Tetrahedron Vol 47, No 10/11, pp 2027-2040, 1991
Printed in Great Britain

0040-4020/91 $3 00+00

REACTION OF 2-NITRO AND 3-NITRO-2-CYCLOHEXENONE ACETALS: PREPARATION OF USEFUL INTERMEDIATES[1,§]

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(*Received in UK 21 November* 1990)

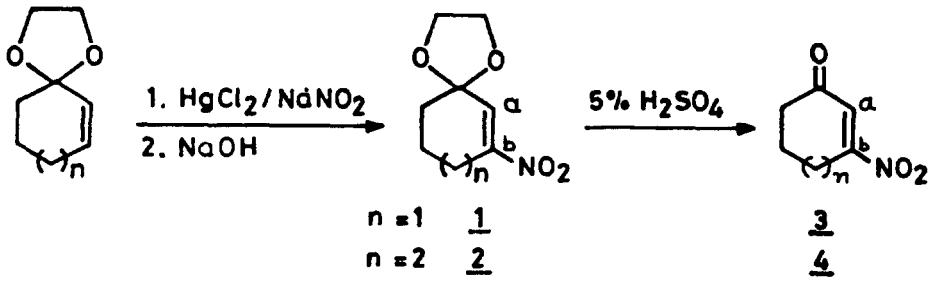
Abstract: *Preparation of 2-nitro-2-cyclohexenone acetal 31 starting from 2-nitrocyclohexanone acetal 29 has been reported for the first time. This compound as well as 3-nitro-2-cyclohexenone acetal 1, whose synthesis has been reported by us earlier, react with a variety of nucleophiles to form highly functionalised intermediates. One of them viz. 21 is converted into a bicyclic α-methylene-γ-lactone 24 using radical chemistry.*

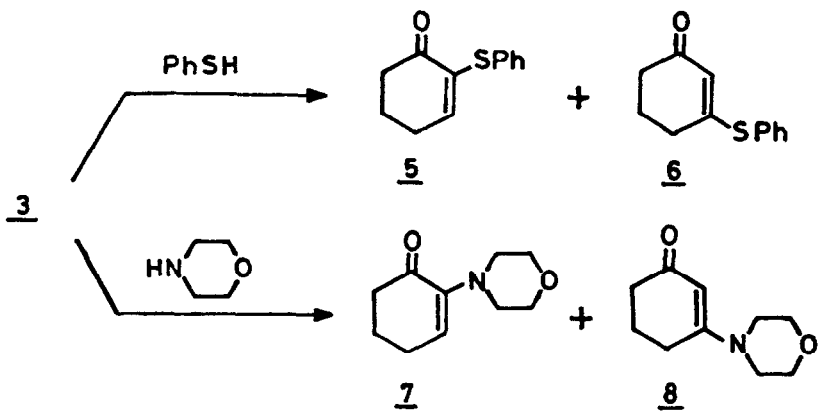
Recently we have reported[2] an easy approach to the synthesis of 3-nitro-2-cyclohexenone **3** and 3-nitro-2-cycloheptenone **4** by using nitromercuration[3] chemistry on the corresponding olefinic acetals. In the process we have synthesised two new acetals viz. **1** and **2** (scheme 1) in addition to the new nitroenone **4**. In this paper we wish to report the preparation of a number of interesting synthetic intermediates from the reactions of **1** with various nucleophiles. Besides this, we also wish to report the first synthesis of a new compound viz. 2-nitro-2-cyclohexenone acetal **31**. A few useful reactions of this compound have also been reported.

Corey and Estreicher[4] reported the synthesis of **3** and showed its usefulness in Diels-Alder chemistry where regiochemistry in the product was found to be of high degree. It became especially interesting to us to find out the behaviour of **3** as a Michael acceptor since two electron withdrawing groups (>C=O and $-NO_2$) were at the two ends of a double bond. We reported[2] a simpler synthesis of **3** avoiding the dangerous and difficult preparation of CF_3CO_3H and 90% H_2O_2. In order to examine the behaviour of **3** as a Michael acceptor it was reacted with thiophenol under different conditions. Varying amounts of the products **5** and **6** were obtained under these conditions. Thus, in the absence of a base, thiophenol reacted with **3** in benzene to give only **6** in 76% yield. On the other hand in the presence of bases such as morpholine or piperidine, a mixture of two products **5** and **6** were obtained in 35:65 and 40:60 ratio respectively. On the other hand when triethylamine was used as a base, product **5** was formed exclusively in 74% yield. With morpholine as a nucleophile products **7** and **8** were found to form in 48% and 16% yields respectively. Formation of these adducts clearly suggests that **3** is capable

§ Dedicated to Prof. E. Wenkert on the occasion of his 65th birthday.

of being attacked by thiophenol at both the carbons 'a' and 'b' with the loss of NO_2 group and the regioselectivity is dependent upon the conditions employed.In view of the fact that compounds of the type **5** and **6** are shown to be versatile intermediates by Trost[5] and Danishefsky[6], the present methods could be useful in their preparation.

