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Bis-(β-diketones)

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Methods of synthesis of various types (including those containing the ferrocene structure) of bis-(β-diketones) which are of interest as intermediates in organic synthesis, owing to their high reactivity, are described. The physical and chemical properties of these tetraketones, due to their structural features, to the presence of four carbonyl groups in the molecule, and to ketol-enol tautomerism are examined. 119 references.

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I. INTRODUCTION

Tetraketones, like other carbonyl compounds, exhibit high reactivity and can therefore serve as intermediates for the synthesis of aliphatic, aromatic, heterocyclic, and high-molecular-weight compounds.

The interest in tetraketones arose in recent years when existing methods for their preparation were perfected and new methods developed. The greatest number of papers relates to the use of tetraketones for the synthesis of new compounds, especially those of the heterocyclic series, which have attracted the attention of both chemists and of investigators in the sciences bordering on chemistry. Tetraketones have been used successfully for the synthesis of a new class of thermally stable polymers containing macromolecules of heterocycles in chains: polypyrazoles, polyquinoxalines, polyquinolines, and also for the obtaining coordination polymers with various metals.

Polycoordination and polyheterocyclisation are comparatively new reactions in macromolecular chemistry and their subsequent development should also extend the regions of use of tetrafunctional compounds, including tetraketones.

The present review considers the most abundant representatives of tetraketones—bis-(β-diketones) of various structures: linear, of the type

$$RCOCH_2CO-Y-COCH_2COR$$

and branched, of the types

$$[(RCO)(R'CO)CH]_2CHR'' \text{ and } (RCO)(R'CO)CH-Y-CH(RCO)(R'CO).$$

Other tetracarbonyl compounds are not considered here, since they have been studied less and are little used.

The review covers the periodical literature on these tetraketones up to 1st January 1968.

II. SYNTHESIS OF BIS-(β-DIKETONES)

1. The $RCOCH_2CO-Y-COCH_2COR$ Type

a. The Claisen condensation. Bis-(β-diketones) of the general formula

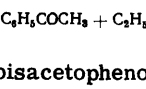
$$RCOCH_2CO-Y-COCH_2COR\ ,$$

can be obtained by two main methods: the Claisen condensation and direct acetoacetylation of aromatic compounds. The most prevalent method is the Claisen condensation, which consists in the treatment of a dicarbonyl compound, usually an ester of a dicarboxylic acid ($R'OOC-Y-COOR'$) with a ketone ($RCOCH_3$) or ethyl acetate in the presence of sodium or potassium amide[1-13]. For example[1]:

$$CH_3OOC-Y-COOCH_3 + 2C_6H_5COCH_3 \rightarrow C_6H_5COCH_2CO-Y-COCH_2COC_6H_5 + 2CH_3OH.$$

Despite its universality this method has several limitations: the Claisen condensation is accompanied by side-processes, which considerably reduce the yield of the final bis-(β-diketone), make it more difficult to isolate in a pure form, and sometimes make the synthesis completely impossible. For example, the Claisen condensation cannot be used for making adipylbisacetophenone and pimelylbisacetophenone ($Y = [CH_2]_4$ and $[CH_2]_5$; $R = C_6H_5$), because under these conditions the Dieckmann reaction takes place more readily, leading to the formation, in the first example, of 2-ethoxycarbonylcyclopentanone in 77% yield[1]:

$$C_6H_5COCH_3 + C_2H_5OCO(CH_2)_4COOC_2H_5 \rightarrow$$



.

Adipylbisacetophenone and pimelylbisacetophenone were obtained by treatment of a suspension of the sodium salt of the ketone in ether with the dichloride of the corresponding

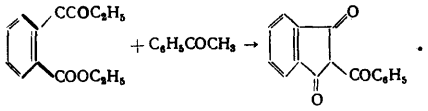
acid[1]. This method was used earlier for the synthesis of certain β-diketones[14-17]. It was then noted that the use of three equivalents of the sodium salt of the ketone per one equivalent of the acid chloride ruled out any possibility of further acylation.

The Claisen condensation also has other limitations: esters of malonic and succinic acids usually undergo an aldol condensation and a Stobbe condensation respectively. For example, with diethyl succinate the condensation with acetophenone leads to the formation of an ester of an unsaturated acid in 92% yield:

$$C_6H_5COCH_3 + C_2H_5OOC(CH_2)_2COOC_2H_5 \xrightarrow{NaH} \rightarrow C_6H_5C(CH_3)=C(COOC_2H_5)CH_2COOC_2H_5.$$

It is interesting to note that in the condensation of di-t-butyl succinate with acetophenone in the presence of NaH succinylbisacetophenone was obtained in 19–34% yield in addition to the half-ester (yield 56–64%).[9]

Several bis-(β-diketones) cannot be obtained by the Claisen condensation owing to the occurrence of intermolecular cyclisation. For example, 2-benzoyl-1,3-diketoindane was obtained in the reaction of diethyl phthalate and acetophenone in the presence of sodium ethoxide[18]:

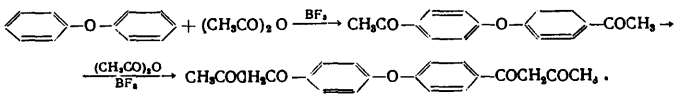


The reactions with acetone and ethyl methyl ketone take place in a similar fashion.

The mechanism of the Claisen condensation in the synthesis of bis-(β-diketones) is analogous to the mechanism of the acylation of ketones by esters. The acylation probably takes place by a three-stage mechanism, as for the formation of acetoacetic ester[15].

b. Direct acetoacetylation. This method is suitable for the synthesis of only aromatic bis-(β-diketones) in which R = CH_3, and Y = an aryl biradical of various structures. The method consists in the direct acetoacetylation of aromatic compounds with two benzene rings by an excess of acetic anhydride in the presence of BF_3.[19,20]

In comparison with the Claisen condensation this method does not require the use of solvents and metallic sodium (or sodium amide), is simple and convenient to use, and gives higher yields and purer bis-(β-diketones). With diphenyl oxide as an example the reaction can be represented by the following overall equation:

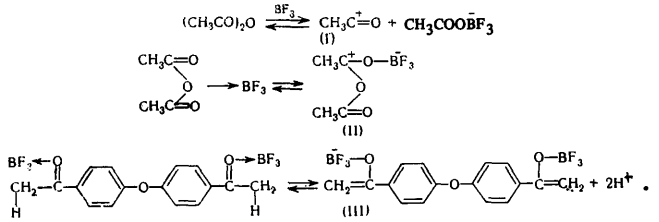


The first stage of the reaction is evidently the formation of diacetyl compounds by a Friedel-Crafts reaction.

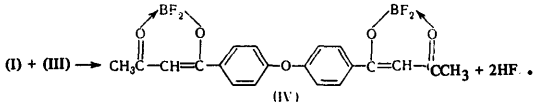
The formation of bis-(β-diketones) from diketones can occur either as a result of their direct *C*-acylation or by the *O*-acylation of the diketone with subsequent *C*-acylation of the resulting ester of the enol form of the diketone[21].

The large consumption of boron trifluoride is probably due to the *C*-acylation of the diketone being connected with the conversion of both the acid anhydride and also the diketone into reactive intermediate compounds, which then participate further in the condensation.

The mechanism of this reaction has not been investigated. Presumably, as for the synthesis of β-diketones[22] the acid anhydride forms a carbonium ion—of type (I) or (II)—and the diketone a complex of the enol type, which by analogy with ordinary enols should correspond to structure (III):



Condensation of the carbonium ion (I) with the enol complex (III) leads to the formation of a complex of the tetraketone (IV):



The *O*-acetylation of a diketone evidently leads to the proton-catalysed enolisation of the diketone accompanied by the acylation of the enol formed. Subsequently *C*-acylation of the ester of the enol form of a diketone by carbonium ions (I) or (II) lead to the formation of an ester of the enol form of a bis-(β-diketone), which after removal of the acid fluoride also forms the complex (IV).[20-22]

In the initial period of the reaction when there is still little acid in the reaction mixture, a bis-(β-diketone) can be formed only by *C*-acylation of a diketone. However, with the accumulation of acid in the reaction mixture formation of a bis-(β-diketone) can also take place indirectly and in the last period of the reaction this second path can become dominant. Since the acid which is formed as a side-product of the reaction catalyses not only the *O*-acetylation of ketones but also their self-condensation (aldol type) the best yields of bis-(β-diketones) were obtained when the rate of introduction of BF_3 into the reaction was maximal[20].

The direct acetoacetylation of diphenyl oxide, diphenylmethane, diphenylethane, diphenyl disulphide, and diphenyl esters of ethylene glycol and diethylene glycol by acetic anhydride in the presence of BF_3 gave the corresponding bis-(β-diketones), the structure of which was confirmed by a counter-synthesis by the Claisen condensation[20].

2. Bis-(β-diketones) of the $[(RCO)(R'CO)CH]_2CHR''$ Type

Bis-(β-diketones) of this type are obtained by the reaction of β-diketones with aldehydes in the presence of the appropriate catalyst[23-39].

