CHAPTER III

NITRATION OF SOME HYDROXYXANTHONES

THEORETICAL

NITRATION OF SOME HYDROXYXANTHONES

Nitroxanthones such as 1,7-, 1,5- and 1,6-dinitroxanthone and the diaminoxanthones from them are found to be active against Mycobacterium tuberculosis[1]. Some of the amino- and nitroxanthones have shown antiplasmodial activity[2]. Similarly, some aminoxanthones are active against schistosomia mansoni infection in mice[3]. 2,7-Diaminoxanthone gives polymers with isophthaloylchloride and with 1,2,4,5-benzene tetracarboxylic-1,2,4,5-dianhydride, which are found to be good heat resistants[4]. Similarly, the same xanthone also gives heat-stable fibres with 4,4'-diphenylcarboxylic acid, isophthalic acid, 2,7-naphthalene dicarboxylic acid and terephthalic acid[5].

It was thought of interest to study the nitration of xanthones with a view to study the pattern of substitution and to use the nitro compounds for further synthetic work. It will be seen from the review of the previous work on the nitration of xanthones given in Chapter I that there have been no systematic studies on the nitration of xanthones. Some nitroxanthones have however been prepared by starting with appropriately substituted starting materials. Kurdukar and Subba Rao[6] have reported, however, that nitrobenzophenones such as 2,2',4,4'-tetrahydroxy-5-nitrobenzophenone and 2,2',4,4'-tetrahydroxy-3,3',5,5'-tetranitrobenzophenone could not be cyclised to the nitroxanthones by usual methods. In this laboratory 3-hydroxy-4-nitroxanthone has been

prepared by cyclising 2,2',4-trihydroxy-3-nitrobenzophenone in water under pressure, as mentioned in Chapter II, where no difficulty was observed.

Many aminoxanthones have been synthesised by cyclising the suitable acetamido-o-phenoxybenzoic acids or by reducing the nitroxanthones. For reducing the nitroxanthones reagents such as tin and hydrochloric acid, stannous chloride, ammonium sulphide, ferrous sulphate and ammonia, ammonia and hydrogen sulphide are used. In the present work the reduction is effected by dithionite in alcohol.

Although, in the literature there is no reference to coupling of hydroxyxanthones with aryldiazonium chlorides, xanthoneazo derivatives have been obtained by coupling xanthonediazonium chlorides, obtained from the aminoxanthones, with phenols, β-naphthol, etc. Purgotti[7] has prepared m-nitroxanthone, reduced it to aminoxanthone and then diazotised and coupled it with phenol to get a yellow dye. With β-naphthol it gave a scarlet dye. Many dye intermediates such as aminoxanthones have been patented[8,9]. A number of azo compounds have been prepared by coupling diazotised 3-aminoxanthone[10] with various phenols and amines such as phenol, resorcinol, salicylic acid, β-naphthol, 2-hydroxy--3-naphthoic acid, G-acid, R-acid and dimethyl aniline. 4-Aminoxanthone on diazotisation and coupling with o-toluidine gave a scarlet shade on cotton, while 3-phenoxy--2-aminoxanthone on coupling with o-anisidine gave a bright red shade[11]. Similarly, 2-aminoxanthone, 4-aminoxanthone, 3-phenoxy-2-aminoxanthone, 3-carboxy-4-aminoxanthone and

their sulphonated products were diazotised and coupled with naphthols and naphthol-sulphonic acids[12]. Dhar[13,14] has also prepared some azocompounds from aminoxanthones. Kiyoshi[15] has prepared dyes from aminoxanthones and studied their dyeing properties.

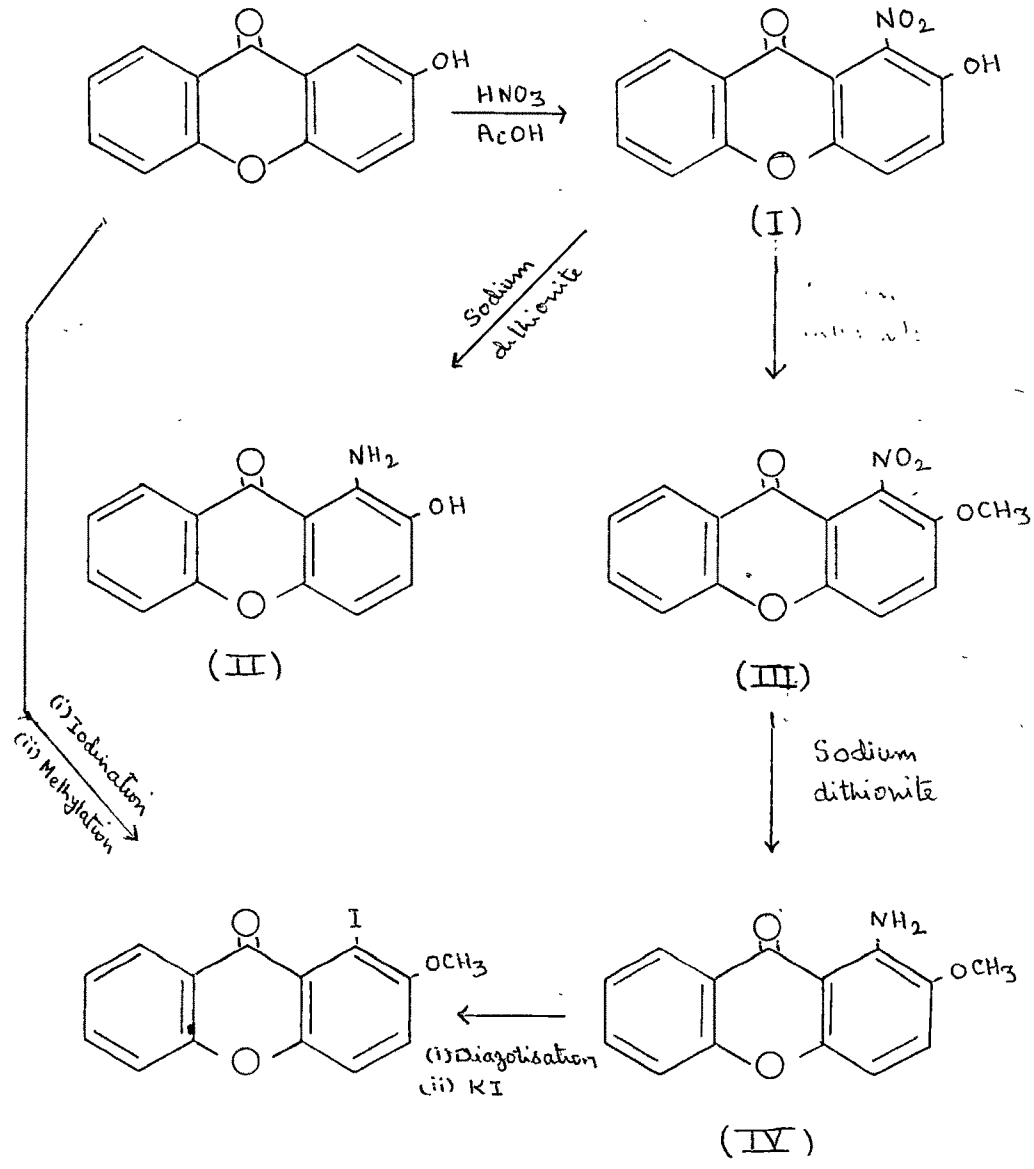
The present work deals with the nitration of 2-hydroxy-, 3-hydroxy-, 3,6-dihydroxy-, 3-hydroxy-6-methoxy- and 2-methoxyxanthone. The nitration was carried out with fuming nitric acid in acetic acid and with sulphuric acid-fuming nitric acid mixture at 0-5°. Reduction of the nitroxanthones proceeded well. Conversion of the aminoxanthones to hydroxyxanthones was not successful. The coupling of phenyldiazonium chloride with 3-hydroxyxanthone, 2-hydroxyxanthone and 3,6-dihydroxyxanthone has also been studied.

Nitration of 2-hydroxyxanthone

Nitration of 2-hydroxyxanthone was carried out in acetic acid with a few drops of fuming nitric acid. The mixture on dilution with water gave a yellow compound, which on crystallisation gave a pure mononitroxanthone. The structure of this mononitro derivative was established on the basis of the NMR data and it was found to be the 1-nitro derivative. This was confirmed by its conversion into 2-methoxy-1-iodoxanthone through its 2-methoxy-1-amino derivative as described later and comparing the iodo derivative obtained with the directly iodinated product discussed in Chapter II.

The NMR spectrum of this compound in dimethyl

sulphoxide (Fig. 1) shows a one-proton doublet in the low field region at δ 8.05, in which meta-coupling is also visible (J = 3Hz), indicating that this proton is at peri position to the carbonyl and there is also a proton present meta to this proton. This situation is possible with the proton at 8-position. There is no signal in the low field region for the proton at 1-position, which is also peri to



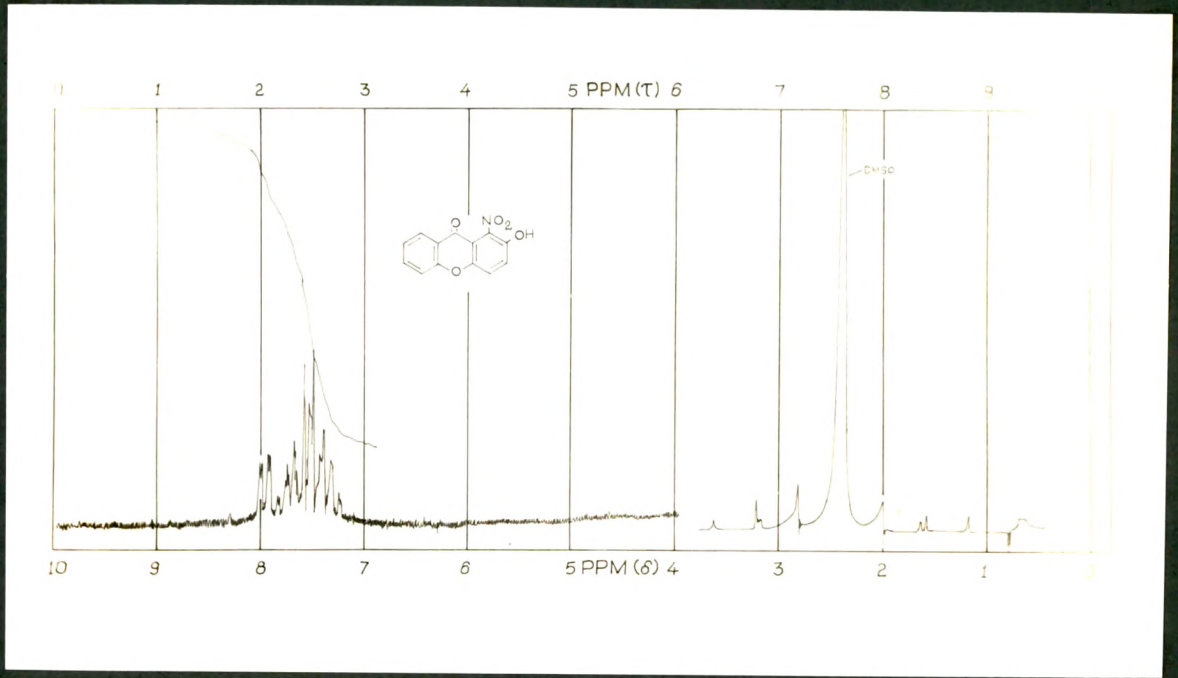


Fig. 1 :- NMR spectrum of 2-hydroxy-1-nitroxanthone (I) in DMSO (90 MHz).

the carbonyl group, indicating that the nitro group has entered the 1-position. The other aromatic protons appear as a multiplet between δ 7.95-7.35. Thus the NMR data establishes the 2-hydroxy-1-nitroxanthone structure (I).

