CHAPTER - 3

SCOPE OF ZEOLITE CATALYSIS:
SYNTHESIS OF PUSH - PULL ETHYLENE SYSTEMS

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3.1 Abstract:

The scope of the zeolite catalyzed condensation between carbonimidodithioic acid esters and various active methylene compounds has been fully explored. This has led to the synthesis of several functionalized ketene N,S-acetals in more than 70% yields. Our efforts to synthesize push-pull systems with a longer conjugation using this zeolite catalyzed process has however, not succeeded.
3.2 Introduction:

3.2.1 Background:

Functionalized ketene N,S acetals belong to the general class of push-pull ethylene systems. In such molecules one end of the double bond is attached to an electron donating group (amine) and the other end to an electron withdrawing group (nitro or carbonyl). Consequently, there is delocalization of π-electrons over the entire system. Such compounds have been synthesized in order to study their intrinsic properties. They have also been utilized as versatile intermediates for the synthesis of heterocyclic compounds. There are only two methods known in the literature for the synthesis of such functionalized ketene N,S-acetals. One is the substitution of one of the S-alkyl groups of ketene S,S-acetals by amines through an addition-elimination mechanism. The other is the addition of active methylene compounds to alkyl or aryl isothiocyanates followed by S-alkylation. The drawbacks in these two routes are the formation of unwanted side products and the necessity of using isothiocyanates as starting materials.

3.2.2 Earlier synthetic methods:

3.2.2a Synthesis of α-oxoketene N,S-acetals

The doubly activated ketene S,S-acetals (1) undergo an addition-elimination sequence with amines (2) to give the corresponding N,S-acetals (3). The reaction however, cannot be stopped cleanly at this stage, it always leads to some amount of the further displacement product, the N,N-acetals (4). The formation of the side product can be controlled to some extent by controlling the stoichiometry of the added amines (Scheme 3-1). However, the less reactive α-oxoketene S,S-acetals (5) required more vigorous conditions for their reaction with amines and generally offered a mixture of N,S and N,N-acetals 6 and 7 (Scheme 3-2)

The second method involves the reaction of enolate ions of active methylene compounds (8) with isothiocyanates (9) followed by S-alkylation to give the required ketene N,S-acetals (10) (Scheme 3-3)
Scheme 3-1

\[ \text{Scheme 3-1} \]

\[ \text{1} \quad \text{SMe} \quad \text{SMe} \quad + \quad \text{H}_2\text{N-R} \quad \rightarrow \quad \text{3} \quad + \quad \text{4} \]

Scheme 3-2

\[ \text{Scheme 3-2} \]

\[ \text{5} \quad \text{SMe} \quad \text{SMe} \quad \text{H}_2\text{N-R} \quad \text{H}_2\text{N-R} \quad \rightarrow \quad \text{6} \quad + \quad \text{7} \]

Scheme 3-3

\[ \text{Scheme 3-3} \]

\[ \text{8} \quad \text{CH}_3 \quad + \quad \text{R-}_\text{N}=_\text{C}=\text{S} \quad \xrightarrow{1) \text{NaH/DMF}} \quad \xrightarrow{2) \text{R'}X} \quad \text{10} \]
3.2.2b  Synthesis of nitroketene N,S-acetals: 3,13-16

In 1967 Gompper et al. 13 reported for the first time the synthesis of nitroketene N,N-acetals. The method employed was the reaction of secondary amines with nitroketene S,S-acetals (11). Later, such compounds were also synthesized by Rajappa et al. 14 in 1977. Their method involved the condensation of S-alkyl isothioureas with nitromethane. Schafer et al. 15 reported the first compound belonging to the group of nitroketene N,S-acetals. This was the synthesis of 1-methylthio-1-para nitro anilino-2-nitroethylene (13) in 63% yield. The formation of this reflected the lower nucleophilicity of p-nitroaniline (12) compared to the aliphatic secondary amines employed earlier. In 1990 Rajappa et al. 16 reported the synthesis of a series of nitroketene N,S-acetals (14) as intermediates for the synthesis of N-nitroacetyl derivatives of various amines and amino acid esters (Scheme 3-4).

The second method for the synthesis of such nitroketene N,S-acetals is the addition of nitromethane to arylisothiocyanate (15) followed by S-alkylation; this leads to the required compound (16) (Scheme 3-5).

