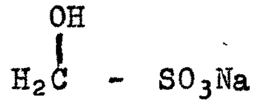
PART II

Formation of methylene bis-derivatives of cyanacet arylamides by means of sodium hydroxy methane sulphonate.

PART II

THEORETICAL

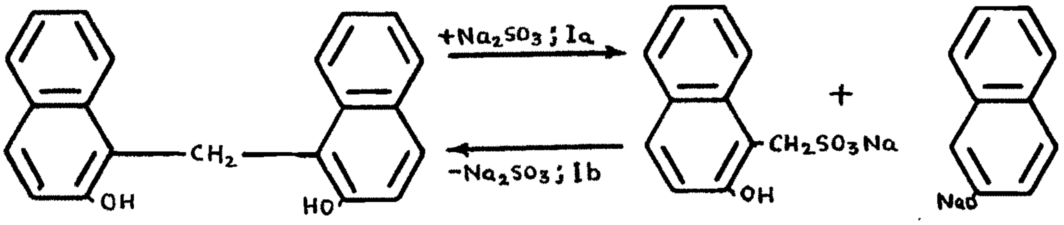
The experiments of Raschig and Prahl (1), Backer and Mulder (2) and the recent work of Lauer and Langkammerer (3) leave no doubt that the sodium bisulphite compound of formaldehyde is best represented by the hydroxysulphonate structure given below.



$$H_2\overset{OH}{\overset{|}{C}} - SO_3Na$$

Raschig and Prahl (1) have further reported that the action of potassium hydroxy methane sulphonate with compounds, containing reactive methylene group and few phenols, gave their sulphomethylated products, where the hydrogen atom of the reactive methylene group is replaced by alkali sulphomethyl group ($-CH_2SO_3M$). Suter, Bair and Bordwell (4) carried out the sulphomethylated reaction of compounds containing active methylene group. Shin Matsuura (5) condensed formaldehyde with malonic ester in presence of sodium acetate (or sodium ethoxide) and obtained methylene bis-ethylmalonate $-(EtO_2C)_2CH.CH_2.CH(CO_2Et)_2$.

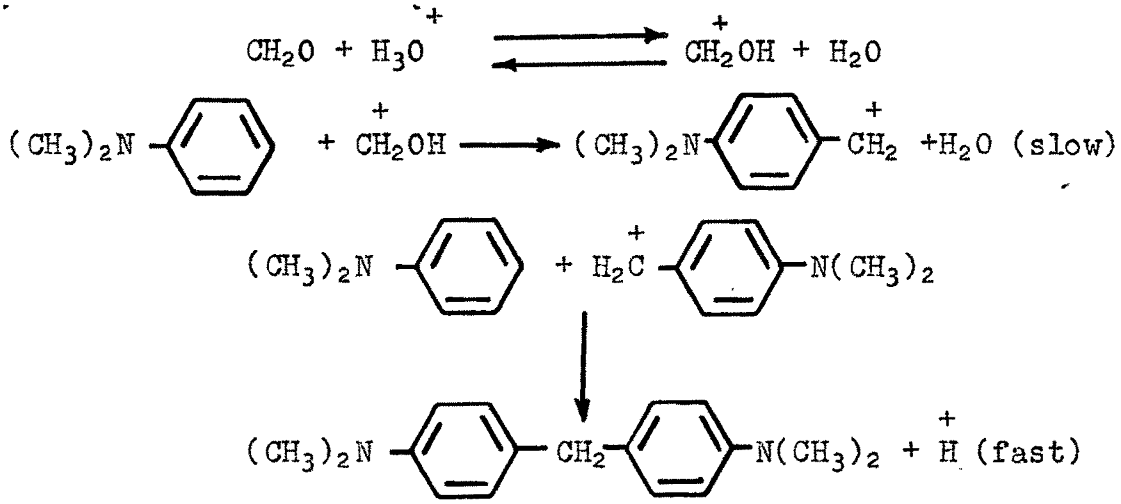
Shearing and Smiles (6) carried out the experiment of 2-naphthol with formaldehyde and sodium sulphite and obtained sodium 2-hydroxy-1-naphthylmethane-sulphonate with di-2-hydroxynaphthyl-1-methane (I). Further experiment has established the fact that di-2-hydroxynaphthyl-1-methane is resolved by hot aqueous sodium sulphite into sodium-2-naphthoxide and sodium-2-naphthol-1-methane-sulphonate according to reaction (Ia) ; moreover, the process is reversible and according to reaction (Ib) ; the methane derivative being readily formed from the sulphonate with excess of naphthoxide as under :



(I)

Similarly, 6-bromo-2-naphthol when treated with formaldehyde and sodium sulphite, bis-(6-bromo-2-hydroxynaphthyl)-1-methane was obtained, which was found to be identical to the sample prepared by the method of Fries (7). Cohen and Clutterbuck (8) have found that the action of 2-naphthol with formaldehyde and sodium sulphite gave 2-hydroxynaphthyl-1-methanol, but hydroxymethyl derivative was not obtained by others. According to Patent literature (D.R.P. 87385), the sodium 2-naphthol-1-methane sulphonate from formaldehyde and sodium sulphite supports the process of Shearing and Smiles (6) in the formation of di-2-hydroxynaphthyl-1-methane.

Yoshiro Ogata and Masaya Okano (9) studied the condensation of dimethylaniline with formaldehyde and obtained p-p'-tetramethyl-diaminodiphenylmethane (II). The mechanism of the reaction was described as the slow irreversible formation of $p\text{-}(CH_3)_2N.C_6H_4.\overset{+}{CH_2}$ from dimethylaniline and the conjugate acid of formaldehyde, followed by the rapid condensation of the product with a second molecule of dimethylaniline. Thus,



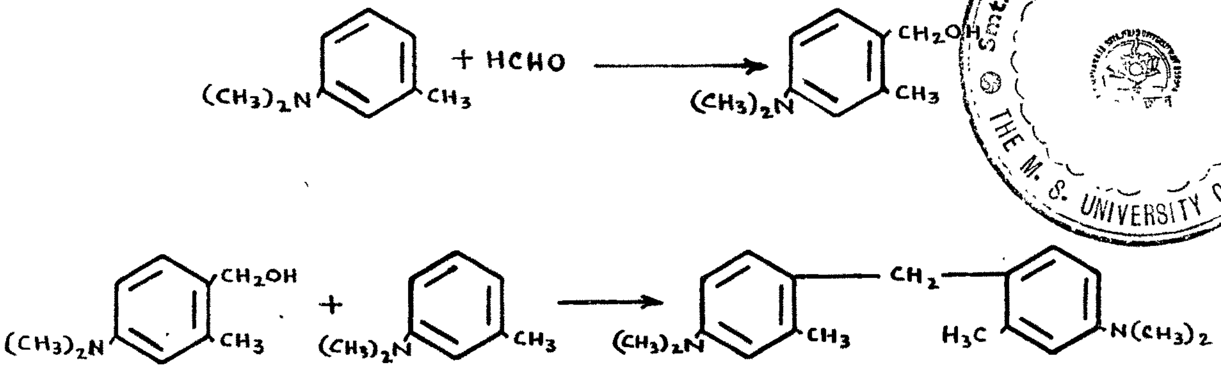
(II)

Pratt and Green (10) treated n-heptaldehyde with dimethylaniline and obtained 1,1-bis-(p-dimethylaminophenyl)-heptane in presence of p-toluenesulphonic acid monohydrate as catalyst in sufficient quantity of benzene.

Smith and Welch (11) prepared methylene bis-o-nitroaniline from p-dimethylaminobenzyl alcohol and o-nitroaniline in the absence of a catalyst at 130°C in one hour, and 4,4'-tetramethyldiaminodiphenylmethane from dimethylaniline and dimethylaminobenzyl alcohol with one drop of hydrochloric acid.

Bruson (12) studied the reaction of acrylonitrile in presence of alkali with acetoacetic ester, viz. acetoacetic ester and acrylonitrile in dioxane with $Me_3(PhCH_2)NOH$ gave ethyl bis-(2-cyanoethyl)acetoacetate. In a similar manner, reaction of acrylonitrile with acetoacetanilide in dioxane containing $Me_3(PhCH_2)NOH$ yielded bis-(2-cyanoethyl)acetoacetanilide and reaction with o-chloroacetoacetanilide gave bis-(2-cyanoethyl)acetoacet-o-chloroanilide.

Burnett and Hammett (13) employed the reaction of dimethyl-m-toluidide with formaldehyde in dioxane-water medium and obtained 4,4'-methylene bis-(dimethyl-m-toluidide) (III). It was expected that the reaction would occur in two stages .

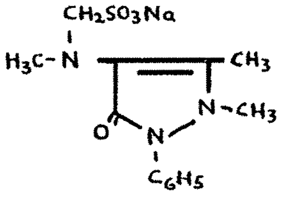


(III)

Here, the major product remaining was the above mentioned diphenylmethane derivative.

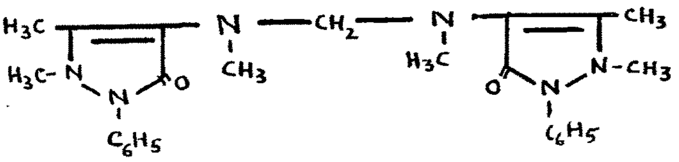
Paul Pastour (14) condensed acetoacetanilide with aliphatic aldehydes and obtained the bis-derivative of the formula, $RCH(COCH_3CHCONHC_6H_5)_2$, in pure or alcoholic pyridine. If traces of piperidine are used, substituted cyclohexanolones are obtained. Thus, acetaldehyde and acetoacetanilide refluxed with alcohol in pyridine gave ethylidene bis-(acetoacetanilide).

Schwarz et al.(15) treated a secondary aromatic-aliphatic amine with CH_2O and bisulphite and obtained Na-1-phenyl-2,3-dimethyl-5-pyrazolone-4-methyl-aminomethylsulphite (IV) and Na-N-methyl-p-phenitidinemethylsulphite (V). Methylene bis-1-phenyl-2,3-dimethyl-4-methylamino-5-pyrazolone (VI) is obtained by heating with CH_2O, the mixtures of amines produced by methylating 1-phenyl-2,3-dimethyl-4-amino-5-pyrazolone, while methylene bis-N-methyl-phenitidine (VII) is obtained by treating with CH_2O, the crude N-methyl-phenitidine obtained by methylating phenitidine.

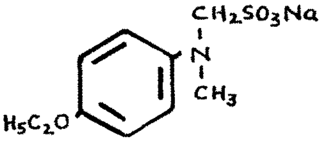


;

(IV)

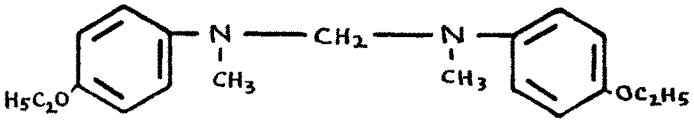


(VI)



;

(V)



(VII)

Knoevenagel and Mercklin (16) prepared diethylaminoacetonitrile from a mixture of CH_2O and $NaHSO_3$ in the presence of NaCN.

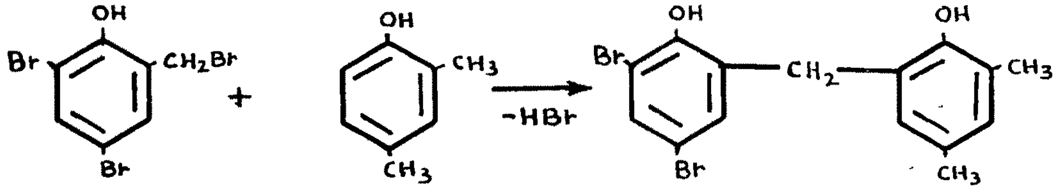
Jean Décombe and Monique Prétot (17) obtained hydroxymethyl acetoacetanilide with equimolecular mixture of alcoholic acetoacetanilide and 30 % formaldehyde without catalyst ; while acetoacetic ester under the same condition did not react with formaldehyde. But acetoacetanilide and formaldehyde when treated with 0.4 N NaOH solution from which on acidification with acetic acid gave the compound of the type ($PhNHCOCH_2CH_2CHCOCH_3CONHPh$). Further they stated that three moles of formaldehyde with two moles of acetoacetanilide gave methylene bis-acetoacetanilide, instead of hydroxymethyl derivative.

Zieglar (18) advanced the successful reaction between a halomethylphenol and a phenol giving a diphenylmethane derivative using halogen acids as catalysts. Pepper (19) and Lilley (20) have independently proposed a mechanism for diphenylmethane formation from phenol alcohols which involves a benzyl cation as the active intermediate. These authors reasoned that if methylene bridges in phenolic resins occur via a benzyl cation then reagents and conditions known to produce such ions should be capable of catalyzing a reaction between a halomethylphenol and another phenol. This was found to be the case when 3,5-dibromo-2-hydroxybenzylbromide and 2,6-dichlorophenol reacts,employing molecular equivalent of silver perchlorate as promoters and nitromethane as solvent.