Reduction of 2-hydroxy-1-nitroxanthone (I) with sodium dithionite in alcohol gave 2-hydroxy-1-aminoxanthone (II). Similarly, 2-methoxy-1-nitroxanthone (III) could be reduced to 2-methoxy-1-aminoxanthone (IV). 2-Hydroxy-1-aminoxanthone was diazotised to get 2-hydroxyxanthone-1-diazonium chloride, but attempt to hydrolyse it failed as it cyclised to give the azoxy compound. No hydrolysis occurred even with 60-80 % sulphuric acid. So the desired 1,2-dihydroxyxanthone could not be obtained. For preparing the iodo- derivative 2-methoxy-1-aminoxanthone was diazotised, excess of nitrous acid was decomposed by adding urea and then potassium iodide was added. This resulted in 2-methoxy-1-iodoxanthone. It was found on direct comparison to be identical with the product obtained from the iodination of 2-hydroxyxanthone and then methylation. Attempts to prepare 2-methoxy-1-hydroxyxanthone from 2-methoxy-1-aminoxanthone were also not successful.

Under the condition discussed above no nitration occurred with 2-methoxyxanthone.

Nitration of 2-hydroxyxanthone with more amount of fuming nitric acid in acetic acid, than that required for the mononitroxanthone, gave a mixture of a dinitroxanthone, the mononitroxanthone and a trace of a third compound,

detectable only in TLC. Most of the dinitroxanthone separated as yellow needles from the reaction mixture. The mother liquor on dilution with water gave a mixture containing the above mentioned three products. On recrystallisation from acetic acid of this mixture more of the dinitroxanthone was obtained. The filtrate on dilution gave a compound, which on crystallisation from aqueous alcohol gave 2-hydroxy--1-nitroxanthone.

The structure of the dinitroxanthone was established on the basis of the NMR data. The NMR taken in dimethyl sulphoxide (Fig. 2) showed a one-proton singlet at δ 8.7 and another one-proton doublet at δ 7.91, in which the meta-coupling (J = 3Hz) is discernible. The rest of the aromatic protons appeared in between δ 7.5-7.2, in which there is broadening due to the -OH proton. To record the NMR spectrum after deuterating the -OH group was not possible, as the compound separated after adding D_2O in the solution of the compound. The above NMR data suggests 2-hydroxy-1,3-dinitroxanthone structure (V). The singlet can be assigned to H-4 and the doublet to H-8, the position of which is almost identical to that of H-8 in 2-hydroxy-1-nitroxanthone.

2-Hydroxy-1,3-dinitroxanthone on methylation with dimethyl sulphate and potassium carbonate in dry acetone, slowly decomposed. However, pure 2-methoxy-1,3-dinitroxanthone (VII) was obtained in low yield by crystallising the product repeatedly from aqueous alcohol. Reduction of 2-hydroxy-1,3-dinitroxanthone with dithionite in alcohol gave

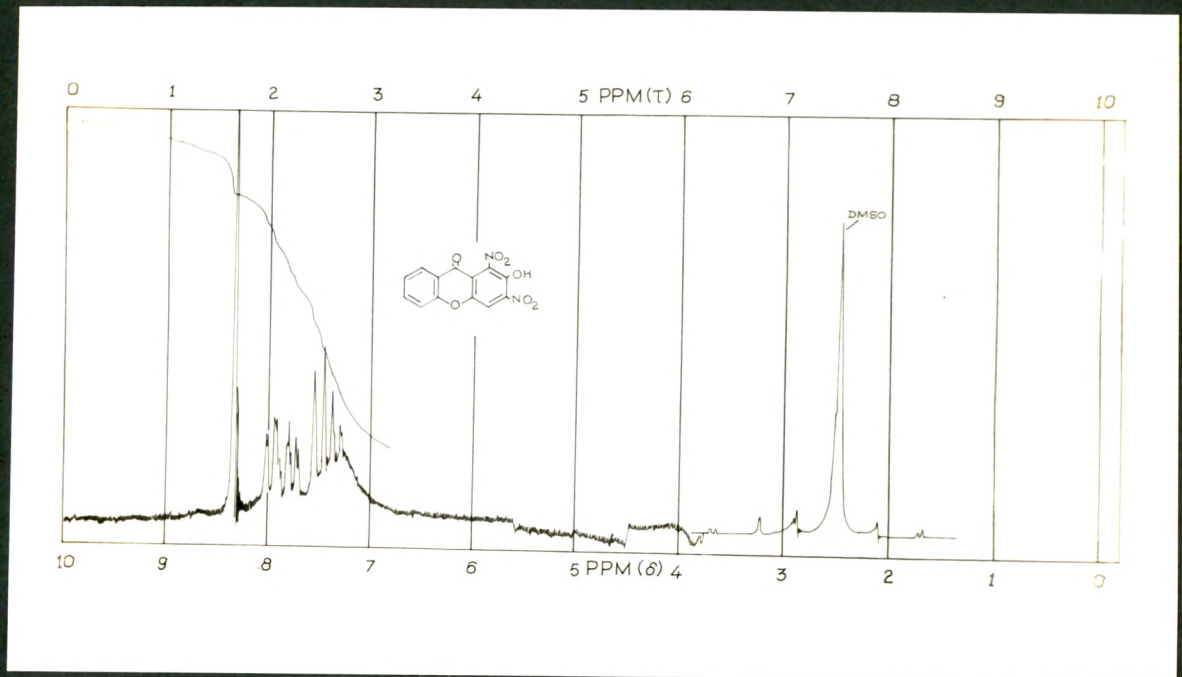
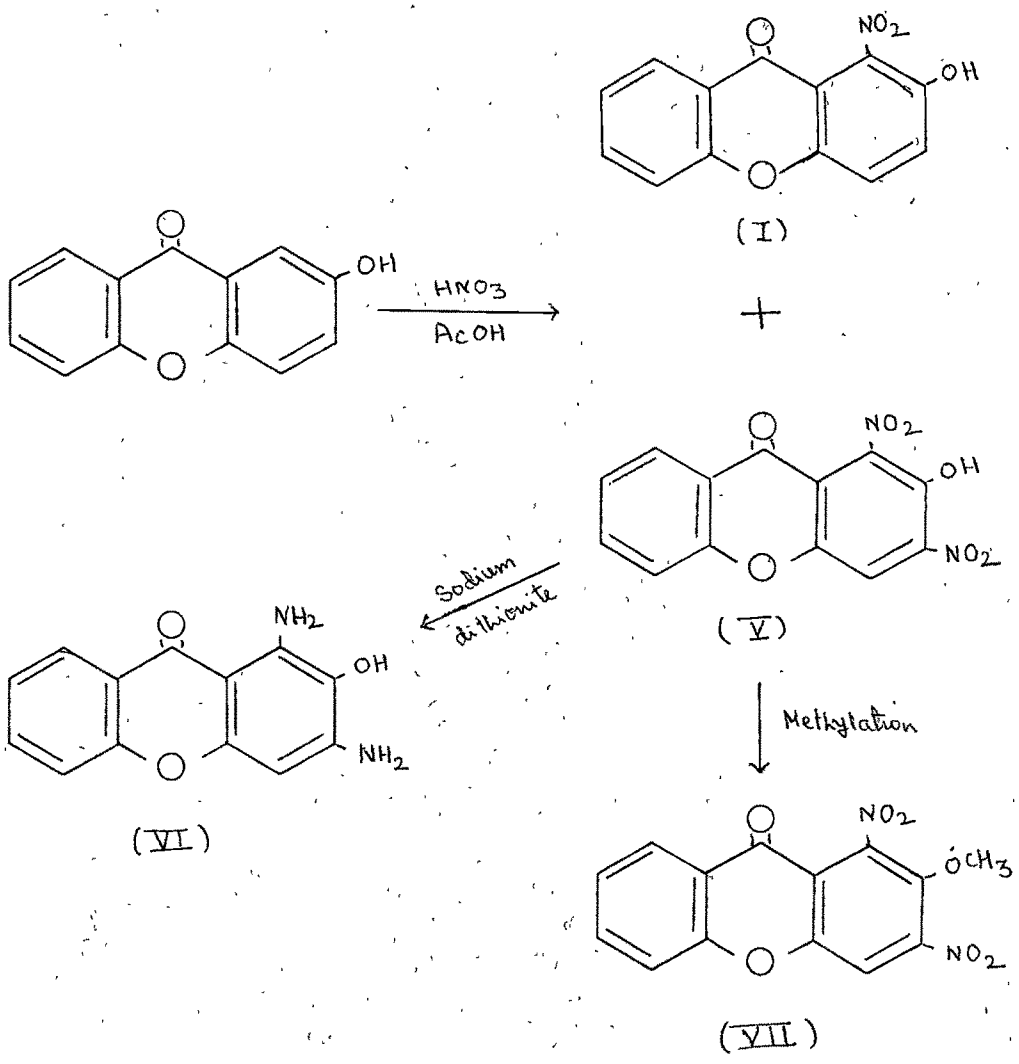


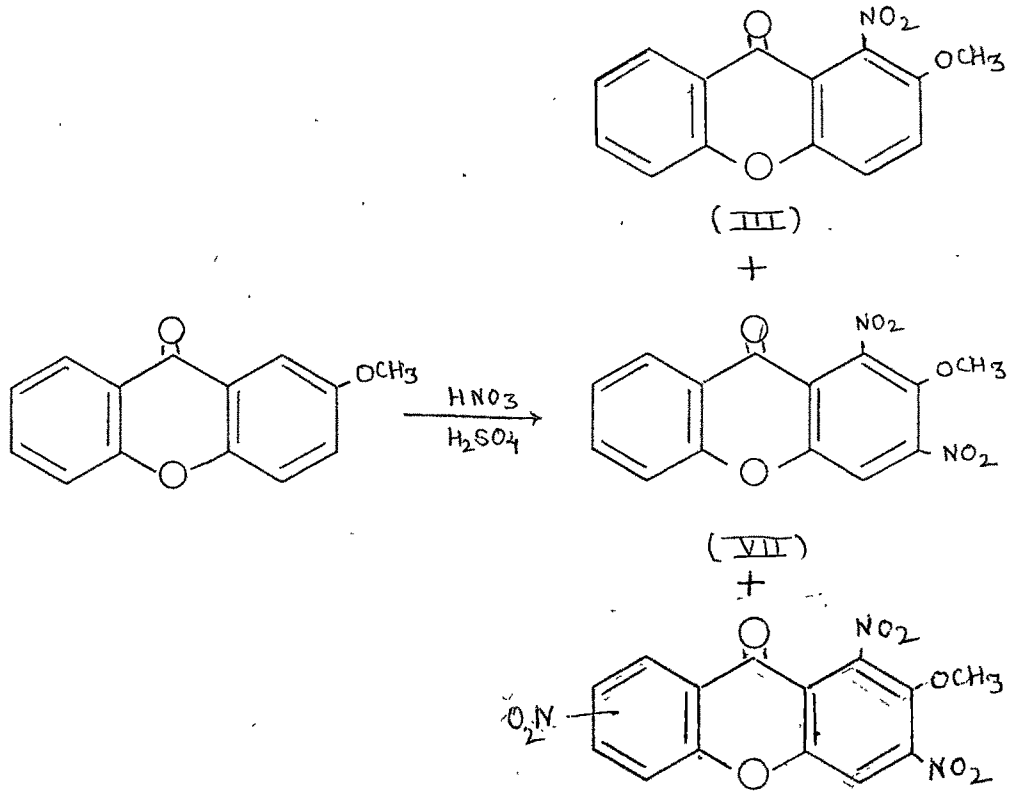
Fig. 2 : NMR spectrum of 2-hydroxy-1,3-dinitroxanthone (V) in DMSO (90 MHz).



2-hydroxy-1,3-diaminoxanthone (VI).

Nitration of 2-methoxyxanthone with sulphuric acid and fuming nitric acid mixture gave a mixture of nitroxanthones. This when treated with cold methanol, partly dissolved. The major fraction which was insoluble in methanol crystallised from acetic acid and was found to be a trinitroxanthone. Because of the insolubility of this trinitroxanthone in usual solvents, the NMR could not

be recorded and definite structure could not be assigned to it.