The synthesis of bis-(β-diketones) of the $[(RCO)(R'CO)CH]_2CHR''$ type, evidently proceeds through the formation of an intermediate product of the $(RCO)(R'CO)CH{=}CHR''$ type, which adds a second molecule of the β-diketone by a Michael reaction, for example, in the formation of 2-phenyl-1,1,3,3-tetra-acetylpropane during the reaction of equimolecular amounts of benzaldehyde and acetylacetone[23]. In a series of instances, for example, in the reaction of acetylacetone with cinnamaldehyde[24], 2-hydroxynaphthaldehyde[25], or salicylaldehyde[26], the formation of an unsaturated β-diketone $(CH_3CO)_2C{=}CHR''$ was not observed.

Bis-(β-diketones) with a trifluoroacetyl group could not be obtained by this method, evidently because of their hydrolytic cleavage, analogous to that of the simple β-diketones containing a trifluoroacetyl group[26-28].

3. Bis-(β-diketones) of the (RCO)(R'CO)CH–Y–CH(RCO)(R'CO) Type

Bis-(β-diketones) in which R=R'=CH_3 and Y is a single bond are obtained by the reaction of a sodium salt of a β-diketone with iodine in ether and ethanol[40-42].

For the synthesis of bis-(β-diketones) with R=R'=CH_3, Y = $[CH_2]_2$, $[CH_2]_6$, $[CH_2]_{10}$, and 1,4-$(CH_2)_2C_6H_4$ a method suitable for the synthesis of monoalkylated β-diketones RCOCHR"COR' was used, consisting in the alkylation of a β-diketone (sodium salt of acetylacetone) with a dihalogenoalkane[43-48,56,57]. The reaction is usually carried out in a sealed ampoule[46-49] or in a high-boiling solvent[50]. The dihalogenoalkane can act as the solvent, which allows the reaction to be carried out at higher temperatures. However, the presence of a large excess of the dihalide is unfavourable for the reaction since it assists intramolecular condensation.

It was found that the best alkylation conditions are the reaction of acetylacetone (3 moles) with the dihalogenoalkane (1 mole) in a medium of t-butyl alcohol in the presence of sodium t-butoxide (2 moles) under reflux with vigorous stirring[40]. 4,4'-Bis-(2,2-diacetoethyl)biphenyl and 4,4'-bis-(2,2-diacetoethyl)diphenyl oxide were obtained by boiling 4,4'-bis(bromomethyl)biphenyl and 4,4'-bis(bromomethyl)diphenyl oxide with sodium acetylacetonate in acetylacetone[51].

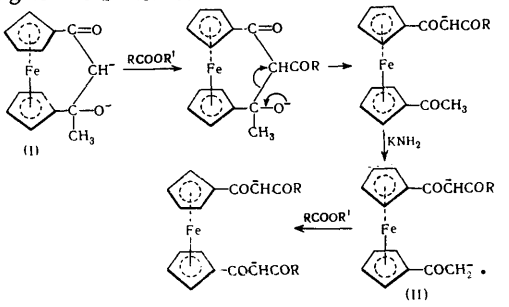
It should be noted that the alkylation of sodium acetylacetonate by dihalogenoalkanes in the synthesis of bis-(β-diketones) takes place exclusively at the carbon atom. Evidently for bis-(β-diketones) a type S_N2 transition state is established preferentially, in which the alkylation is directed towards the less electronegative atom, here carbon.

The observed direction of alkylation agrees with the views of Nesmeyanov and Kabachnik concerning the increasing tendency to reaction with transfer of the reaction centre (from oxygen to carbon) with increase in the ionic character of the bond of an ambidentate anion with a metal. Moreover, in addition to polar factors steric effects have a great effect on the direction of alkylation[52-54].

Neuse and Crossland[57] recently described some ferrocene-containing bis-(β-diketones) having a linear structure of the $RCOCH_2CO–Y–COCH_2COR$ type, where Y = ferrocene.

1,1'-Bis(acetylaceto)ferrocene and 1,1'-bis(benzoylaceto)ferrocene were obtained by a Claisen condensation from 1,1-diacetylferrocene by the method of Hauser and coworkers[16]; 1,1'-bis(formylaceto)ferrocene was synthesised by a modified Schlögl method[17], which included condensation of 1,1'-diacetylferrocene with ethyl formate.

A mechanism has been proposed for the acylation of diacetylferrocene in the presence of potassium amide, which takes place through the formation of the intermediate cyclic carbanion (I) and dianion of the bis-(β-diketone) (II), according to the scheme:



The authors note that the introduction of the second acyl group is easier than the first which can be explained by the better solubility of the dipotassium salt of the dicarbanion (II) compared with the dipotassium salt of the dianion (I), and possibly also the isomerisation of cis-dianion (II) into the trans-configuration as a result of the repulsion of the negative charges of the two side chains[57].

III. PHYSICAL PROPERTIES AND STRUCTURE OF THE BIS-(β-DIKETONES). KETO–ENOL TAUTOMERISM

Most of the bis-(β-diketones) described above are crystalline substances with rather high melting points. The overwhelming majority of the bis-(β-diketones) give a specific cherry-red colour with a methanol solution of $FeCl_3$.

A characteristic feature of the bis-(β-diketones) is the keto–enol tautomerism which has been studied in detail by the example of dicarbonyl compounds[58]. In recent years a significant contribution to the development of a quantitative theory of keto–enol equilibrium by the example of β-diketones has been made by Kabachnik and coworkers[59-62].

Since linear bis-(β-diketones) of the type $RCOCH_2CO–Y–COCH_2COR$ can be regarded as derivatives of benzoyl acetone and branched bis-(β-diketones) of the $[(RCO)_2CH]_2Y$ and $[(RCO)(R'CO)CH]_2CHR'''$ types as 3-substituted acetylacetone. They will possess to a considerable extent the keto–enol equilibrium found for β-dicarbonyl compounds. However, there are some specific features in the keto–enol tautomerism of bis-(β-diketones), owing to the peculiarities of their structure.

As an investigation of their infrared and ultraviolet spectra showed, bis-(β-diketones) of the $RCOCH_2CO–Y–COCH_2COR$ type exist predominantly in the *cis*-enol form in the solid state and in 95% ethanol solution[1]. This is shown by the absence of absorption characteristic for the carbonyl group in the infrared spectra of almost all the bis-(β-diketones) studied (in the range 5.7–5.9 μm), except for oxalyldiacetone and adipyldiacetone. Furthermore, the 16 bis-(β-diketones) studied have either one or two absorption bands of high intensity (in the range 6.2–6.5 μm) ascribable to an enol chelate bond. The absence of hydroxyl absorption in the spectra of ten of the 16 bis-(β-diketones) (2.95 μm region) is evidently due to its displacement and the superposition of the bands of the stretching vibrations of the C–H bonds. A similar effect was observed earlier in the spectra of acetylacetone and other enolised β-diketones, which was explained by the influence of the strong intramolecular hydrogen bonds[22,55,63,64].

The position of the enol-chelate bonds in the infrared spectra is determined by the structural features of the bis-(β-diketones). Thus, the enol-chelate bands in sebacylbisacetone are found at 6.08 and 6.24 μm, and in oxalyldiacetone at 6.25 and 6.33 μm. This displacement is the result of the great degree of conjugation possible in oxalyldiacetone. Replacement of the alkyl terminal groups in the latter by phenyl groups increases the degree of conjugation and correspondingly the oxalyldiacetophenone has an enol–chelate band at 6.25–6.40 μm.[1]

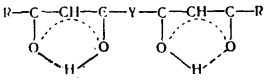
When two β-diketone groups are separated by a methylene chain there is less conjugation. Thus succinyl-, pimelyl-, suberyl-, azeloyl-, and sebacyl-diacetophenone have enol–chelate absorption at 6.20 and 6.34 μm.[1]

The position of the keto–enol equilibrium is significantly affected by the nature of the solvent. It is found that a tendency for bis-(β-diketones) to exist in the keto-form is more pronounced in tetrachloroethylene than in the solid state. As studies of the ultraviolet spectra showed, in

95% ethanol bis-(β-diketones) of this type exist predominantly in the enol form[1]. A displacement of the position of the enol band in the ultraviolet spectra of the bis-(β-diketones) to the side of 310 nm can be qualitatively connected with conjugation, which appears in the presence of terminal phenyl groups and/or phenylene bonds. For example, when R = phenol and Y = a methylene chain, the enol band is noted at ~ 312 nm (succinyldiacetophenone 320 nm, and oxalyldiacetophenone even 333 nm); terephthalyldiacetone has absorption at 340 nm, isophthalyldiacetophenone at 357 nm, and terephthalyldiacetophenone at > 360 nm.

For certain bis-(β-diketones) the enol content has been determined quantitatively from the ratio $\varepsilon_m/\varepsilon_e$ (ε_m is the observable extinction at 310 nm, where the absorption of the keto-form should be insignificant, and ε_e is the extinction of the pure enol), and on the basis of PMR spectra. The calculated concentrations of the enol in 95% ethanol for the following bis-(β-diketones) are: suberyldiacetophenone 77.8%; azelyldiacetophenone 82.8%; sebacyldiacetophenone 88.4%; and 4,4'-bis(acetoacetyl)diphenyl oxide 100%.[1,65]

On the basis of the results of spectroscopic investigations and also the inertness of bis-(β-diketones) of the $RCOCH_2CO-Y-COCH_2COR$ type in certain reactions in which the ketonic form is absent, the following structure was attributed to them:



Evidently, as a result of the enolisation of the bis-(β-diketones) a claw-shaped complex (chelate) is formed and the fractional negative charge arising on the carbon is delocalised between the carbon and carbonyl-oxygen atoms, which leads to the stabilisation of the molecule and a decrease in its reactivity[19].

