

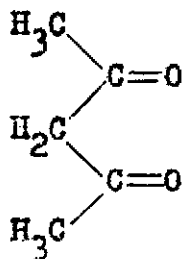
Chapter 4

USES OF SOME β -KETOANILIDES

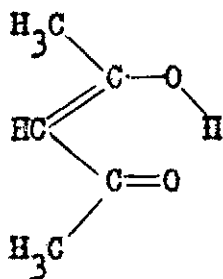
Organic reagents of the following types, β -diketones, β -ketoesters and β -ketoanilides have more or less similar activities as all of them contain two oxygen as ligand atoms separated from each other in an analogous fashion. Thus, a brief mention about the first two types is necessary before discussing the analytical uses of β -ketoanilides.

4.1. β - Diketones

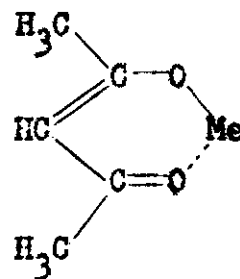
Among the oxygen-containing ligands, β -diketones of general formula, $R.CO.CH_2.CO-R'$ constitute one of the most important classes, finding wide applications. Acetylacetone (4-I,II) is the simplest member of the family forming complexes (4-III) with various metal ions, which are extractable in organic solvents or may be volatilised, providing important methods of separation. The properties, structures,



(keto-form)
(4 - I)



(enol- form)
(4 - II)

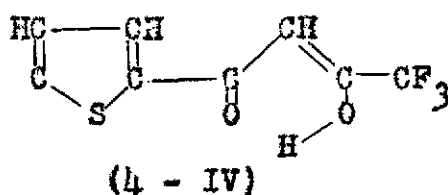


(Me metal equivalent)
(4 - III)

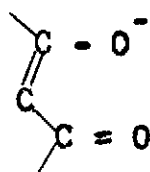
stabilities and spectra of various acetylacetonates have been studied and numerous derivatives of the reagent have been prepared and used.

Substitution of one of the hydrogen atoms of the central methylene group of acetylacetonone often fails to give the characteristic reactions. Thus, isopropyl or sec-butyl substitution prevents the usual colour reactions with Cu(II) or Fe(III), although α -n-alkyl and α -isobutyl substituted reagents give normal complexes.¹ Probably steric factors (section 1.7) prevent the planar configuration in the former reagents and reduce the stability of the complexes.² However, the more important derivatives of acetylacetonone are obtained by substituting varied types of groups in the positions of the terminal methyl groups (R or R'). The effects of such substitution are manifested in three ways.

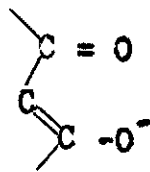
First, the nature of the substituents (solubilising, chromophoric, hydrophobic groups etc.) in the positions R or R' will determine the suitability of the new reagent for complexometric titration, spectrophotometry, gravimetry etc. (Chapter 3). Secondly, the substituent may also effect the ratio of the keto- and enol-forms. This may influence the stability of the metal derivatives as this is related to the acid dissociation constants³ (section 1.5). As the substitution of fluorine on the terminal carbon atoms has been found to increase the amount of enol-form in aqueous solutions^{4,5}, thenoyl trifluoroacetone (4 - IV)



has been found to be a better reagent for extractions than acetylacetonone. Thirdly, the enolate resonance (4 - V,VI) may also be influenced by the substitution and the stability of the complexes may be affected.

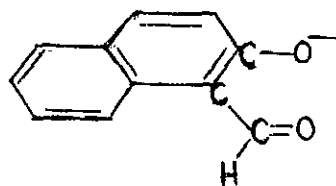


(4 - V)

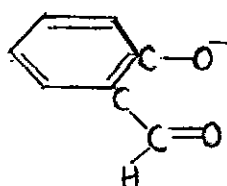


(4 - VI)

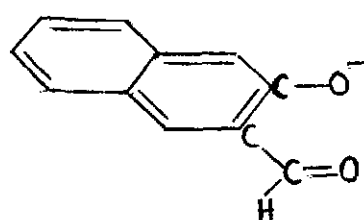
The resonating double bond between the two carbon atoms attached to the enolate oxygen in acetylacetonone will have a bond order⁶ of 2. But for comparable cases in 2-hydroxy-1-naphthaldehyde (4- VII), salicylaldehyde (4-VIII) or 2-hydroxy-3-naphthaldehyde (4 - IX)



(4 - VII)



(4 - VIII)

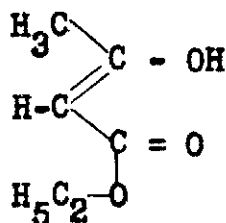


(4 - IX)

the bond order will be reduced to 1.67, 1.5 and 1.33 respectively, as these double bonds also become a part of a resonating aromatic ring⁷. This gradual decrease in the bond order from 2 to 1.33 is also reflected in the stability order of the corresponding copper chelates.