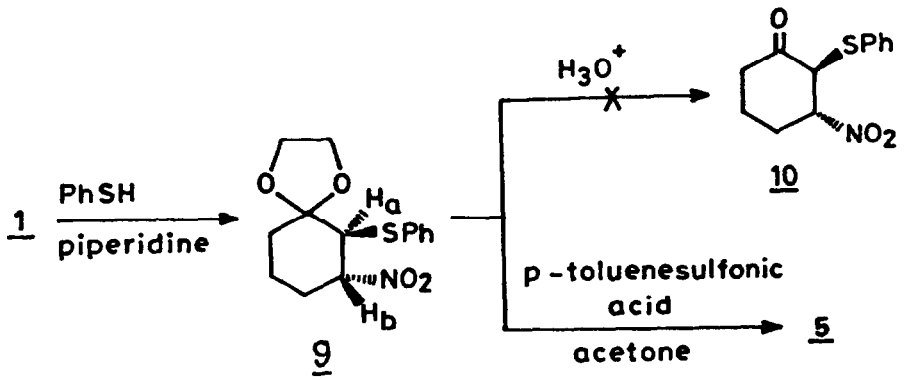




Scheme 1

In order to assess the reactivity of carbon nucleophiles with **3**, diethyl malonate was reacted with it in the presence of a catalytic amount of NaH. This reaction did not yield any product even after a prolonged time. On the other hand when one equivalent of NaH was used, even at -10°c to 0°c, a complex mixture of products was formed. Similar observations were made when ethyl(phenylthio)acetate was used instead of diethyl malonate.Failure of reactions with carbon nucleophiles and the fact that hetero nucleophiles react with **3** with the loss of the nitro group prompted us to look **1** as an alternate and a milder Michael acceptor.Retention of the nitro group is important as this could be of further utility for functional group transformations. Thus, when **1** was treated with thiophenol in the presence of catalytic amount of piperidine in refluxing benzene the corresponding adduct **9** was obtained in 78% yield. This clearly showed that **1** is a better Michael

acceptor than 3. Also the nucleophile attacked only at C-a. Compound 9 is found to possess trans configuration as is evident on the basis of its ^{1}H NMR spectral analysis. Thus, H_a appeared as a doublet at δ3.5 with J=12 Hz, a typical value for vicinal diaxial coupling. On the other hand, as expected, H_b appeared as ddd at δ (4.3-4.8) with J=4 Hz and 12 Hz due to two diaxial and one axial equatorial interactions.



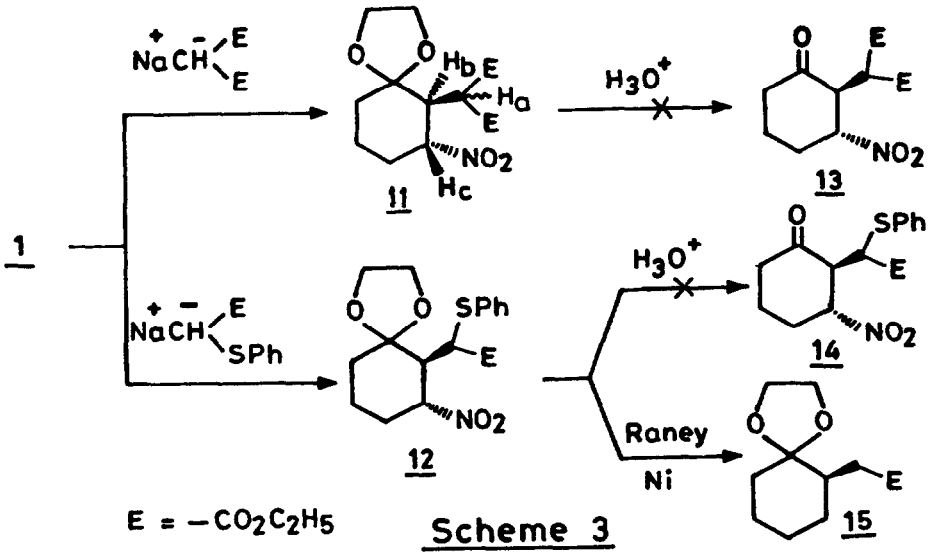
Scheme 2

Hydrolysis of the acetal function of 9, however, did not yield 10 under a variety of conditions that were employed. Thus, it was found unchanged under acid hydrolysis conditions[7]. With p-toluenesulphonic acid in acetone (transacetalisation conditions[8]), although the hydrolysis did occur, elimination of the nitro group also took place to give 5. Recently it has been reported that hydrolysis of acetal with NaI-BF_3.Et_2O[9] (or with NaI-$ClSiMe_3$[10]) is a non aqueous alternative for deprotecting the acetals. Using these conditions also 9 again yielded only 5 as the major product.

To explore the reactivity of 1 towards carbon nucleophiles it was reacted with the anions of diethyl malonate and ethyl (phenylthio) acetate separately. The corresponding Michael adducts 11 and 12 were obtained in 56% and 61% yields respectively. As found in the case of compound 9, ^{1}H NMR analysis of compound 11 and 12 also revealed that they possess trans stereochemistry. For example the proton H_b in 11 appeared as a dd at δ3.02 with J=12 Hz and 4.5 Hz whereas H_c appeared as a ddd at δ 5.1-5.4 with J=12 Hz and 4.5 Hz.

Treatment of 11 with aqueous alkali followed by acid catalysed decarboxylation gave a complex mixture of products from which it was difficult to obtain any pure product.Also the acid catalysed hydrolysis of 11 to obtain 13 was not clean. These results clearly indicate that compounds of the type 11 and 12 are both acid and base sensitive. Even with NaI-BF_3.Et_2O compound

12 did not give any desired product. Although it underwent desulphurisation with Raney Ni, there was also a loss of the nitro group to obtain 15 in 50% yield.However,when 12 was converted into its sulphoxide 16 and heated a single