Scheme 3-4

Scheme 3-5
3.3 Present work:

Chapter-2 had described a new synthesis of 1-methylamino-1-methylthio-2-nitroethylene by the condensation of nitromethane with N-methyl carbonimidodithioic acid dimethyl ester. This condensation was brought about through a specific zeolite catalysis. In the present chapter, we have explored the scope of this condensation by varying the primary amines involved in the carbonimidodithioic acid dimethyl esters as well as the active methylene moieties. In an earlier literature report, the condensation of various active methylene compounds such as malononitrile and methyl cyanoacetate with N-methyl carbonimidodithioic acid dimethyl ester had been described. No catalyst was used in this reaction. However, as mentioned in chapter-2 of this thesis, this reaction failed completely when nitromethane was the active methylene component. The reaction was successful when a specific zeolite catalyst RE(70%)NaY was added to the reaction medium. We have therefore, now extended the scope of this particular condensation and used it to synthesize several other functionalized ketene N,S-acetals. Various active methylene compounds such as ethyl cyanoacetate, acetylacetone, dimeredone and Meldrum's acid have been condensed with the N-methyl carbonimidodithioic acid (17) to give the corresponding α-oxoketene N,S-acetals. In all these condensations the yields of the products have been either higher than or at least equal to those reported in the earlier publication. Thus the uncatalyzed condensation of compound 17 with methyl cyanoacetate has been reported to give the required product in 42% yield. The same reaction with the zeolite catalysis has given the product in 85% yield. However, reaction of 17 with ethyl acetoacetate, diethyl malonate resulted in the formation of polymeric material. In the case of nitroethane, even after prolonged refluxing with 17, only starting material 17 was recovered. Various other N-alkyl carbonimidodithioic acid dimethyl esters 23a-f prepared from several primary amines (22a-f) have been condensed with nitromethane to give the corresponding nitroketene N,S-acetals (24a-f). Finally, an attempt was
made to synthesize a push-pull butadiene system with the nitro group at one terminus and an amine at the other, by the condensation of 1-nitrocyclohexene; however, this only gave polymeric material. These efforts have been discussed below in greater detail.

3.4 Results and discussion:

3.4.1 Synthesis of α-oxoketene N,S-acetals (18-21):

N-Methyl carbonimidodithioic acid dimethyl ester (17) was prepared as described in the earlier chapter. This was heated with active methylene compounds such as ethyl cyanoacetate, acetyl acetone, dimedone and Meldrum’s acid in presence of the zeolite RE(70%)NaY to give the corresponding α-oxoketene N,S-acetals (18-21) (Scheme 3-6). The solid products obtained were characterised by the $^1$H NMR spectra, infrared and mass spectra. Thus ethyl cyanoacetate gave the product 18 in 85% yield. The product exhibited the following bands in the $^1$H NMR spectrum 10.10 (NH), 4.23 (q, 2H, CH$_2$), 3.23 (d, $J = 2.7$ Hz, 3H, NCH$_3$), 2.70 (s, 3H, SCH$_3$), 1.34 (t, $J = 7.14$ Hz, 3H, CH$_3$). Similarly dimedone gave the product 20 in 60% yield as a colourless crystalline solid. It exhibited $^1$H NMR signals at 9.80 (NH), 3.00 (d, $J = 4.8$ Hz, 3H, NCH$_3$), 2.80 (s, 3H, SCH$_3$), 2.35 (s, 4H) and 1.10 (s, 6H). The product from Meldrum’s acid (21) was obtained as a white crystalline solid in 78% yield. It exhibited $^1$H NMR signals at 11.00 (NH), 3.20 (d, $J = 4.5$ Hz), 3H NCH$_3$), 2.60 (s, 3H, SCH$_3$) and 1.70 (s, 6H). The product from acetylacetone was however, not the expected compound 19a but the deacetylated product derived from this. The product is obtained as a crystalline solid in 70% yield. This exhibited $^1$H NMR (Spectrum No. 3-1) signals at 11.20 (NH, 4.96 (s, 1H), 2.98 (d, $J = 4.89$ Hz, 3H, NCH$_3$), 2.36 (s, 3H, SCH$_3$), 2.03 (s, 3H, COCH$_3$). The presence of the olefinic signal at 4.96 and the fact that only one acetyl methyl group was seen in $^1$H NMR spectrum prove the structure of the product to be 19b. This obviously arises from 19a by deacetylation, most probably induced by the nucleophilic action of the methyl mercaptan$^{18}$ liberated in the first step (Scheme 3-7). The structure of 19b was further confirmed by the $^{13}$C NMR spectrum (Spectrum No. 3-2), in which, using the DEPT technique, the =CH carbon was seen at 88.70 ppm. Furthermore in the mass spectrum the molecular ion peak (M$^+$) appeared at m/z 145.
Scheme 3-6

\[
\text{Me} \equiv N \equiv \text{SMe} + X \xrightarrow{\text{Zeolite, 110°C, 24 h}} Y \equiv \text{SMe} \equiv \text{NHMe}
\]

