoximes or isonitroso-ketones, formed by the action of nitrous acid on ketones $RCOCH_2R'$; as well as via dioximes, which are produced by replacing the nitrous acid by an alkyl nitrite, hydroxylamine, or an aromatic nitroso-compound[103]. Condensation of isonitroso-ketones with diazo-compounds has been used to obtain several aryl methyl α-diketones[1]:

$$MeCOC\begin{matrix}H\\ \diagdown\\ NOH\end{matrix} \xrightarrow{ArN_2Cl} \left[MeCOC\begin{matrix}N:N\cdot Ar\\ \diagdown\\ NOH\end{matrix}\right] \rightarrow MeCOC\begin{matrix}Ar\\ \diagdown\\ NOH\end{matrix} \rightarrow MeCOCOAr\ .$$

α-Diketones can be prepared by the action of organomagnesium compounds on vinylidenoxanilide[1]:

$$\begin{matrix}O{=}C{-}N\\ |\\ O{=}C{-}N\end{matrix}\begin{matrix}Ph\\ \diagdown\\ C{=}CH_2\\ \diagup\\ Ph\end{matrix} \xrightarrow{2\ MeMgI} MeCOCOMe\ .$$

αβ-Unsaturated monoketones (e.g. vinyl ketones) will yield α-diketones by the series of reactions[1]

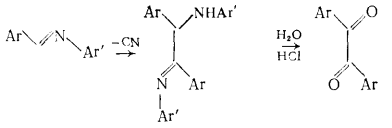
$$RCOCH{=}CHR' \xrightarrow{Br_2} RCOCHBrCHBrR' \xrightarrow{-HBr} RCOCBr{=}CHR' \xrightarrow{+\ piperidine} \rightarrow RCOCBr(NC_5H_{10})CH_2R' \xrightarrow{-HBr} RCOC(NC_5H_{10}){=}CHR' \xrightarrow{+H_2O} RCOC(OH){=}CHR' \xrightarrow{-H_2O} RCOCOR'.$$

Several α-diketones can be obtained by the Friedel–Crafts condensation of phenyl ethers, e.g. anisole, with oxalyl chloride[104]:

$$2\ MeOC_6H_5 + ClOC{-}COCl \xrightarrow[CS_2]{AlCl_3} \underset{(90\%)}{4\text{-}MeOC_6H_4COCOC_6H_4OMe\text{-}4'}\ .$$

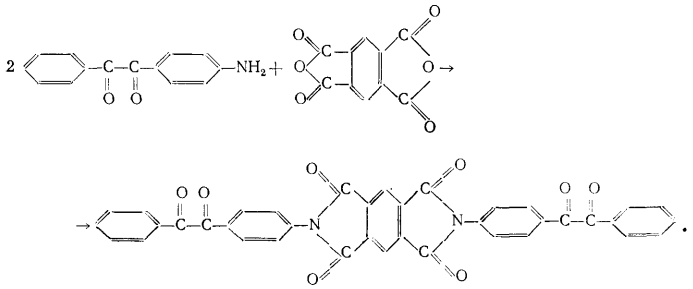
In most cases, however, the ethers are insufficiently reactive, and the oxalyl chloride decomposes under the influence of the aluminium chloride before it can react with the ether.

A convenient method published recently involves oxidative dimerisation of several aromatic aldimines in the presence of the cyanide ion, followed by hydrolysis of the α-diketimines formed as intermediates[105]:

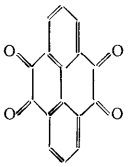


The reaction is usually conducted in dimethyl sulphoxide or dimethylformamide at room temperature, when the yield of α-diketones reaches 85–95%.

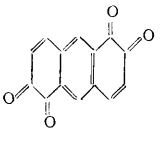
Bis-α-diketones containing imide rings (Table 3, No.13 and 14) have been prepared by an original route consisting in the action of *p*-aminobenzil on the dianhydride of a tetracarboxylic acid[70,106]. In the case of pyromellitic dianhydride the reaction can be written



The di-*o*-quinones used in the synthesis of ladder polyphenylquinoxalines—4,5,9,10-tetrahydro-4,5,9,10-tetraoxopyrene (I) and 1,2,5,6-tetrahydro-1,2,5,6-tetraoxoanthracene (II)



I

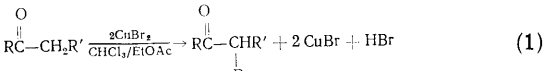


II

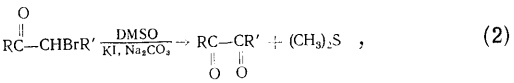
(Table 3, No. 27 and 28)—are obtained by special methods. The first step in the preparation of (I) is oxidation by ozone of pyrene to 5-formylphenanthrene-4-carboxylic acid, which on treatment with phenylhydrazine followed by reduction is converted into 4-amino-5-hydroxypyrene, and this is oxidised to the 4,5-quinone. The most difficult step is the further oxidation of this diketone to the diquinone, conducted in acetic acid by means of aqueous chromium trioxide. After crystallisation from nitrobenzene the total yield of (I) does not exceed 15%.[107]

The second di-*o*-quinone (II) is obtained by treating anthracene-2,6-diol with a solution of zinc chloride and sodium nitrite. Subsequent reduction of the resulting 1,5-dioxime with sodium dithionite forms 1,5-diaminoanthracene-2,6-diol, whose oxidation with sodium dichromate in dilute sulphuric acid gives the 1,2,5,6-tetraketone (II) in a total yield of 3% (after crystallisation from dioxan)[108].

A two-stage preparation of α-diketones from α-methylene-ketones involves intermediate formation of α-bromoketones, which are then oxidised with dimethyl sulphoxide in the presence of iodide ions[109]:



(1)



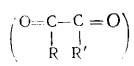
(2)

where R and R′ = Alk or Ar. The total yield of α-diketones reaches 65–92%.

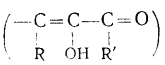
III. REACTIONS OF α-DICARBONYL COMPOUNDS

The simultaneous presence of two carbonyl groups ensures that α-diones are able to undergo not only all the reactions of simple aldehydes and ketones but also reactions leading to the formation of heterocyclic systems. Either one or both carbonyl groups may react depending on the conditions[110].

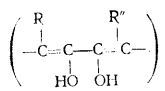
The contiguity of the two carbonyl groups is responsible for the colour of α-diketones. These compounds may exist either in the diketonic form



in the monoenolic form



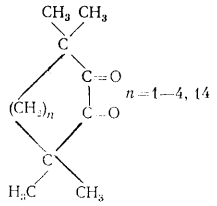
or in the dienolic form



depending on several factors, primarily the nature of substituents adjacent to the carbonyl groups. Thus acyclic α-diketones (e.g. butane-2,3-dione) are true diketones and possess a yellow colour: cyclic α-diketones are usually colourless and react typically tautomerically, forming both monoximes and dioximes[111]. When enolisation is sterically hindered, as e.g. in camphorquinone, cyclic diketones also have a yellow colour.