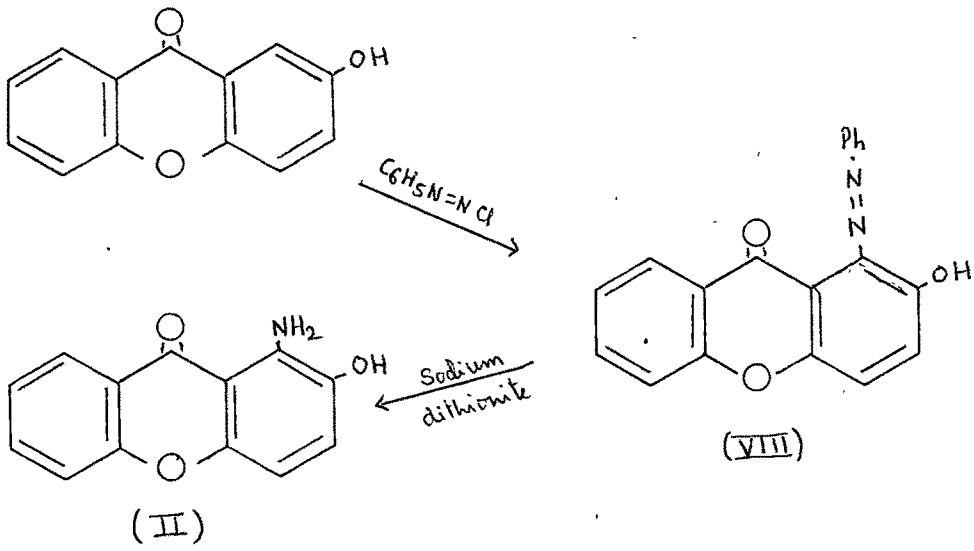


The methanol soluble fraction was found to contain 2-methoxy-1-nitroxanthone, 2-methoxy-1,3-dinitroxanthone and the trinitroxanthone as seen by TLC with chloroform-methanol (70 : 30), and by comparing the spots with the spots of 2-hydroxy-1-nitroxanthone and 2-methoxy-1,3-dinitroxanthone run side by side. The R_f value and the fluorescence of these under UV light were identical.

Diazocoupling of 2-hydroxyxanthone

Coupling of phenyldiazonium chloride with 2-hydroxyxanthone gave a monophenylazoxanthone. This on

reduction with excess of sodium dithionite in alcohol gave 2-hydroxy-1-aminoxanthone, same as the one obtained by reducing 2-hydroxy-1-nitroxanthone. Therefore 2-hydroxy-1-phenylazoxanthone (VIII) structure has been assigned to the coupling product. Methylation of it gave monomethyl ether, which could also be reduced to get 2-methoxy-1-aminoxanthone.



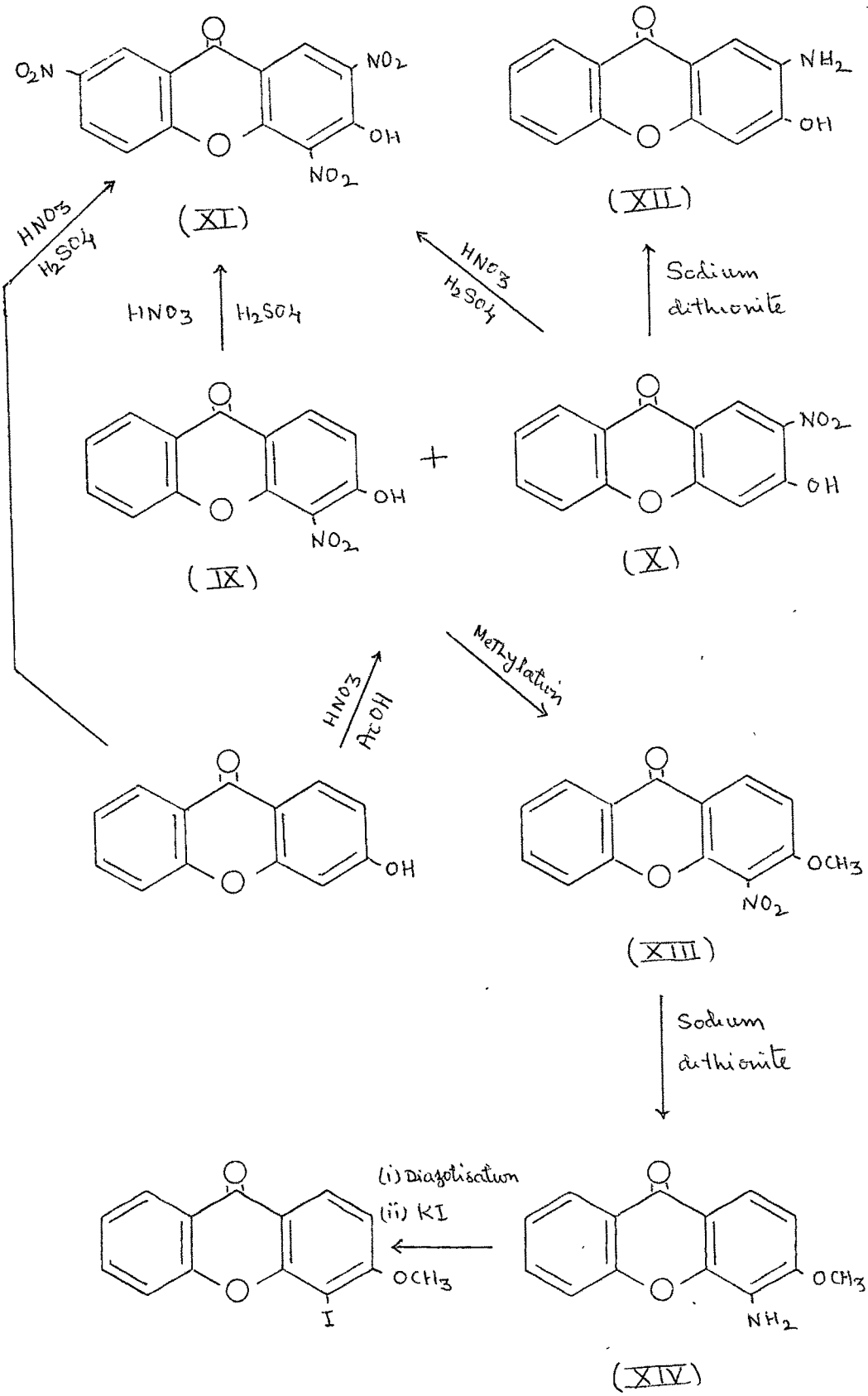
(II) (VIII)

Nitration of 3-hydroxyxanthone

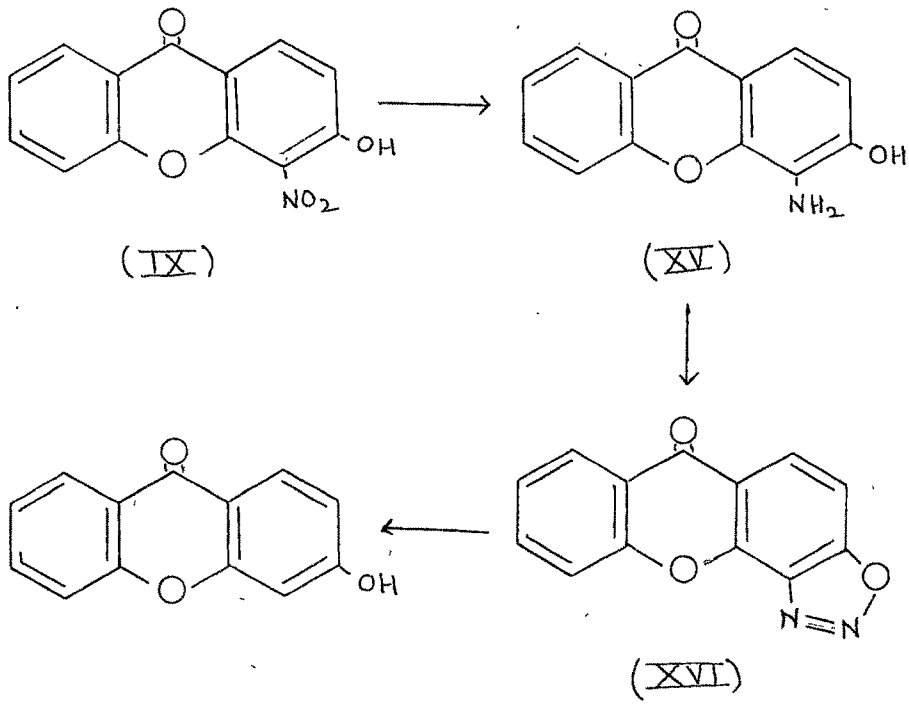
Nitration of 3-hydroxyxanthone with fuming nitric acid in acetic acid gave yellow needles of 3-hydroxy-4-nitroxanthone (IX), same as that synthesised from 2-nitroresorcinol and salicylic acid as described in Chapter II. The mother liquor on dilution with water was found to contain a mononitroxanthone, the original 3-hydroxyxanthone and a third product, which is formed in traces, as seen by TLC with chlofoform-methanol (95 : 5). In actual separation on a column of silica gel only the mononitroxanthone and

3-hydroxyxanthone could be isolated. The mixture was eluted first with first benzene, and then with benzene-chloroform (50 : 50) mixture. The first band eluted was a yellow compound, which analysed for a mononitroxanthone, which was different from 3-hydroxy-4-nitroxanthone. The second band was colourless, which was found to be 3-hydroxyxanthone. The last band remained strongly adsorbed, which may be the trinitroxanthone as can be seen by TLC comparison with the spot of the 2,4,7-trinitro-3-hydroxyxanthone (XI) obtained by nitration of 3-hydroxyxanthone by sulphuric acid and nitric acid mixture described later. The second mononitroxanthone has been assigned tentatively 3-hydroxy-2-nitroxanthone (X) structure. Both these mononitroxanthones could not, however, be nitrated further with fuming nitric acid in acetic acid to get the dinitro derivative. But when nitrated with sulphuric acid and nitric acid mixture both gave the same trinitroxanthone. 3-Hydroxyxanthone, with more fuming nitric acid gave a better yield of 3-hydroxy-4-nitroxanthone (IX). Here, the nitroxanthone separated as yellow needles in a pure form.

When 3-hydroxy-4-nitroxanthone was reduced with dithionite in alcohol it gave 3-hydroxy-4-aminoxanthone (XV). Similarly, 3-hydroxy-2-nitroxanthone was reduced to aminoxanthone (XII). 3-Hydroxy-4-aminoxanthone, however, could not be converted into 3,4-dihydroxyxanthone, as after diazotisation and treatment with dilute sulphuric acid it cyclised to give an azoxy compound, which was isolated and

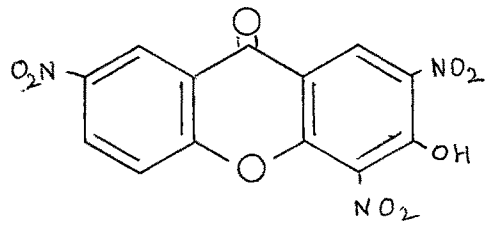

O2N
NO2
OH
NO2
(XI)
NH2
OH
(XII)
HNO3
H2SO4
HNO3
H2SO4
HNO3
H2SO4
Sodium dithionite
OH
NO2
(IX)
+
NO2
OH
(X)
HNO3
AcOH
Methylation
OH
OCH3
NO2
(XIII)
Sodium dithionite
(i) Diazotisation
(ii) KI
OCH3
I
OCH3
NH2
(XIV)

analysed. In one experiment the azoxy compound (XVI) was prepared and treated with hot boiling 60 % sulphuric acid in order to hydrolyse it as reported in the literature[16], but no dihydroxy compound was obtained. Treatment with dilute sodium hydroxide solution in the presence of alcohol results in the loss of nitrogen, even at room temperature, and original 3-hydroxyxanthone is obtained back. The methyl ether of 3-hydroxy-4-nitroxanthone (XIII) could be reduced easily to the amino derivative (XIV), but the aminomethoxy-xanthone could not be converted into 3-methoxy-4-hydroxy-xanthone through diazotisation. But 3-methoxyxanthone-4-diazonium chloride could be converted into 3-methoxy-4-iodoxanthone by treatment with potassium iodide as described in Chapter II.

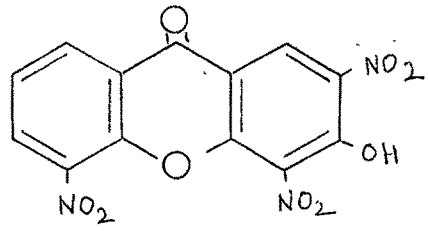


(IX) (XV) (XVI)

Nitration of 3-hydroxyxanthone with sulphuric acid and nitric acid mixture gave a mixture of trinitroxanthone and the other two mononitroxanthones along with the unreacted 3-hydroxyxanthone. The trinitroxanthone being insoluble in cold methanol could be easily separated from the mixture. On crystallisation from acetic acid pure trinitroxanthone was obtained. The NMR of this compound was taken in dimethyl sulphoxide (Fig. 3). There are two possibilities for the trinitroxanthone (XI) and (XVII).