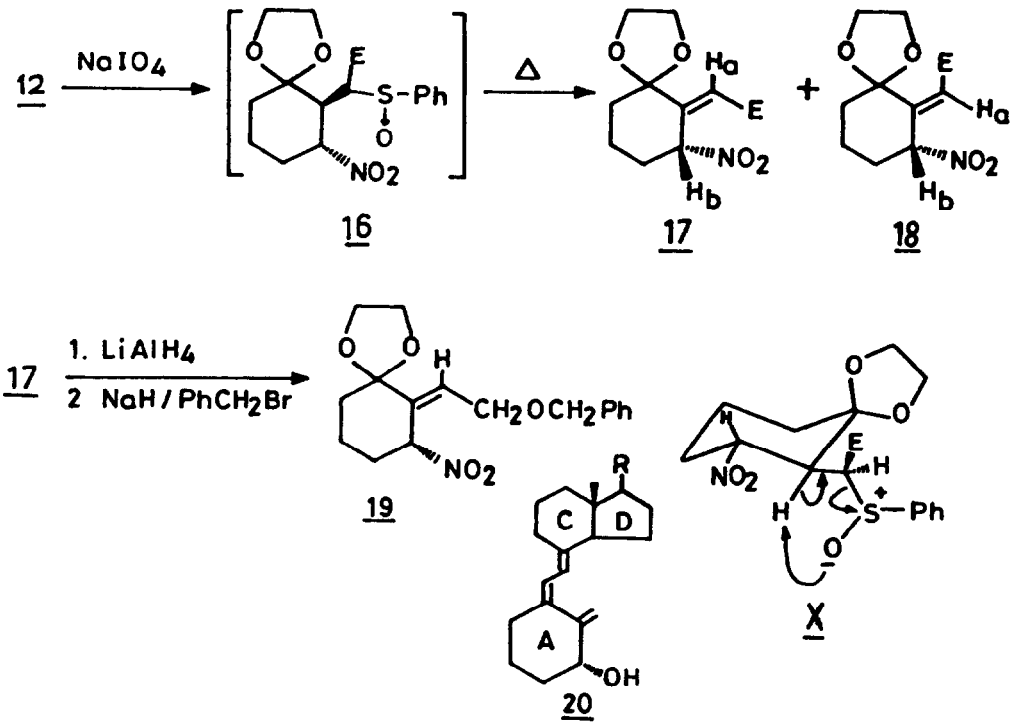


Scheme 3

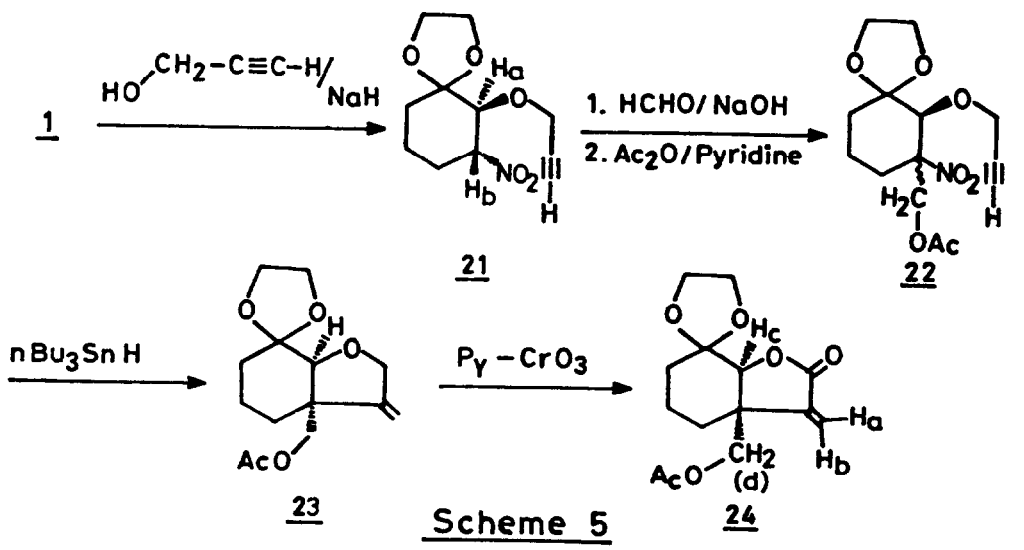
compound was formed in 81% yield whose ^{1}H NMR spectrum showed absorption at δ6.73 as a multiplet due to H_b, at δ6.35 as a doublet (J=1.5 Hz) due to H_a. The ethyl ester showed a triplet for $-CH_3$ at δ1.3 and quartet for $-OCH_2-$ at δ4.25 clearly indicating that only one of the stereoisomers 17 or 18 was formed. From the inspection of its model the most stable conformation,in which the transition state required for the cis elimination of a molecule of sulphenic acid is possible, appears to be X (scheme 4). This conformation favours the formation of 17.However more analysis is needed to confirm the stereochemistry. Reduction of this compound with $LiAlH_4$ followed by benzylation of the alcohols obtained thereby gave 19 which, with its potential carbonyls from the nitro and acetal groups,provides entry to 'A' ring of vitamin 'D_3' metabolites skeleton 20 or its derivatives.

Reaction of propargyl alcohol under basic conditions with 1 gave 21 which ,in turn, was converted into α-methylene-γ-lactone 24 through a series of reactions[12] as shown in scheme 5. Thus hydroxymethylation of 21 with formaldehyde followed by acetylation gave 22 in excellent yield which upon treatment with n-bu_3SnH resulted in the formation of 23. Finally, oxidation of 23 with pyridine-CrO_3 gave the α-methylene lactone 24.

The stereochemistry in 21 is expected to be trans as is found in the earlier cases such as 9, 11 and 12. In the ^{1}H NMR spectrum in this case,however, the protons H_a and H_b did not separate out to be properly assigned.