17 \hspace{1cm} 18 \hspace{1cm} 19b \hspace{1cm} 20 \hspace{1cm} 21

Scheme 3-7

\[
\text{Me} \equiv N \equiv \text{SMe} + \text{H}_2\text{C} \equiv \text{CMe} \xrightarrow{-\text{MeSH}} \text{MeCO} \equiv \text{NHMe}
\]

17 \hspace{1cm} 19a \hspace{1cm} 19b
3.4.2 Synthesis of 1-substitutedamino-1-methylthio-2-nitroethylenes (24a-f):

Several primary amines (22a-f) were condensed with carbon disulfide by the usual procedure\textsuperscript{19} and then methylated to give the N-alkyl carbonimidodithioic acid dimethyl esters (23a-f). These compounds condensed with nitromethane in presence of the zeolite RE(70%)NaY to give the products 24a-f. Thus n-propyl amine (22a) was condensed with carbon disulfide in CH\textsubscript{2}Cl\textsubscript{2} solution in the presence of triethylamine as the basic catalyst. The product was methylated with methyl iodide to give 23a as a liquid in 72% yield (Scheme 3-8). The \textsuperscript{1}H NMR spectrum of the purified sample of 23a showed the following five signals 3.40 (t, \textit{J} = 7.2, Hz, 2H, NCH\textsubscript{2}), 2.55 (s, 3H, SCH\textsubscript{3}), 2.35 (s, 3H, SCH\textsubscript{3}), 1.65 (m, 2H, CH\textsubscript{2}) and 1.00 (t, \textit{J} = 7.2 Hz, 3H, CH\textsubscript{3}). The above data confirm the structure assigned. Furthermore, the compound 23a showed the molecular ion (M\textsuperscript{+}) peak in its mass spectrum at \textit{m/z} 163.

The carbonimidodithioic acid dimethyl esters of the following primary amines (22b-f) were synthesized by a similar procedure: Sec.butylamine cyclohexylamine, benzylamine, \textalpha; -methyl benzylamine and furfurylamine. The yields and spectral data of all these compounds are given in the experimental section.

The above carbonimidodithioic acid dimethyl esters (23a-f) were then condensed with nitromethane in presence of the zeolite RE(70%)NaY to yield nitroketene N,S-acetals (24a-f) (Scheme 3-8). Thus the n-propyl derivative (24a) was obtained by heating N-n-propyl carbonimidodithioic acid dimethyl ester (23a) with excess nitromethane at 100°C in presence of zeolite RE(70%)NaY for 24 h. Separation of the catalyst by filtratoin and removal of excess nitromethane left the product 24a as a solid in 76% yield. The \textsuperscript{1}H NMR spectrum (Spectrum No. 3-3) of the purified sample showed two signals at 6.60 and 2.35 corresponding to =CH and SCH\textsubscript{3} protons respectively, and three signals at 3.35 (q, 2H, NCH\textsubscript{2}), 1.60 (m, 2H, CH\textsubscript{2}) and 1.00 (t, \textit{J} = 6.72 Hz, 3H, CH\textsubscript{3}) corresponding to protons of N-n-propyl group. The NH proton resonated at 10.60 \textbf{6}. In the mass spectrum, the molecular ion (M\textsuperscript{+}) peak was seen at \textit{m/z} 176. The above spectral data clearly indicate that the structure 24a assigned to this product is the right one. Similarly, the nitroketene N,S acetals 24b-f were prepared in 52-85% yield from the starting materials 23b-f. All the products were characterized by analytical and special data.
Scheme 3-8

\[ \text{H}_2\text{N} - \text{CH} \rightarrow \text{CS}_2 \rightarrow \text{MeS} - \text{NH} \]

1) \( \text{Et}_3\text{N} / \text{CH}_2\text{Cl}_2 \)
2) \( \text{MeI} \)

\[ \text{MeS} - \text{N} \rightarrow \text{MeS} - \text{NH} \]

1) \( \text{Et}_3\text{N} / \text{CH}_3\text{Cl}_2 \)
2) \( \text{MeI} \)

\[ \text{MeS} - \text{N} \rightarrow \text{MeS} - \text{NH} \]

\[ \text{MeS} - \text{N} \rightarrow \text{MeS} - \text{NH} \]

\[ \text{MeS} - \text{N} \rightarrow \text{MeS} - \text{NH} \]