Investigation on a series of α-substituted diketones have shown that the ultraviolet spectra of all the compounds contain two maxima, at 219–269 and 391–421 nm, which are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electron transitions respectively. The position of the second maximum depends on the nature of the substituent governing the spatial arrangement of the carbonyl groups. The same factors determine absorption by the carbonyl groups in the infrared spectra[112].

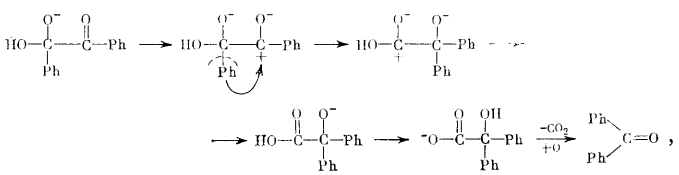
Study of the influence of steric configuration on the ultraviolet spectra of α-diketones of the type



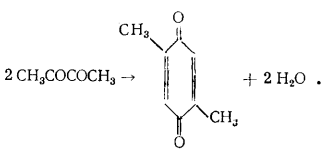
has shown that the position of absorption bands at the longer wavelengths correlates with the relative steric orientation of the carbonyl groups, which is supported by inspection of molecular models. The position of the bands varies with the angle between the planes of the carbonyl groups: a band moves to shorter wavelengths with increase in the angle from 0 to 90°, and moves back to longer wavelengths with further increase in the angle (>90°).[113]

1. Action of Alkalis

Under the influence of alkalis α-diketones tend to undergo a so called benzil rearrangement. This has been studied in greatest detail on and named after benzil itself. The benzil rearrangment compares formally with the pinacol rearrangement

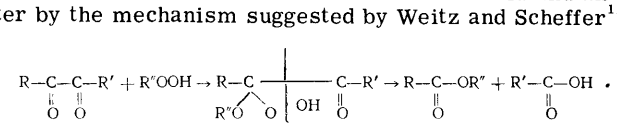


where the benzil molecule is written in hydrated form. Butane-2,3-dione is characterised by condensation, in the presence of an alkali, to a cyclic xyloquinone[37]:

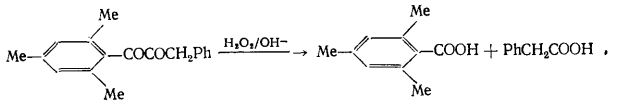


2. Action of Acids and Peroxides

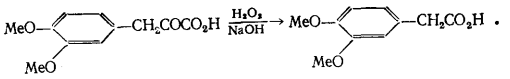
The carbonyl–carbonyl bond undergoes cleavage when α-dicarbonyl compounds are treated with peroxy-acids or peroxides[116–118]. The first stage probably involves 1,2- or 1,4-addition of hydroxy-groups to the system with formation of an unsymmetrical product, subsequent cleavage of which (e.g. in the case of ethyl hydroperoxide) yields either two acid molecules or a mixture of an acid and an ester by the mechanism suggested by Weitz and Scheffer[119].



Alkaline hydrogen peroxide also splits α-dicarbonyl compounds to give high yields of the corresponding carboxylic acids[120,121]:

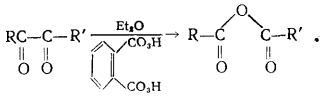


α-Keto-acids are readily decarbonylated under these conditions[122]:



Complicated mixtures are obtained by the action of a hydroxamic acid in the presence of concentrated sulphuric acid. The example of benzil shows that this reaction also involves bond rupture between the two carbonyls. The main product, N-benzoyl-N'-phenylurea, is then accompanied by 5-anilinotetrazole, 5-amino-1-phenyltetrazole, 5-benzamido-1-phenyltetrazole, and minute quantities of benzoic acid, aniline, and other products[123].

α-Dicarbonyl compounds react rapidly with peroxyacids. The structure of the anhydrides isolated from the reaction was regarded[124] as indicating migration of an acyl group:



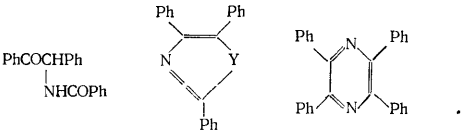
3. Hydrogenation

The selectivity of the hydrogenation of α-diketones is determined by the nature of the catalyst and the conditions of the reaction[125-128]. Thus reduction at a copper cathode in aqueous medium converts benzil into benzoin[125]. 1,2-Diphenylethane is formed when zinc amalgam is used as cathode in an aqueous–alcoholic solution of an acid (sulphuric) at 70–90°C.[125] The use of relatively inactive catalysts—platinum on carbon, Raney nickel, palladium on poly(methyl methacrylate)—enables hydrogenation to be arrested after 80 min, at the *meso*-1,2-diphenylethane-1,2-diol stage. Further saturation with hydrogen (for 30 h) also yields 1,2-diphenylethane[125].

When benzil is heated with sodium tetrahydroborate or lithium tetrahydroaluminate in methanol at 60°C, *meso*-1,2-diphenylethane-1,2-diol is formed[126]. Heating benzil with potassium iodide, red phosphorus, and concentrated hydrochloric acid for 15 h enabled deoxybenzoin to be isolated, together with minute quantities of 1,2,3,4-tetraphenylbutane-2,3-diol[127].

4. Action of Ammonia and Amines

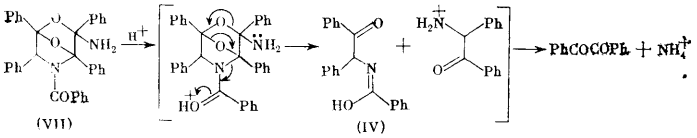
The action of ammonia on benzil has led to the isolation of various products depending on the solvent, the temperature, and the duration of the reaction—ethyl benzoate, benzamide, N-desylbenzamide (IV), and three aromatic heterocycles—2,4,5-triphenyloxazole (Va), 2,4,5-triphenylimidazole (Vb), and tetraphenylpyrazine (VI)[129]



(IV) (V) (VI)

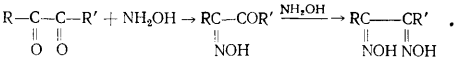
a) Y=O;
b) Y=NH

Later another product (VII), of high molecular weight and empirical formula $C_{35}H_{28}O_3N_2$, was isolated. It was regarded as formed via an intermediate complex containing three benzyl groups per ammonia molecule, whose disproportionation gave compounds (IV) and (VII). The latter was assumed to be labile, readily decomposing in the presence of acids and alkalis to form (IV), benzil, and other products[130,131]:

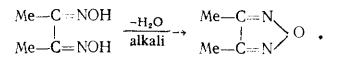


(VII) (IV)

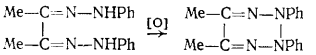
α-Dicarbonyl compounds react vigorously with hydroxylamine at one or both carbonyl groups to form monoximes and dioximes[132,133]:



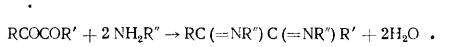
Alkalis abstract a water molecule from dioximes and convert them into furazans[134]:



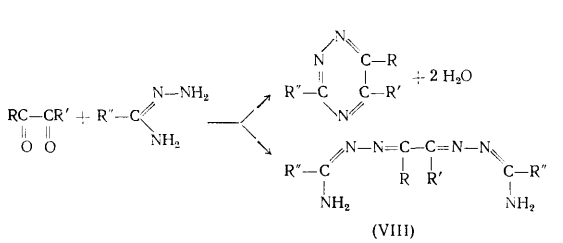
The action of semicarbazide on α-diketones is similar: mono- or di-semicarbazones or cyclic condensation products are formed depending on the reaction conditions. With phenylhydrazine mono- or bis-phenylhydrazones are obtained also depending on the conditions[135-138]. Oxidation of the latter products (osazones) can be represented as



Several reports have appeared of the formation of Schiff bases by the action of amines on glyoxal and biacetyl[139,140]:



The reaction between α-dicarbonyl compounds and amidrazones, yielding either 1,2,4-triazines or acyclic products such as (VIII)



(VIII)

has been discussed in a review by Rusanov[141].