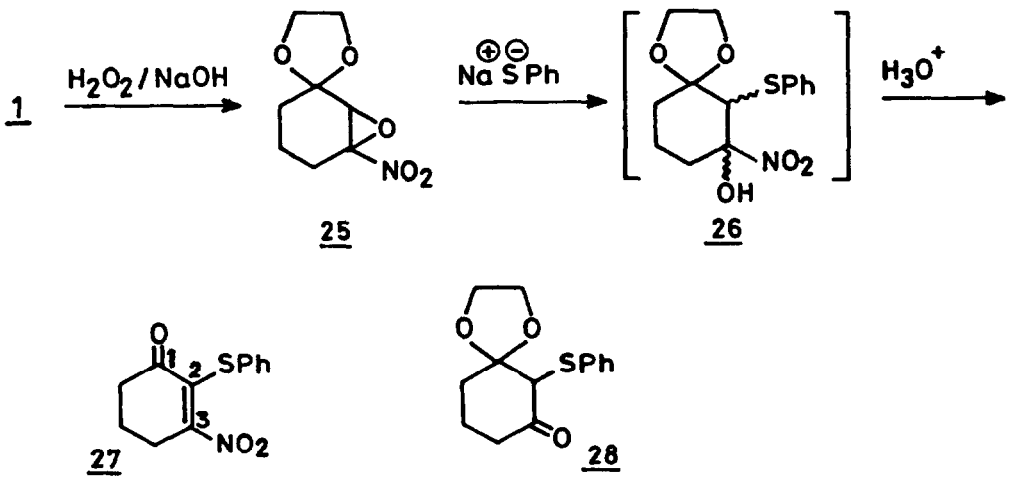
Scheme 4



Scheme 5

Compound **24**, on the other hand, typically showed signals at δ 6.40 as a singlet for H_a, at δ 5.55 as a singlet for H_b, at δ 4.4 as a singlet for H_c, and at δ 3.85-4.3 as a multiplet for H_d and acetal methylenes. On the basis of these spectral values it is difficult to predict if the stereochemistry at the the junction is cis or trans. Literature reports[13], however, indicate that such kinds of cyclisations yield only the cis products. It is ,therefore, likely that **24** possesses cis geometry at the junction.

Epoxidation of nitroolefins is not a very well studied[14] reaction. However recently we have reported the epoxidation[15] of several cyclic and some acyclic nitroolefins and studied their reactions. It was thus of interest to us to prepare α-nitroepoxide **25** from **1** which indeed was obtained in 95% yield. Its IR spectrum showed an absorption at 1550 cm^{-1} clearly indicating it to be a saturated nitro group. Reaction of **25** with Na^+S^-Ph was found to be rather interesting. On the basis of earlier reports[14] it was expected that **25** gave **28** by the loss of nitro group as shown in scheme 6.However it first gave

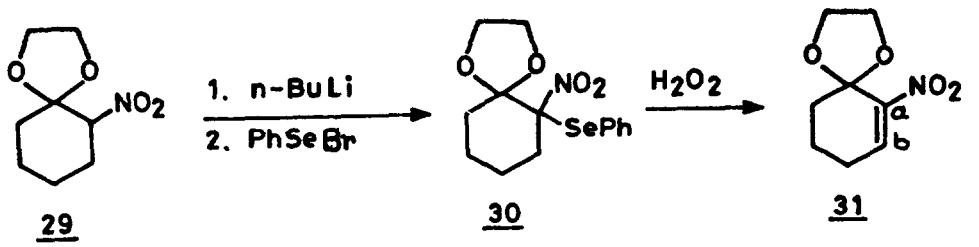


Scheme6

26, as revealed by the IR and ^1H NMR spectral data but it slowly got converted into **27** upon standing or rapidly upon treatment with protic acid.

Prompted by the usefulness of **1** in developing important synthetic intermediates, we explored the possibility of preparing another nitro olefinic acetal i.e. **31** in which the nitro function is at C-2. Thus structural variations are possible with **1** and **31**. With this view the nitro acetal **29** was treated with n-BuLi followed by PhSeBr to obtain **30** which upon further treatment with 30% H_2O_2 gave **31** in 51% yield. Its ^1H NMR spectrum showed a typical multiplet for the olefinic protons at δ7.2. As expected, in its IR spectrum the nitro group appeared as a strong absorption band at 1510 cm^{-1}.

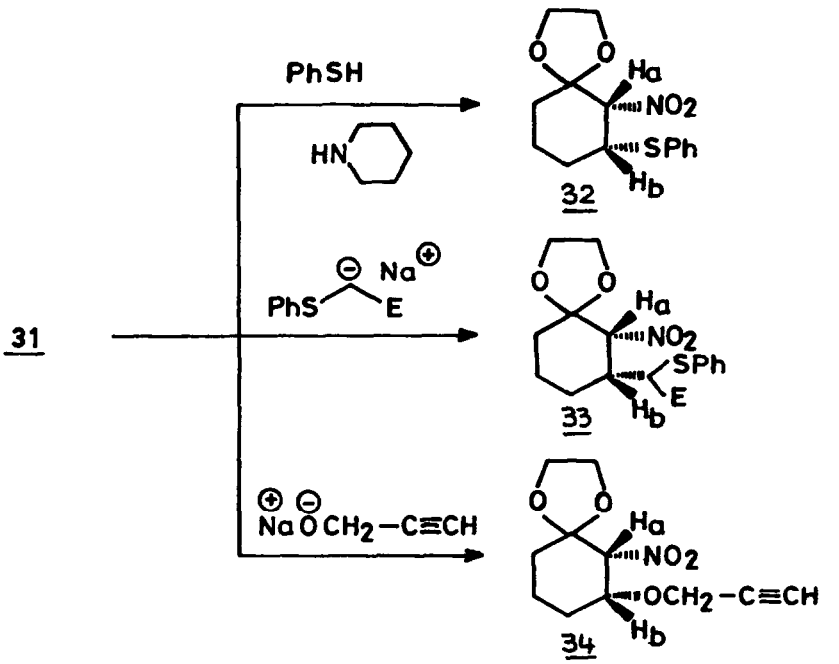
Further, the mass spectrum and the microanlytical data confirmed its molecular weight. To our knowledge this compound is not known so far.



29 30 31

Scheme 7

Compound **31**, as expected, underwent Michael additions with PhSH, $PhSCH_2CO_2Et$ and $HC{\equiv}CH_2OH$ under basic conditions to give adducts **32**, **33** and **34** in 88, 53 and 85% yields respectively (scheme 8).

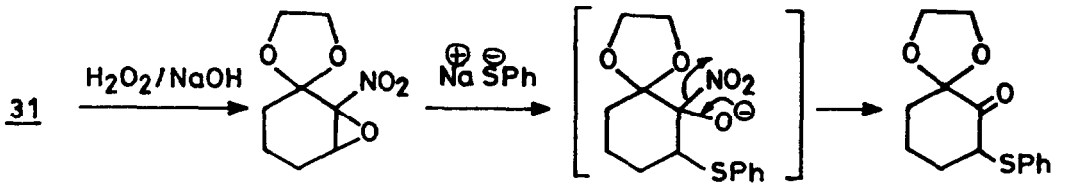


Scheme 8

Their spectral data (cf. experimental section) were in complete agreement with the structures assigned to them. Thus, ^1H NMR spectral analysis of these adducts indicated that these are cis products in contrast to similar adducts **9**, **13** and **21** formed with **1** which were trans. Thus, for example

in **32**, H_a appeared as a doublet at δ 4.48 with J=5 Hz indicating that H_a and H_b experience equatorial axial coupling. Proton H_b, on the other hand, appeared as a ddd at δ 3.2-3.51 with J=3 Hz,5 Hz and 16 Hz. Likewise examination of the ^{1}H NMR spectra of **33** and **34** also revealed that they are cis compounds as in each case the coupling constant value for H_a-H_b corresponded to axial-equatorial coupling.

Compound **31** also underwent epoxidation with H_2O_2/NaOH to give **35** whose reaction with PhS^-Na^+, in sharp contrast to the reaction of **25** with PhS^-Na^+, gave **37**, perhaps via the sequence of steps as shown in scheme **9**. It is rather surprising that the intermediate **36**, in contrast to **26** (scheme 6) undergoes decomposition to give **37** rather than dehydration. All these intermediates



Scheme 9

could be expected to be useful in organic synthesis. Specific applications of these compounds are being explored and will form the subject of future publications.

Experimental

General Methods: ^{1}H NMR spectra were recorded on Varian EM 390,Jeol PMX 60 and Bruker WP 80 spectrometers with $(CH_3)_4Si$ as internal standard. IR spectra were recorded on Perkin-Elmer 580 and 1320 spectrophotometers by using samples as neat liquids or in $CHCl_3$. Mass spectra were recorded at 70 ev on a Jeol JMS-300 D mass spectrometer. All the chromatographic separations were done by using TLC grade silica gel obtained from E.Merck. Benzene was distilled from CaH_2. Methylene chloride was distilled from P_2O_5 prior to use. Actonitrile was also distilled from P_2O_5 and stored over molecular sieves (4°A).

2- and 3-Phenylthio-2-cyclohexenone 5 and 6: A mixture of **3** (141 mg, 1 mmol) and thiophenol (118 mg, 1 mmol) in dry benzene with or without base was stirred under nitrogen atmosphere at room temperature for an appropriate time (see below). The reaction mixture was diluted with water and extracted with ether (3 x 15 ml). It was then dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a crude product which was purified by preparative layer chromatgraphy (PLC) (eluent:benzene). Compound **5**: IR (neat) 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ7.61-7.15 (m, 5H), 6.25 (t, J= 4.5 Hz, 1H), 2.62-1.81 (m, 6H). Compound **6**: IR(neat)

1660 (s) cm^{-1}; ^1H NMR ($CDCl_3$):δ7.5-6.9 (m, 5H), 5.35 (s, 1H), 2.64-1.64 (m, 6H); mass spectrum, m/e 204.

Base	Reaction Time (hr)	% of 5	% of 6	Overall Yield (%)
-	45	-	100	76
morpholine	12	35	65	70
piperidine	14	40	60	71
triethylamine	8	100	-	74

2-N-Morpholino-2-cyclohexenone 7 and 8: These compounds were prepared in analogy to **5** and **6** from **3** (50 mg, 0.35 mmol) and morpholine (40 mg, 0.45 mmol). Yield: 30 mg (48%) of **7** and 10 mg (16%) of **8**.Compound **7**: IR (neat) 1670 cm^{-1} ; ^1H NMR ($CDCl_3$) : δ5.86 (t, J= 4.5 Hz, 1H), 3.6-3.2 (m, 4H), 2.9-2.63 (m, 4H), 2.7-2.6 (m, 4H), 2.1-1.8 (m, 2H); mass spectrum, m/e 181; Anal. Calcd. for $C_{10}H_{15}NO_2$: C,64.86; H,8.11; N,7.57. Found: C,64.79; H,8.19; N,7.5. Compound **8**: IR (neat) 1670 cm^{-1}; ^1H NMR ($CDCl_3$):δ5.41 (s, 1H), 3.92-3.61 (m, 4H),2.98-2.61 (m, 4H),2.63 -2.21 (m, 4H), 2.1-1.8 (m, 2H); mass spectrum, m/e 181.

trans-3-Nitro-2-phenylthiocyclohexanone acetal 9: As above from **1** (925 mg, 5 mmol), thiophenol (660 mg, 6 mmol) and a drop of piperidine compound **9** was prepared. Yield: 1.1 gm (78%), m.p. 114°c (pet.ether:chloroform).IR (neat) 1545 cm^{-1}; ^1H NMR (CCl_4):δ7.5-7.1 (m, 5H), 4.8-4.3 (ddd, J= 12 Hz, 4 Hz, 1H), 4.3-3.9(m, 4H), 3.5 (d, J= 12 Hz, 1H), 2.5-1.25 (m, 6H); mass spectrum,m/e 295; Anal. Calcd. for $C_{14}H_{17}NSO_2$: C,56.95; H,5.74; N,4.75; S,10.85. Found: C,56.90; H,5.85; N,4.80 ; S,10.81.