It should also be noted that the keto-enol equilibrium in the bis-(β-diketones) is extremely stable. Unlike the usual mobile keto-enol equilibrium known in acetylacetone, acetoacetic ester, and other β-diketones, the principal enol form is retained and reacts even in solutions of these bis-(β-diketones).

Bis-(β-diketones) of the $[(RCO)(R'CO)CH]_2CHR''$ type (the so-called branched tetraketones) exist predominantly in the keto-form in the solid state according to the infrared spectra. This is shown by the intense carbonyl absorption at 5.77–5.85 μm and the weak absorption in the 6.25 μm range, characteristic of enol–keto absorption. In the infrared spectra of the bis-(β-diketones) of this type there are maxima at ~ 2.95 μm, corresponding to the vibrations of the strained hydroxyl bonds. In nine examples it was found that the hydroxyl bonds can be shifted, bringing about displacements of the vibrations of the CH-bonds analogous to the displacement observed in the spectrum of acetylacetone and other enolised β-diketones, and also bis-(β-diketones), which form strong intramolecular hydrogen bonds[63,64].

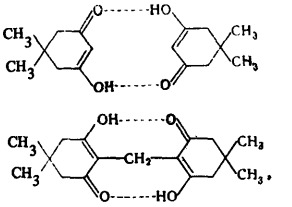
The structure of R and R' has a considerable influence on the position of the normal carbonyl bond in these bis-(β-diketones). In 11 compounds in which R = R' + CH_3 five have two carbonyl maxima at 5.78 and 5.85 μm, and six of the compounds have only one intense maximum at ~ 5.85 μm. The compounds

$[(CH_3CO)(C_6H_5CO)CH]_2CHC_6H_5$ and $[(C_6H_5CO)_2CH]_2CH_2$

have two carbonyl group absorption maxima in the ranges 5.83 and 5.94 μm and 5.91 and 5.97 μm, respectively. These changes in the position of the carbonyl bonds are evidently due to an increase in the carbonyl conjugation.

The enol-chelate absorption of these compounds is very weak. Only in three compounds of the $[(CH_3CO)_2CH]_2CHR''$ type, where R'' = 2-ClC_6H_4, 2-CH_3O-C_6H_4, or 2-C_5H_4N, is the intensity of the enol-chelate absorption and carbonyl absorption comparable. The reason for this is not clear. Possibly here there is the effect at all the R'' of these three compounds of heteratoms or substituting groups in the *ortho*-position, which creates steric and/or polar effects favourable for an enol-chelate structure.

In the infrared spectra of solid methylenebis(dimedone) there are present the vibrations of weak intensity of conjugated carbonyl at 5.90 μm and of enol-chelate bonds of high intensity at 6.10 and 6.30 μm. This picture is completely analogous to the dimedone spectrum, which suggested an analogy in their structure: an enol-chelate structure resulting from dimerisation has been proposed for dimedone and an intramolecular enol-chelate structure for methylenebis(dimedone)[63]:



Methylenebis(dimedone) does not form the cherry-red colour characteristic of bis-(β-diketones) with a methanol solution of $FeCl_3$.

An investigation of the ultraviolet spectra of bis-(β-diketones) of the $[(RCO)(R'CO)CH]_2CHR''$ type in 95% ethanol showed the dependence of the extinction coefficient on concentration; in some instances the extinction coefficient increases with increase in concentration—for example, for the compound

3,4-$(CH_3O)_2C_6H_3CH[CH(COCH_3)_2]_2$

—in other instances it decreases as the concentration is raised—for example,

$[(CH_3CO)_2CH]_2CHC_5H_4N$,

—in a third group it is independent of concentration—methylenebis(dimedone) and certain other compounds[40].

Such anomalies, which are explicable for acyclic β-diketones by their low acidity and inability to form enol-chelates[68] unsuitable for finding differences in the spectra of bis-(β-diketones) since they are all capable of forming enol-chelate structures. The differences in the extinction coefficients can be best explained by a change in the conjugation of the enol with change in concentration[67].

A comparison of the ultraviolet spectra of the β-diketones and the related bis-(β-diketones) of the $[(RCO)(R'CO)CH]_2CHY$ type that the latter have much less tendency to enolisation, with the structure and spectroscopic characteristics of the bis-(β-diketones) determined by the nature of R, R', and the –Y bonds. Thus benzoyldiacetone in 95% ethanol has mixed keto–enol absorption in the 245.5 nm range ($\lg\varepsilon_m = 3.78$) and the pure absorption of the enol form at 310 nm ($\lg\varepsilon_m = 4.14$).[68] The bis-(β-diketone)

$[(CH_3CO)(C_6H_5CO)CH]_2CHC_6H_5$

has only one intense maximum, at 248.5 nm ($\lg\varepsilon_m = 4.30$), which shows the absence of an enol form. Dibenzoylmethane exists in ethanol almost exclusively in the enol form

($\lg \varepsilon_m = 4.36$ at 345 nm and $\lg \varepsilon_m = 3.92$ at 250 nm); tetra-acetylpropane, on the other hand, has intense absorption at 249 nm ($\lg \varepsilon_m \simeq 4.6$) and weak absorption at 340 nm ($\lg \varepsilon_m = 3.0-3.4$).

Hence unlike the $RCOCH_2CO-Y-COCH_2COR$ type of bis-(β-diketones), which exist in the solid state predominantly in the enol form, the bis-(β-diketones) of the $[(RCO)(R'CO)CH]_2CHR''$ type (where $R'' \neq H$) have a much less expressed tendency to enolisation in the solid state.

Bis-(β-diketones) of the $[(RCO)(R'CO)CH]_2Y$ type show great differences amongst themselves in physical properties and structure. Tetrabenzoylethane is hardly enolised at all (there is no absorption at 340 nm, an intense absorption at 247.5 nm, $\lg \varepsilon_m = 4.89$); tetra-acetylethane, on the other hand, has an intense enol-chelate absorption at 6.27 μm but no carbonyl absorption in the 5.85 μm range. Tetra-acetylpropane has maximum absorption of approximately the same intensity both in the range of vibrations of the ketonic groups and in the enol-chelate region.

In an investigation of the PMR spectra of 1,1,2,2-tetra-acetylethane, 1,1,3,3-tetra-acetylpropane and 1,4-bis-(2',2'-diacetoethyl)benzene a signal for a hydroxyl proton of *cis*-enol form was observed. The chemical shifts of the protons of the OH group measured on the δ scale were 16.85, 15.80, and 16.90 respectively. Our calculations showed that the first is 100% *cis*-enol, the second contains 50% *cis*-enol and 50% ketonic form, and the third 20% *cis*-enol and 80% ketonic form. The PMR results are in complete agreement with the results obtained in studying the infrared spectra of these bis-(β-diketones), and also with their reactivity.

For all three types of bis-(β-diketones) the dissociation constants in water–dioxan mixtures with 75 or 50 vol. % dioxan at 30°C were determined using tetramethylammonium hydroxide as a base[69-71].

It was found that linear bis-(β-diketones) of the $[RCOCH_2CO]_2Y$ type are evidently stronger acids than branched ketones of the $[(RCO)(R'CO)CH]_2CHR''$ and $[(RCO)(R'CO)CH]_2Y$ types, as is shown primarily by the fact that the dissociation constants of branched bis-(β-diketones) were so low that they could not be determined in 75% dioxan.

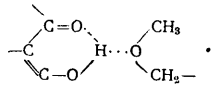
The lower acidity of the branched bis-(β-diketones) is probably connected with the fact that both the β-diketone functions are displaced from the active methylene position. An analogous picture is observed with simple β-diketones: the pK_D of acetylacetone (10.35) in 50% dioxan is less than the pK_D of butylpentane-2,4-dione (12.07).[69]

In general the relative acidity of linear and branched bis-(β-diketones) can be linked with their relative tendency to exist in the enol form in the solid state: linear bis-(β-diketones), which exist in the solid state predominantly in the enol form, are weaker acids than the branched bis-(β-diketones), which have less tendency to enolisation.

In the $C_6H_5COCH_2CO-[CH_2]_n-COCH_2COC_6H_5$ series (n = 4–8) it is interesting to note the peculiar dependence of the value of pK_{D_1} (but not pK_{D_2}) on the chain length *n*. Thus the dissociation of the first proton takes place more slowly for pimelyl ($n = 5$) than for adipyl ($n = 4$), suberyl ($n = 6$) or sebacyl-diacetophenone ($n = 8$) and even more slowly for azelayldiacetophenone ($n = 7$). The difference between the values of pK_{D_1} and pK_{D_2} increases linearly with increase in the chain length from 4 to 8. We were unable to determine pK_{D_2} for azelayldiacetophenone. The fact that the second proton of linear bis-(β-diketones) dissociates with greater difficulty with increase in the chain length, differs from what is to be expected from their behaviour[69].