Table 4. Data on bisquinoxalines[64,67,68].

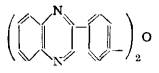
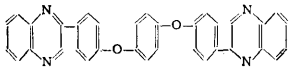
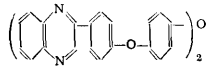
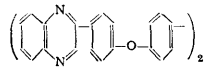
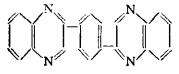
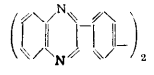
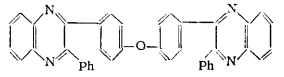
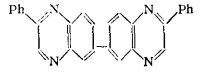
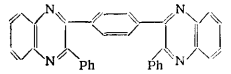
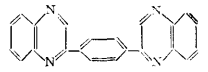
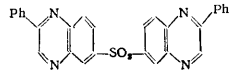
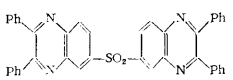
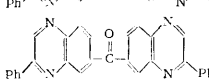
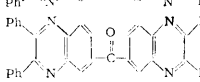
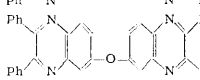
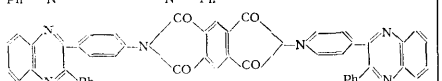
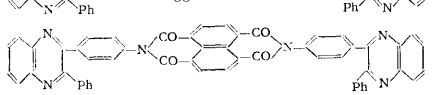
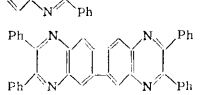
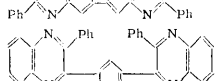
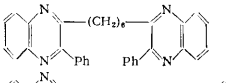
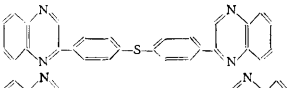
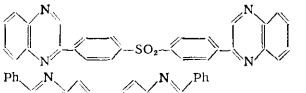
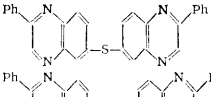
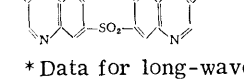
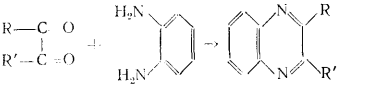
No.	Compound	M.p., °C	Ultraviolet spectra* λ_{max}, nm	$10^3\epsilon$
1	2	3	4	5
1		171—173	315	38.0
2		222—224	315	46.9
3		190—191	315	56.8
4		229—231	310	50.5
5		266—267	276	39.0
6		261—262	312	39.8
7		292—294	350	45.2
8		226—227	280	32.0
9		314—315	303	68.0
10		260—260.5	323	85.0
11		272—274	280	101.0
12		257—258.5	381	29.0
13		295—304	295	40.3
14		247—247.5	323	85.3
15		260—260.5	268	66.5
16		266—267	292	28.4
17		264—265.5	—	—
18		436—437	—	—
19		460—462	—	—
20		309—310	—	—
21		224—225	—	—

Table 4 contd.

No.	Compound	T. пл., °C	Ultraviolet spectra* λ_{max}, nm	$10^3\epsilon$
1	2	3	4	5
22		151.5—152.5	355	22.7
23		194—195	264	29.8
24		297—298	261	34.0
25		306—307	368	17.6
26		274—275	345	12.0

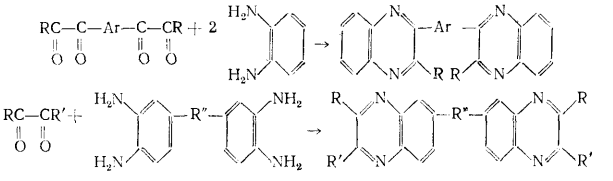
*Data for long-wavelength absorption maximum.

The reaction of greatest interest and practical importance is the quantitative cyclocondensation of α-dicarbonyl compounds with aromatic o-diamines, which led to the discovery in 1884 of a new class of heterocyclic compounds—the quinoxalines[142,143]:



The chemistry of quinoxaline has been actively developed since then: diverse derivatives have been prepared, their physical and chemical properties have been studied, and possible practical applications have been examined[144].

The reaction of bis-α-dicarbonyl compounds with aromatic o-diamines or of α-dicarbonyl compounds with bis-o-diamines yields bisquinoxalines of diverse structure (Table 4):

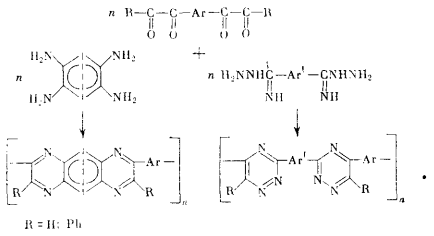


R=R′=H, Ph; R″=CH_2; O; SO_2; CO; S; —; Ar = arylene

Spectral investigations show that wavelengths λ_{max} are the same for compounds containing p-diphenylene ether units between unsubstituted quinoxaline rings. Replacement of these bridges by p-phenylene units produces a bathochromic shift in λ_{max}, which increases on passing from p-phenylene to p-biphenylylene and to p-terphenylylene, which is evidence of the presence of conjugation in the system. Introduction of phenyl substituents into the pyrazine ring has an analogous effect[65], which indicates that the quinoxaline and phenyl units are coplanar.