4.2. β -Ketoesters

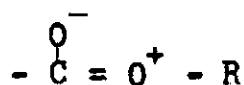
The substitution of an ethoxy-group in the position R or R' of a β -diketone will result in β -ketoester, e.g., ethylacetoacetate (4 - X). The strong ester resonance (4 - XI, XII) would normally strengthen the bond by increasing the negative charge on



(4 - X)



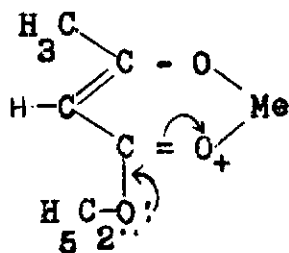
(4 - XI)



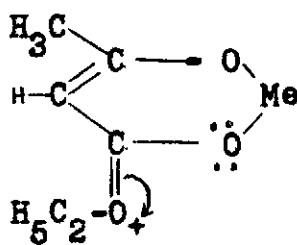
(4 - XII)

the oxygen of the 'O-metal' bond. Harries⁸ has shown that in 50% dioxan medium the stability of the Be-ethyl acetoacetate complex ($\log K = 16.2$) is slightly higher than the corresponding acetyl-acetone complex ($\log K = 15.7$), the acid dissociation constants ($\text{p}K_a$) for the reagents being 11.9 and 10.3 respectively.

However, in these β -ketoesters, the participation by the carbonyl groups in the ester resonance (4-XIII, XIV) may greatly interfere with the chelate resonance. As a result



(4 - XIII)



(4 - XIV)

the tendency of the increment in the oxygen-metal bond strength by ester resonance may be out weighed by the effect of the weakening of the bond due to participation of carbonyl resonance with the ester resonance. Thus, Calvin and Wilson⁹ observed that the acetylacetonate complex of copper (II) ($\log K = 17.4$) is more stable than the ethylacetoacetate complex ($\log K = 14.2$).

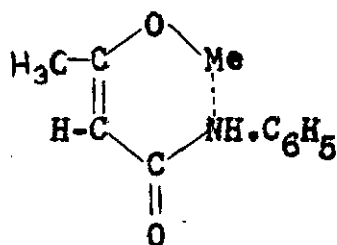
The analytical uses of the β -ketoesters are, however, restricted to extraction processes, as these substances are, in general, liquid at ordinary temperature and insoluble in water. Moreover, the low stability of such compounds towards heat, hydrolysis etc., and the difficulty in purification contribute to additional disadvantages.

4.3. β -Ketoanilides

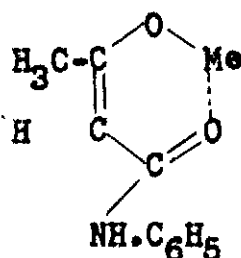
The substitution of hydrocarbon groups and of hydrophobic groups in general decreases water solubility (and increases solubility in organic solvents) of the chelates (section 3.1.). The introduction of an anilide group in the place of the ethoxy-group in β -Ketoesters also increases the molecular weight and the resulting β -ketoanilides, in general, will be better reagents for gravimetry, extraction processes etc. Das et al used acetoacetanilide, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, having pK_a ⁹ 11.6, in the gravimetric determination of beryllium¹⁰ and copper¹¹ as well as for the extraction and spectrophotometric determinations of copper¹² and vanadium(IV)¹³. The advantages of introducing the anilido group has further been utilised in

developing a titrimetric method for beryllium¹⁴, where the anilide group is quantitatively brominated and from the amount of bromine consumed the metal is estimated.