(XI)



(XVII)

Structure (XI) will give two ortho-coupled doublets for the two protons H-5 and H-6 and two singlets for H-1 and H-8. While (XVII) will give rise to a singlet and a doublet in the low field region due to H-1 and H-8 and the protons H-6 and H-7 will appear as multiplets, H-6 being shifted slightly downfield due to the proximity of the nitro group at C-5. The NMR of the trinitro compound shows two doublets and two singlets confirming structure (XI). There are two one-proton singlets at δ 8.58 and δ 8.45 which can easily be assigned to H-8 and H-1 respectively. The singlet at δ 8.58 shows meta coupling (J = 3Hz) due to the presence of m-proton

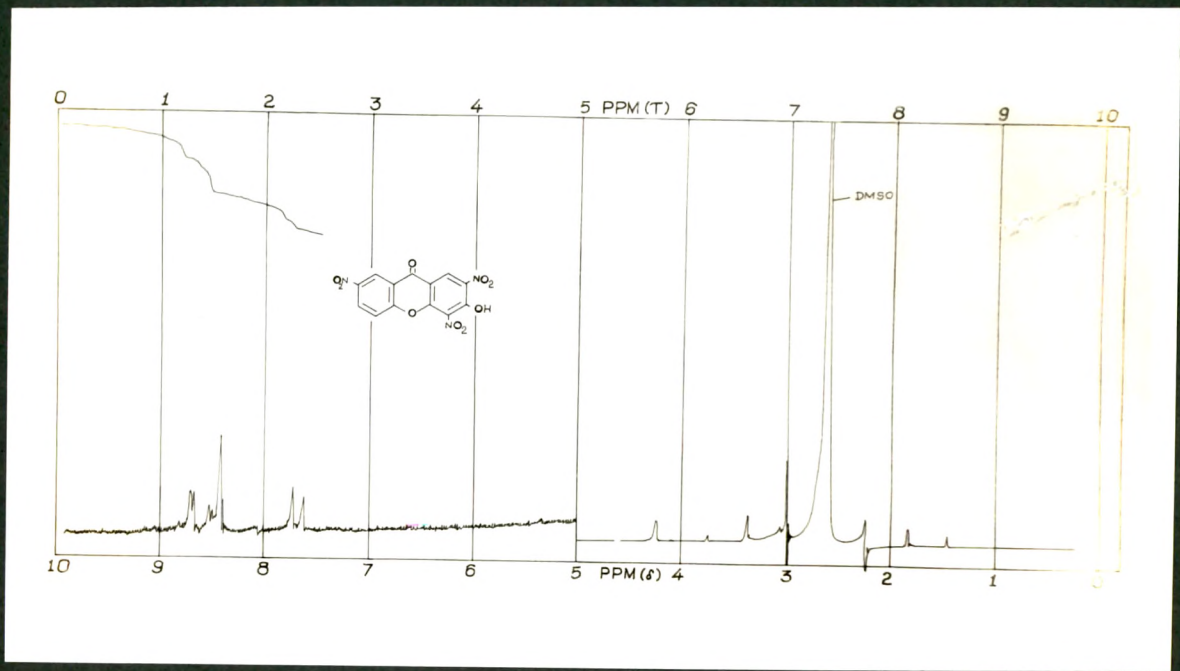


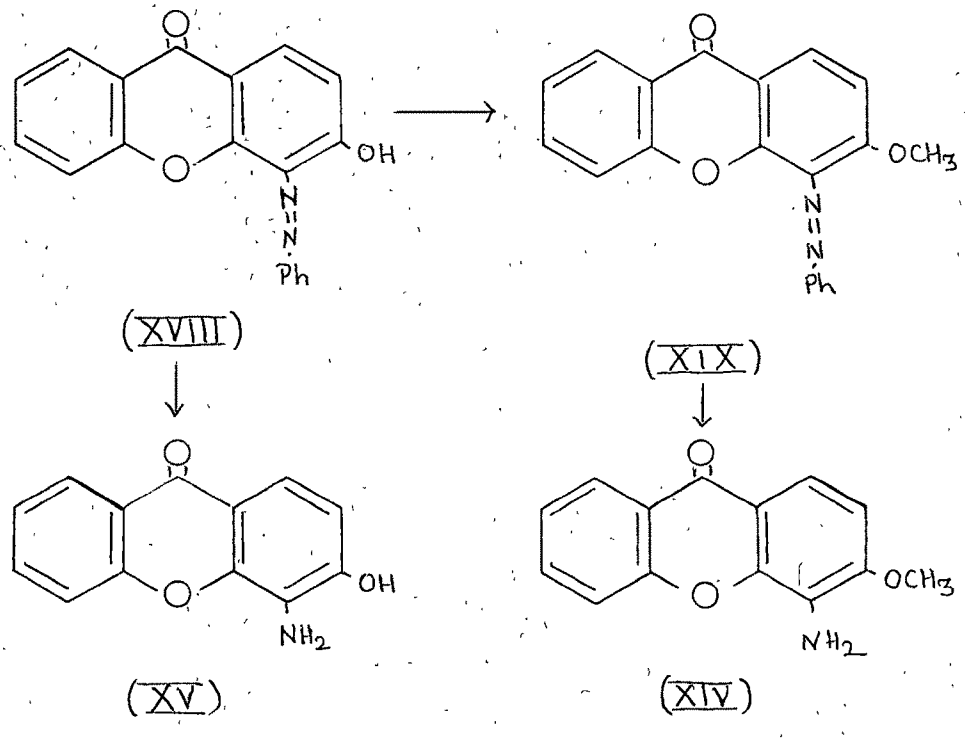
Fig. 3 : NMR spectrum of 3-hydroxy-2,4,7-trinitroxanthone(XI) in DMSO (90 MHz).

H-6, the fact which is also in favour of the structure (XI). The doublets at δ 7.68 and δ 8.58 with ortho coupling J of 9Hz can be assigned to H-5 and H-6 respectively. Eventhough, the doublet due to H-6 is overlapped by the singlet of H-1, the meta coupling of H-6 with H-8 is visible in the other half of the doublet (J = 3Hz).

No nitration occurred when 3-methoxyxanthone was treated with fuming nitric acid in acetic acid, under the conditions given for 3-hydroxyxanthone.

Diazocoupling of 3-hydroxyxanthone

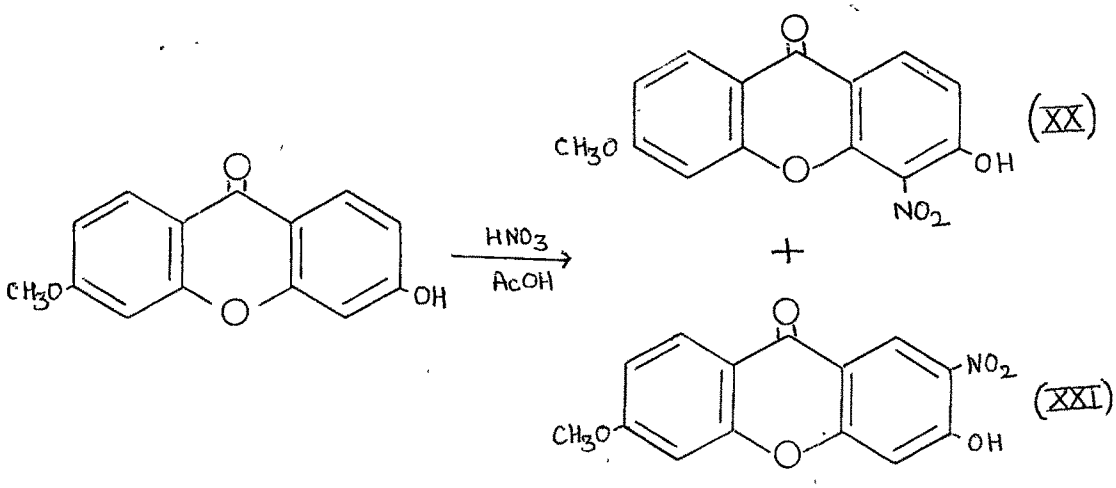
3-Hydroxyxanthone on coupling with phenyldiazonium chloride gave an orange dye which analysed for monoazoxanthone. This on reduction gave 3-hydroxy-4-aminoxanthone (XVI), same as obtained from 3-hydroxy-4-nitroxanthone on

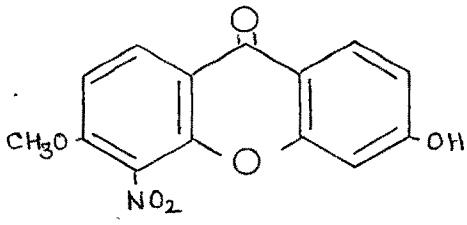


reduction. So, it has been assigned 3-hydroxy-4-phenylazoxanthone (XVIII) structure. Methylation of it gave 3-methoxy-4-phenylazoxanthone (XIX), which could also be reduced to 3-methoxy-4-aminoxanthone (XIV).

Nitration of 3-hydroxy-6-methoxyxanthone

Nitration of 3-hydroxy-6-methoxyxanthone has been carried out only with fuming nitric acid in acetic acid. The product separated was a mononitroxanthone with m.p. 290°. The mother liquor on dilution with water gave a mixture of this xanthone and another nitroxanthone as seen by TLC. The mixture showed a m.p. 235°. This mixture on separating on a column of silica gel by chloroform-methanol





(XXII)

(95 : 5) mixture gave two bands the lower yellow one and the upper brownish one. These were separated by removing the column and cutting the zones and extracting the two zones in methanol separately. The solvent was removed and the products were crystallised from alcohol. The lower band was of a mononitro derivative which had m.p. 238°, while the upper one was of the same mononitroxanthone described above with m.p. 290°

The NMR spectrum (Fig.4) of the product with m.p. 290° showed two one-proton doublets, appearing as triplet due to overlapping of the two at δ 7.95 and δ 7.85 (each with J = 9Hz) in the down field peri proton region indicating that the two peri protons H-1 and H-8 have their ortho-protons H-2 and H-7 unsubstituted. This means that the nitration has taken place in the 4-position and not in the 2-position. The doublet due to H-2 is also discernible. The other protons H-5 and H-7 have appeared as a multiplet between δ 6.94-6.78, in which a singlet at δ 6.8, which has appeared prominently may be attributed to H-5. This NMR data also agrees with the structure (XXII), in which the nitration may occur at 5-position. But this can be ruled out as 3,6-dimethoxyxanthone is not nitrated under these conditions. Therefore, the structure 3-hydroxy-4-nitro-6-methoxyxanthone (XX) is more favourable. The other mononitroxanthone with m.p. 238° has been assigned tentatively 3-hydroxy-2-nitro-6-methoxyxanthone structure (XXI) on the same grounds. The NMR spectrum of this compound

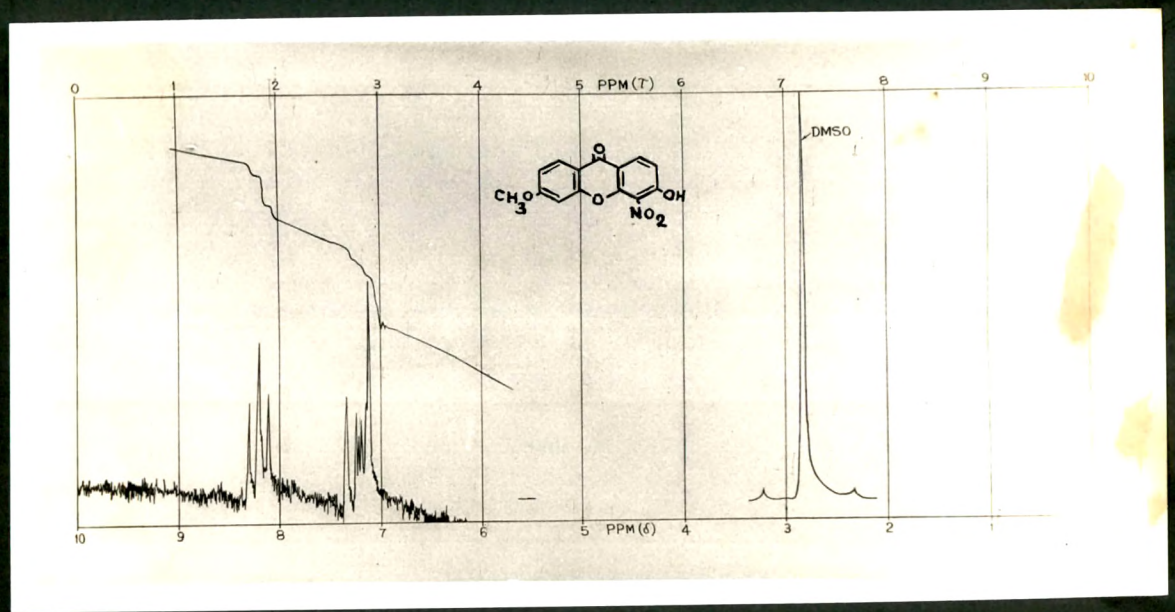


Fig. 4 : NMR spectrum of 3-hydroxy-4-nitro-6-methoxyxanthone (XX) in DMSO (90 MHz).

could not be taken due to its poor solubility in dimethyl sulphoxide and chloroform.