IV. BIS-α-DICARBONYL COMPOUNDS IN THE PREPARATION OF HETEROCYCLIC POLYMERS

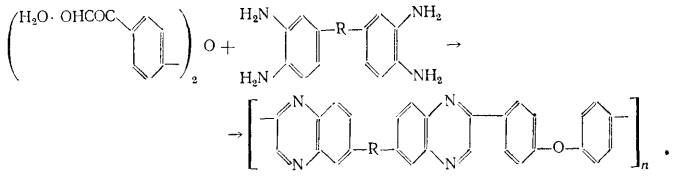
Whereas α-dicarbonyl compounds have as yet found limited practical application only for obtaining certain quinoxaline derivatives exhibiting pharmacological activity[144], bis-α-dicarbonyl compounds are acquiring increasing value as monomers for the synthesis of thermostable heterocyclic polymers, in particular polyquinoxalines and poly-1,2,4-triazines[145-153]:



R = H; Ph

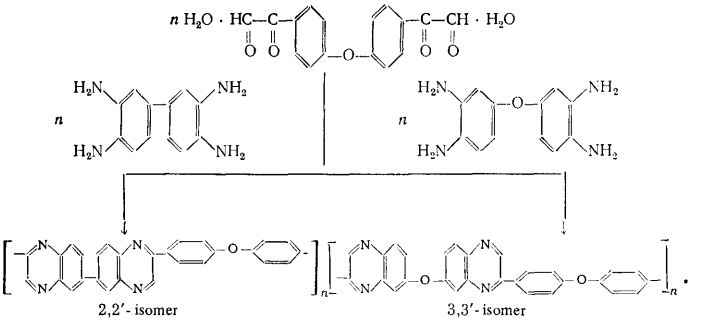
In the opinion of Hergenrother[146] phenylated quinoxalines are among the most promising heterocyclic systems known at the present time, whose structure has the potentiality for high thermal, thermo-oxidative, and hydrolytic stability.

The route to the synthesis of polyquinoxalines was mapped out by Sorenson[147] in 1961, since when the reaction of bis-α-dicarbonyl compounds with bis-o-diamines has been widely used to obtain polymers containing quinoxaline rings. To this period belong papers by Stille[59-61] and a patent[148] on the method of obtaining polyquinoxalines by the reaction of bis-o-phenylenediamines with aromatic bisglyoxals or their hydrates:



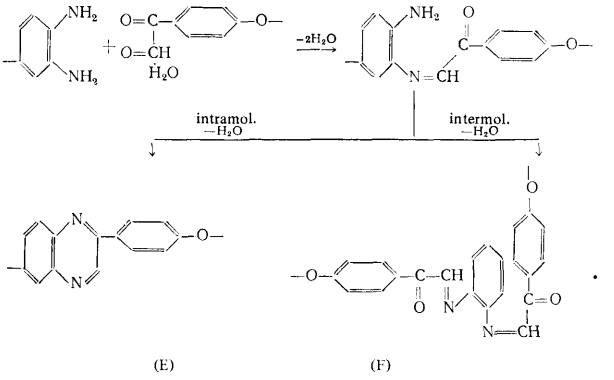
The same process for synthesising polyquinoxalines was suggested simultaneously by some French chemists[62,63,149].

The reaction of aromatic bisglyoxals with aromatic bis-o-diamines can obviously yield a mixture of position isomers (2,2'-, 2,3'-, and 3,3'-polyquinoxalines), a possibility investigated by Stille et al.[59-61]. From the ultraviolet spectra of model compounds and X-ray examination of polyquinoxalines obtained from 3,3'-diaminobenzidine and p-diglyoxyloylbenzene dihydrate these workers concluded that the 2,2'-isomer predominated in the mixture. They considered that preferential formation of a particular isomer could be predicted from the relative nucleophilicity of the o-amino-groups and the relative reactivity of the aldehydic and ketonic carbonyls in the aromatic bisglyoxals. For example, the p-amino-groups in bis-3,4-diaminophenyl ether should be more nucleophilic than those in 3,3'-diaminobenzidine (owing to the electron-donating effect of the ethereal oxygen), which would lead to predominant formation of the 3,3'-isomer, whereas mainly the 2,2'-isomer should be formed from 3,3'-diaminobenzidine[72]. However, it seems more probable that the formation of isomers is governed by the difference in nucleophilicity of the o-amino-groups within the tetramine itself:



2,2'-isomer 3,3'-isomer

Intermolecular interaction of the more reactive aldehydic part of the bisglyoxal with the unreactive amino-group often leads to the formation of branched and cross-linked polyquinoxalines, having diminished resistance to oxidation owing to incompleteness of cyclisation:

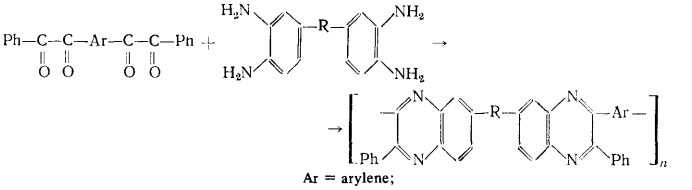


(E) (F)

When the reaction between the starting materials is conducted in suspension (not in solution), the less reactive keto-group of the intermediate product is able to react intramolecularly to give the required product (E).[64,72]

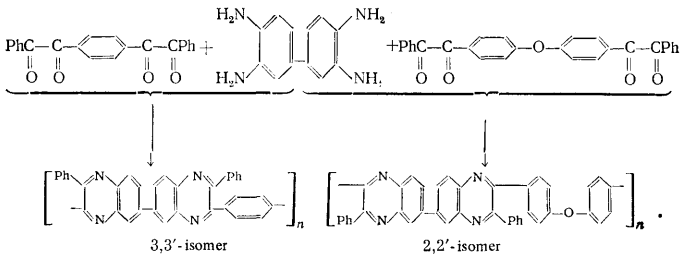
Table 5 shows that increasing the number of p-phenylene ether units in the polymer lowers both the softening temperature and the glass point of the polyphenylquinoxalines. The decomposition temperatures determined by dynamic thermogravimetric analysis exhibit no definite trend, but a sharp difference is evident under isothermal conditions in air at 400°C: polyquinoxalines containing p-phenylene links were more resistant to oxidation than those containing p-phenylene ether links. The former, as was to be expected, had higher softening temperatures and were less soluble in organic solvents[65].

In order to improve the thermo-oxidative stability of the pyrazine ring, which is readily oxidised at a methine group, phenylated polyquinoxalines were synthesised[69] from bis-α-diketones instead of bisglyoxals:



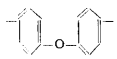
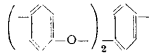
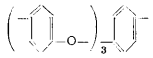
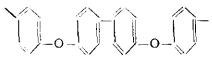
Ar = arylene;
R = —, O, CO, SO_2, CH_2, S, etc.

The possibility of isomeric structures is even greater with polyphenylquinoxalines than with polyquinoxalines. The relative reactivity of the adjacent carbonyl groups in bis-α-diketones (Table 3) is independent of steric factors, in contrast to glyoxals, but inductive and electromeric effects are more significant. For example, the reaction of 3,3′-diaminobenzidine with *p*-bisphenylglyoxyloylbenzene or with dibenzyl ether may be expected to yield the isomers[72]



The influence of isomerism on the properties of polyphenylquinoxalines will be discussed later.