However, for compounds of the $[(CH_3CO)_2CH]_2[CH_2]_n$ type the second proton dissociates more readily with increase in the chain length: thus the difference between the values of pK_{D_1} and pK_{D_2} equals 4.11 ($n = 0$), 0.49 ($n = 6$), and 0.06 ($n = 10$). The value of pK_D of bis-(β-diketones) of the $[(RCO)(R'CO)CH]_2CHR''$ type is greatly affected by the nature of R, R', and R''. For a given R'' group the derivatives of acetylacetone ($R = R' = CH_3$) have lower pK_D than derivatives of methoxyacetylacetone ($R = CH_3$, $R' = CH_3OCH_2$), although acetylacetone itself has a higher pK_D (10.35) than methoxyacetylacetone (9.66 in 50% dioxan).

To explain this non-correspondence it is suggested that a structure with an intermolecular hydrogen bond between an ethereal oxygen and a chelate hydrogen is formed:



Hence the third oxygen reduces the lability of a proton and increases pK_D itself.

In the bis-(β-diketones) series $[(RCO)(R'CO)CH]_2CHR''$ with $R = R' = CH_3$ the compound with $R'' = 4\text{-}CH_3OC_6H_4$ has a higher value of pK_D than the compound with $R'' = C_6H_5$ (11, 62, and 11.1 respectively), which is attributed to the activating influence of a methoxy-group. An increase in the electronic density at an α carbon atom in relation to the methylene group leads to a decrease in the lability of the proton. The influence of other electron-repelling substituents can be explained similarly[69]. The differences in the structure of bis-(β-ketones) appear not only in the physical properties but also in their behaviour in chemical reactions.

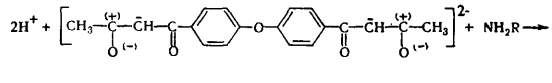
IV. CHEMICAL PROPERTIES OF THE BIS-(β-DIKETONES)

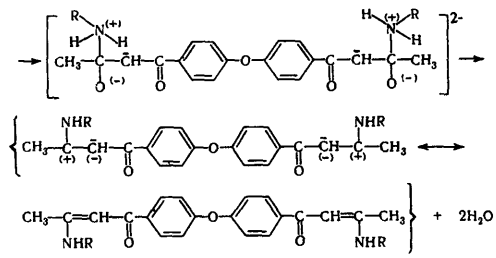
The reactivity of bis-(β-diketones) has been little investigated. As might have been expected from the analogy in structure, the bis-(β-diketones) are greatly reminiscent of β-dicarbonyl compounds. However, there are significant differences in the reactivity of these classes of compounds, which are evidently due to the presence of four carbonyl groups in the molecule of bis-(β-diketones) and of structural features connected primarily with keto-enol tautomerism.

1. Reaction of Bis-(β-diketones) with Amines. Ketoimide–Enamine Tautomerism

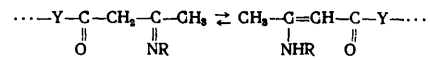
The reaction of linear bis-(β-diketones) of the $RCOCH_2CO-Y-COCH_2COR$ type with some aromatic amines has been studied. Thus 4,4'-bis(acetoacetyl)diphenyl oxide reacts vigorously on heating with aniline, 2-naphthylamine, 4-aminobiphenyl, and other amines, forming the corresponding dianils in high yields[72].

Since the initial 4,4'-bis(acetoacetyl)diphenyl oxide exists predominantly in the enol form, this reaction evidently proceeds owing to polarisation of the bonds of the principal form of the enol, which adds on the amine with subsequent loss of water from the addition product and stabilisation by conjugation:

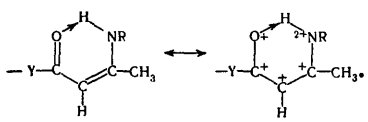




Like the initial 4,4′-bis(acetoacetyl)diphenyl oxide the product of its reaction with an amine can exist in two tautomeric forms, enamine and ketimide:

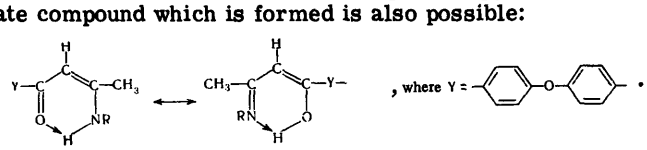


And, finally, the enamine form, like the enol form of the bis-(β-diketone), forms a pseudoaromatic chelate compound:



The "aromatisation" of the enamine-chelate form with the formation of an aromatic system of 6π-electrons should proceed more readily here than in ordinary enols, since the p-electrons of nitrogen are less firmly held than those of oxygen in the enols.

The existence of intramolecular prototropy in the chelate compound which is formed is also possible:

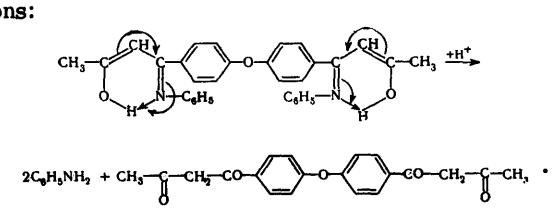


A noteworthy feature, which is characteristic for bis-(β-diketones) and probably for their derivatives, is the complete displacement of the tautomeric equilibrium in solutions, in the solid state, and in melts to the side of one of the possible tautomeric forms.

2. Kolbe Synthesis

Unlike the derivatives of aniline and acetylacetone, the products of the reaction of 4,4′-bis(acetoacetyl)diphenyl oxide with amines are cyclised into derivatives of quinoline with much greater difficulty[72].

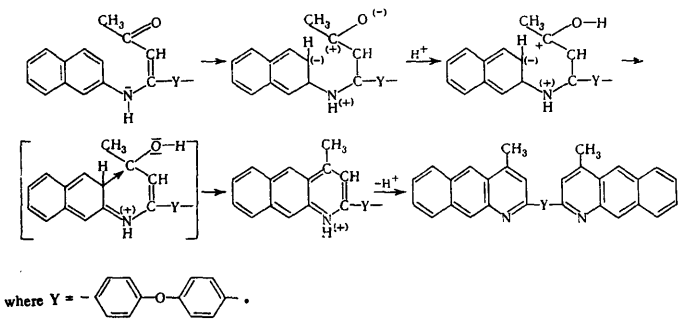
As a result of the reaction the fission of the original dianil into its constituent components is often observed. Evidently, such a direction of reaction can be explained by the fact that displacement of one CH_3 group (acetylacetone) by an aromatic radical (diphenyl oxide residue) leads to the weakening of the nitrogen–carbon bond in the β-arylaminoketone. The presence of an unshared pair of electrons at the nitrogen determines the nucleophilic nature of the NH group and facilitates attack at the side of the hydrogen ions:



The product of the reaction of 4,4′-bis(acetoacetyl)diphenyl oxide with 2-naphthylamine readily undergoes cyclisation under the action of anhydrous HF at 0°C and also on heating with a mixture of 2-naphthylammonium chloride with 2-naphthylamine, forming derivatives of benzoquinoline in ~ 35% yield in both instances. The action of conc. H_2SO_4 brought about hydrammine splitting of the original dianil.

The benzoquinolines obtained by these two methods were not identical in their properties[72]. Evidently under different conditions cyclisation proceeds in different ways.

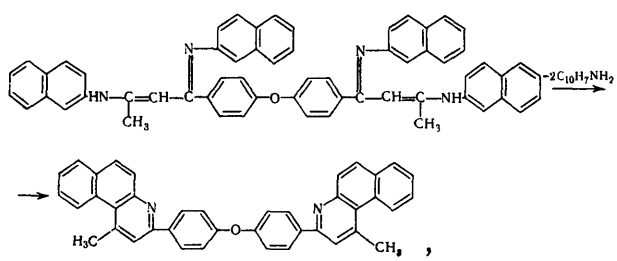
Evidently, under the action of HF a hydroxycarbonium ion is formed which cyclises into an aromatic system when water is lost:



where Y = .

In this system the closure of the naphthalene ring takes place in position 3 and a linear derivative of dibenzo(*g*)quinoline is formed. Its structure is confirmed by the similarity of the ultraviolet spectra of benzoquinoline with the spectra of anthracene, by the characteristic colour of its salts and by fluorescence in ultraviolet light[72].

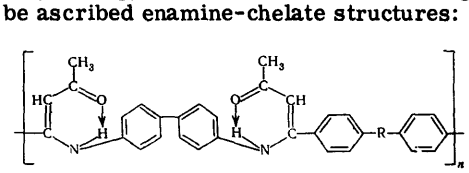
On heating 4,4′-bis(acetoacetyl)diphenyl oxide with 2-naphthylamine in the presence of an equimolecular amount of the amine hydrochloride after Petrov[73], an angular derivative of dibenzo(*f*)quinoline is obtained. Here the reaction evidently proceeds throughout the formation of an intermediate addition compound at the four carbonyl groups:



with subsequent loss of two molecules of 2-naphthylamine.

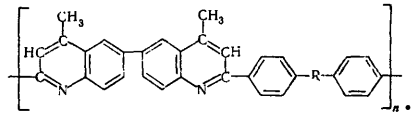
These reactions were extended to aromatic diamines; in particular the reaction of 4,4′-bis(acetoacetyl)diphenyl oxide and 4,4′-bis(acetoacetyl)diphenylethane with benzidine were studied.

Heating a mixture of the initial products leads to the formation of high-molecular-weight polyanils (η_{pr} = 0.6–0.8) which by analogy with the low-molecular-weight products can be ascribed enamine-chelate structures:



where R = –O– or $-[CH_2]_2-$.

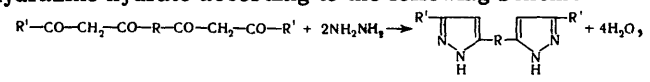
Further heating of the polyanils in a vacuum leads to intramolecular cyclisation and the formation of polyquinolines, with the degree of cyclisation here depending on the temperature and the time of heating in a vacuum[74].



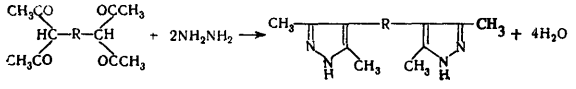
3. Reaction of Bis-(β-diketones) with Hydrazines and Hydrazides of Acids

Bis-(β-diketones) readily undergo condensation, especially with nitrogen-containing compounds (such as hydrazine and its derivatives, hydroxylamine, amidines, urea, etc.), forming addition products at two opposite carbonyl groups of two molecules of the nitrogen-containing compound, with subsequent cyclisation of the addition product and formation of heterocyclic systems: pyrazole, isoxazole, etc. The condensation products, like the original bis-(β-diketones), exhibit tautomerism.

a. Bispyrazoles. 3,5-Bispyrazoles are formed in the reaction of linear and branched bis-(β-diketones) with hydrazine hydrate according to the following scheme[55,75-77]:



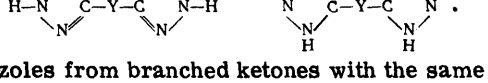
where R′ = CH_3 or C_6H_5; R = C_6H_4–$[CH_2]_2$–C_6H_4, $[CH_2]_3$, C_6H_4–O–C_6H_4, or C_6H_4–S_2–C_6H_4.



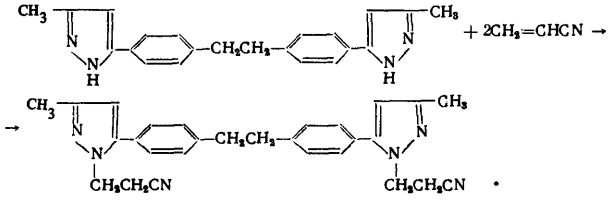
where R = CH_2–C_6H_4–CH_2, $CH_2[C_6H_4]_2CH_2$, or CH_2–C_6H_4–O–C_6H_4–CH_2.

An intermediate product of the reaction is evidently the bishydrazone formed in the reaction of the carbonyl groups of the ketone with the amino-group of the hydrazine, which then closes into a pyrazole ring.

Since the bispyrazoles of linear bis-(β-diketones) have different substituents in positions 3 and 5, two structural isomers are possible:



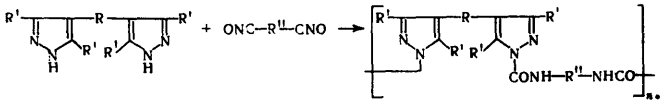
Bispyrazoles from branched ketones with the same substituents do not have isomers, thanks to the symmetry of the molecule. Bispyrazoles, like pyrazoles, form salts with strong bases (for example, hydrochlorides) they are capable of undergoing cyanoethylation, acylation, etc. The cyanoethylation of 4,4′-bis-[3(5)-methylpyrazolyl-5(3)]diphenylethane on heating it with acrylonitrile in an ampoule has been described[75]:



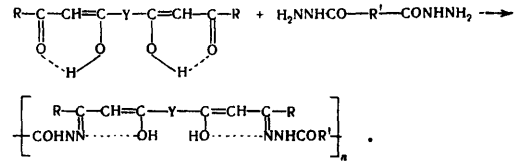
When bispyrazoles react with acetyl chloride, the corresponding *N*-acyl derivatives are formed[75,78-80].

The replacement of the acetyl chloride in this reaction by the acyl chlorides of dicarboxylic acids leads to the formation of polyacylpyrazoles[76].

When di-isocyanates are used instead of the dicarboxylic acid chlorides polymers containing pyrazole rings and amide bonds –CO–NH– in a chain were obtained[87]:



b. Polyacylhydrazones and polyacylpyrazoles of linear bis-(β-diketones). The reaction of linear bis-(β-diketones) with hydrazides of dicarboxylic acids leads to the formation of polyacylhydrazones:

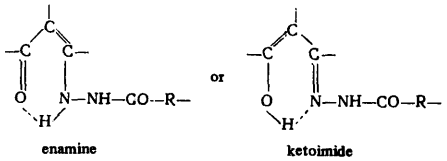


Evidently the formation of polyacylhydrazones takes place analogously to the reactions of monocarbonyl compounds with such reagents as semicarbazide, hydroxylamine, amines, etc., that is, through the addition of the amino-group of the hydrazide at the >C=O bond, with subsequent loss of water. Therefore such reaction will proceed more readily with a ketonic or *trans*-enolic form of a bis-(β-diketone) having a free carbonyl group and with greater difficulty with *cis*-enols in which the carbonyl group is connected by an intramolecular hydrogen bond into a stable six-membered ring.

The polyacylhydrazones which have been formed also have a chelate structure stabilised by an intramolecular hydrogen bond, which is shown by the presence in the ultraviolet spectrum of a polyacylhydrazone of absorption in the range λ_{max} = 335 nm; the band with λ_{max} at 300 nm is ascribed to the presence of a *cis*-enol with a stable hydrogen bond[40].

In the infrared spectrum of polyacylhydrazone as well as an intense absorption band in the 1720 cm^{-1} range attributable to the vibrations of a hydrazide C=O group there is a maximum in the range 1600–1620 cm^{-1} characteristic for a *cis*-enol[75].

The enolisation of polyacylhydrazones can be effected both as a ketomide and as an enamine structure[82]



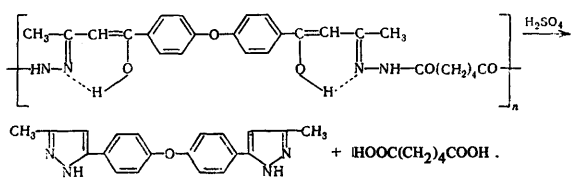
enamine ketoimide

and it is difficult to choose between these. Both these structures are stabilised by intramolecular hydrogen bond, which makes further attack by nitrogen on the carbonyl oxygen more difficult in the formation of a pyrazole ring.

Having investigated the kinetics of the formation of polyacylhydrazones by the example of the reaction of 4,4′-bis-(acetoacetyl)diphenyl oxide with the dihydrazide of adipic

acid in dimethylformamide solution at 90–120° was investigated by ultraviolet spectroscopy. It was shown that under the chosen conditions the process obeys the laws of a first order irreversible reaction. The rate constants and the activation energy of the process (17 kcal mole^{-1}) were determined[83].

The polyacylhydrazones are stable to long boiling in water and also to brief action by conc. H_2SO_4 (5–10 min). After 24 h in a solution in H_2SO_4 at room temperature polyacylhydrazones form the corresponding bispyrazoles and an acid, in quantitative yield:



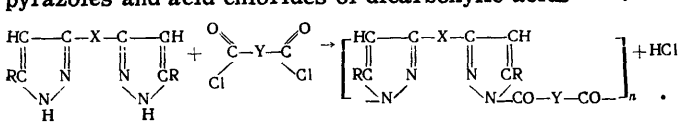
On treating polyacylhydrazones with hot hydrochloric acid the bispyrazolium chloride is formed. Concentrated solutions of alkalis also decompose the polyacylhydrazones.

The structure of the polyacylhydrazones was confirmed by comparing their ultraviolet spectra in H_2SO_4 with the ultraviolet spectrum of a model compound—4,4′-bis(acetoacetyl)diphenylethane acetylhydrazone. The ultraviolet spectrum of the polyhydrazone based on sebacylbisacetophenone in methanol is similar to the spectrum of the model compound in methanol, but has a bathochromic shift of 40 nm.[75]

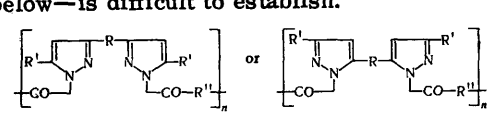
Heating polyacylhydrazones in an atmosphere of inert gas in a vacuum at 200–250°C for 3–5 h leads to the formation of polyacylpyrazoles in quantitative yield. Polyacylpyrazoles are yellow powders soluble in cresol, dimethyl sulphoxide, dimethylformamide, and sulphuric and formic acids.

Polyacylhydrazoles exhibit stability to hydrolysis by boiling water and to the brief action of conc. H_2SO_4. At room temperature polyacylpyrazoles are unchanged after several days action by 25% KOH solution; boiling for 12 h in the same alkali solution leads to complete destruction of the polymer. The bispyrazole formed as a result of hydrolysis is identical with the known product obtained from a ketone and hydrazine hydrate.

The production of bispyrazoles in the hydrolysis of polyacylpyrazoles with almost quantitative yield is confirmation of the structure of the polymers as linear macromolecules with repeated pyrazole rings. Proof of the correctness of the structure attributed to the polymers was also obtained in studying their ultraviolet and infrared spectra and also by counter-synthesis of the polyacylpyrazoles from bispyrazoles and acid chlorides of dicarboxylic acids[84–86]:



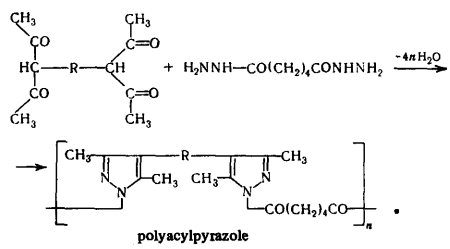
It is noteworthy that the precise position of the enol hydroxyl in bis-(β-diketones)—which determines whether the polyacylpyrazoles formed have one of the two structures shown below—is difficult to establish.



poly-1,3-pyrazole poly-1,5-pyrazole

However, Lowe and Ferguson[87] have shown convincingly that in benzoylacetone the carbonyl adjacent to the phenyl ring is enolised. Therefore of the two possible isomeric structures the poly-1,5-pyrazole structure must be considered the more probable, since linear bis-(β-diketones) can be considered to be analogues of benzoylacetone.

c. Branched bis-(β-diketones). The reaction of branched bis-(β-diketones) with hydrazides of dicarboxylic acids can be effected both in solution and in the melt. Branched bis-(β-diketones), as might have been expected, were much more reactive than the linear ones. 1,4-Bis-(2,2′-diacetoethyl)benzene, 4,4′-bis-(2,2-diacetoethyl)biphenyl, and 4,4′-bis-(2,2-diacetoethyl)diphenyl oxide exist predominantly in the ketonic form and react with adipic hydrazide very vigorously, forming polyacylpyrazoles directly under mild conditions; the intermediate polyacylhydrazones could not be isolated.

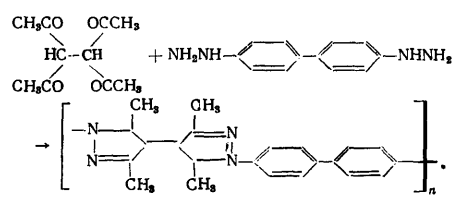


polyacylpyrazole

1,1,2,2-Tetra-acetylethane is an exception to the series of branched bis-(β-diketones), since it exists exclusively in the *cis*-enol form. On reacting with the hydrazide of adipic acid it forms a polyhydrazone comparatively readily, but attempts to cyclise this were unsuccessful. 1,1,3,3-Tetra-acetylpropane behaves similarly: it readily forms a polyhydrazone, which under different cyclisation conditions forms the same product, corresponding to a mixture of 50% polyhydrazole and 50% polyhydrazone.

According to the infrared and PMR spectra this ketone is 50% enolised[51]. However, tetra-acetylethane and tetra-acetylpropane readily form bispyrazoles with hydrazine hydrate, from which the corresponding polyacylpyrazoles were obtained by polycondensation with adipoyl chloride[85].

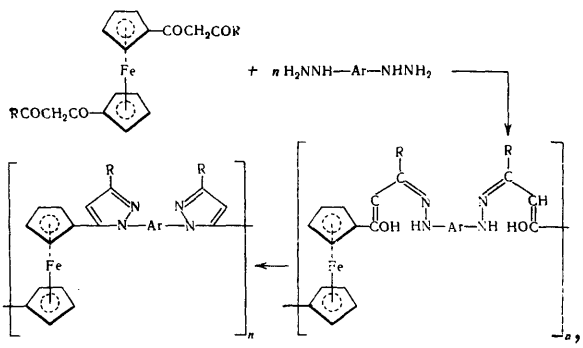
High-molecular-weight thermally stable polyarylenepyrazoles were obtained by heating bis-(β-diketones) with dihydrazines (for example, with 4,4′-dihydrazinobiphenyl). They exhibit high stability to hydrolysis by water and the action of acids and alkalis[88]. Their formation can be represented in general by the following scheme:



The structure of these polymers was demonstrated by the investigations of Mosby[55], and of Schaefer and Bertram[89].

By low-temperature condensation of 1,1′-bis(diketo)ferrocenes with aromatic or pseudoaromatic dihydrazines in solution, Neuse[90] obtained soluble polyhydrazones with a molecular weight of 1500–2000 and a viscosity of ~ 0.1–0.2 dl. g^{-1}. By thermal treatment at 200–240°C these polyhydrazones undergo cyclisation with the formation of

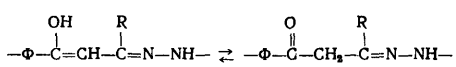
polymers containing pyrazole heterocycles substituted in positions 1 and 5:



where R = H, CH_3, C_6H_5; Ar = *m*-C_6H_4, *p*-C_6H_4, *p*-C_6F_4-C_6F_4-*p*, and *p*-C_6H_4-SO_2-C_6H_4-*p*.

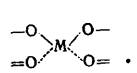
Infusible, but usually soluble, polypyrazoles had a reduced viscosity of 0.15–0.40 dl. g^{-1} and exhibited high thermal stability, exceeding that of other known ferrocene-containing polymers with heterocycles in chains[90].

The investigation of the infrared and electronic spectra of the polyferrocenylhydrazones shows the possibility of the existence in them of keto–enol equilibrium of the type:



and that the formation of a hydrazone includes the predominance of the γ-carbonyl groups of the initial bis-diketo-compound. When R = H the formation of a hydrazone takes place exclusively through the γ-carbonyl; the polymer has weak absorption in the 6.02–6.05 μm range, which is characteristic for aliphatic acyl derivatives of ferrocene in which the Φ–CO–CH_2 group is present. The additional vibrations at 5.75–5.80 μm which show the formation of a hydrazone through the α carbonyl are absent[90].

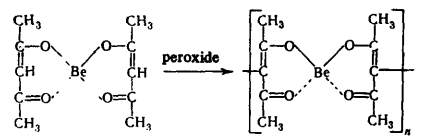
d. Coordination polymers based on bis-(β-diketones). Bis-(β-diketones) of various structure were used in polycoordination which led to the use for the construction of polymeric molecules of coordinate bonds, as well as the ordinary covalent bonds, and to the inclusion of metal atoms in the macromolecule. In this instance the bond between the metal and the ligand is effected through oxygen:



A large number of review articles and original papers deal with the synthesis of coordination polymers are the study of the polycoordination[91–99].

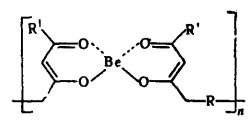
Metals with coordination number 4: copper, beryllium, zinc, magnesium, cadmium, calcium, and also transitional metals: nickel, cobalt, manganese, chromium, titanium, etc., have mainly been used for the synthesis of the coordination polymers.

The production of coordination-chain polymers can be brought about by the reaction of aqueous solutions of salts of the corresponding metals with alcoholic solutions of the bis-(β-diketones)[100] or by heating stoichiometric amounts of the metal acetylacetonate with the bis-(β-diketone) in vacuo or in a high-boiling solvent[101–103]. In the latter procedure the acetylacetone is liberated and a metal derivative of the original tetraketone is formed. Coordination polymers were also obtained by interfacial polycondensation (polycoordination)[104–106] and by polyrecombination of beryllium acetylacetonate[107]:

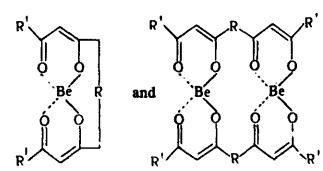


The coordination polymers obtained by the above methods are infusible and insoluble products, which makes it extremely difficult to investigate the mechanism for their formation, and to study their properties and field of application. The molecular weights of these polymers varied within the range 1000–5000, which impeded the appearance of the main polymeric properties: mechanical strength, and ability to form films and fibres.

The coordination polymers of the type:

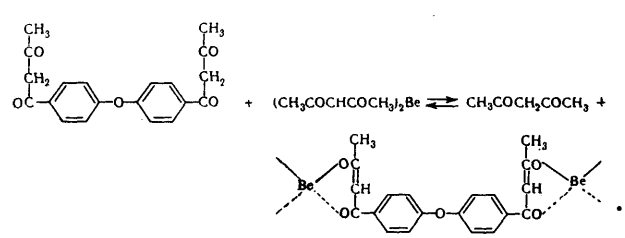


with the highest molecular weights were obtained by the polymerisation of cyclic coordination compounds of beryllium formed in the thermal destruction in vacuo of the low-molecular-weight coordination polymers of the corresponding bis-(β-diketones) and beryllium[13]:



where R′ = CH_3, CF_3; R = $[CH_2]_6$, $[CH_2]_7$, $[CH_2]_{10}$, $[CH_2]_{12}$, $NH[CH_2]_6NH$, $NH[CH_2]_{10}NH$, *p*-$[O(CH_2)_2O]_2C_6H_4$, $O[CH_2]_6O$ (R = CF_3).

The detailed investigation of polycoordination by the example of the reaction of 4,4′-bis(acetoacetyl)diphenyl oxide with beryllium acetylacetonate both in the melt and in solution allowed the main rules for this process to be established. It was found that polycoordination is a form of polycondensation process, which can be carried out at elevated temperature and which is an equilibrium process[101–117]:



Under polycoordination conditions the coordination polymers are capable of undergoing exchange reactions both with the low-molecular-weight product of the polycoordination (acetylacetone) and with low-molecular-weight substances which are similar in chemical nature to the coordination polymer (the acetylacetonate of another metal); exchange reactions also of individual polymeric molecules

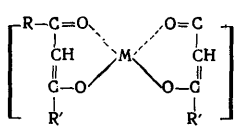
with one another also occur. Finding the main rules of polycoordination made it possible to obtain coordination polymers of high molecular weight[98,99].

A study of the kinetics of polycoordination of 4,4′-bis(acetoacetyl)diphenyl oxide with beryllium acetylacetonate in dimethylformamide solution and in Dinyl showed that this process is a second-order reaction with an activation energy of 25 kcal mole^{-1}.[109]

The properties of the coordination polymers, as for other types of high-molecular-weight compounds, are determined by the flexibility of the polymeric chain, the interfacial interaction, and the stereochemical regularity of the macromolecule. The ionic radius of the metal participating in the formation of the polymeric chain has a considerable effect on the strength of the interchain interaction and the packing density of the macromolecules of coordination polymers of the bis-(β-diketones). When the radius of the metal differs considerably from those of other atoms forming the chain (for the polymers of beryllium) this results in a disturbance of the packing density of the polymeric chains, a weakening of the force of interchain interaction, which in turn determines their best solubility and fusion[112].

The melting point of the coordination polymers of 4,4′-bis(acetoacetyl)diphenyl oxide, 4,4′-bis(acetoacetyl)diphenylmethane and 1,1,2,2-tetra-acetylethane with various metals decreases in the order: Be > Mg > Ca > Zn. The nature of the metal also affects the colour of the polymer[113].

The properties of the coordination polymers of the bis-(β-diketones) depend considerably on the chemical structure of the initial tetraketone, since in all the polymers of the bis-(β-diketones) the same coordination ring



is present, which is a comparatively stable formation in view of the fact that the donor groups coordinated with the metal ion occupy positions fixed relative to one another, the observable differences in the properties of these polymers are determined by the flexibility of the initial ligand and the packing density of the polymeric chains. The flexibility of the bis-(β-diketone) ligand will increase with increase in the number of methylene groups it contains, with decrease in the concentration of aromatic nuclei, with inclusion of aliphatic links between the aromatic nuclei of the tetraketone; the packing density of the polymeric chains will decrease on going from bis-(β-diketones) with aromatic nuclei substituted in the *para*-position, to bis-(β-diketones) with aromatic units substituted in the *meta*-position[99].

An increase in the flexibility of the polymeric chains or a decrease in their packing density owing to the corresponding changes in the structure of the initial bis-(β-diketone) is usually accompanied by a decrease in the thermal stability and an increase in the solubility of the coordination polymers[100,106,111,112].

An improvement in the solubility of the coordination polymers of the bis-(β-diketones) is brought about by the introduction into the ligand molecule of polar substituents on using a six-coordinated metal, four bonds of which participate in the creation of a coordination ring and two are occupied by aromatic radicals[118]. For example, the coordination polymers of terephthalyldiacetoacetic ester with copper, nickel, cobalt, magnesium, zinc, and mercury of the general formula:

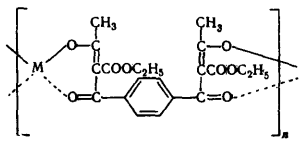
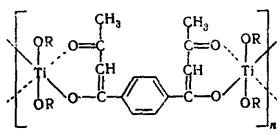


exhibit better solubility than the polymers of terephthalyldiacetone.

The coordination polymers of tetraethyl and tetra-t-butyl orthotitanates and terephthalyldiacetone of the structure



exhibited solubility in xylene[118].

The infrared spectra of polymeric copper chelates of bis-(β-diketones) have been studied[119].

REFERENCES

1. D. F. Martin, M. Shamma, and W. C. Fernelius, J. Amer. Chem. Soc., 80, 4891 (1958).
2. L. Lowg and H. Heuze, J. Amer. Chem. Soc., 63, 1939 (1941).
3. L. Claisen, Annalen, 291, 1361.
4. L. Claisen and N. Stylos, Ber., 21, 1141 (1888).
5. O. Diels, J. Sielisch, and E. Müller, Ber., 39, 1331 (1906).
6. J. Algar, Proc. Roy. Irish Acad., 33B, 86 (1916); Chem. Abs., 10, 2577 (1916).
7. E. Bröme and L. Claisen, Ber., 21, 1131 (1888).
8. O. Widman and E. Virgin, Ber., 42, 2794 (1909).
9. G. H. Daub and W. S. Johnson, J. Amer. Chem. Soc., 72, 501 (1950).
10. A. I. Vogel, J. Chem. Soc., 333 (1934).
11. H. Wieland and J. Drishaus, Annalen, 474, 102 (1929).
12. L. Berend and P. Herms, J. prakt. Chem., 2, 74, 131 (1906).
13. R. W. Kluiber and J. W. Lewis, J. Amer. Chem. Soc., 82, 5777 (1960).
14. B. O. Linn and C. R. Hauser, J. Amer. Chem. Soc., 78, 6066 (1956).
15. H. G. Walker, J. J. Sanderson, and C. R. Hauser, J. Amer. Chem. Soc., 75, 4109 (1953).
16. C. E. Cain, A. Mashburn, and C. R. Hauser, J. Org. Chem., 26, 1030 (1961).
17. K. Schlögl and H. Egger, Monatsh. Chem., 94, 1054 (1963).
18. E. Schwerin, Ber., 27, 104 (1894).
19. V. V. Korshak, E. S. Krongauz, and V. E. Sheina, USSR P. 126488 (1959), Byull. Izobr., No. 5 (1960).
20. V. V. Korshak, E. S. Krongauz, P. N. Gribkova, V. E. Sheina, and V. A. Vasnev in "Sbornik Instituta Neftekhimicheskogo Sinteza AN SSSR im. A. V. Topchieva" (Collected Papers of the Topchiev Institute of Petrochemical Synthesis of the Academy of Sciences of the USSR), Izd. Nauka, Moscow, 1964, p. 173.
21. F. G. Joung, F. C. Frostick, J. J. Sanderson, and C. R. Zauser, J. Amer. Chem. Soc., 72, 3635 (1958).

22. C. R. Hauser, F. C. Frostick, and E. H. Man, J. Amer. Chem. Soc., 74, 3231 (1952).
23. D. F. Martin, M. S. Shamma, and W. C. Fernelius, J. Amer. Chem. Soc., 80, 5851 (1958).
24. W. Renard and A. Maquinay, Bull. soc. chim. Belg., 55, 98 (1946).
25. E. Knoevenagel and F. Schröter, Ber., 37, 4484, 4496 (1904).
26. R. G. Pearson and E. A. Mayerle, J. Amer. Chem. Soc., 73, 926 (1951).
27. R. G. Pearson and A. C. Sandy, J. Amer. Chem. Soc., 73, 931 (1951).
28. E. H. Cook and R. W. Taft, J. Amer. Chem. Soc., 74, 6301 (1952).
29. E. Knoevenagel, Ber., 36, 2136 (1903).
30. E. Knoevenagel and F. Albert, Ber., 37, 4476 (1904).
31. E. Knoevenagel and R. Werner, Annalen, 281, 79 (1894).
32. R. Schiff, Annalen, 309, 206 (1899).
33. K. Bodendorf and G. Koralowski, Arch. Pharm., 271, 101 (1903).
34. G. Issoglio, Atti. accad. sci. Torino, 41, 1755 (1906).
35. E. Knoevenagel and A. Erler, Ber., 36, 2131 (1903).
36. S. Ruheman, J. Chem. Soc., 83, 1376 (1903).
37. S. V. Lieberman and E. C. Wagner, J. Org. Chem., 14, 1001 (1949).
38. W. Dieckmann, von K. Fischer, Ber., 44, 974 (1911).
39. E. C. Horning and M. G. Horning, J. Org. Chem., 11, 95 (1946).
40. D. F. Martin, W. C. Fernelius, and M. Shamma, J. Amer. Chem. Soc., 81, 130 (1959).
41. S. P. Milliken, Amer. Chem. J., 15, 523 (1893).
42. E. Fischer and C. Bülow, Ber., 18, 2131 (1885).
43. G. T. Morgan and C. J. Taylor, J. Chem. Soc., 43 (1926).
44. U. S. P. 2659711 (1953); Chem. Abs., 48, 11105 (1954).
45. J. P. English, J. Amer. Chem. Soc., 68, 453 (1946).
46. G. T. Morgan and R. W. Thomason, J. Chem. Soc., 754 (1924).
47. G. T. Morgan, J. Chem. Soc., 2611 (1925).
48. H. F. Holtzclaw, K. W. R. Johnson, and F. W. Hengekeld, J. Amer. Chem. Soc., 74, 3776 (1952).
49. H. Adkins, W. Kutz, and D. D. Coffman, J. Amer. Chem. Soc., 52, 3213 (1930).
50. H. F. Holtzclaw and J. P. Collman, J. Amer. Chem. Soc., 78, 3318 (1957).
51. V. V. Korshak, E. S. Krongauz, and A. M. Berlin, Vysokomol. Soed., 6, 1078 (1964).
52. S. T. Ioffe, K. V. Vatsuro, E. E. Kugucheva, and Zh. I. Kabachnik, Zhur. Org. Khim., 2, 381 (1966).
53. A. N. Nesmeyanov and M. I. Kabachnik, Zhur. Obshch. Khim., 25, 41 (1955).
54. N. Kornblum and R. Seltzer, J. Amer. Chem. Soc., 83, 3688 (1961).
55. W. L. Mosby, J. Chem. Soc., 3997 (1957).
56. E. Knoevenagel, Ber., 36, 2154 (1903).
57. E. W. Neuse and R. K. Crossland, Chem. and Ind., 2005 (1965).
58. H. Henecka, "Chemie der Dicarbonylverbindungen", Springer, Berlin, 1950.
59. M. I. Kabachnik, Dokl. Akad. Nauk SSSR, 83, 407, 859 (1952).
60. M. I. Kabachnik, S. T. Ioffe, and K. V. Vatsuro, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 755 (1957).
61. Yu. N. Molin, S. T. Ioffe, E. E. Zaev, E. K. Solov'eva, E. E. Kosucheva, V. V. Voevodskii, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 1556 (1965).
62. M. I. Kabachnik and S. T. Ioffe, Izv. Akad. Nauk SSSR, Ser. Khim., 339 (1963).
63. R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, J. Amer. Chem. Soc., 71, 1061 (1949).
64. R. Mecke and E. Funck, Z. Elektrochem., 60, 1124 (1956).
65. E. S. Krongauz, Doctoral Thesis, Institute of Organoelemental Compounds, Academy of Sciences of the USSR, Moscow, 1968.
66. E. R. Blout, V. W. Eager, and D. C. Silverman, J. Amer. Chem. Soc., 68, 566 (1946).
67. A. E. Gillam and E. S. Stern, "An Introduction to Elęctronic Absorption Spectroscopy in Organic Chemistry", Arnold, London, 1954, p. 223.
68. R. A. Morton, A. Hassan, and T. C. Calloway, J. Chem. Soc., 83 (1934).
69. D. F. Martin and W. C. Fernelius, J. Amer. Chem. Soc., 81, 1509 (1953).
70. L. G. Van Uibert, J. Amer. Chem. Soc., 75, 451, 455 (1953).
71. B. P. Block and G. H. McIntyre, J. Amer. Chem. Soc., 75, 5667 (1953); 76, 5887 (1954).
72. E. S. Krongauz, A. M. Berlin, and A. P. Travnikova, Khim. Get. Soed., 301 (1969).
73. V. A. Petrov, J. Chem. Soc., 693 (1942).
74. V. V. Korshak, E. S. Krongauz, A. M. Berlin, and A. P. Travnikova, Vysokomol. Soed., 9B, 171 (1967).
75. A. M. Berlin, Candidate's Thesis, Institute of Organoelemental Compounds, Academy of Sciences of the USSR, Moscow, 1966.
76. V. V. Korshak, E. S. Krongauz, A. M. Berlin, and A. P. Travnikova, Vysokomol. Soed., 6, 1087 (1964).
77. P. Pabe and F. Elze, Annalen, 323, 110 (1902).
78. F. Siedel, W. Thier, A. Uber, and J. Dittmer, Ber., 68B, 1913 (1935).
79. R. Hüttel, Ber., 70B, 2024 (1937).
80. H. Fox and J. E. Gibas, J. Org. Chem., 20, 60 (1955).
81. V. V. Korshak, E. S. Krongauz, A. M. Berlin, and T. Ya. Smirnova, Vysokomol. Soed., 6, 1195 (1964).
82. Yu. P. Kitaev and A. E. Arbuzov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk., 1037 (1957).
83. E. S. Krongauz, A. M. Berlin, and V. V. Korshak, Vysokomol. Soed., 11A, 48 (1969).
84. V. V. Korshak, E. S. Krongauz, A. M. Berlin, and P. N. Gribkova, Dokl. Akad. Nauk SSSR, 149, 602 (1963).
85. V. V. Korshak, E. S. Krongauz, and A. M. Berlin, J. Polym. Sci., A3, 2425 (1965).
86. V. V. Korshak, E. S. Krongauz, A. M. Berlin, P. N. Gribkova, and V. E. Sheina, Izv. Akad. Nauk SSSR, Ser. Khim., 1281 (1964).
87. J. U. Lowe and L. Ferguson, J. Org. Chem., 30, 3000 (1965).
88. E. S. Krongauz, V. V. Korshak, A. M. Berlin, and A. P. Travnikova, Khim. Get. Soed., 880 (1967).
89. J. P. Schaefer and J. Z. Bertram, J. Polymer. Sci., B3, 95 (1965).
90. E. W. Neuse, Macromol., 1, 171 (1968).
91. A. A. Berlin, in collected papers "Uspekhi Khimii i Tekhnologii Polimerov" (Progress in the Chemistry and Technology of Polymers), Goskhimizdat, Moscow, 1960, p. 3.
92. M. M. Koton, in collected papers "Uspekhi Khimii i Tekhnologii Polimerov" (Progress in the Chemistry and Technology of Polymers), Goskhimizdat, Moscow, 1960, p. 122.
93. V. V. Rode, E. G. Rukhadze, and A. P. Terent'ev, Uspekhi Khim., 32, 1488 (1963) [Russ. Chem. Rev., No. 12 (1963)].

94. N. G. Matveeva, Khim. Prom., No. 12, 39 (1962).
95. A. A. Berlin and N. G. Matveeva, Uspekhi Khim., 29, 277 (1960) [Russ. Chem. Rev., No. 3 (1960)].
96. I. Haiduc, Uspekhi Khim., 30, 1124 (1961) [Russ. Chem. Rev., No. 9 (1961)].
97. H. Kiehne, Gummi, Asbest, Kunststoffe, 15, 969, 1088 (1962).
98. M. G. Vinogradov, Candidate's Thesis, Institute of Organoelemental Compounds, Academy of Sciences of the USSR, Moscow, 1964.
99. S. V. Vinogradova, in collected papers, "Uspekhi v Oblasti Sinteza Elementoorganicheskikh Polimerov" (Progress in the Synthesis of Organoelemental Polymers), Izd. Nauka, Moscow, 1966, p. 59.
100. V. V. Korshak, E. S. Krongauz, A. M. Sladkov, V. I. Sheina, and L. K. Luneva, Vysokomol. Soed., 1, 1764 (1959).
101. V. V. Korshak, S. V. Vinogradova, and M. G. Vinogradov, Vysokomol. Soed., 5, 1771 (1963).
102. V. V. Korshak and S. V. Vinogradova, Dokl. Akad. Nauk SSSR, 138, 1353 (1961).
103. V. V. Korshak, S. V. Vinogradova, and V. S. Artemova, Vysokomol. Soed., 4, 492 (1962).
104. F. W. Knobloch and N. H. Ranscher, J. Polymer Sci., 38, 261 (1959).
105. B. P. Block, S. H. Pose, C. W. Schaumann, E. S. Koth, and J. Simkin, J. Amer. Chem. Soc., 84, 3200 (1962).
106. V. V. Korshak, E. S. Krongauz, P. N. Gribkova, and V. A. Vasnev, Vysokomol. Soed., 4, 815 (1962).
107. V. V. Korshak, S. V. Vinogradova, V. S. Artemova, T. M. Babchinitser, and S. A. Pavlova, Vysokomol. Soed., 3, 1116 (1961).
108. T. S. Patterson, F. J. Pavlik, A. A. Baldoni, and R. L. Frank, J. Amer. Chem. Soc., 81, 4213 (1959).
109. S. V. Vinogradova, M. G. Vinogradov, and V. V. Korshak, Kinetika i Kataliz, 5, 247 (1964).
110. V. V. Korshak, S. V. Vinogradova, and M. G. Vinogradov, Vysokomol. Soed., 7, 729 (1965).
111. V. V. Korshak, E. S. Krongauz, and V. E. Sheina, Vysokomol. Soed., 3, 1456 (1961).
112. V. V. Korshak, E. S. Krongauz, and V. E. Sheina, Vysokomol. Soed., 2, 662 (1960).
113. N. A. Glukhov, M. M. Koton, and Yu. V. Mitin, Vysokomol. Soed., 2, 791 (1960).
114. C. S. Marvel, J. H. Rassweiler, M. M. Martin, and K. V. Martin, J. Amer. Chem. Soc., 80, 233, 1197, 6600 (1958).
115. M. G. Vinogradov, S. V. Vinogradova, Yu. A. Davidovich, and V. V. Korshak, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2023 (1963).
116. V. V. Korshak, A. A. Slinkin, S. V. Vinogradova, and T. M. Babchinitsev, Vysokomol. Soed., 3, 1624 (1961).
117. S. Randa and I. Saito, Bull. Chem. Soc. Japan, 30, 192 (1957).
118. V. V. Korshak, A. M. Sladkov, L. K. Luneva, and I. A. Bulgakova, Vysokomol. Soed., 5, 1288 (1963).
119. Z. Wolf and C. Troltzsch, J. prakt. Chem., 24, 305 (1964).

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