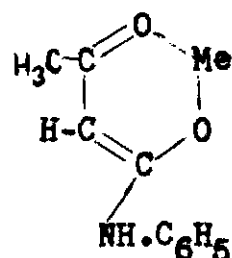
The β -keto group is effective in acetoacetanilide in forming metal chelates, However an alternative way of coordination through nitrogen (4 - XV) in addition to the expected linkage through oxygen (4 - XVI, 4 - XVII) is possible making acetoacetanilide an ambidentate ligand. By studying the effects of substitution



(4 - XV)

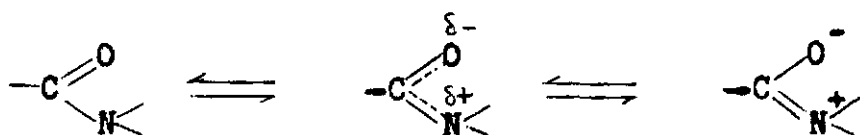


(4 - XVI)



(4 - XVII)

in the benzene ring Harries concluded that in the beryllium chelate the bonding takes place through oxygen atoms. Infrared studies have also indicated similar possibility. The resonating structure of the amide group (XVIII) suggest the donation through oxygen because of its higher electronegativity than nitrogen¹⁵. However, with



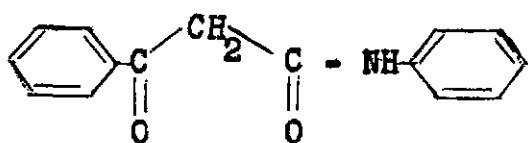
(6 - XVIII)

metal ions having greater affinity for nitrogen, the picture may be somewhat different and all the three forms (6 - XV, -XVI- and -XVII)

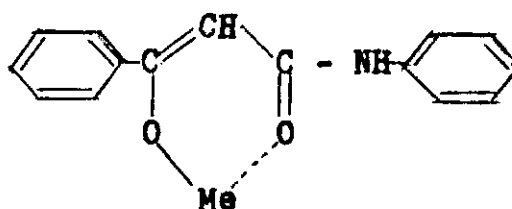
may have some contributions. Investigations are in progress to establish this.

4.3.1. Benzoylacetanilide

Sarkar and Das observed that by changing the terminal methyl group of acetoacetanilide a superior reagent, benzoylacetanilide (4-XIX) is obtained. The introduction of the benzene-ring does not only decrease the solubility of the complexes when compared to acetoacetanilide, the increased conjugation in the



(4 - XIX)



(4 - XX)

chelates (4 - XX) also renders the reagent more promising for spectrophotometry. Moreover, from the consideration of the effect of the benzene ring on the enolate resonance, this compound is supposed to be more dissociated than acetoacetanilide. The pKa values of benzoylacetanilide and some comparable reagents are given in Table 4-1.

Table 4 - I

Reagent	pK _a	Reference
Acetylacetone, CH ₃ COCH ₂ COCH ₃	10.3	8
Ethyl acetoacetate, CH ₃ COCH ₂ COOC ₂ H ₅	11.9	8
Benzoyl acetate, C ₆ H ₅ COCH ₂ COOC ₂ H ₅	11.27	16
Acetoacetanilide, CH ₃ COCH ₂ CONHC ₆ H ₅	11.6	8
Benzoylacetanilide, C ₆ H ₅ COCH ₂ CONHC ₆ H ₅	9.6	17

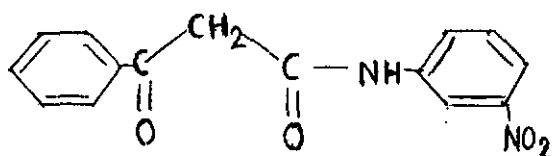
Like other reagents of the same series (section 1.5.) the change in stability constants of metal chelates of different β -ketoanilides follow a linear relationship with their pK_a values^{8,18,19}. This happens as in this structurally similar series, the entropy of reaction does not change much with substitution, so that changes of free energy which are related to changes in equilibrium constant (equations 1.7,1.8) will depend mainly on changes of enthalpy of the reaction, which in turn depend on the donor power of the chelating atoms (Section 1.8).

Sarkar and Das have used benzoylacetanilide for the gravimetric determination of beryllium²⁰, titanium(IV)²⁰, mercury(II)²¹, vanadium(IV)²¹ and aluminium²² as well as for the

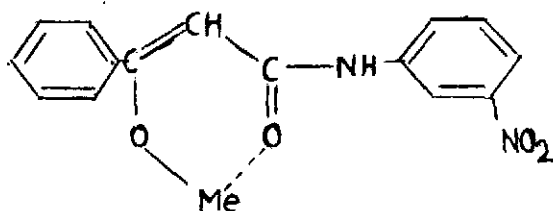
extraction and spectrophotometric estimation of titanium(IV)²⁰, molybdenum(VI)²³ and iron(III)²². This reagent has been found to be useful in the spectrophotometric determination of uranium(VI) and its separation from other commonly associated elements by extraction in nonaqueous solvents in the presence of suitable masking agents. (Chapter 5).