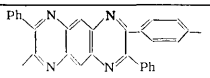
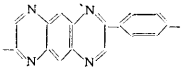
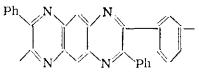
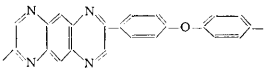
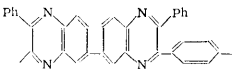
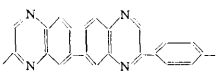
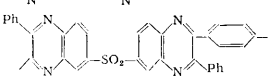
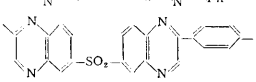
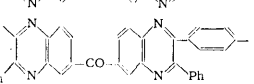
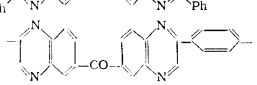
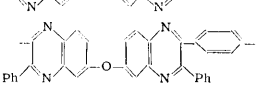
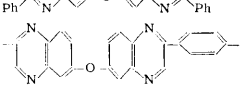
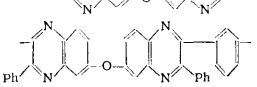
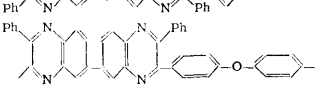
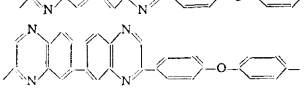
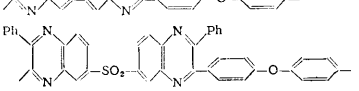
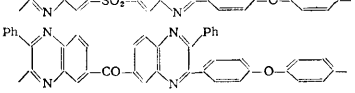
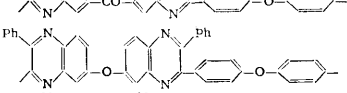
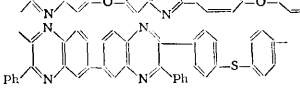
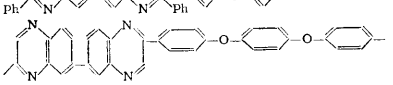
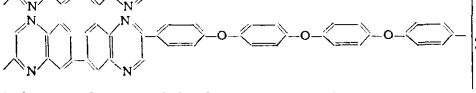
Table 5. Data on polyquinoxalines[65].

No.	Ar	η_{log},* dl g^{-1}	T_{gl},** °C	T_{soft},*** °C	T_{decomp}, °C in**** N_2	T_{decomp}, °C in**** air	Ultraviolet spectra***** λ_{max}, nm	Ultraviolet spectra***** $10^3\epsilon$
1		1.62	280	315	550	530	280;331	22.0;35.2
2		1.21	195	262	530	510	283;333	29.9;42.3
3		1.27	133	240	520	510	286;337	30.0;46.0
4		0.82	213	253	560	535	280;327	34.0;78.5
5		1.07	350	>350	575	535	292	29.0
6		1.03	305	330	565	515	275;330	20.0;34.0
7		0.91	—	340	600	525	284;365	24.0;36.0

* Viscosity of 0.5% solution in sulphuric acid at 25°C.
** Glass point determined from dielectric losses.
*** Softening temperature determined by means of a Fisher–John apparatus.
**** Decomposition points determined from thermogravimetric analysis (ΔT = 5 deg min^{-1}).
***** Measured in sulphuric acid.

The thermo-oxidative stability of phenylated polyquinoxalines was indeed considerably greater than that of their non-phenylated analogues. This is made especially clearly apparent by comparing the behaviour of the polymers under isothermal conditions. Thus the polyphenylquinoxaline obtained by the reaction of *p*-bisphenylglyoxylbenzene with 3,3′-diaminobenzidine (Table 6, No. 5) has lost only 6% of its original weight after being heated

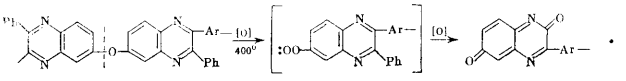
Table 6. Values of ΔC_p for quinoxaline polymers.

No.	Structure	T_{gl}, °C	Flexible bonds*	ΔC_p, cal deg^{-1}	ΔC_p, cal deg^{-1} mole^{-1}	ΔC_p, cal deg^{-1} bond
1	2	3	4	5	6	7
1		395	4	0.063	25.9	6.48
2		392	2	0.050	12.7	6.67
3		365	4	0.065	26.7	6.32
4		353	4	0.059	20.6	5.18
5		372	5	0.060	28.4	5.78
6		376	3	0.56	18.5	6.15
7		345	6	0.058	31.8	5.33
8		242	4	0.059	22.1	5.52
9		325	6	0.063	32.1	5.37
10		318	4	0.067	23.9	6.00
11		304	6	0.066	33.3	5.56
12		306	4	0.061	39.8	5.43
13		270	6	0.067	33.6	5.56
14		300	7	0.074	42.7	6.11
15		305	5	0.070	29.6	5.94
16		290	8	0.070	45.0	5.63
17		271	8	0.077	46.5	5.85
18		258	8	0.071	41.6	5.23
19		283	7	0.067	39.4	5.67
20		235	8	0.081	42.0	6.00
21		216	9	0.089	54.4	6.00

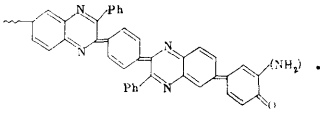
* A single bond linking aromatic rings is regarded as flexible.

in air at 400°C for 200 h, whereas the loss of weight of its unsubstituted analogue (No. 6) under the same conditions is 50%. In differential thermogravimetric analysis phenylated and non-phenylated polyquinoxalines show the same behaviour: they begin to decompose above 500°C. Polyphenylquinoxalines have the advantages of easier preparation of initial monomers and of the polymers themselves, better solubility, and ability to be converted into articles in the cyclised form. Great attention has been paid during recent years to research on the preparation and properties of polyphenylquinoxalines[66-72,150,151].

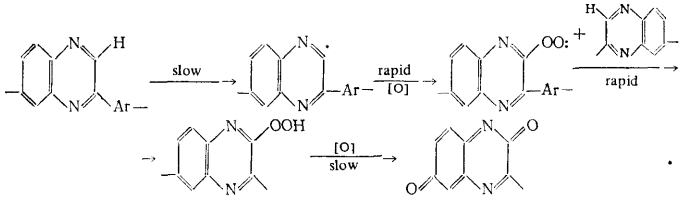
As would be expected, the introduction of ethereal oxygen into the main polymer chain produces a considerable decrease in the resistance to oxidation of polyphenylquinoxalines, accelerates the formation of volatile products, and increases their yield[150,151]. Wrasidlo[150] suggested a mechanism for the action of oxygen in which oxidation is initiated by radicals formed slowly by rupture of a carbon–oxygen bond:



The appearance of radicals is accompanied by degradation of the main chain, resulting ultimately in loss of film flexibility and strength. The phenoxy-radicals formed are rapidly converted by molecular oxygen into peroxy-radicals, whose decomposition and isomerisation liberate phenyl side-groups and yield quinonoid structures[151]

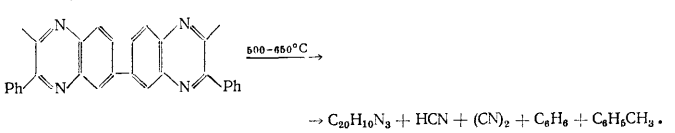


Oxidative degradation of unsubstituted polyquinoxalines proceeds differently: oxidation is initiated in the heterocycle by the action of molecular oxygen, and leads to formation of peroxy-radicals of the type[150]



These peroxy-radicals interact with a hydrogen atom of the heterocycle, to form a more stable hydroperoxy-radical. This is followed by a slow stage, which determines the rate of decomposition of the hydroperoxide and produces a resonance-stabilised quinonoid structure.