Reaction of 3-nitro-2-cyclohexenone acetal with diethyl malonate: To a solution of sodium ethoxide (54 mg, 1 mmol) in ethanol was added diethyl malonate (160 mg, 1 mmol) in ethanol at 0°c. The resultant mixture was stirred at room temperature for 30 min. Compound **1** (185 mg, 1 mmol) in ethanol was added dropwise at 0°c and the stirring continued at room temperature for 2 hr. Ethanol was then removed under vacuum and the residue diluted with water (5 ml), neutralised with satd. NH_4Cl solution and extracted with CH_2Cl_2 (3 x 15 ml).Work up in usual manner gave 240 mg of crude product which was purified by PLC (eluent: 10% acetone-benzene) to obtain pure **11**, yield: 193 mg (56%). IR ($CHCl_3$) 1725,1550 cm^{-1}; ^1H NMR (CCl_4):δ5.31-5.04 (m, 1H), 4.32-3.71 (m, 9H), 3.03 (dd,J= 12 Hz, 4 Hz, 1H), 2.70-1.41 (m, 6H), 1.3 (t, 6H); mass spectrum,m/e 299; Anal.Calc. for $C_{15}H_{23}NO_8$: C,52.17; H,6.67; N,4.06. Found:C,52.11; H,6.72; N,4.12.

Reaction of 3-nitro-2-cyclohexenone acetal with ethyl(phenylthio) actate: To a suspension of NaH (64 mg, 1.3 mmol) in THF was added ethyl(phenylthio) acetate (225 mg, 1.3 mmol) in THF at 0°c and stirred at room temperature for 30 min. when **1** (185 mg, 1 mmol) in THF was added dropwise. Stirring was continued at room temperature for additional 2 hr. It was then neutralised with satd. aq. NH_4Cl and extracted with ether (3 x 15 ml). Work up as described above gave

390 mg of crude product which was purified by chromatography (eluent: benzene -chloroform) to obtain pure **12**, yield: 234 mg (61%). IR (neat) 1725, 1545 cm^{-1}; ^1H NMR($CDCl_3$ + CCl_4):δ7.72-7.21 (m, 5H), 5.65-5.25(ddd, J= 12 Hz, 4.5 Hz, 1H),4.45 -3.85 (m, 6H), 3.75 (d, J=4.5 Hz, 1H), 3.35 (dd, J= 12 Hz, 4.5 Hz, 1H), 2.7-1.5(m, 6H), 1.25 (t, 3H); mass spectrum, m/e 381; Anal. Calcd. for $C_{18}H_{23}NSO_6$: C,56.69; H,6.04; N,3.67; S,8.40. Found: C,56.64; H,6.10; N,3.75; S,8.51.

Reaction of 3-nitro-2(α-carbethoxy,α-phenylthiomethyl)cyclohexanone acetal 12 with Raney nickel: To a suspension of Raney nickel (900 mg) in dry ethanol was added **12** (285 mg, 0.75 mmol) and the resultant mixture was refluxed for 3 hr. The reaction mixture was then cooled and filtered through a pad of celite. Evaporation of the solvent gave 180 mg of crude product which was purified by PLC to obtain pure **15**, yield: 82 mg (50%). IR($CHCl_3$) 1725 cm^{-1}; ^1H NMR ($CDCl_3$): δ4.3-3.7 (m, 6H), 2.8-1.65 (m, 11H), 1.25 (t, 3H); mass spectrum, m/e 228; Anal. Calcd. for $C_{12}H_{20}O_4$: C,63.43; H,8.38: Found: C,63.49; H,8.31.

Oxidative elimination of 12: To a suspension of sodium metaperiodate (53 mg, 0.25 mmol) in 4 ml of 1:1 mixture of water-methanol was added **12** (95 mg, 0.25 mmol) at 0°c and stirred for an additional 12 hr at 0°c and 5 hr at room temperature. After filtration the filtrate was evaporated under reduced pressure and the residue extracted with chloroform (3 x 15 ml) to give 100 mg of the crude product. Usual work up gave pure sulphoxide **16**, yield 90 mg (98%). Without purification sulphoxide **16** (200 mg, 0.5 mmol) in anhydrous benzene (5 ml) was refluxed under nitrogen atmosphere for 9 hr. The reaction mixture upon work up gave a crude product which was purified by PLC(eluent:benzene), yield: 110 mg(82%). IR($CHCl_3$) 1710, 1550 cm^{-1}; ^1H NMR ($CDCl_3$):δ6.8-6.52 (m, 1H), 6.35 (d, J= 1.5 Hz, 1H), 4.35-3.6 (m, 6H), 2.7-1.8 (m, 6H), 1.3 (t, 3H); mass spectrum, m/e 271; Anal. Calcd. for $C_{12}H_{17}NO_6$: C,53.13; H,6.27; N,5.17. Found: C,53.03 ; H,6.22; N,5.20.

Preparation of compound 19: To a suspension of $LiAlH_4$ (40 mg, 0.8 mmol) in dry ether (5 ml) was added compound **17** (360 mg, 1.2 mmol) in ether at 10°c and the resultant mixture stirred at room temperature for 10 hr. Excess of $LiAlH_4$ was then destroyed by satd. NH_4Cl solution. The ether extract was dried over anhydrous Na_2SO_4. Evaporation of the solvent gave 292 mg of the crude product which was purified by PLC (eluent: 10% acetone-benzene), yield: 128 mg (42%). The purified alcohol (110 mg, 0.5 mmol) was then added to a suspension of NaH (48 mg, 0.5 mmol) in dry THF (2 ml) and the resultant mixture stirred at room temperature for 30 min. Benzyl bromide (86 mg, 0.5 mmol) at 0°c was added to the above mixture and further stirred at room temperature for 20 hr. It was then diluted with water (5 ml) and extracted with ether (3 x 15 ml). The combined organic layer upon further usual work up gave 140 mg of crude product which was purified by PLC, yield: 92 mg (60%). IR (neat) 1550 cm^{-1}; ^1H NMR($CDCl_3$) : δ7.5-7.2 (m, 5H), 6.8 (m, 1H), 5.28 (m, 1H), 4.5-3.6 (m, 8H), 2.9-1.4 (m, 6H);

mass spectrum, m/e 212; Anal. Calcd. for $C_{17}H_{21}NO_5$: C,63.95; H,6.58; N,4.39. Found: C,63.64; H,6.23; N,4.61.

3-Nitro-2-propargyloxycyclohexanone acetal 21: To a suspension of NaH (300 mg, 6 mmol) in dry THF at 0°c and the resultant mixture stirred at 0-10°c for 1 hr. Compound **1** (925 mg, 5 mmol) in THF was added dropwise at -10°c to the above mixture and stirring continued for another 30 min. The reaction mixture on work up gave a product which was purified by chromatography (SiO_2), yield: 1 gm (83%). IR (neat) 3280, 2110, 1540, 1370 cm^{-1}; ^1H NMR (CCl_4): δ 4.95-3.85(m,8H), 2.35 (s, 1H), 2.25-1.3 (m, 6H); mass spectrum, m/e 195; Anal. Calcd. for $C_{11}H_{15}NO_5$: C,54.77; H,6.22; N,5.81. Found: C,54.70; H,6.28; N,5.76.

2-Propargyloxy-3-acetoxymethyl-3-nitrocyclohexanone acetal 22: A mixture of **21** (480 mg, 2 mmol), 37% HCHO (75 mg, 2.5 mmol) and NaOH (13 mg) in isopropanol (10 ml) was stirred at room temperature for 20 hr. The reaction mixture was then diluted with water (5 ml) and extracted with ethyl acetate (3 x 15 ml). Further work up gave 540 mg of the crude product which was stirred at room temperature with acetic anhydride (0.38 ml, 4 mmol) in pyridine (1 ml) for 14 hr. It was then diluted with water and extracted with CH_2Cl_2 (3 x 15 ml).Further work up in usual manner gave a crude product which was purified by chromatography (SiO_2), yield: 480 mg (75%). IR (neat) 3280, 2110, 1740, 1540 cm^{-1}; ^1H NMR (CCl_4): δ 4.65-4.45 (m, 1H), 4.45-4.25 (m, 2H), 4.25-3.8 (m, 6H), 2.05 (s, 3H),2.75 -1.4 (m, 6H); mass spectrum, m/e 267; Anal. Calcd. for $C_{14}H_{19}NO_7$: C,53.67; H,6.07 ; N,4.47. Found: C, 53.75; H,6.00; N,4.39.

Preparation of compound 23: A mixture of **22** (185 mg, 0.59 mmol), n-bu_3SnH(224mg , 0.77 mmol) and AIBN (29 mg, 0.17 mmol) in benzene (4 ml) was refluxed under nitrogen atmosphere for 5 hr. Solvent was evaporated and the residue purified by chromatography (SiO_2) (eluent: pet.ether: ether= 80:20) to obtain a thick oil, yield: 80 mg (51%). IR (neat) 1735 cm^{-1}; ^1H NMR (CCl_4):δ4.95-4.8 (m, 2H), 4.4(s, 2H) , 4.1-3.8 (m, 6H), 3.7 (s, 1H), 2.0 (s, 3H), 1.85-1.15 (m, 6H); mass spectrum, m/e 195; Anal.Calcd. for $C_{14}H_{20}O_5$: C,62.68; H,7.46. Found: C,62.72; H,7.50.

Oxidation of 23 with pyridine-chromium trioxide: A stirred mixture of pyridine (0.45 ml) in CH_2Cl_2 (5 ml) was treated with CrO_3 (450 mg, 4.5 mmol) and stirring continued for 20 min. at 20°c. Compound **23** (60 mg, 0.22 mmol) in CH_2Cl_2 (1 ml) was added to the above mixture and refluxed for 1 hr. After cooling it was treated with satd. $NaHCO_3$ solution (20 ml) and extracted with CH_2Cl_2 (3 x 25 ml). Work up as described earlier gave a crude product which was purified by PLC (eluent: benzene-acetone= 95:5),yield: 40 mg (65%). IR (neat) 1770, 1740 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.4 (s, 1H), 5.55 (s, 1H), 4.4 (s, 1H), 4.3-3.85 (m, 6H),2.05 (s, 3H),2.0-1.55 (m, 6H); mass spectrum, m/e 282; Anal. Calcd. for $C_{14}H_{18}O_6$: C, 59.53; H,6.38. Found: C,59.52; H,6.43.

3-Nitro-2,3-epoxycyclohexane-1-one acetal 25: To a stirred solution of **1** (185 mg, 1 mmol) in methanol containing 30% H_2O_2 (0.23 ml, 2 mmol) was added 2N NaOH solution (0.25 ml, 0.5 mmol) at 0°c. The stirring was continued for addi-

tional 10 min. (a turbidity developed during this time). The reaction mixture was then extracted with ether (3 x 15 ml) and further worked up to obtain a crude product which was purified by PLC, yield: 190 mg (95%). IR (neat) 1550, 1350 cm^{-1}; ^1H NMR (CCl_4): δ 4.06-3.50 (m, 4H), 3.26 (s, 1H), 2.88-1.16 (m, 6H); mass spectrum, m/e 201; Anal. Calcd. for $C_8H_{11}NO_5$: C,47.76; H,5.47; N,6.96. Found: C, 47.81; H,5.43; N,6.89.

3-Nitro-2-phenylthio-2-cyclohexenone 27: A stirred solution of Na^+S^-Ph(prepared in-situ from thiophenol ,110 mg and Na, 23 mg in CH_3OH at 0°c) in methanol was added compound **25** (200 mg, 1 mmol) at 0°c and the resultant mixture was stirred at room temperature for further 2 hr. The reaction mixture was then poured on cold water, neutralised with satd. NH_4Cl solution and extracted with CH_2Cl_2 (3 x 15 ml). Usual work up gave the hydroxy acetal which was treated with 5% H_2SO_4 (2 ml) and stirred for 30 min. at room temperature. The reaction mixture was then diluted with water (5 ml) and extracted with ether (3 x 15 ml). It gave a crude product after evaporating ether which was purified by PLC, yield: 178 mg (73%). IR neat) 1650, 1550 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.2 (br. s,5H), 2.9-2.4 (m, 4H), 2.25-1.9 (m, 2H); mass spectrum, m/e 220; Anal. Calcd. for $C_{12}H_{11}NSO_3$: C,57.83; H,4.42; N,5.62; S,12.85. Found: C,57.79; H,4.50; N,5.70;S, 12.88.

2-Nitro-2-cyclohexenone acetal 31: To a stirred solution of **29** (374 mg, 2 mmol) in THF (5 ml) at 0°c was added n-BuLi(1.75 ml, 15% solution in hexane, 4 mmol). After stirring for 30 min., a solution of PhSeBr in anhydrous THF prepared from PhSeSePh (662 mg, 4.2 mmol) and Br_2 (0.1 ml, 4.2 mmol) was added during 10 min. After 1 hr., 30% H_2O_2 (2 ml) was added and the resultant mixture was stired at room temperature for 4 hr. It was then diluted with water (20 ml) and extracted with ether (3 x 25 ml). Its further work up gave a crude product which was purified by chromatography (eluent: pet. ether:ether= 90:10), yield: 190 mg (51%). IR (neat) 1510, 1340 cm^{-1}; ^1H NMR (CCl_4): δ 7.35-7.10 (m, 1H), 4.35-3.85 (m, 4H), 2.55-2.2 (m, 2H), 2.1-1.7 (m, 4H); mass spectrum, m/e 185; Anal. Cal. for $C_8H_{11}NO_4$: C,51.89; H,5.95; N,7.57. Found: C,51.93; H,6.02; N,7.51.

2-Nitro-3-phenylthiocyclohexanone acetal 32: To a mixture of **31** (50 mg, 0.27 mmol) in CH_2Cl_2 (2 ml) at 0°c under nitrogen atmosphere was added a drop of piperidine and stirred for 1 hr. Its further work up in the usual manner gave a crude product which was purified by PLC to obtain a thick oil,yield: 70 mg (88%). IR (neat) 1550, 1370 cm^{-1}; ^1H NMR (CCl_4): δ 7.7-7.25 (m, 5H), 4.48 (d, J= 5 Hz, 1H), 4.15-3.8 (m, 4H), 3.51-3.2 (m, 1H), 2.4-1.35 (m, 6H); mass spectrum, m/e 295; Anal. Calcd. for $C_{14}H_{17}NSO_2$: C,56.95; H,5.76; N,4.75; S,10.85. Found: C, 56.98; H,5.82; N,4.70; S,10.87.

2-Nitro-3(α-carbethoxy,α-phenylthiomethyl)cyclohexanone acetal 33: To a suspension of NaH (18 mg, 50% suspension in oil, 0.37 mmol) inTHF at 0°c was added ethyl(phenylthio)acetate (64 mg, 0.33 mmol). The resultant mixture was stirred at room temperature for 30 min. Compound **31** (50 mg, 0.27 mmol) in THF was added

dropwise with ice-water cooling and stirred for another 30 min. The reaction mixture was neutralised with satd. NH_4Cl solution and extracted with CH_2Cl_2. The crude product obtained after work up was purified by PLC to get a thick oil, yield: 55 mg (53%). IR (neat) 1725, 1545 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.71-7.25 (m, 5H), 4.8 (d, J= 5 Hz, 1H), 4.5-3.9 (m, 6H), 3.65-3.2 (m, 2H), 2.4-2.2 (m, 1H), 2.15-1.45 (m, 6H), 1.2 (t, 3H); mass spectrum, m/e 381; Anal. Calcd. for $C_{18}H_{23}NSO_6$: C, 56.69; H,6.04; N,3.67; S,8.40. Found: C,56.73; H,5.97; N,3.59; S,8.45.

2-Nitro-3-propargyloxycyclohexanone acetal 34: To a stirred suspension of NaH (16 mg, 50% suspension in oil, 0.33 mmol) in 3 ml of THF was added propargyl alcohol (18 mg, 0.32 mmol) at 0°c and the stirring continued till the evolution of gas ceased (15 min.). Then , 2-nitro-2-cyclohexenone acetal **31** (50 mg, 0.27 mmol) in THF was added to the reaction mixture and the resultant mixture was stirred for further 15 min. Usual work up gave the crude product which was purified by PLC, yield: 55 mg (85%). IR (neat) 3270, 2110, 1545, 1365 cm^{-1}; ^1H NMR (CCl_4 + $CDCl_3$): δ 4.9 (d, J= 5 Hz, 1H), 4.55-3.9 (m, 7H), 2.45 (s, 1H), 2.2-1.3 (m, 6H); mass spectrum, m/e 195; Anal. Calcd. for $C_{11}H_{15}NO_5$: C,54.77; H,6.22; N, 5.81. Found: C,54.85; H,6.28; N,5.87.

2-Keto-3-phenylthiocyclohexanone acetal 37: To a stirred solution of compound **31** (50 mg, 0.27 mmol) in methanol containing 30% H_2O_2 (0.06 ml, 0.54 mmol) at 5°c was added aq. NaOH (0.07 ml, 2N, 0.14 mmol) rapidly. Stirring was continued at the same temperature for additional 10 min. (turbidity developed this time), then the raection mixture was extracted with ether (3 x 15 ml). The crude product obtained after work up was treated with sodium thiophenolate, prepared in-situ from thiophenol (30 mg, 0.27 mmol) and sodium (6 mg, 0.27 mmol), in CH_3OH at 0°c and stirred for 2 hr. The crude product was purified by PLC (eluent: benzene-acetone = 95:5) to obtain a thick oil, yield : 60 mg (47%). IR(Neat)1725 cm^{-1}; ^1H NMR (CCl_4): δ 7.6-7.1 (m, 5H),4.3-3.65 (m, 5H), 2.0-1.4 (m, 6H); mass spectrum, m/e 264; Anal. Calcd. for $C_{14}H_{16}SO_3$: C,63.64; H,6.06; S,12.12. Found: C,63.-70; H,6.12; S,12.14.

Acknowledgement:

We are grateful to the Department of Science and Technology and Council of Scientific and Industrial Research, New Delhi for financial support.

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