Nitration of 3,6-dihydroxyxanthone

3,6-Dihydroxyxanthone on nitration with sulphuric acid and nitric acid mixture gave a compound which crystallised from acetic acid to give a pure tetranitroxanthone. The NMR spectrum of this compound (Fig. 5) showed only a singlet at δ 8.4, quite down field indicating that it is due to the two peri protons, overlapping each other, being identical. This shows that all the four ortho-positions have been nitrated, and so 3,6-dihydroxy-2,4,5,7-tetranitroxanthone structure (XXIII) has been assigned to it.

In the literature Kurdukar and Subba Rao[6] have reported that the nitration of 3,6-dihydroxyxanthone gave 3,6-dihydroxy-2,4,5,7-tetranitroxanthone with m.p. 240°. On repetition of their work, the m.p. was found to be 298°, same as that of the tetranitroxanthone obtained in the present work. The mixed m.p. was also not depressed. They prepared this by nitrating 3,6-dihydroxyxanthone with conc. nitric acid on a steam bath for 3 hr. and reported aqueous alcohol as a solvent for crystallisation, but it was found to be inconvenient, as the xanthone did not crystallise out of it. Methylation of this product gave a dimethyl ether which exploded violently before melting. Similarly, the inorganic salts of the hydroxytetranitroxanthone also exploded. Acetylation gave the acetoxy derivative.

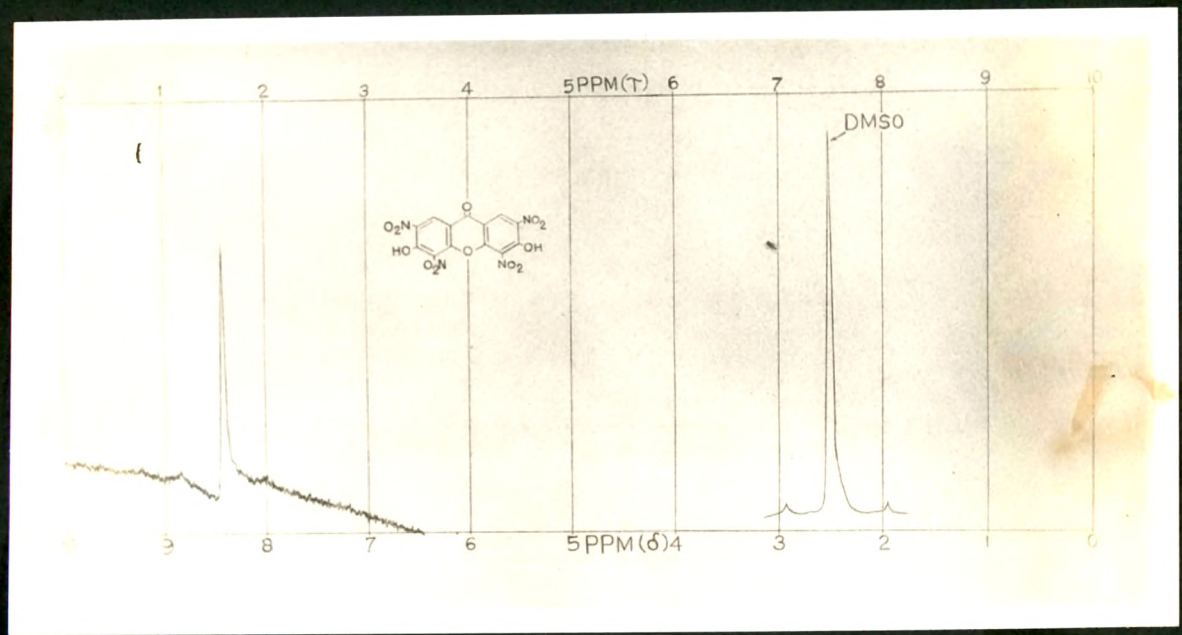
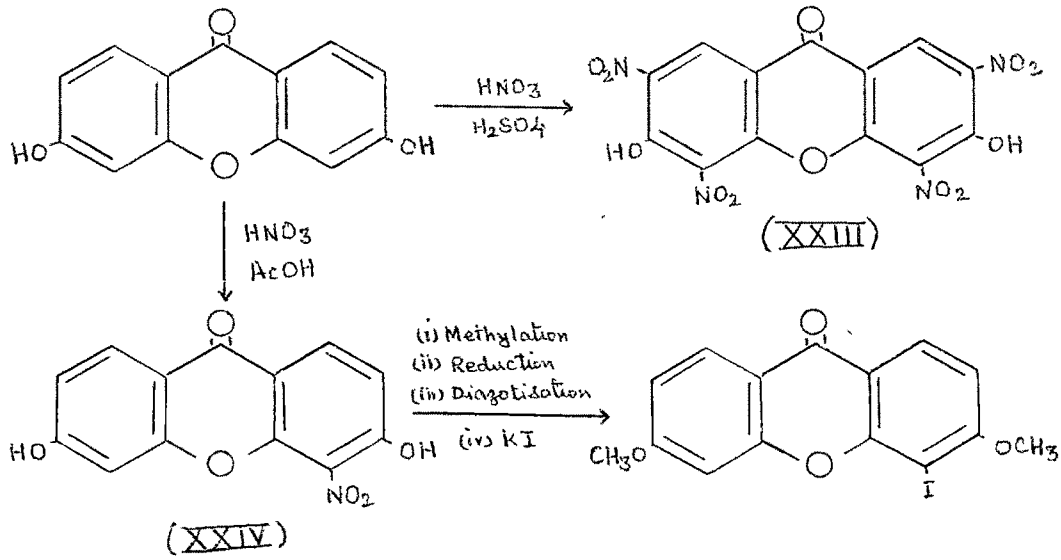


Fig. 5 : NMR spectrum of 3,6-dihydroxy-2,4,5,7-tetranitro-xanthone (XXIII) in DMSO (90 MHz).

Nitration of 3,6-dihydroxyxanthone with fuming nitric acid in acetic acid gave only a mononitroxanthone. Methylation of this gave dimethoxy derivative which when reduced, diazotised and subjected to Sandmeyer reaction with potassium iodide gave 3,6-dimethoxy-4-iodoxanthone, identical with the product obtained from direct iodination of 3,6-dihydroxyxanthone described in Chapter II. Therefore, the mononitroxanthone has been assigned 3,6-dihydroxy-4-nitroxanthone structure (XXIV).



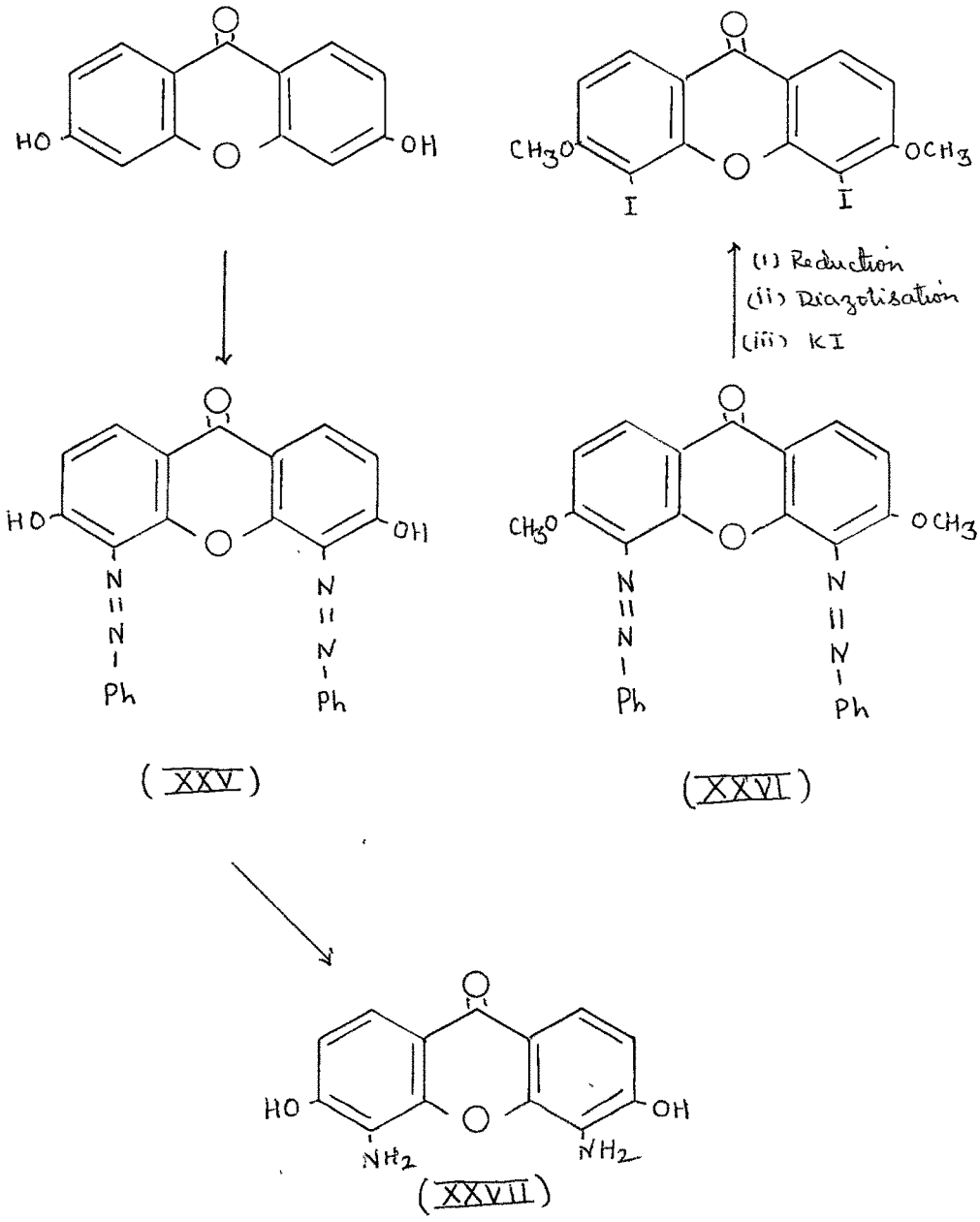
(XXIII)

(XXIV)

Diazocoupling of 3,6-dihydroxyxanthone

Coupling of 3,6-dihydroxyxanthone with phenyldiazonium chloride gave a di(phenylazo)xanthone as an orange dye. This, when reduced with sodium dithionite in aqueous alcohol gave a dihydroxydiaminoxanthone. The NMR spectrum (Fig. 6) of this diamino derivative in trifluoroacetic acid, showed two doublets (J = 9Hz) at δ 8.08, and δ 6.76, similar

to the doublets observed in the case of 3,6-dihydroxy-4,5-diiodoxanthone (Fig. 5 ,Chapter II) and that of 3,6-dimethoxy-4,5-diallylxanthone (Fig. 4 , Chapter IV). The fact favours 3,6-dihydroxy-4,5-diaminoxanthone structure (XXVII). Therefore,