23a

24a

24b

24c

24d

24e

24f
3.4.3 An attempt to synthesize a push-pull butadiene system (26):

In order to delineate the scope of the zeolite catalyzed condensations, it was decided to see whether a push-pull butadiene system could be generated by a similar reaction. The appropriate starting materials for this projected synthesis are 1-nitrocyclohexene (25) and N-methyl carbonimidodithioic acid dimethyl ester (17). In a recent review of conjugated aliphatic nitro compounds, it has been explicitly stated that there are very few examples of such nitrovinyl compounds acting as nucleophiles on carbon atom C3. 1-Nitrocyclohexene, prepared by the standard procedure was heated with carbonimidodithioic acid dimethyl ester (17) in presence of RE(70%)NaY. There was no evidence for the formation of the required compound 26. However, in one of the experiments, a small quantity of a solid product was isolated, which from its analytical and spectral data (Spectrum No.3-4a & 3-4b) seemed to have the structure 27 corresponding to an oxime (Scheme 3-9). The formation of this however, was not reproducible and no mechanistic conclusions can be drawn from this observation. However the authentic sample of this oxime 27 was prepared by the reaction of 1-nitrocyclohexene (25) with isoamyl nitrite (28) as earlier reported (Scheme 3-10) and compared with the \textsuperscript{1}H NMR spectrum of the sample obtained by zeolite catalysis. The two were identical.
Scheme 3-9

\[
\begin{align*}
\text{NO}_2 + 17 &\xrightarrow{\text{RE (70\% NaY)}} \text{O}_2\text{N} \quad \text{NHMe} \\
&\xrightarrow{\text{RE (70\% NaY)}} \text{26} \\
\end{align*}
\]

Scheme 3-10

\[
\begin{align*}
\text{NO}_2 + \text{28} &\xrightarrow{\text{K}_2\text{CO}_3 / \text{DMSO} \at 20-25^\circ\text{C}}} \text{27} \\
\end{align*}
\]
3.5 Summary:

The synthesis of functionalized ketene N,S-acetals as described here is a general and mild method proceeding under almost neutral conditions. This method gives exclusively a single product (>90% selectivity). Workup and purification are easy. The catalyst can be reactivated and recycled without affecting its efficacy.
3.6 Experimental:

Synthesis of α-oxoketene N,S-acetals (18-21):

**General:** A mixture of N-methyl carbonimidodithioic acid dimethyl ester (17), (10 mmol), active methylene compound (3 mmol) and zeolite RE(70%)NaY (half the weight of the active methylene compound) was stirred at 100°C for 24-48 h. The reaction mixture was cooled, catalyst filtered off and washed with dichloromethane (2x15 ml). The filtrate was concentrated at reduced pressure. The residue was taken in n-hexane and stirred for a few mins to precipitate the product and most of the unreacted starting material was dissolved. Final purification was carried out by column chromatography to give the pure product (18-21) in 60-85% yield.

**3-Methylamino-3-methylthio-2-cyano acrylic acid-ethylester (18):**

Yield : 85%, colorless crystalline solid.

mp : 93°C (EtOH-n-hexane).

$^1$H NMR (300 MHz) : δ 10.10 (br, 1H, NH), 4.23 (q, 2H, CH$_2$), 3.23 (d, J = 2.7 Hz, 3H, NC$_2$H$_5$), 2.70 (s, 3H, SCH$_3$), 1.34 (t, J = 7.1 Hz, 3H, CH$_3$).

IR (Nujol) : cm$^{-1}$ 3100, 2120, 1690, 1570, 1360.

MS : m/z 200 (M$^+$, 90%), 153, 125 (100), 107, 81.

Analysis : C$_4$H$_2$N$_2$O$_2$S. Calcd. : C, 48.00; H, 6.00; N, 14.00.

Found : C, 48.08; H, 6.12; N, 14.06.

**3-Methylthio-3-methylamino butan-3-ene-2-one (19b):**

Yield : 70%, crystalline solid.

mp : 65°C (EtOH).

$^1$H NMR (300 MHz) : δ 11.20 (br, d, 1H, NH), 4.96 (s, 1H), 2.98 (d, J = 4.89 Hz, 3H, NC$_2$H$_5$), 2.36 (s, 3H, SCH$_3$), 2.03 (s, 3H, COCH$_3$).
$^{13}$C NMR (75.5 MHz) : ppm 194.40, 168.65, 88.70, 29.54, 28.45, 13.56.