Thermo-oxidative degradation is influenced by the nature of the terminal groups[150,151,163]. In the absence of air both types of polyquinoxalines decompose between 500 and 640°C by a mechanism involving cleavage of the heterocycle[150]:



These polymers have potential uses as highly thermostable adhesives[152,153].

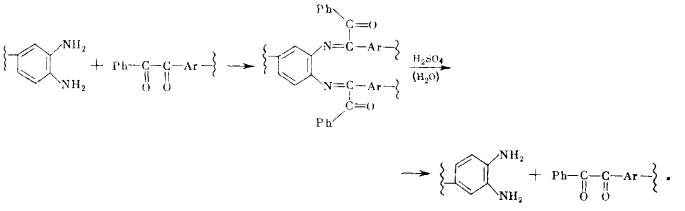
The ease of formation of polyphenylquinoxalines is extraordinary: in contrast to methods used to obtain other polyheteroarylenes, it takes place only in a single stage even at room temperature and yields completely cyclised final polymers. In no case have uncyclised intermediate products, including fragments like Schiff bases, been isolated, which evidently indicates a high degree of completeness of cyclisation. This is obviously promoted by the relatively similar nucleophilic reactivity of the *o*-amino-groups of bis-*o*-phenylenediamines and electrophilicity of the bis-α-diketones used, and also by thermodynamic and kinetic factors favouring closure of the six-membered pyrazine ring.

Polyphenylquinoxalines have been obtained in quantitative yield both in the melt and in solution. In the former case equimolecular quantities of the tetramine and the bis-α-diketone were heated in an inert atmosphere to 180–280°C, with the evolution of volatile products and the formation of polymers of relatively low molecular weight (η_{log} = 0.46 dl g^{-1}). Polycondensation in solution involves the use of various solvents (dimethylformamide, dimethylacetamide, and *m*-cresol) over the range 10–202°C. However, polymers of high molecular weight ($\eta_{log} > 1$ dl g^{-1} in sulphuric acid at 25°C) could not be obtained by boiling the initial compounds directly in dimethylformamide or in dimethylacetamide, owing to the sparing solubility of the polymers formed, which separated from the reaction mixture in the initial stages[68].

The most suitable solvent for this reaction proved to be *m*-cresol, in which polyphenylquinoxalines of high molecular weight were readily formed at room temperature (within 2–3 h); subsequent heating (boiling for 72 h) produced hardly any increase in viscosity or molecular mass of the polymers. With η_{log} = 2.16 dl g^{-1} the scattering of light gave the molecular mass M_n = 247 000. *m*-Cresol probably not only is a good solvent for polyphenylquinoxalines but also catalyses their formation. This conclusion forms the basis of a method for synthesising these polymers in a cresol-free medium, e.g. a chlorinated hydrocarbon, with proton-donating compounds—methanol, acetic acid, phenols—as catalysts[154]. Reaction takes place readily and rapidly in solution at room temperature to give polymers of high molecular weight (η_{log} = 1.5 dl g^{-1}).

Kinetic investigation of the formation of polyphenylquinoxalines in dilute media indicates[155] the second order for the reaction catalysed by *m*-cresol; similar results have been obtained by other workers[156]. From a study of the molecular-weight distribution and the hydrodynamic properties of dilute solutions of the polymers it was concluded that one branch point was present in ~180 ± 10 chain units[155].

Analogous conclusions were reached by Hergenrother[157], who observed gel formation during synthesis of the polymers in concentrated solutions, as well as a decrease in the viscosity of their solutions in concentrated sulphuric acid. He related this to the possibility of the formation of side-chains containing azomethine bonds, which are easily broken by the action of an acid:

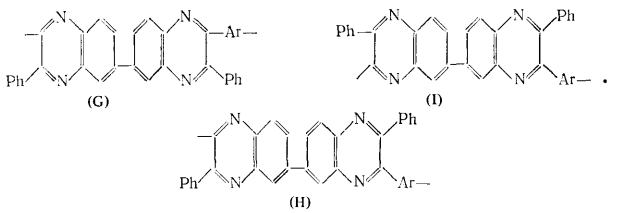


Such an explanation appears unconvincing, however, since it contradicts the good solubility of the polymers, as well

as the formation of Schiff bases usually at high temperatures[158]. It is quite possible that the branching, gel formation, and fall in viscosity mentioned by several investigators[155,157] may be due to contamination of the initial tetraketone by small amounts of impurities of functionality ≳4. This seems likely, as the method used to prepare the bis-α-diketones involved a stage of acylation in the presence of aluminium chloride, leading to formation of the required product with difficulty separable products of incomplete or excessive acetylation. Furthermore, the oxidation of deoxybenzoins by selenium dioxide may be incomplete. When bis-α-diketones obtained via diethynyl compounds are used to prepare the polymers, gel formation and the fall in viscosity of solutions in sulphuric acid are not observed[76,88,159].

Polyphenylquinoxalines are distinguished from other polyheteroarylenes in being true thermoplasts. However, their plastic properties become undesirable when the polymers are used at high temperatures (above 300°C). Numerous and varied attempts have therefore been made to overcome this defect by raising the glass point T_{gl} of polyphenylquinoxalines, which usually lies below 300°C and prevents realisation of the high thermal stability inherent in the polymers.

Three main factors—molecular flexibility (mobility) of the chains, molecular symmetry, and intermolecular interaction, i.e. polar interactions and hydrogen bonds—determine the glass points of polymers. This is clearly evident from results obtained by Wrasidlo[160] and by other workers[161], who studied the molecular mobility of phenylated and non-phenylated polyquinoxalines. Position isomerism is possible with these polymers:

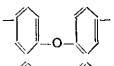
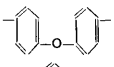
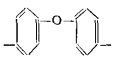


The probability of formation of these isomers decreases from (G) to (I), owing to the reactivity of the active groups in the initial reactants (i.e. the inductive and electromeric effects); they are all randomly distributed in the polymer chain. As a result, configurational disorder is observed, intensified by the introduction of flexible groups— O, CO, and SO_2— into the chain, with loss of crystallinity.

It is noteworthy that structurally similar phenylated and non-phenylated polyquinoxalines have almost the same glass points (Table 6). Wrasidlo[160] considers that the mobility responsible for the second-order transition in these polymers corresponds to movement of the main chain, since the barrier to internal rotation in them (measured by ΔC_p) is extremely high owing to the effects of *ortho*-substitution and resonance, while depending little on the structure of the monomer unit. Table 6 shows that increasing the number of single bonds in the unit from two to nine (No. 1 and 21) results in a fall in the glass point from 395 to 216°C, caused mainly by the introduction of hinge groups—ether bonds, carbonyl and sulphonyl groups.