4.3.2 Benzoyl - m- nitroacetanilide

It is evident from the previous discussions that the introduction of a nitro-group in the benzene nucleus of the anilido-group in benzoylacetanilide will result in a reagent forming chelates with low solubilities. It will also form coloured complexes with many colourless ions like Be(II), Hg(II) etc., due to the expected shift of the absorption spectra of the chelates to longer wave lengths. Thus, benzoyl-m-nitroacetanilide (4-XXI) has been prepared and its pK_a value has been found to be 9.36 (chapter 6)



(4 - XXI)



(4 - XXII)

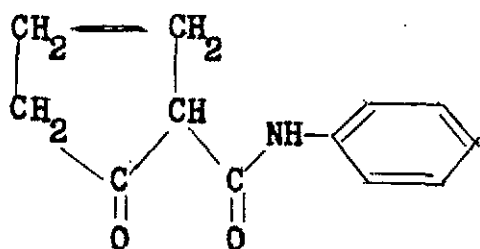
The expected structure of a chelate is given above (4 - XXII). This reagent has been used in the gravimetric and/or spectrophotometric determinations of beryllium, uranium(VI) and mercury(II). The

absorption spectra of the chelates showed the expected batho - chromic shifts rendering the spectrophotometric determination of beryllium in visible range feasible. In the case of uranium(VI) also, the λ_{max} was higher when compared to the corresponding benzoylacetyl complex though the molar absorptivity and sensitivity values did not change much. There was an additional advantage over the benzoylacetyl complex. The complex was extractable in the presence of sulphosalicylic acid, in addition to magnesium - EDTA and iodide. As a gravimetric reagent, the nitro - compound formed an uranium(VI) complex of definite composition which was easily coagulated, while benzoylacetyl gave only a colloidal precipitate of indefinite composition with the same ion. Probably the steric effect due to the nitro-group played a part in removing the sphere of hydration of the large uranyl ion.

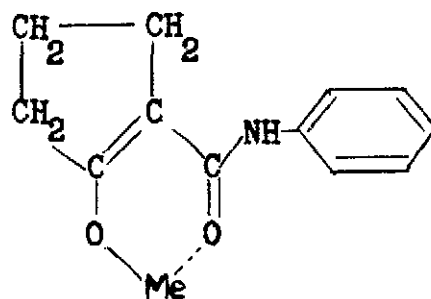
4.3.3. Cyclopentanone-2-Carboxyanilide

The fusion of alicyclic rings with the chelate rings has shown interesting effects in many cases. Thus, 1,2-cyclohexane - dione dioxime²⁴ is a more sensitive reagent for nickel than dimethylglyoxime and 1,2-diaminocyclohexane tetraacetate²⁵ forms a stronger chelate with calcium than ethylenediamine tetraacetate does. The enhanced stabilities are probably due to the difference in entropies of the two comparable reactions and are related to the restriction of free rotation of the two carbon bridges between the nitrogen atoms when they occur in the cyclohexane ring.

The structures of cyclopentanone -2-carboxyanilide(4 - XXIII) and its probable metal chelates (4-XXIV) show that the effective β -diketo group is retained intact, but it forms a part of an



(4 - XXIII)



(4 - XXIV)

alicyclic ring in contrast to the same in acetoacetanilide, benzoyl - acetanilide or benzoyl-m-nitroacetanilide. The pK_a value of the compound is 10.14 (chapter 7) and this has been introduced as a new reagent through its application in the quantitative estimations of beryllium, uranium (VI) and mercury (II).

A summary of the procedures developed for the determinations of these ions, viz., Be(II), U(VI) and Hg(II) including separation from allied ions using benzoylacetanilide, benzoyl-m-nitroacet - anilide and cyclopentanone-2-carboxyanilide has been given in chapter 8, while a brief resume is presented in a tabular form (Table 4 - II) on pages 44-45.

Table 4 - II

Analytical uses of three β -ketoanilides.