IR (CHCl$_3$) : cm$^{-1}$ 3200-3350, 1560, 1470, 1280.

MS : m/z 145 (M$^+$, 100%), 130, 98, 82.

Analysis : C$_6$H$_4$NOS. Calcd. : C, 49.65; H, 7.58; N, 9.65.

Found : C, 50.11; H, 7.68; N, 9.79.

2-[(Methylamino, methylthio) methylene] dimerone (20):

Yield : 60%, colorless crystalline solid.

mp : 142°C (EtOH).

$^1$H NMR (80 MHz) : δ 9.80 (br, 1H, NH), 3.00 (d, J = 4.8 Hz, 3H, NCH$_3$), 2.80 (s, 3H, SCH$_3$), 2.35 (s, 4H), 1.10 (s, 6H).

IR (Nujol) : cm$^{-1}$ 3160, 1670, 1540, 1450, 1200.

MS : m/z 227 (M$^+$, 05%), 210 (100), 180, 153, 138, 123, 83.

Analysis : C$_{11}$H$_{17}$NOS. Calcd. : C, 58.15; H, 7.48; N, 6.16.

Found : C, 58.22; H, 7.51; N, 6.21.

2,2-Dimethyl-5-[(methylamino)(methylthio)methylene]-1,3-dioxane-4,6-dione(21):

Yield : 78%, white crystalline solid.

mp : 119°C (MeOH).

$^1$H NMR (90 MHz) : δ 11.00 (br, 1H, NH), 3.20 (d, J = 4.5 Hz, 3H, NCH$_3$), 2.60 (s, 3H, SCH$_3$), 1.70 (s, 6H).

IR (Nujol) : cm$^{-1}$ 3200, 1700, 1650, 1550, 1450, 1200.

MS : m/z 231 (M$^+$, 20%), 184, 173, 126 (100), 82.

Analysis : C$_9$H$_{14}$NO$_2$S. Calcd. : C, 46.70; H, 5.60; N, 6.06.

Found : C, 46.51; H, 5.61; N, 6.11.
Synthesis of carbonimidodithioic acid dimethyl esters of various primary amines (23a-f):

**General:** To a solution of the primary amine (10 mmol) and carbon disulfide (10 mmol) in dichloromethane (50 ml), triethylamine (10 mmol) was added slowly at 20°C. The reaction mixture was stirred for 30 min at room temperature. Methyl iodide (12 mmol) was then added dropwise and the resulting mixture was refluxed for 2-3 h. The reaction mixture was then cooled to room temperature; triethylamine (12 mmol), methyl iodide (12 mmol) were successively added dropwise and it was again refluxed for 2-4 h. After complete conversion of dithiocarbamate to carbonimidodithioate, the reaction mixture was cooled, washed with water (2 X 30 ml) and concentrated under vacuum. The residue was taken in ether (50 ml) and again washed with water (3 X 20 ml) and brine, dried (anhydrous Na₂SO₄) and concentrated to give the product (23a-f) in 70-90% yield.

**N-n-Propyl carbonimidodithioic acid dimethyl ester (23a):**

- **Yield**: 72%. Yellow coloured liquid.
- **bp**: 47°C/0.17 mm.
- **¹H NMR (80 MHz)**: δ 3.40 (t, J = 7.2 Hz, 2H, NCH₂), 2.55 (s, 3H, SCH₂), 2.35 (s, 3H, SCH₂), 1.65 (m, 2H, C₃H₂), 1.00 (t, J = 7.2 Hz, 3H, CH₃).
- **IR (Neat)**: cm⁻¹ 1590.
- **MS**: m/z 163 (M⁺, 20%), 116 (100), 74.
- **Analysis**: C₆H₁₃NS₂. Calcd.: C, 44.17; H, 7.97; N, 8.58. Found: C, 43.98; H, 8.02; N, 8.27.

**N-sec-Butyl carbonimidodithioic acid dimethyl ester (23b):**

- **Yield**: 78%. Yellow coloured liquid.
- **bp**: 61°C/0.21 mm.
$^1$H NMR (80 MHz) : δ 3.70 (m, 1H), 2.50 (s, 3H, SCH$_3$), 2.30 (s, 3H, SCH$_3$), 1.45 (m, 2H, CH$_2$), 1.10 (d, $J = 6.4$ Hz, 3H, CH$_3$), 0.80 (t, $J = 7.2$ Hz, 3H, CH$_3$).