Additional support for the carbonium ion theory was obtained by the experiment in which toluene was substituted for nitromethane as solvent. In this case the main product of the reaction was found to be a methyl,monohydroxydiphenylmethane. Here the phenyl nucleus in toluene is sufficiently activated by the presence of the methyl group.

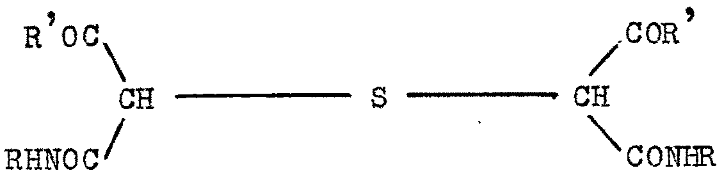
In cases where the addend is of enhanced reactivity i.e. contains ring positions of relatively increased electron density, due to the presence of substituent groups as the methyl group, the relative yield of diphenylolmethane is increased and the reaction conditions are correspondingly less severe. Thus, 3,5-dibromo-2-hydroxybenzylbromide combines readily with 2,4-dimethylphenol to form the diphenololmethane derivative (VIII).

Finally, they concluded that the presence of carbonium ion in neutral or acidic medium is capable of accounting for the conversion of methylolphenol to dibenzyl ether as well as to diphenylmethane.



(VIII)

Naik et al. (21) studied the reaction of thionyl chloride with organic compounds containing reactive methylene group and concluded that the course of reaction entirely depended on the conditions of the experiment. The reaction of thionyl chloride with phenols, phenetoles and alcohols in presence of anhydrous aluminium chloride gave rise to sulphides, but sulphoxides are also obtained under changed conditions. Here, thionyl chloride behaves, as if it was a mixture of sulphur dichloride and sulphuryl chloride, ($2SOCl_2 \longrightarrow SCl_2 + SO_2Cl_2$), and its reaction with acetoacet arylamides and malon diarylamides respectively is found to give thio-bis-derivatives of the type (IX) as under:

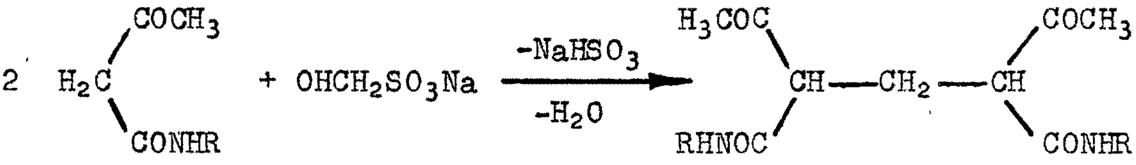


(IX)

(Where, R is phenyl,tolyl,xylyl etc. groups ; and R' is CH_3 or NHR group).

The above cause of reaction, where only one hydrogen atom of the molecule takes part, is explained on the fact that the second hydrogen atom becomes sluggish after the first one is replaced by a substitution of compounds containing reactive methylene group.

Mehta and Patel (22) have carried out the reaction in absence of a catalyst, between acetoacet arylamides and sodium hydroxy methane sulphonate and obtained a number of corresponding methylenebis-derivatives (X).



(X)

(Where, R is phenyl,tolyl,xylyl and naphthyl groups).

Methylene bis-cyanacetarylamides :

In the present investigation the cyanacet arylamides, containing the reactive methylene group, have been condensed with sodium hydroxy methane sulphonate, without using a trace of potassium cyanide as catalyst, yielding the methylene bis-derivatives; whereas the reaction in presence of a trace of potassium cyanide as catalyst, gave the sulphomethylated products as described in part I. The formation of both these products support the processes of Suter,Bair and Bordwell(4) as well as Shearing and Smiles (6).

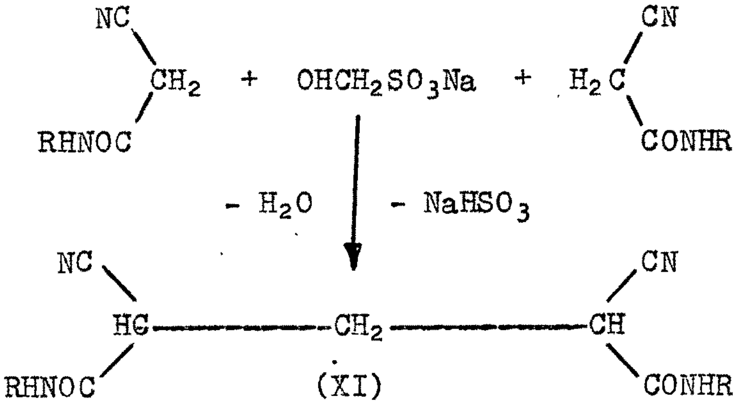
Preparation of cyanacet arylamides :

Cyanacetanilide (23),cyanacet-p-toluidide (24) have been known, but no reliable details of the methods employed in their preparation could be found. Therefore, in the preparation of the substituted amides of cyanacetic acid, Whiteley's method (25) with the modification described by Naik (26) was followed.

Requisite amount of ethyl cyanacetate and pure arylamine were mixed in a round bottom flask,which was heated with an air condenser at 160-170 °C for six hours. The contents of the flask when hot were then poured into a mortar, where the whole mass solidified. The solid was broken and triturated with a mixture of equal volumes of benzene and light petrolium. It was then filtered and the process was repeated until the reddish colour of the solid disappeared, and then it was crystallised from acetic acid. In this way, the other members of cyanacet arylamides have been prepared.

Preparation of methylene bis-(cyanacet arylamide)

Two moles of cyanacet arylamide and one mole of sodium hydroxy methane sulphonate were refluxed in 90 % methyl alcohol for 3 hours on a sand-bath. It was then diluted with water and a white precipitate appeared on cooling. The crude product, after filtering the reaction mixture was crystallised from acetic acid. A number of other methylene bis-cyanacet arylamides of the type (XI) are similarly prepared. The reaction may be expressed as under:

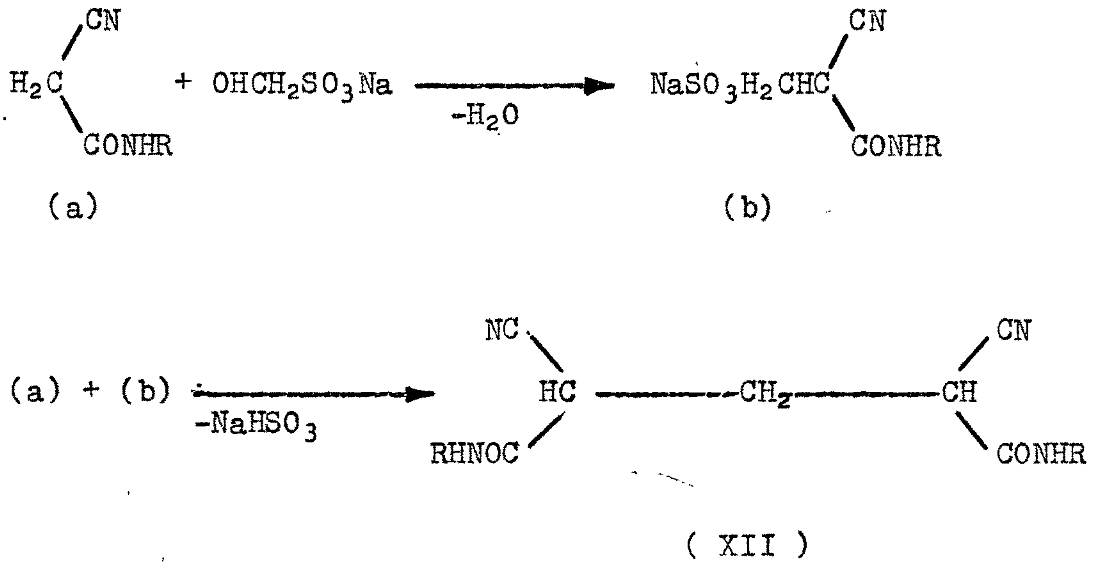


(XI)

(Where,R is phenyl,tolyl,xylyl and naphthyl groups).

The above reaction is believed to have taken place according to the following two courses :

First course may be visualized first through the elimination of water by the intermediate formation of sulphonate(b), with which the reactive hydrogen atom of the methylene group $-CH_2-$ of the unreacted molecule of the amide (a) simultaneously interacts, yielding only the corresponding methylene bis-derivatives (XII), with the elemination of sodium bisulphite, and then the overall reaction is expressed as :



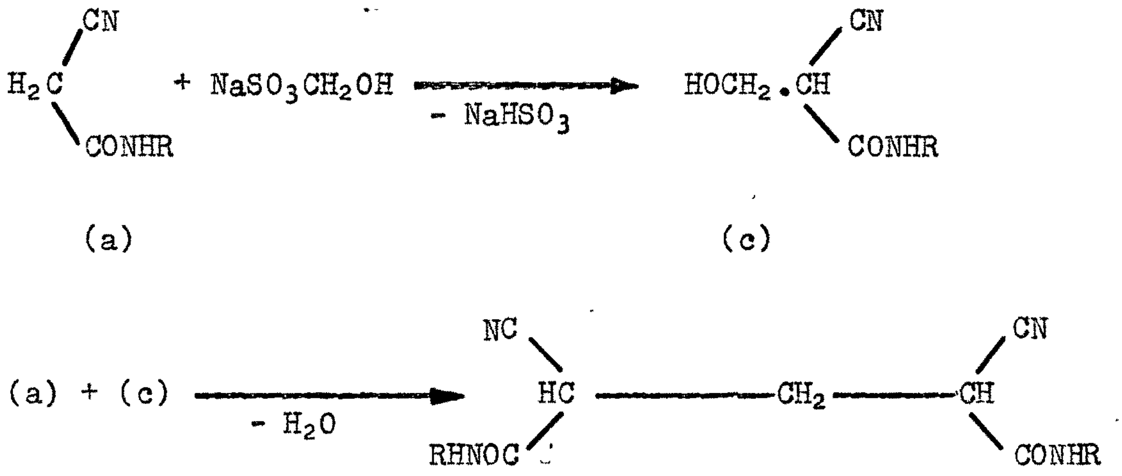
$$H_2C(CN)(CONHR) + OHCH_2SO_3Na \xrightarrow[-H_2O]{} NaSO_3H_2CHC(CN)(CONHR)$$

(a) (b)

$$(a) + (b) \xrightarrow[-NaHSO_3]{} (NC)(RHNOC)HC-CH_2-CH(CN)(CONHR)$$

(XII)

The second course may take place first through the elemination of sodium bisulphite by the intermediate formation of hydroxy methyl derivative of cyanacet arylamide (c), with which the reactive hydrogen atom of the unreacted molecule of the amide (a) simultaneously interacts with the elimination of water, yielding only the corresponding methylene bis-derivatives (XII) as under :



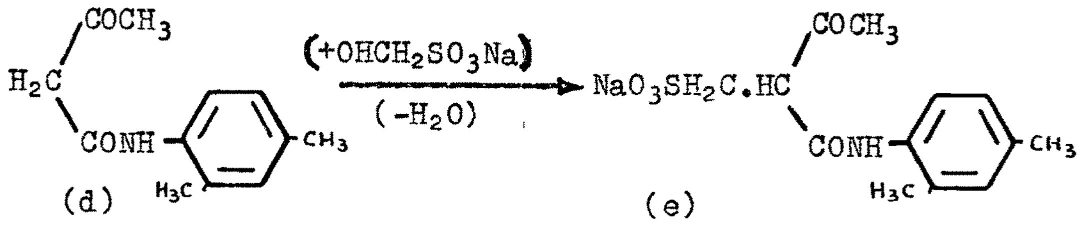
(XII)

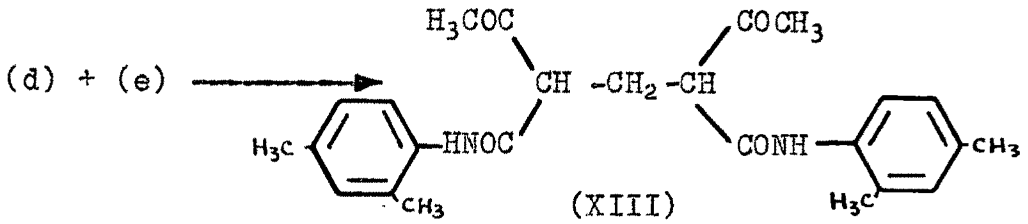
As has been observed by Suter et al. (4) in the sulphomethylation reaction of 2-naphthol with formaldehyde and sodium bisulphite, the intermediate formation of 2-hydroxy 1-naphthol methanol is unlikely ; and in the formation of di-2-hydroxy-naphthyl-1-methane by Shearing and Smiles (6), the occurrence of hydroxy methyl compound was not confirmed. Hence the first course of reaction, which takes place through the intermediate formation of a sulphonate is supported. Moreover, sulphomethylation of acetoacet arylamides by means of sodium hydroxy methane sulphonate described in part I, have been prepared by Mehta and Trivedi (27) also supports the first course of the reaction (b) taking place in this case.