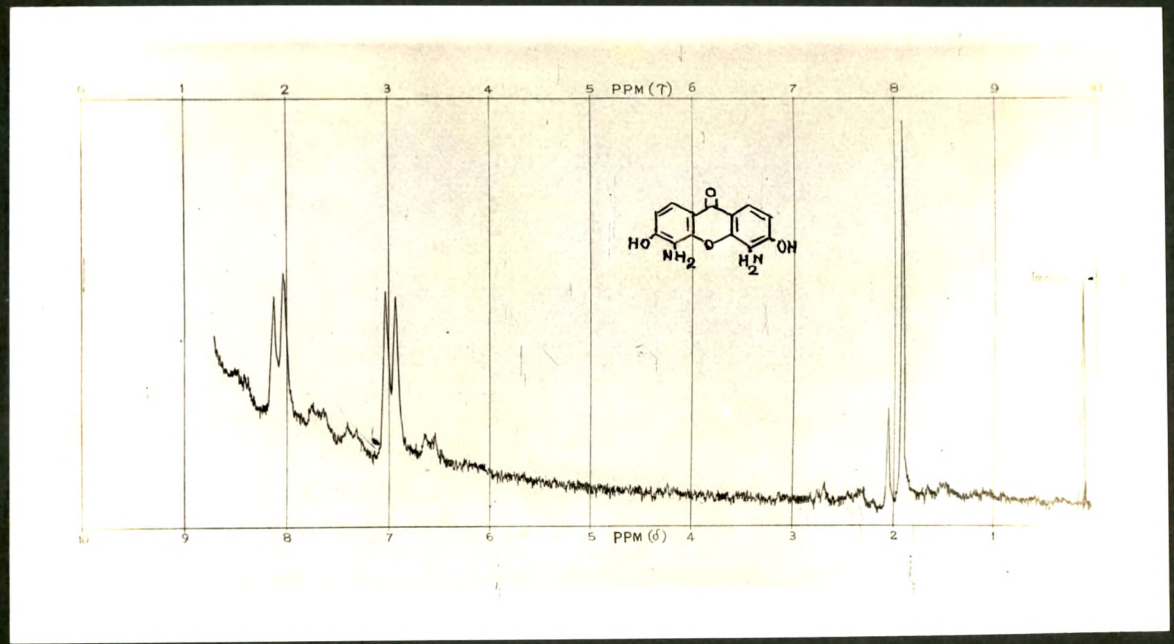


Fig. 6 : NMR spectrum of 3,6-dihydroxy-4,5-diaminoxanthone (XXVII) in CF_3COOH (90 MHz).

3,6-dihydroxy-4,5-di(phenylazo)xanthone structure (XXV) has been assigned to the azo-dye. Methylation of the dye gave a dimethyl ether (XXVI), which when reduced with sodium dithionite, diazotised and treated further with potassium iodide, gave 3,6-dimethoxy-4,5-diiodoxanthone. This was found identical with the dimethyl ether of 3,6-dihydroxy-4,5-diiodo-xanthone obtained by direct iodination.

The IR data for the nitroxanthones and the amino-xanthones has been summerised in Table 1 and Table 2 respectively.

Table - 1

IR data of the nitroxanthones

The IR spectra are recorded on Perkin-Elmer model in KBr.

	Xanthone	-OH stretching $cm.^{-1}$	-C=O * stretching $cm.^{-1}$	$-NO_2$ stretching $cm.^{-1}$	-C-O-C- stretching $cm.^{-1}$
1)	2-Hydroxy-1-nitroxanthone (I)	3200 (broad)	1630; 1610	1545; 1345	1235; 1225
2)	3-Hydroxy-4-nitroxanthone (IX)	3400 (broad)	1670; 1630	1535; 1330	1230; 1190
3)	2-Hydroxy-1,3-dinitroxanthone (V)	3400 (broad)	1680; 1660	1556; 1325	1255; 1230
4)	3-Hydroxy-2,4,7-trinitroxanthone (XI)	3400 (broad)	1690; 1650	1550; 1350	1225; 1200
5)	3,6-Dihydroxy-2,4,5,7-tetranitroxanthone (XXIII)	3400 (broad)	1700; 1630	1560; 1360	1230; 1215
6)	3-Hydroxy-4-nitro-6-methoxy-xanthone (XX)	3400 (broad)	1630; 1615	1540; 1350	1240; 1200

* Second band is the intense -c=c- stretching.

Table - 2

IR data of the aminoxanthones

The IR spectra are recorded on Beckman IR-20 model in nujol.

Xanthone	-OH stretching $cm.^{-1}$	$-NH_2$ stretching $cm.^{-1}$	-C=O * stretching $cm.^{-1}$	-NH bending $cm.^{-1}$	-C-N stretching $cm.^{-1}$	-C-O-C- stretching $cm.^{-1}$
1) 2-Methoxy-1-amino-	-	3420;	1630;	1650	1350;	1230;
xanthone (IV)		3320	1615		1270	1190
2) 2-Hydroxy-1-amino-	3450 (broad)		1620;	1645	1345;	1225;
xanthone (II)			1605		1295	1195
3) 3-Methoxy-4-amino-	-	3440;	1650;	1650	1350;	1230;
xanthone (XIV)		3340	1615		1290	1180
4) 3-Hydroxy-4-amino-	3480	3380;	1635;	1650	1340;	1240;
xanthone (XV)		3280	1615		1300	1185
5) 2-Hydroxy-1,3-di-	3420	3300;	1630;	1655	1320;	1235;
aminoxanthone (VI)		3150	1610		1270	1185
6) 3,6-Dihydroxy-4,5-di-	3350 (broad)		1625;	1650	1350;	1235;
aminoxa nthone(XXVII)			1610		1300	1195

* Second band is the intense -c=c- stretching.

EXPERIMENTAL

Nitration of 2-hydroxyxanthone : 2-Hydroxy-1-nitroxanthone :

2-Hydroxyxanthone (0.5g.) was dissolved in acetic acid (110 ml.) by warming and the solution cooled to room temperature (30°). To this fuming nitric acid (d. 1.5 ; 0.05 ml.) was added with stirring and the stirring continued for 2 hr. Next day the solution was diluted with water and the separated product crystallised from aqueous alcohol in yellow needles (0.18 g.), m.p. 244-45° (decomp.).

Analysis : Found : C, 60.06 ; H, 2.83 ; N, 5.38 %
$C_{13}H_7O_5N$ requires : C, 60.70 ; H, 2.73 ; N, 5.45 %.

The methyl ether :

2-Hydroxy-1-nitroxanthone (0.2 g.), dimethyl sulphate (0.2 ml.) and anhydrous potassium carbonate (0.6 g.) were refluxed in acetone (30 ml.) for 2 hr. The product crystallised from aqueous alcohol in yellow needles (0.16 g.), m.p. 276-78°.

Analysis : Found : C, 61.81 ; H, 3.44 ; N, 4.92 %
$C_{14}H_8O_5N$ requires : C, 61.97 ; H, 3.34 ; N, 5.16 %.

2-Hydroxy-1-aminoxanthone :

2-Hydroxy-1-nitroxanthone (0.5 g.) in alcohol (30 ml.) together with sodium dithionite (1.0 g.) was refluxed for 5 min. and water (10 ml.) was added. Heating was continued for half an hour and then alcohol was removed.

The separated product was taken in 2N hydrochloric acid and reprecipitated with ammonia. The separated product crystallised from aqueous alcohol in yellow needles (0.28 g.), m.p. 262°. This was analysed after drying at 110° in vacuum.

Analysis : Found : C, 68.87 ; H, 3.98 ; N, 6.08 %

$C_{11}H_9O_3N$ requires : C, 68.72 ; H, 3.99 ; N, 6.17 %.

2-Methoxy-1-aminoxanthone :

2-Methoxy-1-nitroxanthone (0.5 g.) in refluxing alcohol (30 ml.) was treated with sodium dithionite (1.0 g.). This was followed by addition of water (10 ml.). The solution was refluxed for half an hour, when the colour changed to light yellow. Alcohol was removed and the solution diluted. After the chemical purification the product crystallised from aqueous alcohol in brown needles (0.21 g.), m.p. 159-60°.

Analysis : Found : C, 69.60 ; H, 4.63 ; N, 5.45 %

$C_{14}H_{11}O_3N$ requires : C, 69.70 ; H, 4.59 ; N, 5.80 %.

Attempted conversion of 2-hydroxy-3-aminoxanthone into 1,2-dihydroxyxanthone :

To a solution of 2-hydroxy-1-aminoxanthone (0.5 g.) in 2N hydrochloric acid (20 ml.) kept at 0°, sodium nitrite (0.3 g. in 4 ml. water) was added and the solution stirred for half an hour. The solution was then boiled after adding sulphuric acid (60 % ; 50 ml.). On cooling needles separated which were insoluble in dilute alkali and which decomposed to a brownish product. But when the diazotised solution was added to boiling sulphuric acid (60 % or 80 % ; 80 ml.),

the brownish product was obtained which could not be purified. This product slowly dissolved when kept in dilute alkali solution.

2-Methoxy-1-aminoxanthone under similar conditions gave no pure product.

2-Methoxy-1-iodoxanthone :

2-Methoxy-1-aminoxanthone (0.4 g.) was dissolved in sulphuric acid (20 % ; 20 ml.), cooled to 0° and treated with sodium nitrite solution (0.4 g. in 5 ml. water). The separated diazonium salt was stirred for half an hour at this temperature and treated with urea (0.5 g.). Next the solution of potassium iodide (0.5 g. in 5 ml. water) was added slowly. The solution was stirred and brought to room temperature and then kept at 60° for 1 hr. The separated solid was treated with sodium sulphite solution and taken in chloroform. The chloroform solution was passed through a small column of silica gel and the product obtained after removal of chloroform crystallised from acetic acid and was found identical with 2-methoxy-1-iodoxanthone obtained after direct iodination and methylation.

Attempted nitration of 2-methoxyxanthone :

To a solution of 2-methoxyxanthone (0.5 g.) in acetic acid (45 ml.) was added fuming nitric acid (d. 1.5 ; 0.1 ml.) and the solution was left overnight. The solid separating after dilution was found to be the original 2-methoxyxanthone.

2-Hydroxy-1,3-dinitroxanthone :

When 2-hydroxyxanthone (0.5 g.) in acetic acid (110 ml.) was treated with fuming nitric acid (d. 15 ; 0.8 ml.) at 30° and left overnight, yellow needles separated. These were collected and crystallised from acetic acid in yellow shining needles (0.18 g.), m.p. 250-51°. This showed brown colouration with the alcoholic ferric chloride. It in mu/oil :

Analysis : Found : C, 51.40 ; H, 2.43 ; N, 8.98 %

$C_{13}H_6O_7N_2$ requires : C, 51.65 ; H, 1.98 ; N, 9.27 %.

The mother liquor on pouring in water gave a yellow solid which when crystallised from acetic acid gave needles of dinitroxanthone (0.08 g.). When these were filtered off and the filtrate diluted, yellow solid was obtained which crystallised from aqueous alcohol in yellow needles (0.05 g.), which were found to be of 2-hydroxy-1-nitroxanthone.

2-Methoxy-1,3-dinitroxanthone :

Methylation of 2-hydroxy-1,3-dinitroxanthone (0.5 g.) with dimethyl sulphate (1 ml.) in acetone (50 ml.) in the presence of anhydrous potassium carbonate by refluxing on a steam bath for 2 hr. gave a yellow compound which on repeated crystallisation from aqueous alcohol gave yellow buds (0.16 g.), m.p. 177-79°.

Analysis : Found : C, 53.90 ; H, 2.90 ; N, 9.21 %

$C_{14}H_8O_7N_2$ requires : C, 53.60 ; H, 2.53 ; N, 8.86 %.

2-Hydroxy-1,3-diaminoxanthone :

2-Hydroxy-1,3-dinitroxanthone (0.4 g.) was dissolved in aqueous alcohol (30 % ; 40 ml.) and sodium dithionite (5.0 g.) was added. The reaction mixture refluxed for half an hour. After removing alcohol, the product obtained was crystallised from aqueous alcohol in black needles (0.16 g.), m.p. 244-45°.

Analysis : Found : C, 64.46 ; H, 4.61 ; N, 11.28 %

$C_{13}H_{10}O_3N_2$ requires : C, 64.46 ; H, 4.13 ; N, 11.57 %.

Nitration of 2-methoxyxanthone : 2-Methoxy-trinitroxanthone :

To a mixture of sulphuric acid (3 ml.) and fuming nitric acid (1 ml.) at 0-5° was added powdered 2-methoxy-xanthone(0.5 g.) slowly with stirring and the mixture was kept overnight. Next day the reaction mixture was poured over ice and the separated solid was dried and treated with cold methanol and filtered. The insoluble solid crystallised from acetic acid in white needles (0.21 g.), 240-42°.

Analysis : Found : C, 46.95 ; H, 2.05 ; N, 10.59 %

$C_{14}H_7O_9N_3$ requires : C, 46.53 ; H, 1.93 ; N, 10.36 %.

The alcoholic filtrate when run on TLC plate along with the spots of above xanthone, 2-methoxy-1,3-dinitroxanthone, and 2-methoxy-1-nitroxanthone and kept in a chamber containing chloroform-methanol (70-30). The mixture gave three spots, as seen under UV light, the upper one matching with the mononitroxanthone, the middle one with the dinitroxanthone and the last one with the above trinitroxanthone.

Diazocoupling with 2-hydroxyxanthone : 2-Hydroxy-1-phenylazoxanthone :

Aniline (2 ml.) was dissolved in hydrochloric acid (50 % ; 8 ml.) and cooled to 0-5°. To this was added sodium nitrite solution (1.5 g. in 10 ml. water) slowly, when a yellow product separated. Cold solution of 2-hydroxyxanthone (1.1 g.) in sodium hydroxide 4 % ; 20 ml.) which was diluted with water (150 ml.) was added slowly to the diazotised solution when an orange dye separated. The solution was stirred for 1 hr. The product was collected and crystallised from acetic acid in crimson-red needles (0.9 g.), m.p. 208-10°.

Analysis : Found : C, 71.71 ; H, 4.09 ; N, 8.84 %

$C_{19}H_{12}O_3N_2$ requires : C, 72.14 ; H, 3.82 ; N, 8.86 %.

2-Methoxy-1-phenylazoxanthone :

Methylation of 2-hydroxy-1-phenylazoxanthone as usual gave 2-methoxy-1-phenylazoxanthone which crystallised from acetic acid in shining crimson plates, m.p. 196-98°.

Analysis : Found : C, 72.93 ; H, 4.69 ; N, 8.62 %

$C_{20}H_{14}O_3N_2$ requires : C, 72.72 ; H, 4.27 ; N, 8.48 %.

Reduction of 2-hydroxy-1-phenylazoxanthone : 2-Hydroxy-1-aminoxanthone :

To 2-hydroxy-1-phenylazoxanthone (0.5 g.) in alcohol (30 ml.) sodium dithionite (0.8 g.) was added and the solution refluxed. To this solution water (10 ml.) followed by further quantity of sodium dithionite (0.8 g.)

was added and the solution refluxed for further 15 min. Alcohol was removed and the separated solid was purified by taking in hydrochloric acid. The solid obtained on neutralising the extract with ammonia crystallised from aqueous alcohol in yellow needles (0.15 g.). This was identical with 2-hydroxy-1-aminoxanthone obtained from 2-hydroxy-1-nitroxanthone after reduction.

Reduction of 2-methoxy-1-phenylazoxanthone : 2-Methoxy-1-aminoxanthone :

2-Methoxy-1-phenylazoxanthone (0.5 g.) was reduced as described above and the product obtained crystallised from aqueous alcohol when it gave yellow needles (0.21 g.) of 2-methoxy-1-aminoxanthone.

Nitration of 3-hydroxyxanthone : 3-Hydroxy-4-nitroxanthone :

3-Hydroxyxanthone (0.5 g.) was dissolved in acetic acid (45 ml.) by warming and then cooled to 30° and fuming nitric acid (0.08 ml.) was added. Stirring was continued for 1 hr. and then the reaction mixture was left overnight. The separated product was crystallised from aqueous alcohol in tiny needles (0.15 g.), m.p. 222°. It was identical with 3-hydroxy-4-nitroxanthone synthesised from 2-nitroresorcinol and salicylic acid as described on page 84.

3-Hydroxy-4-nitroxanthone was obtained in better yield (0.25 g.) when 3-hydroxyxanthone in acetic acid (40 ml.) was kept overnight with fuming nitric acid

(1 ml.). The xanthone separated as yellow needles.

Analysis : Found : C, 56.70 ; H, 3.53 %
(before drying)

$C_{13}H_7O_5N.H_2O$ requires : C, 56.72 ; H, 3.27 %.

Analysis : Found : C, 60.75 ; H, 2.67 ; N, 5.17 %
(after drying at 110° in vacuum)

$C_{13}H_7O_5N$ requires : C, 60.70 ; H, 2.72 ; N, 5.45 %.

3-Hydroxy-2-nitroxanthone :

The mother liquor from the above reaction mixture on dilution gave a yellow product. This showed three spots on TLC with chloroform-methanol (95 : 5). Under the UV light the upper spot appeared brown, the middle one showed blue fluorescence and the lower one was brown. The middle one was 3-hydroxyxanthone as was a seen by comparing this spot with the spot of 3-hydroxyxanthone. The upper yellow spot was different from the spot of 3-hydroxy-4-nitroxanthone, while the last spot and the spot from 3-hydroxy-2,4,7-trinitroxanthone did not migrate with this solvent system.

The yellow solid obtained after dilution was dried and taken in methanol and applied over a column of silica gel. Elution was first carried out with benzene alone, when the lower yellow band migrated and then with chloroform-benzene (1 : 1) when the yellow band was completely eluted. This was crystallised from methanol in yellow needles (0.02 g), m.p. 238°. Further elution by chloroform alone gave 3-hydroxy-

xanthone. The last product which was in traces remained strontly adsorped on column as brown band. The mixed m.p. of the isolated mononitroxanthone with 3-hydroxy-4-nitroxanthone was depressed by 30°.

Analysis : Found : C, 61.06; H, 2.82 ; N, 5.06 %

$C_{13}H_7O_5N$ requires : C, 60.70 ; H, 2.73 ; N, 5.45 %.

Attempted nitration of 3-hydroxy-4-nitroxanthone :

3-Hydroxy-4-nitroxanthone (0.3 g.) was dissolved in acetic acid (40 ml.) and fuming nitric acid (0.1 ml.)was added. The mixture was poured into water after 20 hr. The separated product was found to be the original 3-hydroxy-4-nitroxanthone.

Attempted nitration of 3-hydroxy-2-nitroxanthone :

This was also recovered unchanged, when it was treated with nitric acid as described above.

Nitration of 3-hydroxy-4-nitroxanthone : 3-Hydroxy-2,4,7-trinitroxanthone :

Powdered 3-hydroxy-4-nitroxanthone (0.5 g.) was added slowly to a mixture of sulphuric acid (2 ml.) and fuming nitric acid (1 ml.) kept at 0-5°. The reaction mixture was kept at this temperature for 3 hr. more and poured over ice. The separated product crystallised from acetic acid in light yellow needles (0.48 g.), m.p. 252-53°. This was identical with 3-hydroxy-2,4,7-trinitroxanthone, which is described later.

Nitration of 3-hydroxy-2-nitroxanthone : 3-Hydroxy-2,4,7-trinitroxanthone :

Nitration of 3-hydroxy-2-nitroxanthone (0.5 g.) under the conditions described above resulted in the same trinitro derivative (0.48 g.) described above.

3-Hydroxy-4-aminoxanthone :

3-Hydroxy-4-nitroxanthone (0.5 g.) dissolved in alcohol (15 ml.) containing a water (8 ml.) was treated with sodium dithionite (1.0 g.) and refluxed for half an hour. The alcohol was removed. The separated product was taken in hydrochloric acid and the solution was then neutralised. The product obtained crystallised from aqueous alcohol in yellow needles (0.26 g.), m.p. 238-40°.

Analysis : Found : C, 69.11 ; H, 4.05 ; N, 6.09 %

$C_{13}H_9O_3N$ requires : C, 68.70 ; H, 3.97 ; N, 6.17 %.

Attempted conversion of 3-hydroxy-4-aminoxanthone to 3,4-dihydroxyxanthone : Formation of an azoxy derivative :

3-Hydroxy-4-aminoxanthone (0.3 g.) was taken in water (125 ml.) and conc. sulphuric acid (3 ml.) and acetic acid (3 ml.) were added. The solution was boiled and cooled when the solid separated. This was cooled to 0° and treated with cold sodium nitrite solution (0.3 g. in 5 ml. water). The stirring was continued for half an hour. A yellow solid started separating which separated completely when the solution was heated at 40° for a few minutes. This solid crystallised from water as yellow needles (0.1 g.), m.p. 193°

(decomp.). It was decomposed by light.

Analysis : Found : C, 65.92 ; H, 2.38 ; N, 11.26 %

$C_{13}H_6O_3N_2$ requires : C, 65.55 ; H, 2.54 ; N, 11.76 %.

Hydrolysis :

When the above azoxy derivative (0.1 g.) was taken in sulphuric acid (60 % ; 10 ml.) and added to boiling sulphuric acid (60 % ; 50 ml.) slowly during 15 min. and the solution refluxed further for 3 hr., a brown product separated. This could neither be crystallised nor chemically purified. The crude product showed a melting range 240-50°.

When the azoxy derivative (0.1 g.) was taken in alcohol (5 ml.) and sodium hydroxide solution (10 % ; 2 ml.) was added, nitrogen was evolved. The solution was acidified and the separated product crystallised from alcohol. It was identical with 3-hydroxyxanthone.

3-Methoxy-4-aminoxanthone :

This has already been described on page 85.

Attempted preparation of 3-methoxy-4-hydroxyxanthone :

3-Methoxy-4-aminoxanthone was diazotised under the conditions described for the diazotisation of 3-hydroxy-4-aminoxanthone. The diazonium salt, however, could not be hydrolysed by sulphuric acid (60 %) to any pure product.

3-Hydroxy-2-aminoxanthone :

3-Hydroxy-2-nitroxanthone (0.2 g.) and sodium dithionite (0.5 g.) in alcohol (40 ml.) were refluxed for

half an hour. The solution was diluted and the separated product crystallised from aqueous alcohol in yellow needles (0.08 g.), m.p. 256-58°. This was analysed after drying at 110° in vacuum.

Analysis : Found : C, 69.16 ; H, 4.26 ; N, 6.02 %

$C_{13}H_9O_3N$ requires : C, 68.72 ; H, 3.99 ; N, 6.17 %.

3-Hydroxy-2,4,7-trinitroxanthone :

To a mixture of sulphuric acid (3 ml.) and fuming nitric acid (1 ml.) at 0°, powdered 3-hydroxyxanthone (0.5 g.) was added with stirring and the reaction mixture was left overnight. Next day it was poured on ice and the separated solid collected. The solid when treated with cold methanol (5 ml.) partially dissolved. The insoluble material crystallised from acetic acid in white needles (0.22 g.), m.p. 252-53° (decomp.).

Analysis : Found : C, 45.40 ; H, 1.85 ; N, 11.76 %

$C_{13}H_5O_9N_3$ requires : C, 44.95 ; H, 1.44 ; N, 12.10 %.

The methanol soluble portion after removing the solvent gave a mixture which showed four spots on TLC with chloroform-methanol (95 : 5). These were compared with the nitroxanthones obtained earlier. The upper most one matched with 3-hydroxy-2-nitroxanthone, the second with 3-hydroxy-4-nitroxanthone, the third with 3-hydroxyxanthone and the fourth with 3-hydroxy-2,4,7-trinitroxanthone. The nitroxanthones appeared brown under UV light while 3-hydroxyxanthone showed blue fluorescence.

Attempted nitration of 3-methoxyxanthone :

3-Methoxyxanthone (0.5 g.) in acetic acid (40 ml.) was treated with fuming nitric acid (0.1 ml.) and left overnight. Dilution of the reaction mixture next day gave the original 3-methoxyxanthone back.

Diazocoupling of 3-hydroxyxanthone : 3-Hydroxy-4-phenylazoxanthone :

Aniline diazonium chloride was prepared from aniline (2 ml.) as before and to this was added slowly 3-hydroxyxanthone(1.1 g.) dissolved in 1N sodium hydroxide solution (20 ml.) and diluted with water (100 ml.). An orange dye separated. This was further stirred for 2 hr. and after acidification filtered and crystallised from acetic acid in dark crimson red needles (0.8 g.), m.p. 213-14°.