IR (CHCl$_3$) : cm$^{-1}$ 1600.

MS : m/z 177 (M$^+$, 05%), 130 (70), 74 (100).

Analysis : C$_7$H$_{15}$NS$_2$. Calcd. : C, 47.45; H, 8.47; N, 7.90.

Found : C, 47.57; H, 8.51; N, 8.02.

N-Cyclohexyl carbonimidodithioic acid dimethyl ester (23c):

Yield : 84%. Colourless liquid.

bp : 93°C/4.5 mm.

$^1$H NMR (80 MHz) : δ 3.60 (m, 1H, NCH), 2.55 (s, 3H, SCH$_3$), 2.35 (s, 3H, SCH$_3$), 1.20-1.80 (br, m, 10H).

IR (Neat) : cm$^{-1}$ 1590.

MS : m/z 203 (M$^+$, 10%), 156 (100), 83, 74.

Analysis : C$_{9}$H$_{19}$NS$_2$. Calcd. : C, 53.20; H, 8.37; N, 6.89.

Found : C, 52.91; H, 8.26; N, 7.10.

N-Benzyl carbonimidodithioic acid dimethyl ester (23d):

Yield : 82%, Yellow coloured liquid.

bp : 124°C/4.5 mm.

$^1$H NMR (80 MHz) : δ 7.30 (m, 5H, aromatic), 4.60 (s, 2H, NCH$_2$), 2.55 (s, 3H, SCH$_3$), 2.40 (s, 3H, SCH$_3$).

IR (Neat) : cm$^{-1}$ 1590.

MS : m/z 211 (M$^+$, 05%), 164 (60), 91 (100).

Analysis : C$_{10}$H$_{11}$NS$_2$. Calcd. : C, 56.87; H, 6.16; N, 6.63.

Found : C, 56.53; H, 6.71; N, 6.72.
(S)-N-α-Methylbenzyl carbonimidodithioic acid dimethyl ester (23e):

Yield : 86%, Yellow coloured liquid.
bp : 105°C/4.7 mm.

$^1$H NMR (200 MHz) : \( \delta \) 7.40 (m, 5H, aromatic), 4.95 (q, \( J = 6.3 \) Hz, 1H), 2.60 (s, 3H, SCH$_2$), 2.50 (s, 3H, SCH$_3$), 1.50 (d, \( J = 6.3 \) Hz, 3H, CH$_3$).

IR (Neat) : cm$^{-1}$ 1585.

MS : \( m/z \) 225 (M$^+$, 00%), 178 (20), 105 (100).

Analysis : C$_{11}$H$_{15}$NS$_2$. Calcd. : C, 58.66; H, 6.66; N, 6.22.

Found : C, 59.09; H, 7.06; N, 6.57.

(+)-N-α-Methylbenzyl carbonimidodithioic acid dimethyl ester:

Yield : 88%, Yellow coloured liquid.
bp : 121°C/4.4 mm.

Analysis : C$_{11}$H$_{15}$NS$_2$. Calcd. : C, 58.66; H, 6.66; N, 6.22.

Found : C, 58.84; H, 6.91; N, 6.55.

N-Furylmethyl carbonimidodithioic acid dimethyl ester (23f):

Yield : 75%, Light yellow coloured liquid.
bp : 100°C/4.65 mm.

$^1$H NMR (200 MHz) : \( \delta \) 7.30 (m, 1H), 6.30 (m, 2H$_3$), 4.55 (s, 2H, CH$_2$), 2.50 (s, 3H, SCH$_2$), 2.30 (s, 3H, SCH$_3$).

IR (CHCl$_3$) : cm$^{-1}$ 1595.

MS : \( m/z \) 201 (M$^+$, 05%), 153 (50), 81 (100).

Analysis : C$_{4}$H$_{11}$NOS$_2$. Calcd. : C, 47.76; H, 5.47; N, 6.96.

Found : C, 47.92; H, 5.73; N, 6.84.
Preparation of 1-substitutedamino-1-methylthio-2-nitroethylene (24a-f):

**General procedure:** Freshly activated zeolite RE(70%)NaY (0.5g) was added to the mixture of carbonimidodithioic acid dimethyl ester (10 mmol) and nitromethane (50 mmol) at room temperature and the suspension was refluxed with stirring for 24 h. The reaction mixture was then cooled to room temperature, the catalyst was filtered off and washed with CH₂Cl₂ (2 X 30 ml). The filtrate was concentrated at reduced pressure. The residue was taken in n-hexane and stirred for a few mins to precipitate the product. Final purification was carried out by column chromatography to give the pure product (24a-f) in 50-82% yield.