The influence of the above factors on the glass points can be traced in polyphenylquinoxalines containing

Table 7. Properties of ordinary and cross-linked polyphenylquinoxalines[75].

No.	R	Ar	X	η_{log}, gl g^{-1}	T_{gl}, °C	
					initial	after * heating
1	—		OH	1.10	375	370
2	—		OCN	1.17	⩽450	none
3	—		—	1.19	280	284
4	—		CN	1.62	340	371
5	>C=O		OPh	0.72	215	219
6	>C=O		4-O-C_6H_4CN	0.51	227	327
7	—		Me	0.63	165	210
8	—		Et	0.64	286	—
9	—		OMe	0.64	305	—
10	—		OPh	0.45	245	—
11	—		Ph	0.81	326	—

* In nitrogen at 400°C for 0.5 h.

various polar groups in the *para*-position of the phenyl substituent.

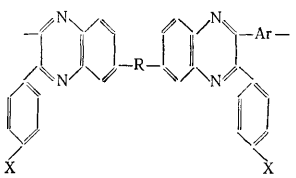
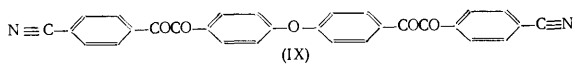


Table 7 [75] shows that such substitution has a significant effect on the glass point in comparison with polymers not containing polar groups (No. 3 and 4). With Ar = *m*-C_6H_4, R representing a singly bonded group, and X = C_2H_5, OCH_3, and OC_6H_5—i.e. groups conferring flexibility on the molecule—the glass point of the polymers falls (286, 305, and 245°C respectively— No. 8–10); with X = C_6H_5 (No. 11) the glass temperature rises to 326°C, but the introduction of hydroxyl (X = OH, No. 1) is accompanied by a rise to 375°C, obviously owing to the strengthening of interchain interaction by hydrogen bonding. The rise to 340°C when X = CN (No. 4) is probably due both to strengthening of polar interaction and to greater molecular symmetry, i.e. a more regular configuration of the chains and hence a more perfect conformation.

Position isomerism in polyphenylquinoxalines provides a good explanation of their solubility, amorphism, and ability to be processed in the cyclised form. However, the carbonyl groups of bis-α-diketones may differ appreciably in electrophilicity owing to non-equivalence of the inductive effects of substituents, which can in principle

lead to preferential formation of one isomer[75]. Thus in the case of the bis-α-diketone

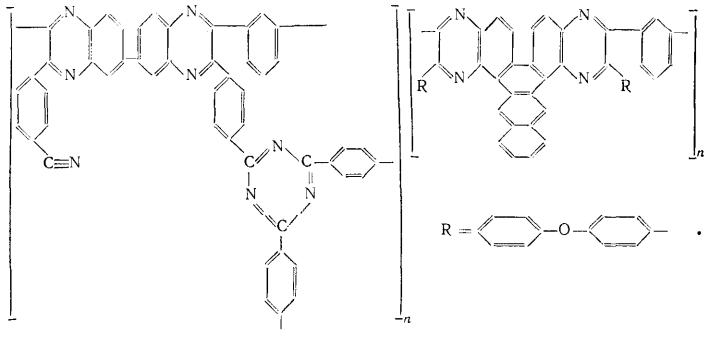


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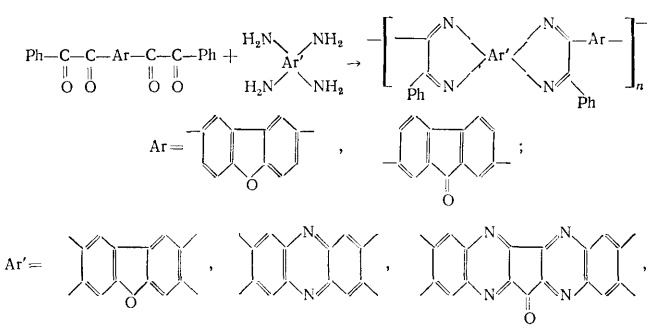
the electron-accepting effect of the cyano-group should increase the reactivity of the nearer carbonyl, whereas the ethereal oxygen atom—an electron donor with respect to the second carbonyl—would lower its reactivity, which should ultimately cause the predominance of one isomer in the polymer chain and increase the molecular symmetry[75].

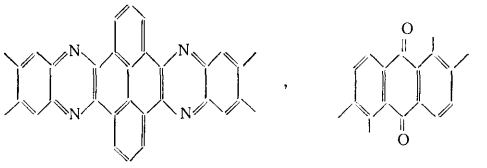
The thermal plasticity of polyphenylquinoxalines can be diminished by heat-treatment above the glass point, which is accompanied by a rise in the temperature at which the mechanical properties of the polymers are maintained. Thus heating films in helium at 400°C for 1, 4, 6, and 8 h gradually moves the temperature dependence of the modulus of elasticity to higher temperatures (the modulus begins to decrease at 316, 347, 375, and 387°C respectively). An analogous effect is achieved by heat-treatment in air, but in a shorter time, The effects are obviously due to pyrolytic cross-linking combined with oxidising processes[162,163].

Another method is available for raising the glass temperature, e.g. by introducing into the polymer functional groups—cyanato, cyano, carbonyl, phenethynyl, etc.—that on subsequent heat-treatment at moderate temperatures or treatment with simple compounds form cross-linked structures. The thermal plasticity and the solubility of the polymers are thereby lowered, and the glass point is raised considerably. In polymers containing nitrile, cyanate, and phenethynyl groups heat-treatment is accompanied by intermolecular trimerisation and formation of 1,3,5-triazine and other rings, yielding highly thermostable rigid systems of the type[75,164]



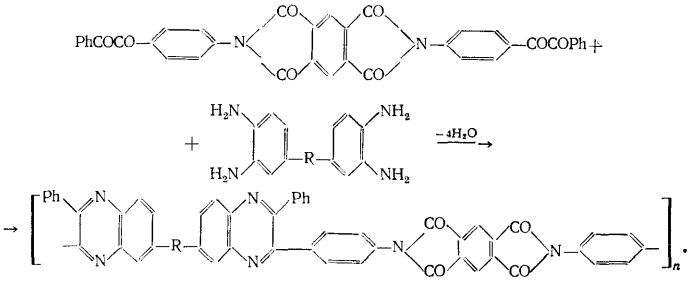
The glass point of polyphenylquinoxalines can be raised also by introducing fused rings into the amine[165] or ketone[166] component:





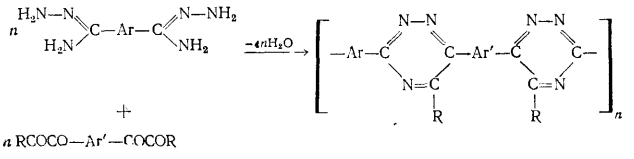
The polymers obtained from tetramines or tetraketones having high melting points possessed glass points of ~400°C and above, but exhibited loss of solubility and workability, as well as considerable impairment of their mechanical properties[165-167].

A more promising approach was the synthesis of polyphenylquinoxaline copolymers[70,168-172], in particular of polyimido-phenylquinoxalines, obtained by Augl et al.[169,170] from $\Lambda\Lambda'$-di-*p*-benzilylpyromellitimide and aromatic tetramines:

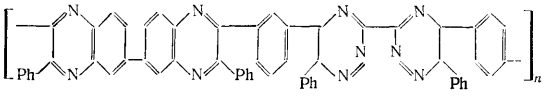


The thermal and other characteristics of the copolymers usually lie between those of the corresponding homopolymers. Table 8 lists glass points and temperatures of maximum mechanical and dielectric losses E'' and ϵ'' for five different compositions, three of which are copolymers obtained from 3,3'-diaminobenzidine and different mixtures of *p*-bisphenylglyoxyloylbenzene and *pp'*-bisphenylglyoxyloylbenzophene.

Poly-1,2,4-triazines have been obtained by reaction between bis-α-dicarbonyl compounds and bisamidrazones of dicarboxylic acids[75,174-176]:



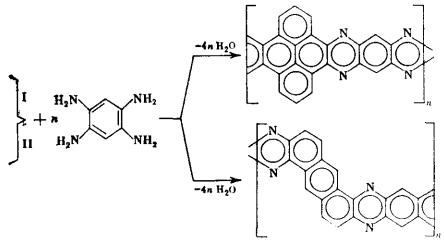
(where R = C_6H_5 and Ar, Ar' represent arylene groups). Copolymers containing quinoxaline and 1,2,4-triazine rings in the macromolecules



have also been prepared[157,177]. The phenylated polytriazines possess better solubility and thermal properties than do their non-phenylated analogues, but both are inferior to polyphenylquinoxalines in thermal and thermo-oxidative stability. Thus phenylated poly-2,2,4-triazines exhibit good stability in air at 260°C, whereas polyphenylquinoxalines retain their properties at 316°C for a long time (1000 h).[157]

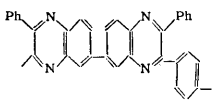
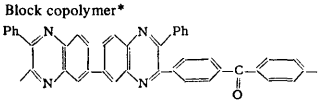
The highest heat resistance and thermal stability are found with "ladder" polyquinoxalines, which have been obtained by the reaction of pyrene-4,5:9,10-diquinone (I)

or anthracene-1,2:5,6-diquinone (II) with benzene-1,2,4,5-tetramine, naphthalene-1,2,5,6-tetramine, anthracene-1,2,5,6-tetramine, or dibenzo-5,10-dioxin-2,3,7,8-tetramine[178,179]. Completely aromatic polymers have been synthesised by the reaction of (I) or (II) with benzene-1,2,4,5-tetramine in hexamethylphosphoramide (or *m*-cresol or polyphosphoric acid) at 180°C for 120 h:



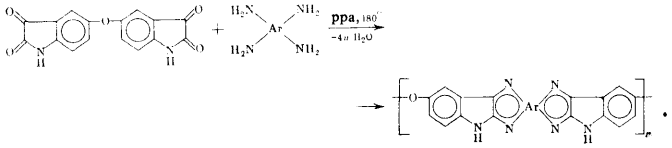
They are readily soluble in the hydrate of dichlorotetrafluoroacetone and possess viscosities $\eta_{log} \leq 2.1$ dl g^{-1}. Thermogravimetric analysis indicates that their degradation begins at 550°C in air and at 700°C in an inert atmosphere; they are regarded as some of the most thermostable heterocyclic polymers known at the present time[178,179].

Table 8. Influence of structure of copolymers on transition temperatures and relaxation maxima[173].

Polymer	Comp., %/%	$T(\Delta C_p)$, °C	$T(E''_{max})$, °C	$T(\varepsilon''_{max})$, °C
	100/0	372	385	435
Block copolymer*	72/25	352	369	415
Block copolymer*	70/50	344	352	408
Block copolymer*	25/75	330	346	391
	0/100	325	340	378

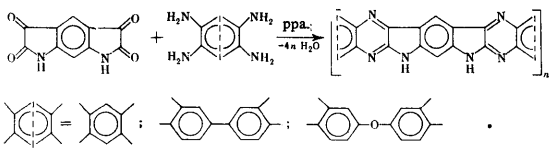
* Mean length of block determined viscosimetrically is 10–20 units[173].

A peculiar variety of this type of polymer comprises polyindoloquinoxalines, obtained by the interaction of tetramines and bi-isatins (e.g. of 5,5′-di-isatinyl ether with 3,3′-diaminobenzidine and bis-3,4-diaminophenyl ether in polyphosphoric acid at 180°C):[180–184]



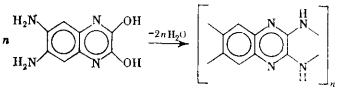
These polymers begin to decompose in air at 420–500°C, dissolve in sulphuric and methanesulphonic acids, and possess comparatively low viscosities (η_{log} = 0.1–0.4 dl g^{-1}).

Ladder polymers of similar structure but higher molecular weight, with η_{log} = 0.86–0.96 dl g^{-1}, have been obtained by the reaction between aromatic tetramines and tetrahydro-2,3,5,6-tetraoxodipyrrolobenzene in polyphosphoric acid[185,186]:

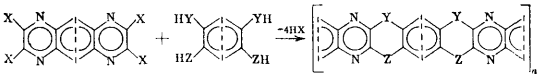


Decomposition of these polymers began in air at 460°C, and in nitrogen at 700°C.

Marvel and his coworkers[187,188] have described ladder polymers formed from tetrasubstituted quinoxalines containing activated functional groups and polymers of graphitic structure based on tetra-aminoanthraquinone and naphthalene-1,8:4,5-bisindanedione. Thus the homocondensation of diaminodihydroxyquinoxaline in polyphosphoric acid gave a ladder polymer containing quinoxaline and dihydrophenazine rings:



Similar polymers have been synthesised by condensing tetrasubstituted bisquinoxalines or anthracenes containing like functional groups with tetramines, diamino-diols, diamino-dithiols, and tetrahydric phenols[189–197]:



X=Cl, OH, OPh; Y=Z=NH; O; Y=S, O; Z=NH

Such polymers are obtained in the melt, in a solvent of high boiling point, or in polyphosphoric acid. They contain alternating quinoxaline and dihydrophenazine, oxazine, triazine, and dioxin rings, and have comparatively good thermal characteristics (they decompose in air at ~450–550°C), but are very sparingly soluble in the usual solvents and have poor workability.

In conclusion it must be remarked that α-dicarbonyl compounds are of undoubted interest as convenient subjects for the study of molecular configuration by conformational analysis[113], electron spectroscopy[198], and photochemical methods[199]. In virtue of their great reactivity they have found application for a wide range of chemical reactions[144,200] yielding in several cases valuable products[201].

The above phenylquinoxaline polymers obtained from bis-α-diketones possess a set of valuable properties, such as ease of formation, solubility, and ability to be processed by the usual technical methods into articles having great heat resistance, theremal stability, and strength against distortion, which makes then extremely promising from practical utilisation.

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