Section No.	Metal ion	Method	pH range	Masking agent used	Selective in presence of	Reported in
* BENZOYLACETANILIDE						
5.1	UO_2^{2+}	Extr., spec.	> 6.5	1,3,11	$Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Bi^{3+}, Fe^{3+}, Al^{3+}, Ce^{3+}, Th^{4+}, VO^{2+}, Zr^{4+}, CrO_4^{2-}, MoO_4^{2-}$	Z. Anal. Chem. (a)
** BENZOYL - m - NITROACETANILIDE						
6.1	Be^{2+}	Grav.	6.5 - 9.0	1,3,4, 5,9	$Co^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Ce^{4+}, Th^{4+}, TiO^{2+}, VO^{2+}, UO_2^{2+}$	J. Ind. Chem. Soc. (a)
6.2	Be^{2+}	Extr., Spec.	> 4.4	1	$Co^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}$	<u>ibid</u> (c)
6.3	UO_2^{2+}	Grav.	> 5.8 or 6.8-7.8	1,3,7	$Pb^{2+}, Ni^{2+}, Be^{2+}, Hg^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Ce^{3+}, Th^{4+}, VO^{2+}, Zr^{4+}$	Ind. J. Chem. (b)
6.4	UO_2^{2+}	Extr., Spec.	> 5.3	1,3,7	$Ni^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Ce^{3+}, Th^{4+}$	<u>ibid.</u> (c)
6.5	Hg^{2+}	Grav.	2.5-9.0	5,6,8, 10	$Ag^+, Tl^+, Cd^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Bi^{3+}, Al^{3+}, Cr^{3+}, Pb^{2+}, UO_2^{2+}, WO_4^{2-}, Fe^{3+}$	J. Ind. Chem. Soc. (c)

contd..

Table 4 - II (contd..)

Analytical uses of three β -ketoanilides.

Section No.	Metal ion	Method	pH range	Masking agent used	Selective in presence of	Reported in
*** CYCLOPENTANONE -2- CARBOXYANILIDE						
7.1	Be ²⁺	Grav.	5.9 - 8.1	2,4,5	Cu ²⁺ , Co ²⁺ , Pb ²⁺ , Ni ²⁺ , Zn ²⁺ , Al ³⁺ , Cr ³⁺ , Fe ³⁺ , Ce ³⁺ , Th ⁴⁺ , TiO ²⁺ , VO ²⁺ , UO ₂ ²⁺	Anal. Chin. Acta (a)
7.2.	Be ²⁺	Titr.	-	-	-	<u>ibid.</u> (a)
7.3	Be ²⁺	Extr., spec.,	7.0 - 10.5	1,2	Ag ⁺ , Tl ⁺ , Cd ²⁺ , Cu ²⁺ , Co ²⁺ , Pb ²⁺ , Hg ²⁺ , Ni ²⁺ , Bi ³⁺ , Al ³⁺ , Ga ³⁺ , In ³⁺ , Cr ³⁺ , Fe ³⁺ , Ce ³⁺ , Th ⁴⁺ , Zr ⁴⁺ , TiO ²⁺ , VO ²⁺ , MoO ₂ ²⁺ , UO ₂ ²⁺ , WO ₄ ²⁻	<u>ibid</u> (a)
7.4	UO ₂ ²⁺	Grav.	6.2 - 8.0	1	Cu ²⁺ , Cd ²⁺ , Co ²⁺ , Hg ²⁺ , Pb ²⁺ , Ni ²⁺ , Zn ²⁺ , Bi ³⁺ , Fe ³⁺ , Al ³⁺ , Th ⁴⁺ , Ce ⁴⁺ , VO ²⁺ , CrO ₄ ²⁻	<u>ibid</u> (c)
7.5	Hg ²⁺	Grav.	5.5 - 8.6	6	Cu ²⁺ , Co ²⁺ , Cd ²⁺ , Ni ²⁺ , Co ²⁺ , Zn ²⁺ , Fe ³⁺ , Al ³⁺	-

1. Mg-EDTA 2. Na₂EDTA 3. Triethanolamine 4. Thioglycolic acid 5. tartrate
 6. Citrate 7. Sulphosalicylate 8. Fluoride 9. H₂O₂ 10. N.T.A.
 11. Ethylenediamine.

(a) published (b) in press (c) communicated

Grav.- Gravimetry; Extr.- Extraction in nonaqueous solvent;

Titr- Titrimetry; Spec.- Spectrophotometry.

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