However, it may here be pointed out that, Mehta and Patel (22) described the reaction of acetoacet-1:2:4-xylidide (d) with sodium hydroxy methane sulphonate in which the product sodium acetoacet-1:2:4-xylidide methane sulphonate (e) melting at 205°C was isolated, which on analysis gave the following results :

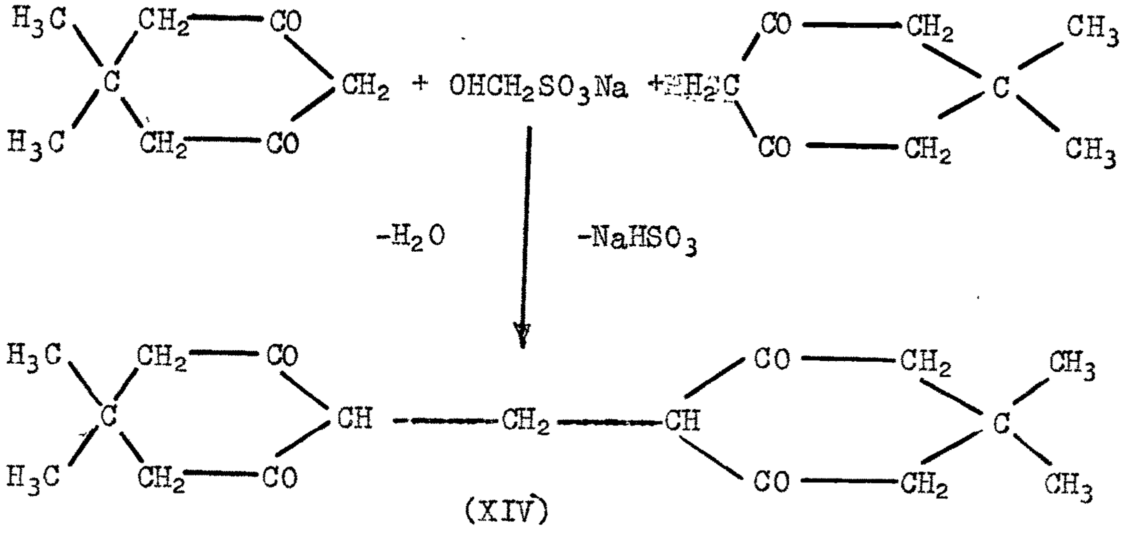
Found : N = 4.45 % , $C_{13}H_{16}O_5NSNa$ requires : N = 4.36 %.

Further, one mole each of (d) and of (e) were condensed in 90 % methanol, when methylene bis-(-acetoacet-1:2:4-xylidide) (XIII) melting at 230°C was formed. Thus,

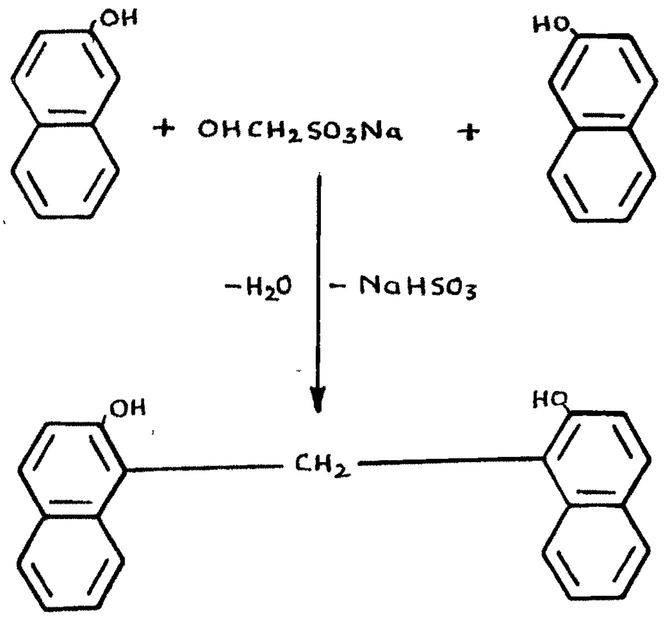




Again, dimedone (5,5-dimethylcyclohexanedione-1,3), containing reactive methylene group, when treated with formaldehyde, gave a known bis-(dimedon)methane, which gave a melting point 188°C (Ber. VII, 888). This very bis-(dimedon)-methane (XIV), melting at 188°C, was prepared from dimedone (2 mols) and sodium hydroxy methane sulphonate (1 mole) by refluxing in 90 % methanol. Thus,



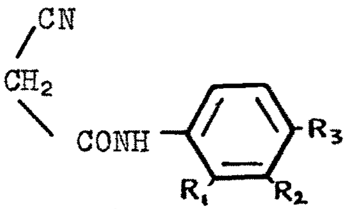
Similarly, 2-naphthol (2 moles) and sodium hydroxy methane sulphonate (1 mole), on condensation, in 90 % methanol, gave di-2-hydroxynaphthyl-1-methane (I), which melted at 199°C. Shearing and Smiles (6) obtained the same di-2-hydroxynaphthyl-1-methane (I) (m.p. 199°C) by condensing 2-naphthol, formaldehyde and sodium bisulphite. Thus,



(I)

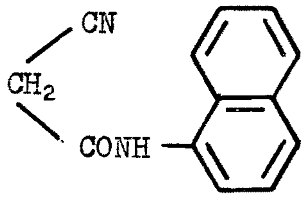
The above reactions indicated that the hydrogen atom of the reactive methylene group in case of dimedone and the α-hydrogen atom in case of 2-naphthol interacted with sodium hydroxy methane sulphonate with the formation of the respective methylene bis-derivatives.

The following cyanacet arylamides, accordingly are obtained:

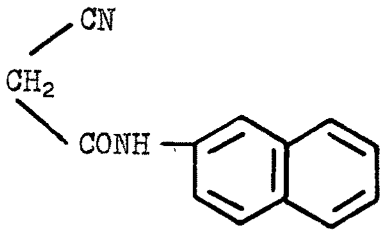


(A)

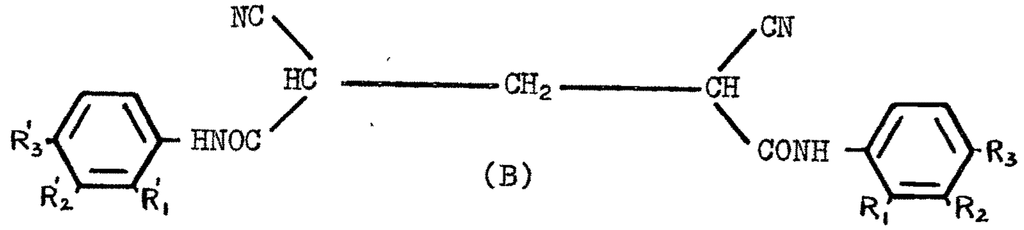
1. Cyanacet anilide : (A, $R_1=R_2=R_3=H$)
2. Cyanacet-o-chloroanilide : (A, $R_2=R_3=H$; $R_1=Cl$)
3. Cyanacet-p-chloroanilide : (A, $R_1=R_2=H$; $R_3=Cl$)
4. Cyanacet-o-toluidide : (A, $R_2=R_3=H$; $R_1=CH_3$)
5. Cyanacet-m-toluidide : (A, $R_1=R_3=H$; $R_2=CH_3$)
6. Cyanacet-p-toluidide : (A, $R_1=R_2=H$; $R_3=CH_3$)
7. Cyanacet-o-anisidide : (A, $R_2=R_3=H$; $R_1=OCH_3$)
8. Cyanacet-1:2:4-xylidide : (A, $R_2=H$; $R_1=R_3=CH_3$)
9. Cyanacet-1:3:4-xylidide : (A, $R_1=H$; $R_2=R_3=CH_3$)
10. Cyanacet-α-naphthylamide :



11. Cyanacet-β-naphthylamide :



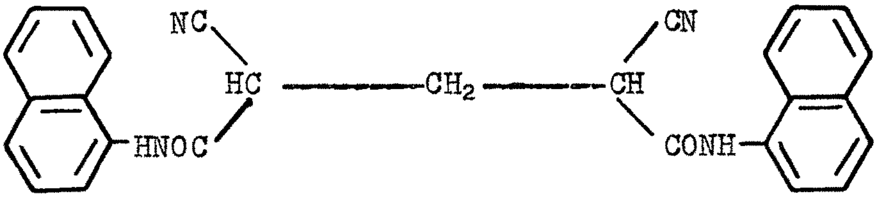
Thus, the methylene bis-cyanacet arylamides prepared from the above mentioned cyanacetarylamides, using sodium hydroxy methane sulphonate, are given as under :



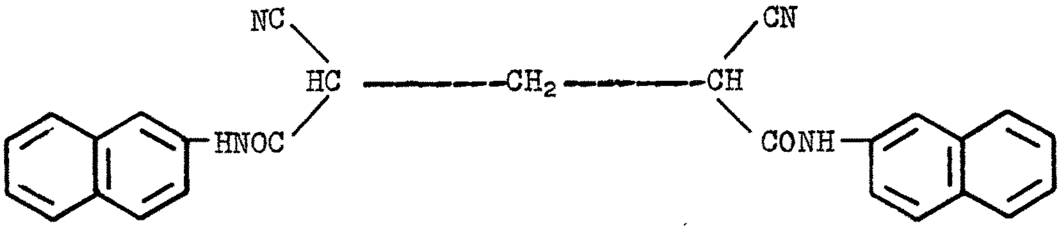
(B)

1. Methylene bis-(cyanacetanilide)
   (B, $R_1=R_1'=R_2=R_2'=R_3=R_3'=H$)

2. Methylene bis-(cyanacet-o-chloroanilide)
   (B, $R_2=R_2'=R_3=R_3'=H$; $R_1=R_1'=Cl$)
3. Methylene bis-(cyanacet-p-chloroanilide)
   (B, $R_1=R_1'=R_2=R_2'=H$; $R_3=R_3'=Cl$)
4. Methylene bis-(cyanacet-o-toluidide)
   (B, $R_2=R_2'=R_3=R_3'=H$; $R_1=R_1'=CH_3$)
5. Methylene bis-(cyanacet-m-toluidide)
   (B, $R_1=R_1'=R_3=R_3'=H$; $R_2=R_2'=CH_3$)
6. Methylene bis-(cyanacet-p-toluidide)
   (B, $R_1=R_1'=R_2=R_2'=H$; $R_3=R_3'=CH_3$)
7. Methylene bis-(cyanacet-o-anisidide)
   (B, $R_2=R_2'=R_3=R_3'=H$; $R_1=R_1'=OCH_3$)
8. Methylene bis-(cyanacet-1:2:4-xylidide)
   (B, $R_2=R_2'=H$; $R_1=R_1'=R_3=R_3'=CH_3$)
9. Methylene bis-(cyanacet-1:3:4-xylidide)
   (B, $R_1=R_1'=H$; $R_2=R_2'=R_3=R_3'=CH_3$)
10. Methylene bis-(cyanacet-α-naphthylamide)



11. Methylene bis-(cyanacet-β-naphthylamide)



Molecular weight by Rast method :

0.0084 gm. of methylene bis-(cyanacetanilide) was intimately mixed with 0.1 gm. purely sublimed camphor in a glass tube. The other end of the tube was sealed, and heated in a paraffin bath till the contents of the tube were completely dissolved. In order to prepare a homogeneous mass of the mixture the tube is cooled and the mass is redissolved by heating. The freezing point of the mixture was found to be 165.8°C and that of the camphor was 175.8°C. The molecular weight of the bis-compound is thus calculated as 336, while its theoretical molecular weight of the formula, $C_{19}H_{16}O_2N_4$, is 332.0

$$\text{Mol. Wt.} = \frac{1000\ gK}{\triangle\ F}$$

Where, g = wt. of the compound taken

K = F.P. constant for camphor

$\triangle$ = observed depression in F.P.

F = wt. of camphor taken.

$$\therefore \quad \text{Mol. Wt.} = \frac{(1000 \times 0.0084 \times 40)}{(10 \times 0.1)} = 336.0$$

EXPERIMENTAL

Methylene bis-(cyanacet anilide)

Cyanacet anilide (3.2 g. ; 0.02 M) dissolved in 90 % methanol to which was added solution of sodium hydroxymethane sulphonate (1.34 g. ; 0.01 M) in 5 ml. of water. The reaction mixture was refluxed on a sand-bath for three hours and 50 ml. of water were added to it at room temperature. The resulting product was then filtered and crystallised from acetic acid in white fine crystals. M.P. 285°C. Yield 1.5 g.

Analysis :

4.106 mg. of the substance gave 10.320 mg. of carbon dioxide and 1.632 mg. of water.

6.108 mg. of the same substance gave 0.90 c.c. of nitrogen at 28°C and 746 mm. pressure.

	Found	: C=68.59 % ; H=4.45 % ; N=16.43 %.
$C_{19}H_{16}O_2N_4$	requires	: C=68.66 % ; H=4.85 % ; N=16.86 %.

Methylene bis-(cyanacet-o-chloroanilide)

Cyanacet-o-chloroanilide (3.88 g. ; 0.02 M) dissolved in 90 % methanol, to which solution of sodium hydroxy methane sulphonate (1.34 g. ; 0.01 M) in 5 ml. of water was added and treated as above. The resulting product was then filtered and crystallised from acetic acid in tiny white crystals. M.P. 241°C. Yield 1.4 g.

Analysis :

5.33 mg. of the substance gave 0.67 c.c. of nitrogen at 28°C and 756 mm. pressure.

Found : N = 14.18 %.

$C_{19}H_{14}O_2N_4Cl_2$ requires : N = 13.97 %.

Methylene bis-(cyanacet-p-chloroanilide)

Cyanacet-p-chloroanilide (3.88 g.) dissolved in 90 % methanol, to which sodium hydroxy methane sulphonate (1.34 g.) in 5 ml. of water was added and treated as above. The resulting product was filtered and crystallised from acetic acid in white crystals. M.P. 226°C. Yield 1.6 g.

Analysis :

4.772 mg. of the substance gave 0.565 c.c. of nitrogen at 28°C and 761 mm. pressure.

Found : N = 13.63 %.

$C_{19}H_{14}O_2N_4Cl_2$ requires : N = 13.97 %.

Methylene bis-(cyanacet-o-toluidide)

Cyanacet-o-toluidide (3.48 g.) dissolved in 90 % methanol to which sodium hydroxy methane sulphonate (1.34 g.) in 5 ml. of water was added and treated as above. The resulting product was filtered and crystallised from acetic acid in white tiny crystals. M.P. 240°C. Yield 1.6 g.

Analysis :

7.492 mg. of the substance gave 1.133 c.c. of nitrogen at 36°C and 753 mm. pressure.

Found : N = 15.90 %.

$C_{21}H_{20}O_2N_4$ requires : N = 15.55 %.

Methylene bis-(cyanacet-m-toluidide)

Cyanacet-m-toluidide (3.48 g.) dissolved in 90 % methanol, to which was added sodium hydroxy methane sulphonate (1.34 g.) in 5 ml. of water and treated as above. The resulting product was then filtered and crystallised from acetic acid in white crystals. M.P. 212°C. Yield 1.7 g.

Analysis :

8.104 mg. of the substance gave 1.222 c.c. of nitrogen at 36°C and 753 mm. pressure.

Found : N = 15.92 %.

$C_{21}H_{20}O_2N_4$ requires : N = 15.55 %.

Methylene bis-(cyanacet-p-toluidide)

Cyanacetacet-p-toluidide (3.48 g. ; 0.02 M) dissolved in 90 % methanol, to which was added solution of sodium hydroxy methane sulphonate (1.34 g. ; 0.01 M) in 5 ml. of water and treated as above. The resulting product was then filtered and crystallised from acetic acid in tiny crystals. M.P. 220°C. Yield 1.6 g.

Analysis :

4.160 mg. of the substance gave 10.642 mg. of carbon dioxide and 2.164 mg. of water.

6.692 mg. of the same substance gave 0.96 c.c. of nitrogen at 30°C and 746 mm. pressure.

Found : C=69.80 % ; H=5.80 % ; N=15.86 %.

$C_{21}H_{20}O_2N_4$ requires: C=69.98 % ; H=5.59 % ; N=15.55 %.

Methylene bis-(cyanacet-o-anisidide)

Cyanacet-o-anisidide (3.78 g. ; 0.02 M) dissolved in 90 % methanol, to which was added solution of sodium hydroxy methane sulphonate (1.34 g. ; 0.01 M) in 5 ml. of water and treated as above. The resulting product was filtered and crystallised from acetic acid in tiny white crystals. M.P. 260°C. Yield 1.6 g.

Analysis :

7.822 mg. of the substance gave 1.010 c.c. of nitrogen at 36°C and 753 mm. pressure.

Found : N = 14.14 %.

$C_{21}H_{20}O_4N_4$ requires : N = 14.28 %.

Methylene bis-(cyanacet-1:2:4-xylidide)

Cyanacet-1:2:4-xylidide (3.76 g.) dissolved in 90 % methanol, and sodium hydroxy methane sulphonate (1.34 g.) dissolved in 5 ml. of water were treated as above. The crude product, after filtration, was crystallised from acetic acid in white tiny needles. M.P. 256°C. Yield 1.6 g.

Analysis :

4.518 mg. of the substance gave 11.740 mg. of carbon dioxide and 2.468 mg. of water.

8.424 mg. of the same substance gave 1.143 c.c. of nitrogen at 35°C and 753 mm. pressure.

Found : C=70.91 % ; H=6.11 % ; N=14.90 %.

$C_{23}H_{24}O_2N_4$ requires : C=71.11 % ; H=6.23 % ; N=14.42 %.

Methylene bis-(cyanacet-1:3:4-xylidide)

Cyanacet-1:3:4-xylidide (3.76 g.) dissolved in 90 % methanol, and sodium hydroxy methane sulphonate (1.34 g.) dissolved in 5 ml. of water were treated as above. The crude product, after filtration, was crystallised from acetic acid in white crystals. M.P. 266°C. Yield 1.5 g.

Analysis :

8.182 mg. of the substance gave 1.118 c.c. of nitrogen at 36°C and 753 mm. pressure.

Found : N = 14.96 %.

$C_{23}H_{24}O_2N_4$ requires : N = 14.42 %.

Methylene bis-(cyanacet-α-naphthylamide)

Cyanacet-α-naphthylamide (4.2 g.) dissolved in 90 % methanol to which was added sodium hydroxy methane sulphonate (1.34 g.) in 5 ml. of water and treated as above. The crude product, after filtration, was crystallised from acetic acid in white crystals. M.P. 236°C. Yield 1.8 g.

Analysis :

11.34 mg. of the substance gave 1.325 c.c. of nitrogen at 28°C and 757 mm. pressure.

Found : N = 13.20 %.

$C_{27}H_{20}O_2N_4$ requires : N = 12.96 %.

Methylene bis-(cyanacet-β-naphthylamide)

Cyanacet-β-naphthylamide (4.2 g.) dissolved in 90 % methanol, to which was added solution of sodium hydroxy methane sulphonate (1.34 g.) in 5 ml. of water and treated as above. The resulting product was filtered and crystallised from acetic acid in tiny white needles. M.P. 227°C. Yield 2.0 g.

Analysis :

9.98 mg. of the substance gave 1.108 c.c. of nitrogen at 32°C and 758 mm. pressure.

Found : N = 12.62 %.

$C_{27}H_{20}O_2N_4$ requires : N = 12.96 %.

Bis- (-dimedone) methane

Dimedone (5,5-dimethylcyclohexanedione-1,3 ; 2.80 g.) dissolved in 20 ml. methyl alcohol to which was added solution of sodium hydroxy methane sulphonate in 5 ml. water(1.34 g.) and the reaction mixture was refluxed on a sand-bath for three hours. 50 ml. of water were added to it at room temperature, the resulting product was then filtered and crystallised from alcohol. M.P. 188°C.

The identity of bis-(-dimedone) methane was established by comparing its melting point and mixed melting point with that of the authentic sample.

Di-2-hydroxynaphthyl-1-methane

2-Naphthol (2.88 g. ; 0.02 M) was dissolved in 20 ml. methyl alcohol to which was added solution of sodium hydroxy methane sulphonate in 5 ml. water (1.34 g. ; 0.01 M) and the reaction mixture was refluxed on a sand-bath for three hours. 50 ml. of water were added to it at room temperature. The resulting product was then filtered and crystallised from acetic acid. M.P. 199°C.

The identity of di-2-hydroxy-naphthyl-1-methane was established by comparing its melting point and mixed melting point with that of the authentic sample.

Table 2

Methylene bis- (cyanacet arylamides)

S.No.	Compound	Molecular Formula	M.P. °C	Yield %	Nitrogen Found %	Nitrogen reqd. %	Carbon Found %	Carbon reqd. %	Hydrogen Found %	Hydrogen reqd. %
1.	Methylene bis-(cyanacet-anilide)	$C_{19}H_{16}O_2N_4$	285	45.4	16.43	16.86	68.59	68.66	4.45	4.85
2.	Methylene bis-(cyanacet-o-chloroanilide)	$C_{19}H_{14}O_2N_4Cl_2$	241	35.0	14.18	13.97	-	-	-	-
3.	Methylene bis-(cyanacet-p-chloroanilide)	$C_{19}H_{14}O_2N_4Cl_2$	226	40.0	13.63	13.97	-	-	-	-
4.	Methylene bis-(cyanacet-o-toluidide)	$C_{21}H_{20}O_2N_4$	240	44.4	15.90	15.55	-	-	-	-
5.	Methylene bis-(cyanacet-m-toluidide)	$C_{21}H_{20}O_2N_4$	212	47.2	15.92	15.55	-	-	-	-
6.	Methylene bis-(cyanacet-p-toluidide)	$C_{21}H_{20}O_2N_4$	220	44.0	15.86	15.55	69.80	69.98	5.80	5.59

Table 2 (Contd.)

S.No.	Compound	Molecular Formula	M.P. °C	Yield %	Nitrogen		Carbon		Hydrogen	
					Found %	reqd. %	Found %	reqd. %	Found %	reqd. %
7.	Methylene bis-(cyanacet-o-anisidide)	$C_{21}H_{20}O_4N_4$	260	42.1	14.14	14.28	-	-	-	-
8.	Methylene bis-(cyanacet-1:2:4-xylidide)	$C_{23}H_{24}O_2N_4$	256	41.0	14.90	14.42	70.91	71.11	6.11	6.23
9.	Methylene bis-(cyanacet-1:3:4-xylidide)	$C_{23}H_{24}O_2N_4$	266	38.4	14.96	14.42	-	-	-	-
10.	Methylene bis-(cyanacet-α-naphthylamide)	$C_{27}H_{20}O_2N_4$	236	41.8	13.20	12.96	-	-	-	-
11.	Methylene bis-(cyanacet-β-naphthylamide)	$C_{27}H_{20}O_2N_4$	227	46.5	12.62	12.96	-	-	-	-

REFERENCES

1. Raschig and Prahl., Ann., 448, 265 (1926) ; Chem.Abst., 20, 3156 (1926).
2. Backer and Mulder., Rec.trav.Chim., 51, 769 (1932).
3. Lauer and Langkammerer., J.Amer.Chem.Soc., 57, 2360 (1935).
4. Suter, Bair and Bordwell., J.Org.Chem., X, 470 (1945).
5. Shin Matsuura., J.Pharm.Soc. Japan., 71, 525-28 (1951); Chem.Abst., 46, 906 (1952).
6. Shearing and Smiles., J.Chem.Soc., 1348 (1937).
7. Fries., Ber., 39, 439 (1906).
8. Cohen and Clutterbuck., J.Chem.Soc., 123, 2510 (1923).
9. Yoshiro Ogata and Masaya Okano., J.Amer.Chem.Soc., 72, 1459 (1950).
10. Pratt and Green., J.Amer.Chem.Soc., 75, 275 (1953).
11. Smith and Welch., J.Chem.Soc., 1136 (1934).
12. Bruson., U.S. 2383444 (1945) ; Chem.Abst., 40, 351 (1946).
13. Burnett and Hammett., J.Org.Chem., 23, 770 (1958).
14. Paul Pastour., Compt.rend., 237, 1094 (1953) ; Chem.Abst., 49, 1614 (1955).
15. Schwarz et al., Brit.Pat. 243,925 (1925) ; Chem.Abst., 21, 592 (1927).
16. Knoevenagel and Mercklin., Ber., 37, 4089 (1904).
17. Jean D'ecombe et al., Compt.rend., 239, 1502 (1954) ; Chem.Abst., 50, 207 (1956).
18. Zieglar., Monatsh., 79, 142 (1948).
19. Pepper., Chem. and Ind.(London)., 866 (1941).
20. Lilley., J.Soc.Chem.Ind., 67, 196 (1948).

21. Naik et al., J.Ind.Chem.Soc., 9, 471 (1932) ;
ibid., 7, 145 (1930).
22. Mehta and Patel., Indian J.Chem., 1, 144 (1963).
23. Quenda., Compt.rend., 121, 189 (1895).
24. Haller., Compt.rend., 108, 1116 (1889).
25. Whiteley., J.Chem.Soc., 83, 24 (1903).
26. Naik et al., J.Chem.Soc., 119, 379 (1921).
27. Mehta and Trivedi., Curr.Sci., 32, 17 (1963).