Analysis : Found : C, 71.67 ; H, 3.45 ; N, 9.04 %

$C_{19}H_{12}O_3N_2$ requires : C, 72.14 ; H, 3.82 ; N, 8.86 %.

Reduction of 3-hydroxy-4-phenylazoxanthone : 3-Hydroxy-4-aminoxanthone :

To the refluxing solution of 3-hydroxy-4-phenylazoxanthone (0.5 g.) in alcohol (140 ml.) and water (20 ml.) was added sodium dithionite (1.25 g.). The mixture was refluxed for half an hour and diluted when a yellow product separated. This after chemical purification was crystallised from aqueous alcohol. Yield 0.2 g. This was found identical with 3-hydroxy-4-aminoxanthone obtained from 3-hydroxy-4-nitroxanthone by reduction.

The methyl ether :

Methylation of 3-hydroxy-4-phenylazoxanthone with dimethyl sulphate as usual gave the methyl ether which crystallised from acetic acid. M.p. 171-73°.

Analysis : Found : C, 73.13 ; H, 4.27 ; N, 8.54 %

$C_{20}H_{14}O_3N_2$ requires : C, 72.72 ; H, 4.27 ; N, 8.48 %.

Reduction of 3-methoxy-4-phenylazoxanthone : 3-Methoxy-4-aminoxanthone :

3-Methoxy-4-phenylazoxanthone (0.5 g.) was dissolved in aqueous alcohol (30 % ; 40 ml.) and sodium dithionite (1.25 g.) was added. After refluxing the solution for half an hour it was diluted and the separated product taken in hydrochloric acid (2N ; 50 ml.). The product obtained after neutralisation with alkali was repeatedly crystallised from aqueous alcohol, m.p. 238-40°. Yield 0.18 g. This was identical with the product obtained after reduction of 3-methoxy-4-nitroxanthone.

Nitration of 3-hydroxy-6-methoxyxanthone : 3-Hydroxy-4-nitro-6-methoxyxanthone :

3-Hydroxy-6-methoxyxanthone (0.5 g.) in acetic acid (125 ml.) was treated with fuming nitric acid (0.8 ml.) and left overnight. The separated needles were collected by filtration and recrystallised from alcohol in yellow needles (0.2 g.), m.p. 290°.

Analysis : Found : C, 59.05 ; H, 3.09 ; N, 4.42 %

$C_{14}H_9O_6N$ requires : C, 58.54 ; H, 3.16 ; N, 4.88 %.

3-Hydroxy-2-nitro-6-methoxyxanthone :

The mother liquor from the above reaction mixture was diluted and the separated product dried. This on TLC showed two spots, the upper one light yellow and the lower one dary yellow. The solvent used was chloroform-methanol (95 : 5) mixture. The lower spot matched with 3-hydroxy-4-nitro-6-methoxyxanthone. In actual separation the mixture was dissolved in methanol and adsorbed over a column of silica gel and developed with chloroform-methanol mixture (95 : 5) when the two zones separated. The column was taken out and the two zones were separated by cutting the column. Both were expected in methanol. The lower yellowish one was different from the upper one which was 3-hydroxy-4-nitro-6-methoxyxanthone. The other xanthones crystallised from alcohol (0.1 g.), m.p. 236-38°.

Analysis : Found : C, 58.24 ; H, 3.09 ; N, 4.68 %

$C_{14}H_9O_6N$ requires : C, 58.54 ; H, 3.16 ; N, 4.88 %.

Nitration of 3,6-dihydroxyxanthone : 3,6-Dihydroxy-2,4,5,7-tetranitroxanthone :

3,6-Dihydroxyxanthone (0.5 g.) was added with stirring to a mixture of sulphuric acid (4 ml.) and fuming nitric acid (2 ml.) kept at 0° and the reaction mixture left overnight. The mixture on pouring over ice gave a yellow solid which crystallised from acetic acid in light yellow needles (0.3 g.), m.p. 298° (decomp.).

Analysis : Found : C, 38.60 ; H, 1.42 ; N, 1322 %

$C_{13}H_4O_{12}N_4$ requires : C, 38.23 ; H, 0.99 ; N, 13.72 %.

The dimethyl ether :

Methylation of the above xanthone by usual method gave a dimethyl ether which crystallised from water as yellow powder and exploded violently above 280° before melting.

Analysis : Found : N, 12.35 %

$C_{15}H\ O_{12}N$ requires : N, 12.84 %.

The diacetoxy ester :

3,6-Dihydroxy-2,4,5,7-tetranitroxanthone (0.5 g.) in pyridine (5 ml.) when treated with acetic anhydride (1 ml.) and the mixture kept at 60° for 2 hr. gave a yellow solid on pouring ice-cold hydrochloric acid. This was crystallised from water in yellow buds (0.32 g.), m.p. 312-15°.

Analysis : Found : C, 41.76 ; H, 1.83 ; N, 11.48 %

$C_{17}H_8O_{14}N_4$ requires : C, 41.46 ; H, 1.62 ; N, 11.38 %.

3,6-Dihydroxy-4-nitroxanthone :

3,6-Dihydroxyxanthone (0.5 g.) was dissolved in acetic acid (200 ml.) by refluxing and the solution was then cooled to 30-32°. To this solution fuming nitric acid (0.8 ml.) was added and the solution stirred for 5 hr. After dilution, the solution was left overnight and then evaporated slowly till a brown product separated. The solid was repeatedly crystallised from aqueous alcohol in brownish needles (0.16 g.), m.p. 248-49°.

Analysis : Found : C, 57.09 ; H, 3.05 ; N, 5.37 %

$C_{13}H_7O_6N$ requires : C, 57.14 ; H, 2.56 ; N, 5.13 %.

The dimethyl ether :

3,6-Dihydroxy-4-nitroxanthone (0.5 g.) and dimethyl sulphate (1 ml.) in dry acetone (60 ml.) were refluxed in the presence of anhydrous potassium carbonate (1.0 g.) for 4 hr. The product crystallised from acetic acid in grey needles (0.4 g.), m.p. 312°.

Analysis : Found : C, 59.68 ; H, 3.67 ; N, 4.75 %

$C_{15}H_{11}O_6N$ requires : C, 59.80 ; H, 3.65 ; N, 4.65 %.

Conversion of 3,6-dimethoxy-4-nitroxanthone into 3,6-dimethoxy-4-iodoxanthone :

The above dimethyl ether (0.5 g.) was taken in aqueous alcohol (20 %); 100 ml.) and refluxed after adding sodium dithionite (1.0 g.) for half an hour. After removing alcohol the solution was extracted with ether . The semi-solid obtained on removal of the ether was treated with hydrochloric acid (2N ; 30 ml.) and filtered. Filtrate was diazotised with sodium nitrite (0.3 g. in 10 ml. water) at 5° and stirred for an hour. This was treated with urea (0.8 g.) followed by potassium iodide solution (0.5 g. in 5 ml. water) and then kept in water bath at 60° for an hour. Further treatment with a little sodium sulphite gave a brown product which filtered, collected and passed through a short column of silica gel after dissolving in benzene. The product obtained thus crystallised from alcohol in white needles

(0.02 g.), m.p. 250°. This was identical with 3,6-dimethoxy-4-iodoxanthone.

Diazocoupling of 3,6-dihydroxyxanthone : 3,6-Dihydroxy-4,5-di(phenylazo)xanthone :-

A cold solution of 3,6-dihydroxyxanthone (1.14 g.) in sodium hydroxide (4 % ; 30 ml.) was added to this stirred solution of aniline diazonium chloride, prepared from aniline (3 ml.) in hydrochloric acid (50 % ; 12 ml.) and sodium nitrite (1.6 g. in 15 ml. water), when an orange dye separated. The solution was stirred further at 5° for 2 hr. and filtered. The solid obtained crystallised from nitrobenzene in orange needles (0.8 g.), m.p. 313-15°.

Analysis : Found : C, 68.95 ; H, 3.41 ; N, 12.60 %

$C_{25}H_{16}O_4N_4$ requires : C, 68.80 ; H, 3.66 ; N, 12.84 %.

The dimethyl ether :

The above dye was methylated with dimethyl sulphate as usual and crystallised from acetic acid in crimson needles, m.p. 184-86°.

Analysis : Found : C, 70.03 ; H, 4.39 ; N, 11.55 %

$C_{27}H_{20}O_4N_4$ requires : C, 69.83 ; H, 4.34 ; N, 12.06 %.

Conversion of 3,6-dimethoxy-4,5-di(phenylazo)xanthone into 3,6-dimethoxy-4,5-diiodoxanthone :

3,6-Dimethoxy-4,5-di(phenylazo)xanthone (0.8 g.) was refluxed in aqueous alcohol (60 % ; 150 ml.) with sodium dithionite (1.0 g.) for 2 hr. After working up the

diaminoxanthone was taken in sulphuric acid (30 % ; 25 ml.) and cooled to 0-5° and treated with cold solution of sodium nitrite (0.3 g. in 20 ml. water). After adding solution of urea (1.0 g. in 15 ml.water), the potassium iodide solution (10 % ; 5 ml.) was added.After stirring the solution for 1 hr. it was heated to 60° and kept at this temperature for half an hour. The separated solid after treating with sodium sulphite was taken in chloroform and passed through a column of silicaa gel. The product further crystallised from acetic acid in white needles (0.03 g.), m.p. 298-300°. The mixed m.p. of this with 3,6-dimethoxy-4,5-diiodoxanthone obtained by direct iodination was not depressed.

Reduction of 3,6-dihydroxy-4,5-di(phenylazo)xanthone : 3,6-Dihydroxy-4,5-diaminoxanthone :

3,6-Dihydroxy-4,5-di(phenylazo)xanthone (0.8 g.) when refluxed in aqueous alcohol (60 % ; 150 ml.) with sodium dithionite (1.0 g.) for 2 hr. and worked up gave a greyish product which crystallised from alcohol in yellow needles (0.35 g.), m.p. 332°.

The xanthone was analysed after drying it at 110° in vacuum.

Analysis : Found : C, 60.86 ; H, 3.87 ; N, 10.62 %

$C_{13}H_{10}O_4N_2$ requires : C, 60.46 ; H, 3.90 ; N, 10.85 %.

REFERENCES

1. A.A.Goldberg and H.A.Walker., Brit., 723,415 (1955); C.A., 50, 5037e (1956).
2. A.A.Goldberg and H.A.Walker., Brit., 708,917 (1954) ; C.A., 49, 14037 (1955).
3. S.D.Sobell and A.Arnold., Proc. Soc. Exptl. Biol. Med., 90, 594 (1955) ; C.A., 50, 5827 (1956).
4. K.K.Mozgova, V.V.Korshak, S.G.Levitskaya., Plast. Massy., 14 (1968).; C.A., 70, 20397h (1969).
5. H.E.Hinderer and R.W.Smith., U.S. 3,467,623 (1969). ; C.A., 71, 114066x (1969).
6. R.Kurdukar and N.V.Subba Rao., Proc.Indian Acad. Sci., 57 A, 280 (1963).
7. A. Purgotti., Portici. Gazz. Chim. Ital., 44, 641 (1914) ; C.A., 9, 70 (1915).
8. Imperial Chemical Industries., Ger., 515,524 (1929) ; C.A., 25, 2442 (1931).
9. E.H.Rodd and H.H.Stocks., Brit., 314,826 (1928).; C.A., 24, 1521 (1930).
10. A.C.Sirkar and S.C.Dutt., J. Indian Chem.Soc., 11, 877 (1934).
11. Compagnie nationale de matieres colorantes et manufacturers de produits chemiques du Nord reunies establisments, Kuhalmann, Fr., 821,275 (1937); C.A., 32, 3628 (1938).

12. Compagnie nationale de matieres colorantes et manufacturers de produits chemiques due Nord reunies establisments, Kuhalmann, Fr., 839,698 (1939); C.A., 33, 8025 (1939).

13. S.N.Dhar., J. Chem. Soc., 109, 744 (1916).

14. S.N.Dhar., J. Chem. Soc., 117, 1053 (1920).

15. H. Kiyoshi, Kogyo Kagaku Zasshi., 71, 463 (1964) ; C.A., 69, 68241j (1968).

16. R.N.Iyer and K.Venkataraman., Proc. Indian Acad. Sci., 37 A, 637 (1953).