**1-Methylthio-1-n-propylamino-2-nitroethylene (24a):**

| Yield       | 76%, Colourless crystalline solid. |
| mp          | 63-64°C (EtOH). |
| ¹H NMR (80 MHz) | δ 10.60 (br, 1H, NH), 6.60 (s, 1H), 3.35 (q, 2H, NCH₂), 2.35 (s, 3H, SCH₂), 1.60 (m, 2H, CH₂), 1.00 (t, J = 6.72 Hz, 3H, CH₃). |
| IR (Nujol)  | cm⁻¹ 3400, 1570, 1470, 1380. |
| MS          | m/z 176 (M⁺, 70%), 129, 87, 74 (100). |
| Analysis    | C₆H₁₂N₂O₂S. Calcd. : C, 40.90; H, 6.82; N, 15.90. |
|             | Found : C, 41.43; H, 6.69; N, 16.22. |

**1-sec-Butylamino-1-methylthio-2-nitroethylene (24b):**

| Yield       | 82%, Colourless crystalline solid. |
| mp          | 116-118°C (EtOH). |
| ¹H NMR (90 MHz) | δ 10.50 (br, 1H, NH), 6.55 (s, 1H), 3.70 (m, 1H), 2.45 (s, 3H, SCH₂), 1.60 (m, 2H), 1.30 (d, J = 6.6 Hz, 3H, CH(CH₃)₂), 1.00 (t, J = 7.2 Hz, 3H, CH₂CH₃). |
| IR (Nujol)  | cm⁻¹ 3350-3450, 1560, 1470, 1330, 1230. |
| MS          | m/z 190 (M⁺, 30%), 135, 74 (100), 57. |
Analysis : C_{9}H_{16}N_{2}O_{2}S. Calcd. : C, 44.21; H, 7.36; N, 14.73.
Found : C, 44.32; H, 7.21; N, 14.57.

1-Cyclohexylamino-1-methylthio-2-nitroethylene (24c):

Yield : 75%, Colourless crystalline solid.
mp : 106°C (EtOH).
$^1$H NMR (80 MHz) : δ 10.50 (br, 1H, NH), 6.50 (s, 1H), 3.60 (m, 1H, NCH), 2.40 (s, 3H, SCH), 1.2-2.0 (br, 11H).
$^{13}$C NMR (50 MHz) : ppm 163.31, 106.13, 53.86, 32.93, 25.21, 24.32, 14.47.
IR (Nujol) : cm$^{-1}$ 3300, 1570, 1480, 1230.
MS : m/z 216 (M$^+$, 20%), 135 (100), 83, 55.
Analysis : C$_{7}$H$_{16}$N$_{2}$O$_{2}$S. Calcd. : C, 50.00; H, 7.40; N, 12.96.
Found : C, 50.21; H, 7.31; N, 13.11.

1-Benzylamino-1-methylthio-2-nitroethylene (24d):

Yield : 80%, Light yellow coloured solid.
mp : 104-105°C (EtOH).
$^1$H NMR (200 MHz) : δ 11.10 (br, 1H, NH), 7.40 (s, 5H, aromatic), 6.65 (s, 1H), 4.70 (d, J = 6.5 Hz, 2H, NCH$_2$), 2.40 (s, 3H, SCH$_2$).
IR (CHCl$_3$) : cm$^{-1}$ 3400, 1580, 1350.
MS : m/z 224 (M$^+$, 10%), 178, 130, 91 (100).
Analysis : C$_{16}$H$_{16}$N$_{2}$O$_{2}$S. Calcd. : C, 53.57; H, 5.35; N, 12.50.
Found : C, 53.61; H, 5.42; N, 12.22.
(S)-1-α-Methylbenzylamino-1-methylthio-2-nitroethylene (24e):

Yield : 52%, Light yellow coloured low melting solid.

**mp** : 44-45°C (EtOH).

**1H NMR (200 MHz)**

δ 10.95 (br, 1H, NH), 7.35 (m, 5H, aromatic), 6.60 (s, 1H), 4.95 (m, 1H), 2.40 (s, 3H, SCH₂), 1.70 (d, J = 7.7 Hz, 3H, CH₃).

**IR (CHCl₃)**

cm⁻¹ 3440, 1580, 1360.

**MS**

m/z 238 (M⁺, 5%), 191, 105 (100).

**Analysis**

C₁₁H₁₄N₂S₂ Calcd. : C, 55.46; H, 5.88; N, 11.76.

