CHAPTER-V

STUDIES ON REDUCTIVE CLEAVAGE OF C-O AND C-S BONDS OF ACETALS AND DITHIOACETALS WITH ZINC IN ACETIC ACID.

V.1. INTRODUCTION

The acetals and dithioacetals are the most commonly used protecting groups for aldehydes and ketones.\textsuperscript{1,2} They also play an important role as precursors of masked acylanions in organic synthesis. In both the cases the ultimate step involves the cleavage of the acetal and dithioacetal functionality to restore the original carbonyl group. Acetals and ketals generally revert to the carbonyl compounds upon treatment with acids, but different types may show widely different sensitivity to cleavage conditions. The stability of the dioxolan group to drastic alkaline reaction conditions has been utilized in synthesis of sensitive $\alpha$, $\beta$-unsaturated carbonyl compounds particularly cyclopentenes, the cleavage of dioxolans is facilitated in the presence of periodic acid, whose further oxidation of the ethylene glycol formed drives the
reaction to completion. Both the selective formation and selective cleavage of dioxolans have been well reviewed in the steroid field.

The reductive cleavage of carbon-sulphur bonds is an established synthetic method of considerable utility. The main interest in dithioacetals and ketals has been in connection with their hydrogenolysis by Raney-Nickel to give the corresponding hydrocarbons, as an alternative to the Clemmensen or Wolff Kishner reduction on the parent carbonyl compound. This subject has been thoroughly reviewed. Hydrogenolysis of thioketals has also been effected by hydrazone and by alkali metals in liquid ammonia. Cleavage of the dithioacetals could better be accomplished using mercury(II) chloride and cadmium carbonate in various solvents.

Although the sulphides and thioacetals are not generally attacked by sodium borohydride or lithium aluminium hydride, the application of these hydrides in combination with transition metal halides have been frequently used in organic synthesis to cleave the carbon-sulphur bond selectively in recent years. Thus the sulphide 1 (Scheme-1) is reported to undergo facile carbon-sulphur bond cleavage in the presence of lithium aluminium hydride and copper(II) chloride to give the corresponding hydrocarbon 2 in 94% yield.

Similarly, 3 underwent complete reduction in the presence of lithium aluminium hydride and either copper(II) chloride or Zinc(II) chloride to give the corresponding hydrocarbon 4 in 84% yield. Another reagent Nickel (II) chloride in the presence of sodium borohydride has been extensively used for selective reduction of carbon-sulphur bonds in yields comparable to those obtained by Raney Nickel methods.
Scheme 1

Ph\(\text{H}^\text{X}\)Ph
\(\text{PhS}^\text{Ph}\) 1

\[
\begin{align*}
\text{PhH} & \quad \text{2CuCl}_2 / 4\text{LAH} \\
\text{PhS}^\text{Ph} & \quad 3h
\end{align*}
\]

\[
\begin{align*}
\text{PhH} & \quad 94\% \\
\text{PhS}^\text{Ph} & \quad 2
\end{align*}
\]

Ph\(\text{H}^\text{X}\)Ph
\(\text{PhS}^\text{Ph}\) 3

\[
\begin{align*}
\text{PhH} & \quad 4\text{CuCl}_2 / 4\text{ZnCl}_2 \\
\text{PhS}^\text{Ph} & \quad +16\text{LAH}
\end{align*}
\]

\[
\begin{align*}
\text{PhH} & \quad 84\% \\
\text{PhS}^\text{Ph} & \quad 4
\end{align*}
\]
Recently numerous reports concerning the cleavage of C-S bonds by using Zinc as promoter have appeared\textsuperscript{17}. The role of Zinc in the selective cleavage of C-O bond of poly acetals and ketals in the steroid field is also well known.

B.C. Ranu et al. reported\textsuperscript{20} a facile selective cleavage of C-O bond of other, tetrahydrofuran and epoxides in the presences of acyl chloride by zinc. Thus dialkyl ethers 5 in the presence of acid chlorides 6 including acyclic, cyclic and aromatic ones underwent cleavage by zinc to produce the corresponding alkyl chlorides 7 and alkanoates 8 (Schemes-2).

Similarly, tetrahydrofuran 9 and epoxides 11 yielded the corresponding alkanoates 10 and 12 respectively in the presence of acylchloride 6 and zinc under the same reaction condition.

A.Schmitt et al. reported\textsuperscript{21} the reduction of activated thiopyridyl compounds by zinc metal in acetec acid. Thus compounds 13 with thiopyridyl functional group was reacted with commercial zinc- powder in acetic acid at 80°C to yield the corresponding partial reduction products 14 in 80-98\% overall yields as shown in Scheme-3.

**Recent works developed in our laboratory for dethioacetalisation, C-S cleavage and Zinc - acetic acid reduction:**

The reagents which could achieve deprotections of both thioacetals and ketals under mild and neutral conditions and ketals under mild and neutral condition in high yields are always on demand. In our laboratory, we have observed\textsuperscript{22} a mild and neutral reagent, dimethyl sulfoxide alone can affect the cleavage of dithioacetals to afford the carbonyl compounds in excellent yields.
Zinc promoted selective cleavage of ethers.

Scheme 2
Scheme 3
Thus the dithioacetals or ketals 15 on merely heating with dry dimethyl sulfoxide at 140-150°C afforded the aldehydes or ketones 16 in high yields as shown in Scheme-4. The probable mechanism proposed depicting transfer of oxygen from the solvent DMSO to regenerate the original aldehydes and ketones 16 is also depicted in Scheme-5.

The use of Nickel (II) chloride in sodium borohydride to reduce C-S bond is already mentioned. The partial dethiomethylation of α-oxoketene dithioacetals 17 was developed in the presence of Nickel (II) chloride to give the corresponding methyl thiomethylene ketones 18 as a mixture of cis and trans isomers 18a and 18b in 60-70% yields (Scheme-6). The reducing agent in this reaction was proposed to be nickel boride derived from the reaction of sodium borohydride and nickel (II) chloride.

In another recent work developed in our laboratory related to zinc-acetic acid reductions, β-oxodithioacetals were obtained in high yields by chemoselective conjugate reduction of β-oxoketene dithioacetals. Thus when β-oxoketene dithioacetals 17 were treated with 2-5 equivalents of zinc in 8ml of acetic acid and water at room temperature for 3-5h to afford the corresponding β-oxodithioacetals 19 in 60-94% overall yields. In fact these β-oxodithioacetals 19 could also be prepared by reducing the β-oxoketene dithioacetals 17 with sodium borohydride in acetic acid (Scheme-7).
Scheme - 4

\[ R^1 = \text{C}_6\text{H}_5; \text{C}_6\text{H}_5 - \text{CH} = \text{CH} -; \text{Et}; \text{Me(CH}_2)_2 -; \text{Me(CH}_2)_10; \]
\[ R^2 = \text{H}, \text{Me}, \text{Et}. \]

\[ R^1 - R^2 = -(\text{CH}_2)_5 -; \]

66-94%
Scheme 5
R₁ = C₆H₅, 4-MeC₆H₄, 4-ClC₆H₄, 4-MeOC₆H₄, Me;
R₂ = H; R₃ = Me, Et.
R₁ = C₆H₅, Me, R₂ = Me, Et, n-C₃H₇, R₃ = Me.
R₁ = R₂ = -(CH₂)₃--; -(CH₂)₄--; 

Scheme-6
V.2. RESULTS AND DISCUSSION

From the literature, it is apparent that many reagents have been used to cleave carbon sulphur and carbon-oxygen bonds. It was further contemplated that the thioacetals could be subjected to partial reduction in the presence of zinc in boiling acetic acid. The cyclic dithioacetals 20a-e which were prepared by treating appropriate aldehyde or ketone with propane 1,3-dithiol according to the reported literature method were examined first. In a typical experiment when dithioacetals 20 (Scheme-8) was refluxed with zinc (10eqv) in acetic acid for 20 hours and the reaction mixture after work up yielded a single compound in 72% yield. The compound was assigned as 4-phenyl-3-thiabutane-1-thiol 21a in 72% yield. The structure of 21a was fully established by its analytical and spectral data: IR (CCl4)υmax : = 3019, 2915, 1535, 1487cm⁻¹, ¹H NMR (CCl): δ ppm 1.13 (t, 1H, J= 7HZ = SH), 1.70 (m, 2H, C CH₂ C), 2.40 (m, 4H, SCH₂), 3.58 (S, 2H, Ph CH₂ -), 7.20 (m, 5H, ArH).

The quantity of zinc (10 mmol) used in these transformations remains critical since any variation made in quantities will affect the quantity of overall yield of product 21. The other acetals 20b-d also underwent partial reduction to yield the corresponding sulphides 21b-d in 72-85%. The structure of these compounds were confirmed by their analytical and spectral data as given in the experimental section. In case of aliphatic acetals and ketals the method fails to observe the C-S bond cleavage reactions.

In case of dithioacetals 20d derived from naphthyldehydro and ketal 20e derived from benzophenone the over reduction and completely sulphur free products were also obtained along with the partially reduced products. Thus under the same reaction conditions 20d yielded 21d and 2-methyl naphthalene 22 as a 1:1 mixture of the
\[ \text{Scheme-8} \]

\[ \begin{align*}
\text{R} & \quad \text{Zn/AcOH, } \Delta \\
\text{20} & \quad 20-24\text{h} \\
\text{R} & \quad \text{H} \\
\text{21} & \quad 72-85\% \\
\text{20,21, a, } & \quad R = \text{C}_6\text{H}_5, R^1 = \text{H} \\
& \quad b, R = 4-\text{ClC}_6\text{H}_5, R^1 = \text{H} \\
& \quad c, R = 4\text{MeOC}_6\text{H}_4, R^1 = \text{H} \\
& \quad d, R = 2-\text{naphthyl}, R^1 = \text{H} \\
& \quad e, R = R^1 = \text{C}_6\text{H}_5
\end{align*} \]
overall 80% yield. Similarly 20e yielded 21e and diphenyl methane 23 in 1:1 ratio of 75% overall total yield as shown in Scheme - 9.

When the thioacetals 24a,b and ketals 24c (Scheme-10) derived from the respective aldehydes, ketone and thiophenol were subjected under the described conditions the corresponding sulphides 25a-c were obtained in 60-70% overall yields along with the traces of thiophenol. The structures of these compounds were confirmed by comparing their spectral properties with the data reported in the literature.
Scheme-10

\[ R \text{SC}_6\text{H}_5 \xrightarrow{\text{Zn/AcOH}} \xrightarrow{\Delta, 24 \text{ h}} R \text{H} + \text{SC}_6\text{H}_5 \text{SH} \]

24, 25, a, \( R = \text{C}_6\text{H}_5 \), \( R^1 = \text{H} \)

b, \( R = \text{C}_6\text{H}_5 - \text{CH} = \text{CH} \), \( R^1 = \text{H} \)

c, \( R = R^1 = \text{C}_6\text{H}_5 \)
Zn-AcOH reduction studies of Cyclic acetals:

A number of 2-(substituted aryl) 1,3-dioxolan 27a-h were prepared by reacting the appropriate aldehydes with ethyleneglycol according to the reported procedure. In a typical study, when 27a was refluxed with 10 equivalent quantity of zinc in acetic acid for 24h after work up yielded two products benzylacetate 28a and benzyl alcohol 29a. The overall yield of the mixture was 80% out of which acetate was 45% and the benzyl alcohol was 35% (Scheme-II).

Both the compounds were separated by column chromatography and the structures were confirmed from analytical and spectral data. Similarly 27b and 27c yielded a mixture of 28b+29b and 28c+29c in 78% and 80% yields respectively. Their further product distributions are shown in Scheme-II. However, the compound 2-(4- methoxy phenyl) 1,3 dioxolan 27d gave a mixture of two products for acetate 28d and completely reduced product 30d instead of the clcohol in 1:1 ratio of overall 80% yield of the mixture. Interestingly compounds 27e-g with more than one alkoxy substituted groups in the aryl ring gave only completely reduced products 30e-g in 63-78% overall yields. 2-Naphthyl 1,3-dioxolan 27 however yielded only the naphthyl alcohol 29h in 82% yield.

The structures of all these compounds were confirmed by comparing their analytical and spectral properties with authentic samples.

The reaction however failed when applied to the corresponding Ketals. Therefore only the aromatic aldehyde acetals were selected to demonstrate the C=O bond cleavage by Zinc in acetic acid. From the results described above, Zn-in acetic acid reduces the acetals to give either a mixture of acetate or the true alcohol or sometimes the
![Chemical structure](image)

**Scheme-11**

<table>
<thead>
<tr>
<th>27</th>
<th>R</th>
<th>28(%)</th>
<th>29(%)</th>
<th>30(%)</th>
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<tr>
<td>a</td>
<td>C₆H₅</td>
<td>(45)</td>
<td>(35)</td>
<td>—</td>
</tr>
<tr>
<td>b</td>
<td>4-MeC₆H₄</td>
<td>(42)</td>
<td>(36)</td>
<td>—</td>
</tr>
<tr>
<td>c</td>
<td>4-ClC₆H₄</td>
<td>(30)</td>
<td>(50)</td>
<td>—</td>
</tr>
<tr>
<td>d</td>
<td>4-MeOC₆H₄</td>
<td>(40)</td>
<td>—</td>
<td>(40)</td>
</tr>
<tr>
<td>e</td>
<td>3,4-(MeO)₂C₆H₃</td>
<td>—</td>
<td>—</td>
<td>(78)</td>
</tr>
<tr>
<td>f</td>
<td>3,4,5-(MeO)₃C₆H₂</td>
<td>—</td>
<td>—</td>
<td>(63)</td>
</tr>
<tr>
<td>g</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>(65)</td>
</tr>
<tr>
<td>h</td>
<td>2-Naphthyl</td>
<td>—</td>
<td>(82)</td>
<td>—</td>
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completely reduced products under similar reaction conditions. It appears that electron donating substituents appear to favour faster rate of reduction by complete cleavage of the C-O bond of the protecting group.

In conclusion, the reduction of dithioacetals under similar reaction condition was more consistent yielding exclusively one product in high yields. Therefore, the method is useful for partial reduction of dithioacetals to the corresponding sulphides.

The plausible reaction pathway is depicted as shown in Scheme-12 assuming a radical mechanism. Initially compound 20 would be protonated to yield the intermediate A which then could be reduced to the radical B by rupture of the alkyl-thio bond. Radical B could then be further reduced to the stabilized carbanion C. Protonation of C would then yield the corresponding partial reduced product 21 (Scheme-12). However the mechanism governing the reduction of acetals (dixolans) appear to be different since in the acetic acid medium the acetals yield the corresponding acetates as one of the products. These studies are still to be concluded.
EXPERIMENTAL SECTION

Melting points were recorded on a Thomas Hoover capillary melting point apparatus and are uncorrected. IR spectra were obtained on Perkin Elmer 983 spectrophotometer. HNMR spectra were recorded on a Varian EM-390 (90 MHz) spectrometer using TMS as internal standard and chemical shifts are expressed in \( \delta \) (ppm) units downfield from TMS. The following abbreviation are used to describe peak patterns when appropriate: br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. Elemental analysis were performed on a Heraeus HN-O-rapid elemental analyser.

Chemical and Reagents:

Zn (AR grade) used in the reaction was supplied by E-Merck (India) and was activated before use. Commercially available AR grade acetic acid, benzaldehyde, cinnamaldehyde, 4-chlorobenzaldehyde, 4-methoxy benzaldehyde 4-methyl, 2-napthyl aldehyde, Thiophene 1,1,3-propan dithiol was supplied by E-Merck, Germany and was used as such.

Starting Materials:

All the starting thioacetals, 1,3-dithianes of the corresponding aromatic aldehydes and ketones and acetals 1,3-dioxolans of the corresponding aromatic aldehydes were prepared according to the reported\(^{1,26,27}\) procedures, and a typical procedure for each class of dithioacetal and acetal mentioned above is given as representative examples in the following sections.
General Procedure for the Preparation of 1,3-dithioactals, (20a-e, Scheme B) from carbonyl compounds:

To a well stirred solution of carbonyl compound (0.01 mol) in dichloromethane (20 ml) was added BF₃·Et₂O (2-3 drops) and stirred for 10-15 min. at room temp. The reaction mixture was cooled to 0°C and was added the 1,3-propanedithiol (0.011 mol) in dichloromethane (10 ml) dropwise over a period of 10 min. The reaction mixture was allowed to come to room temp and stirred for 2-3 hr. (monitored by TLC) worked up with a solution of sat NaHCO₃ and product was chromatographed (silicagel column) using hexane as eluent to obtain pure product. The compounds were characterised by comparison of their physical and spectral data with that of literature methods.

General procedure for the preparation of dithioacetals (24a-c). To a well stirred mixture of corresponding aldehyde or ketone (0.01 mol) and thiophenol (0.022 mol) in dichloromethane (10 ml) was added BF₃·Et₂O (2-3 drops) at 0°C, stirring continued for further 10 min, allowed to come to room temp during a period of 3 hrs (monitored by TLC). The reaction mixture was then poured into a cold sat. NaHCO₃ sol. (50 ml), extracted with dichloromethane 92×50 ml) washed with water (2×50 ml), dried (Na₂SO₄) and evaporated to obtain the corresponding dithioacetals 24a-c, which were purified over silica gel column using hexane as eluent. All the dithioacetals thus prepared were well characterized by comparing their spectral and analytical data with that of reported ones.

General procedure for the preparation of 1,3-dioxolans 27a-h (Scheme-II). 12-(substituted aryl)-1,3-dioxolans were prepared by reacting the appropriate aromatic aldehyde with ethylene glycol in refluxing benzene. A trace of p-toluene sulphonic acid was added as catalyst. Water was removed by azeotrope distillation with the benzene.
At the conclusion of the reaction, the mixture was washed with 1M NaOH solution. The benzene layer was dried (Na₂SO₄) and evaporated to yield the residual liquids which were purified by column chromatography. All these dioxolans prepared were found to be identical in their physical and spectral data with the literature data.

**General Procedure for reduction of dioxolans 27a-h (Scheme-11) with Zinc in acetic acid:**

To a solution of the dioxolane (2 mmol) in acetic acid (10 ml) zinc dust (20 mmol) was added and stirred with refluxing for 24 hours. It was then cooled and poured into crushed ice, extracted with benzene. The benzene layer was washed with saturated aqueous NaHCO₃ and 3-4 times with water, dried (Na₂SO₄) and evaporated to give the corresponding acetals 28a-d, alcohol 29a-c, 29h and completely acetal reduced products 30d-g which were separated and purified by passing through silica gel column using hexane as eluent (Scheme-11 shows the product distribution). All the acetals, alcohols and substituted alkanes are known and were characterised by comparison of their physical and spectral data with those reported in the literature (mixed m.p., b.p., superimposable IR and NMR etc.).

**General Procedure for Reduction of 1,3-dithianes 20a-e, 24a-c (Scheme 10) with zinc in acetic acid:**

Zinc dust (20 mmol) was added to a solution of dithioacetal (2mmol) in 10 ml of acetic acid. The reaction mixture was refluxed for 24 h. It was then cooled and poured into crushed ice, extracted with benzene. The benzene layer was washed with saturated aqueous NaHCO₃ solution, dried (Na₂SO₄) and evaporated to give the corresponding partially reduced products 21a-e & 25a-c and completely reduced products 22 and 23. The column chromatography over silica gel using hexane as eluent afforded the products in very pure form. Their spectral and analytical data are given below:
5-Phenyl-4-thia pentane-1-thiol (21a) was isolated as yellow viscous oil IR $\gamma_{\text{max}}$ (CCl$_4$): 3019, 2915, 1585 cm$^{-1}$ $^1$HNMR (CCl$_4$): 1.13 (t, 1H, J=7Hz, SH) 1.70 (m, 2H, CCH$_2$C), 2.40 (m, 4H, S CH$_2$), 3.58 (s, 2H, Ph CH$_2$). 7.18 (s, 5H, ArH). Anal. Calcd. for C$_{10}$H$_{14}$S$_2$: C 60.56, H 7.11, S 32.33. Found: C 60.54, H 7.09, S 32.57.

5-(4 chloro phenyl)-4 thio pentane-1-thiol (21b) was isolated as thick viscous oil. IR $\gamma_{\text{max}}$(CCl$_4$): 3013, 2900, 2580, 1575 cm$^{-1}$ $^1$HNMR (CCl$_4$): 1.13 (t, 1H, J=7.5Hz, SH). HNMR 41.70 (m,2H, J= 7.5 Hz, -CH$_2$), 2.50 (m, 4H, SCH). 3.50 (s,2H, Ar-CH$_2$), 7.25 (m, 4H, ArH). Anal. Calcd. for C$_{10}$H$_{15}$ClS$_2$.

5-(4-methoxy phenyl)-4 thio pentane-1-thiol (21c) was isolated as thick viscous oil. IR $\gamma_{\text{max}}$(CCl$_4$): 3179, 2923, 2536, 1598, 1102 cm$^{-1}$ $^1$HNMR (CCl$_4$): 1.20 (t, 1H, J= 7Hz, SH). 1.70 (m, 2H, CH$_2$), 2.45 (m, 4H, S-CH$_2$-) 3.50 (s,2H, Ar CH$_2$), 3.70 (s, 3H, OCH$_3$) 6.85 (d,2H, J=9Hz, ArH), 7.20 (d,2H, J=9Hz, ArH). Anal. Calcd. for C$_{11}$H$_{16}$OS$_2$ (228,0), C 57.87 H 7.01, C 58, H 6.6. 11 16.

5-naphthyl-4-thia pentane-1 thiol (21d) was isolated as thick oil. IR (CCl$_4$) 3103, 3057, 2905, 1656, 1616 cm$^{-1}$. $^1$HNMR(CCl$_4$): 1.20 (t, 1H, J= 7Hz, SH), 1.80 (m, 2H, CH), 2.50 (m, 4H, SCH$_2$). 3.80 (s, 2H, Ar-CH$_2$), 7.35 - 7.90 (m, 6H, ArH). Anal. Calcd. for C$_{14}$H$_{16}$S$_2$ (248.0), C 67.74, H 6.41, C 66.5, H 6.7.

5,S-diphenyl-4-thia pentan-1-thiol (21e) was isolated as yellow viscous liquid. IR (CCl$_4$): 3056, 3019, 2918, 1651, 1488 cm$^{-1}$. $^1$HNMR: 1.12 (t,1H, J= 7.5 Hz, SH), 1.65 (m, 2H, CH$_2$), 2.45 (m, 4H, SCH$_2$) 5.0 (s, 1, Ar- CH), 7.20-7.50 (m, 10H, ArH). Anal. Calcd. for C$_{16}$H$_{18}$S$_2$ (274.0) C 70.07, H 6.5, C 71.2, H 6.3.
Benzyl phenyl sulfide (25a) was isolated as a low melting solid (lit. m.p. 41-43.5°C) m.p. 43-44°C. IR$_{\text{max}}$ (KBr): 3015, 1567, 1466, 1075 cm$^{-1}$. $^1$HNMR (CCl$_4$): 3.98 (S, 2H, PhCH$_2$), 7.15-7.20 (m, 10H, ArH). Anal Caled for C$_{13}$H$_{12}$S (200.0) C 78 H 6.0 Found C 76 H 6.5.

1-Phenyl-3(phenylthio)-1-propene (25b) was isolated as low melting solid. IR$_{\text{max}}$ (CCl$_4$): 3014, 2900, 1541 cm$^{-1}$. $^1$HNMR (CCl$_4$): 3.50 (d, 2H, J = 6Hz, -CH$_2$SPh), 5.8 - 6.20 (m, 1H, = CH), 6.30 (d, 1H, J = 15Hz, = CH), 7.20-7.50 (m, 10H, ArH). Anal Caled for C$_{15}$H$_{14}$S (226.0) C 79.64 H 6.19 found C 79.1 H 5.9.

Phenyl-[1,1-diphenyl]methyl sulfide (25c) was isolated as oil. IR$_{\text{max}}$ (neat): 3512 3019, 1481 cm$^{-1}$. $^1$HNMR (CCl$_4$): 5:35 (S, 1H, CH), 7.10 - 7.50 (m, 15H, ArH). Anal Caled for C$_{19}$H$_{16}$S (276) C 82.60, H 5.79. Found: C 82.5 H 5.8.

Diphenyl methane (23) was isolated as low melting solid (lit. m.p. 22-24°C) m.p. 24-25°C. IR (CCl$_4$): 3018, 2907, 1712, 1592. $^1$HNMR (CCl$_4$): 3.8 (S, 2H, CH$_2$), 7.7.25 (m, 10H, ArH). Anal Caled for C$_{13}$H$_{12}$ (168.24) C 82.9, H 7.14. Found C 83.2, H 6.8.

2-Methyl naphthalene (22) was isolated as colourless needles. (m.p lit 34-36) m.p. 35-37°C. IR $\gamma_{\text{max}}$ (CCl$_4$): 3335, 3090, 2901, 1592 cm$^{-1}$. $^1$HNMR (CCl$_4$): $\delta$(ppm: 2.45 (S, 3H, CH$_3$), Anal Caled for C$_{11}$H$_{16}$ (142.20) C 92.9, H 7.04. Found C 92.8, H 7.26.
REFERENCES


   (c) H. Hauptmann, M.M. Campos, Ibid., 72, 1405(1950).