Found : C, 55.32; H, 5.92; N, 11.92.

(+)-1-α-Methylbenzylamino-1-methylthio-2-nitroethylene:

Yield : 50%, Light yellow coloured Crystalline solid.

**mp** : 119°C (EtOH).

**Analysis**

C₁₁H₁₄N₂S₂ Calcd. : C, 55.46; H, 5.88; N, 11.76.

Found : C, 55.32; H, 5.99; N, 11.97.

1-Furfurylamino-1-methylthio-2-nitroethylene (24f):

Yield : 78%.

**bp/mp** : Gum.

**1H NMR (90 MHz)**

δ 10.55 (br, 1H, NH), 7.40 (m, 1H), 6.55 (s, 1H), 6.30 (m, 2H), 4.65 (d, J = 5.9 Hz, 2H, NCH₂), 2.47 (s, 3H, SCH₂).

**IR (CHCl₃)**

cm⁻¹ 3550-3450, 1570, 1360.

**MS**

m/z 214 (M⁺, 10%), 168, 81 (100).

**Analysis**

C₉H₁₀N₂O₂S Calcd. : C, 44.85; H, 4.67; N, 13.08.

Found : C, 44.74; H, 4.79; N, 12.92.
Synthesis of 1-nitrocyclohexene (25):

This was prepared by the reported method. Mductor chloride dissolved in the stirring solution of aqueous sodium nitrite. To this pale green solution, cyclohexene was added slowly. This mixture was stirred vigorously at room temperature for 30 h. Nitro mercurial cyclohexane was filtered out. This solid was then dissolved in aqueous NaOH solution in dichloromethane and stirred for 10-15 minutes. The resulting mixture was acidified with 1N HCl and filtered through a clogged funnel with celite pad. The filtrate was extracted with CH₂Cl₂, dried over Na₂SO₄ and concentrated at reduced pressure. Further purified by distillation (b.p. 61-62°C/1mm) to get pure light yellow coloured 1-nitrocyclohexene in 77.68% yield.

Synthesis of 1-nitrocyclohexene-3-one-oxime (27):

A) By using zeolite catalyst:

Zeolite catalyst RE(70%)NaY was added at room temperature to the mixture of 1-nitrocyclohexene (2 mmol) and N-methyl carbonimidodithioic acid dimethyl ester (1 mmol). This mixture was heated at 100°C for 24 h. The reaction mixture was cooled and the catalyst was filtered out. Filtrate was concentrated and purified by column chromatography to get solid in 15% yield, m.p. 110-112°C (27).

B) By known method:

Isoamyl nitrite (.05 mol) was added dropwise to a solution of the 1-nitrocyclohexene (0.05 moles) and potassium carbonate (.05 mol) in 40 CC of DMSO at 20-25°C. The resulting mixture was stirred at room temperature for 2h. Then the solution was poured into 150 CC of water and extracted with ether. The ether layer was dried over anhydrous sodium sulfate. Evaporation of ether at reduced pressure gave the solid product oxime in 54% yield. Crystalized in CHCl₃, CCl₄ mixture. m.p. 115°C.
1-nitrocyclohexene-3-one-oxime (27):

Yield : Method-A 15%; Method-B 54%; colorless crystalline solid.

H NMR (300 MHz) : δ 8.25 (t, 1H, NOH), 7.45 (t, 1H, =CH), 2.85 (tt, 2H, CH₂), 2.70 (t, 2H, CH₂), 1.95 (m, 2H, CH₂).

IR (Liq. Film) : cm⁻¹ 3300, 1700, 1570, 1500, 1300.

MS : m/z 156 (M⁺, 40%), 80, 65, 53 (100).

Analysis : C₆H₈N₂Ov Calcd. : C, 46.15; H, 5.12; N, 17.94.

Found : C, 46.28; H, 5.22; N, 17.81.

Synthesis of isoamyl nitrite (28):

To a cooled solution of sodium nitrite (2.5 mmol) in water (75 ml) at 0°C, a pre-cooled solution of conc. sulfuric acid (1.25 mmol), water and isoamyl alcohol [mixture prepared by the slow addition of sulfuric acid to water then isoamyl alcohol (2.5 moles) at 0°C] was added dropwise, for a period of 2 h. The resulting mixture was allowed to stand in the ice-salt bath for 15-20 mins, sodium sulfate was filtered off. The filtrate was washed with NaHCO₃ solution and extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate and concentrated at reduced pressure to get light yellow coloured liquid isoamyl nitrite (28).
3.7 References:


