Tetrahedron Vol. 47, No. 42, pp. 8883-8906, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00

CHEMISTRY OF α-NITROEPOXIDES : SYNTHESIS OF USEFUL INTERMEDIATES VIA NUCLEOPHILIC RING OPENING OF α-NITROEPOXIDES[1]

Yashwant D. Vankar*, Kavita Shah, Anita Bawa and Surendra P. Singh

Dept. of Chemistry, Indian Institute of Technology, Kanpur-208016, India

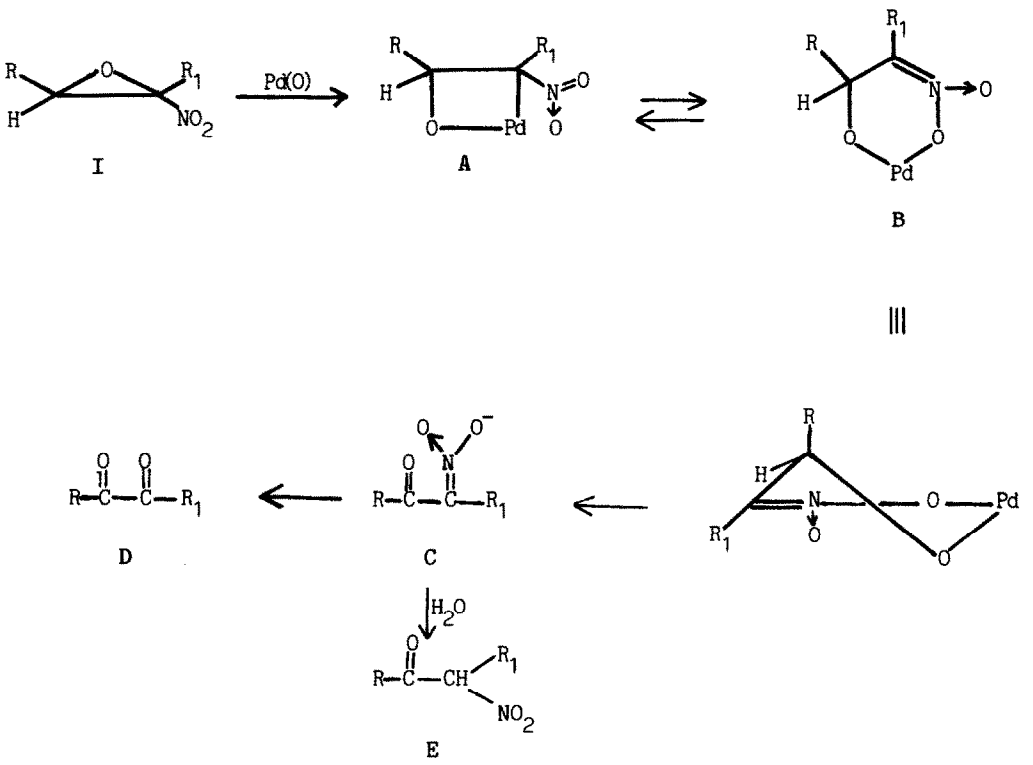
(*Received in UK 24 August* 1991)

Abstract : Various α-nitroepoxides are converted into corresponding 1,2-diketones via two different ways of ring opening viz. with Pd(0) and with $DMSO/BF_3.Et_2O$(or $ClSiMe_3$). In addition to this, a variety of nucleophiles are reacted with α-nitrocyclopentene oxide 6 and α-nitrocyclohexene oxide 7 to form the corresponding α-substituted ketones which are useful intermediates in organic synthesis. Two of the products so obtained viz. 32 and 33 are also transformed further into optically active thialactones 38 and 39 respectively via baker's yeast reduction followed by lactonisation.

Among the epoxides, which contain electron withdrawing groups on one of the epoxy carbons, α-nitroepoxides have received little attention. Newman and Angier[2] were the first ones to systematically study the preparation and some reactions of α-nitroepoxides. Following this report, there have been a few more reports in the literature[3] on the synthesis and uses of α-nitroepoxides in organic synthesis. Jackson and coworkers[4] have recently studied the reactivity of α-nitroepoxides which carry a phenylthio substituent on α-carbon and demonstrated their usefulness in the synthesis of α-substituted S-phenylthio esters. This enhances the utility and scope of α-nitroepoxides even further.

Our interest in the chemistry of α-nitroepoxides led us to study their behaviour towards a range of nucleophiles. In a preliminary account we have recently demonstrated a facile conversion of α-nitroepoxides into α-diketones by using tetrakis(triphenylphosphine)palladium(0)[5]. Such a conversion was expected due to the nucleophilic behaviour of Pd(0) catalysts. The two well studied reactions by Noyori et al. include isomerisation of α,β-epoxy ketones into 1,3-diketones[6] and that of 1,3-diene epoxides into β,γ-unsaturated ketones or dienols[7]. In both of these transformations the mechanistic considerations included nucleophilic attack by Pd(0) on the epoxy carbon adjacent to the ketone or the double bond. It was, therefore, of interest to us to study the reaction of Pd(0) towards α-nitroepoxides. The reaction was found to be extremely slow with Pd(0) alone or with the addition of 1,2-bis(diphenyl-

phosphinoethane). However, it was found to proceed well with the addition of one equivalent of triethylamine in refluxing benzene and the corresponding 1,2-diketones were obtained in fair yields (cf. Table 1). A tentative mechanism to account for this conversion is shown in scheme 1 which is somewhat along the lines suggested earlier by Noyori et al. in their epoxides isomerisations.

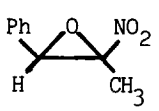
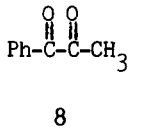
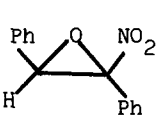
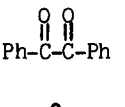
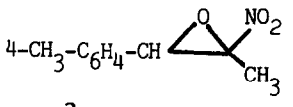
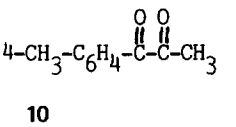
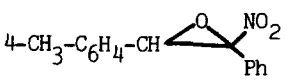
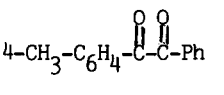
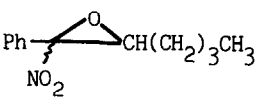
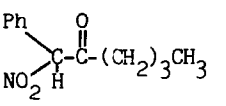
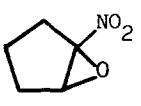
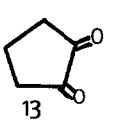
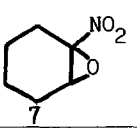
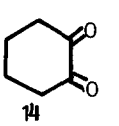


SCHEME 1

It was found by IR spectroscopy and thin layer chromatographic analysis that the reaction did proceed via α-nitroketones. But, the amount of α-diketones was always found to be higher than that of α-nitroketones and towards the end of the reaction almost all the α-nitroketone had disappeared. Interestingly, however, the α-nitroepoxide 5 gave only the α-nitroketone 12 which did not undergo further transformation to the corresponding α-diketone even after prolonged heating. Transformation of the intermediate C (Scheme 1) to the product is an important step. It is not clear how the formation of α-diketone D proceeds but some type of Nef reaction ought to be occurring under the reaction condi-

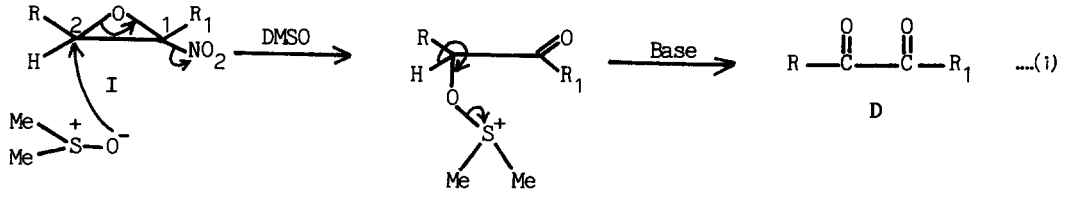
tions[8]. Formation of α-nitroketone E from C is, on the other hand, obvious.

TABLE 1

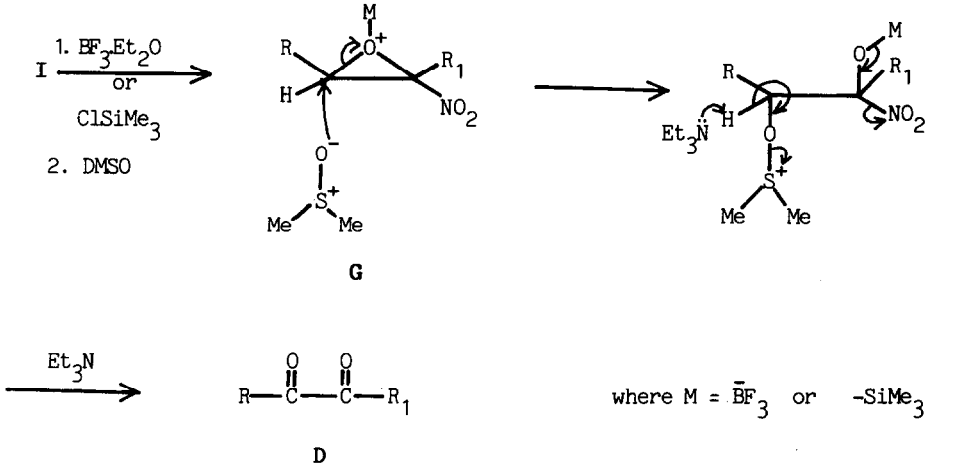
Entry	α-Nitroepoxide	Reaction Time (hr)	1,2-Diketones	Yield(%)	(m.p.)/b.p.°C/mm [Lit. Value]
1.	 1	10	 8	49	102/12 [122][9]
2.	 2	5	 9	64	(92) [95][10]
3.	 3	30	 10	48	100/12[11]
4.	 4	5	 11	75	(31)[12]
5.	 5	7	 12	55	Thick oil
6.	 6		 13	50	(55) [56-58][13]
7.	 7		 14	40	(36) [36-38][13]

As the availability of α-nitroepoxides is relatively convenient and the use of α-diketones[14] in organic synthesis is well known, we sought still a different approach for the conversion of α-nitroepoxides into α-diketones. For this purpose, we considered the possibility of

reactions of α-nitroepoxides with dimethyl sulfoxide (DMSO). It was envisaged that if DMSO attack at C-1 (..eqn.i) of I is followed by the concommitant loss of the nitro group, an intermediate F (Kornblum type) would be formed. Intermediate F upon deprotonation with a base would lead to the diketone D. Initial experiments, however, under different conditions were not successful. α-Nitroepoxides were found to



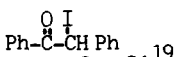
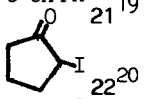
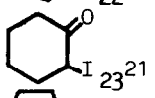
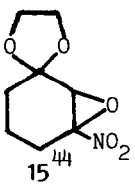
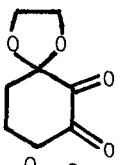
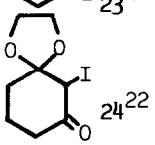
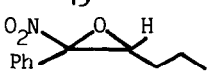
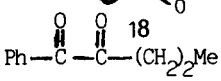
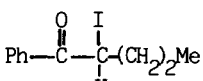
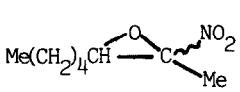
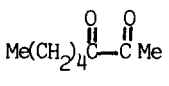
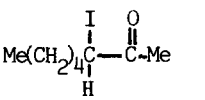
be stable at ambient temperatures and a number of products seemed to form at higher temperatures. The best condition was found[15] to react I with DMSO in the presence of $BF_3.Et_2O$ or $ClSiMe_3$ in CH_2Cl_2 at 0°C followed by the addition of Et_3N to get α-diketones in good yields (see Table 2). Obviously the not so nucleophilic oxygen of DMSO initially required activation of α-nitroepoxides for it to attack. A plausible mechanism to account for the product formation is delineated in Scheme 2.



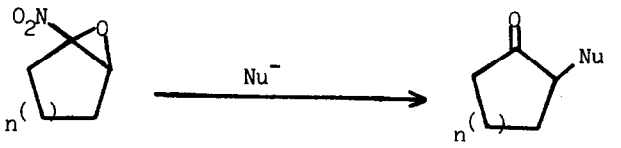
SCHEME 2

Among other nucleophiles, we studied[15] the reaction of α-nitroepoxides with NaI alongwith $BF_3.Et_2O$ in acetonitrile at 0°C and the corresponding α-iodoketones were formed in good yields (cf. Table 2).

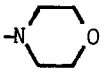
TABLE 2

Entry	α-Nitroepoxide	1,2-Diketone	%Yield using $BF_3.Et_2O$ (Time in hr)	%Yield using $ClSiMe_3$ (Time in hr)	α-Iodoketone	%yield (Time in hr)
1.	2	9[10]	77(7)	87(4)	 21[19]	81(9)
2.	6	13[13]	64(8)	72(5)	 22[20]	72(5)
3.	7	14[13]	64(10)	75(6)	 23[21]	75(6)
4.	 15[44]		61(34)	60(30)	 24[22]	- -
5.	 16	 19[17]	54(10)	57(7)	 25	68(8)
6.	 17	 20[18]	60(11)	65(7)	 26	71(8)

However, further experiments[16] suggested that the use of $BF_3.Et_2O$ was not essential and NaI reacted with the α-nitroepoxides in acetone at 0°-5°C to form α-iodoketones in 5 min. This way α-nitrocyclopentene oxide **6** and α-nitrocyclohexene oxide **7** gave the corresponding α-iodoketones[23] in good yields (cf. Table 3). In view of $I^{\ominus}$ being a good nucleophile it is not surprising that $BF_3.Et_2O$ is not essential. Further, it was also found that these α-nitroepoxides also reacted with LiCl and LiBr to form the corresponding α-chloro and α-bromocycloalkanones[23] 27 (a-**d**) (Scheme 3). Although in the studies by Sokolov[3(vi)] $BF_3.Et_2O$ was used alongwith LiCl, in our experience $BF_3.Et_2O$ was not essential. We believe that Li^+ provides sufficient activation for the epoxide to permit Cl^- and Br^- to react.



6 ; n = 1
7 ; n = 2

27 ; Nu : Cl, Br 22, 23; Nu:I
28 ; Nu :  , C_6H_5NH-

SCHEME 3

Aminolysis of α-nitroepoxides has been studied by Sokolov et al[3(v)]. They have reported the formation of α-aminoketones by the reactions

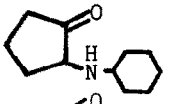
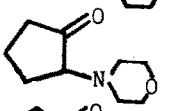
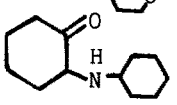
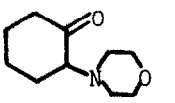
TABLE 3

Entry	α-Nitro-epoxides	MX	α-Halocycloalkanone [27(a-d), 22 and 23]	Yield(%)	B.P. (°C/mm)	Lit. B.P. (°C/mm)
1.	6	LiCl	α-Chlorocyclopentanone 27a	72	78-79/10	82-83/12[24]
2.	7	LiCl	α-Chlorocyclohexanone 27b	88	40-42/0.8	38.5/0.8[24]
3.	6	LiBr	α-Bromocyclopentanone 27c	75	69-70/2	68/2[24]
4.	7	LiBr	α-Bromocyclohexanone 27d	86	48-49/1	95-98/15[24]
5.	6	NaI	α-Iodocyclopentanone 22	81	49-51/1	50/1[20]
6.	7	NaI	α-Iodocyclohexanone 23	84	45-46/0.5	54/1[21]

of α-nitroepoxids with excess of amines for 24 hrs without the use of any other catalyst or a base. In our similar studies we have found that if sodium salts of amines are reacted with α-nitroepoxides, α-aminoketones are very readily formed. Thus 6 and 7 reacted with sodium salts of cyclohexylamine and morpholine whereby the corresponding α-aminoketones 28 (a-d) were formed within 10 min. (cf. Table 4) in reasonably good yields.

The studies described here as well as that by Sokolov et al. make α-nitroepoxides as important compounds for the formation of useful α-halo[26] and α-aminoketones[27].

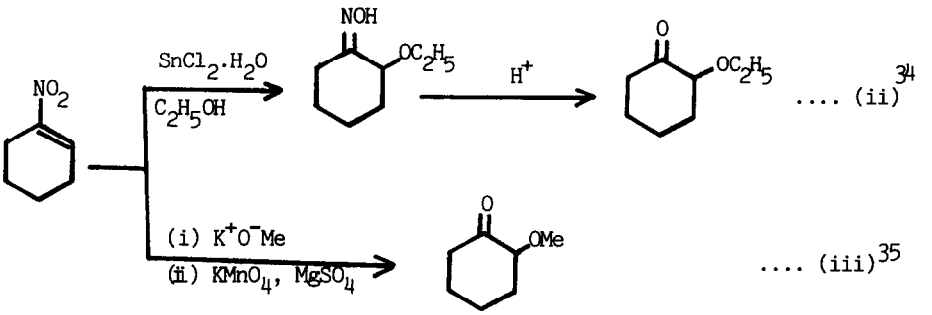
TABLE 4

Entry	α-Nitro-epoxide	Amine	α-Aminocycloalkanone 28(a-d)	Yield(%)	B.P. (°C/mm)
1.	6	Cyclohexylamine	 28a	66	139/20
2.	6	Morpholine	 28b	74	138/20
3.	7	Cyclohexylamine	 28c	68	94-95/1
4.	7	Morpholine	 28d	74	87-89/1 (lit. 148/20)[25]

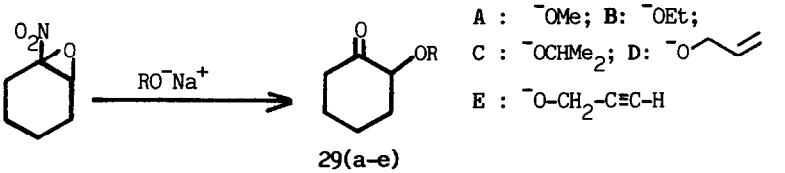
α-Alkoxycarbonyl compounds have been found to be useful in the synthesis of macrolide antibiotics, polyether ionophores[28] and oxaspiro compounds[29]. Although α-alkoxyaldehydes are accessible via several routes[28,30] α-alkoxyketones are not readily available. They are generally prepared by the decomposition of α-diazoketones[30] or the dimers of α-hydroxyketones[31] in the presence of alcohols. α-Alkoxyketones have also been reported to be formed as by-products in the fragmentation of ionic peroxides[32] and in the methanolysis of arylcyclopropanone methyl hemiacetals[33]. In addition to these, recently three new methods from three different laboratories have been reported to convert conjugated nitroolefins to α-alkoxyketones (equations ii,iii and iv;Scheme 4).

Considering the importance of α-alkoxyketones and our interest in studying the nucleophilic ring opening of α-nitroepoxides, a number of alkoxides viz. A to E (Scheme 5) were reacted with 6 and 7. These alkoxides reacted smoothly with 7 to yield the corresponding α-alkoxyketones 29 (Scheme 5) in reasonable yields (see entries in Table 5). Unfortunately, however, 6 yielded a number of products, perhaps, due to its high reactivity towards basic alkoxides.

Methanolysis of α-nitroepoxides has been reported by Sokolov et al[3(iv)]. However, as the reaction is carried out in methanol in the presence $BF_3.Et_2O$, the product obtained is α-methoxyacetals rather than α-methoxy ketones. As the nitroepoxide 6 yielded several products under our conditions of alkoxylations, its reactions under Sokolov conditions[3(iv)] were attempted[23(i),(ii)]. Although with methanol the reaction appeared



SCHEME 4



SCHEME 5

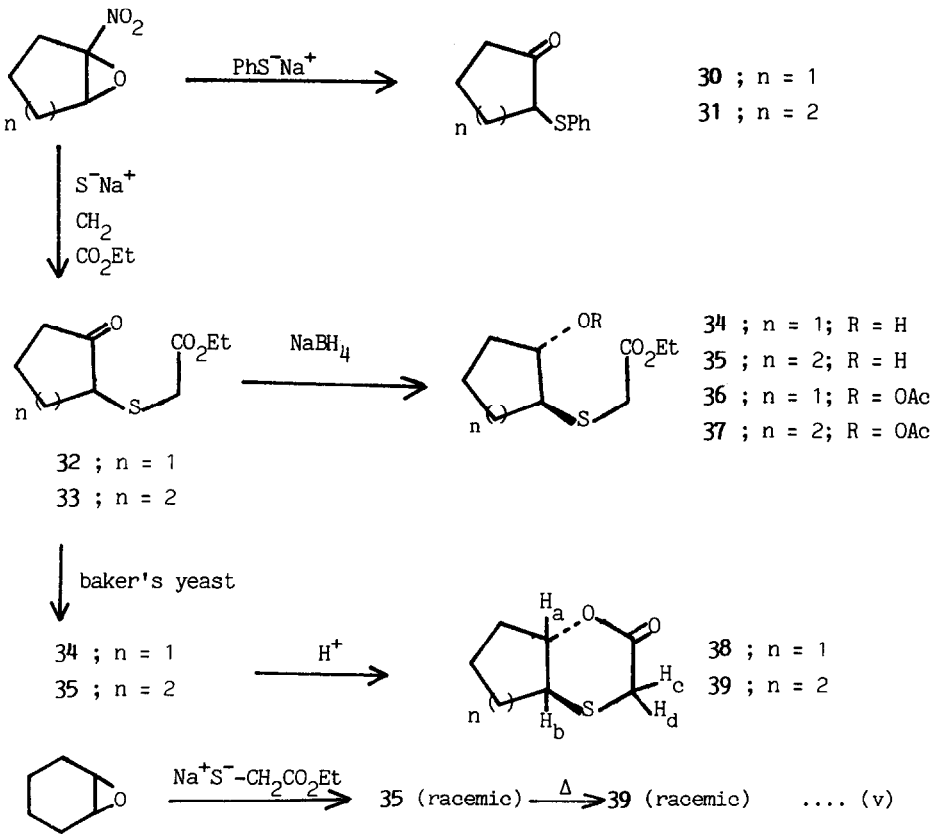
TABLE 5

Entry	α-Nitro-epoxide	Sodium alkoxide	α-Alkoxycycloalkanone 29(a-e)	Yield(%) (%)	B.P. (°C/mm)	Lit.B.P. (°C/mm)
1.	7	NaOMe	α-Methoxycyclohexanone	67	78-79/15	75/15[25]
2.	7	NaOEt	α-Ethoxycyclohexanone	64	86-87/15	85/15[25]
3.	7	$NaOCH(Me)_2$	α-(1-methylethoxy)cyclo-hexanone	53	95/15	---
4.	7	NaO-	α-(prop-2-enyloxy)cyclo-hexanone	60	---(i)	---
5.	7	$NaO-CH_2C\equiv CH$	α-(prop-2-ynloxy)cyclo-hexanone	62	124-127/20(i)	126/20[37]

(i) Purified by PLC (eluent : benzene, acetone = 95,5).

to be relatively cleaner, the product obtained after 24 hrs was a mixture of 1,1,2-trimethoxycyclopentane and 2-methoxycyclopentanone in 70:30 ratio as could be judged by the IR and NMR of the purified product. The reactions, however, appeared more and more unclean with ethanol, isopropanol, allyl alcohol and propargyl alcohol.

α-Keto sulphides have been recognised[38] in recent years as versatile intermediates in organic synthesis. Introduction of an electrophile α to sulphur in these compounds followed by reductive or oxidative removal of sulphur further incorporates many functionalities. As a result of this, several methods of their preparation have been reported in the literature[38]. In the present study two sulphur based nucleophiles viz. derived from thiophenol and ethyl mercaptoacetate were utilised. Thus, sodium thiophenolate reacted with 6 and 7 to give 2-(phenylthio)--cyclopentanone 30 and 2-(phenylthio)cyclohexanone 31 (Scheme 6) in



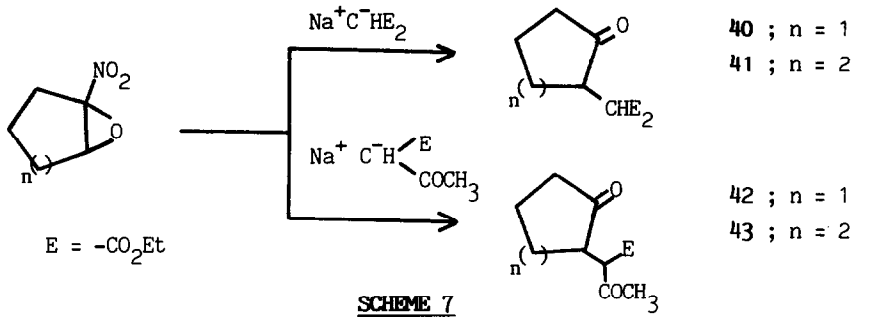
SCHEME 6

90% and 89% yields respectively. Similarly, sodium salt of ethyl mercaptoacetate also reacted with the two α-nitroepoxides to give 2-[(carboethoxy)methylthio]cyclopentanone **32** and 2-[(carboethoxy)methylthio]cyclohexanone **33** in 81% and 80% yields respectively. The products **32** and **33** upon reduction with $NaBH_4$ gave the corresponding alcohols **34** and **35** in 88% and 91% yields which were characterised as their acetates **36** and **37**. The alcohols **34** and **35** were then lactonised[39] in the presence of catalytic amounts of p-toluenesulphonic acid to furnish the lactones **38** and **39** in 81% and 85% yields respectively. These lactones appear to possess trans stereochemistry as supported by their ^{1}H-NMR spectral data and literature comparison[40]. The two thioketones **32** and **33** also were reduced with fermented baker's yeast[41] to obtain the same alcohols **34** and **35** albeit in low yields (ca. 16% and 17%). These alcohols, as expected, underwent lactonisation to form the corresponding optically active lactones **38** and **39** in 96% and 97% yields and optical rotation values as $[\alpha]_D^{25}$ = -122° (C, 0.5, $CHCl_3$) and $[\alpha]_D^{25}$ = -122° (C, 1, $CHCl_3$) respectively. From the ^{1}H-NMR data of these optically active lactones it appears that they also possess trans stereochemistry at the junctions. In its ^{1}H-NMR spectrum **39** had its proton H_a appearing at δ 4.43 - 4.72 as a multiplet and H_b at δ 3.0 - 3.42 as a multiplet. The protons H_c and H_d appeared as an A-B quartet of which one doublet at δ 2.73 with J = 14 Hz and the other at δ 3.33, J = 14 Hz. These values are comparable with the values reported for it in the literature[40] obtained by the epoxide opening followed by lactonisation (equation v, Scheme 6) which ought to be a trans lactone. Similarly **38**, on the basis of its spectral data, was assigned the trans stereochemistry. However, the absolute configuration and enantiomeric purity of these optically active compounds remains to be determined.

Thiodecalins and thiohydrindans have recently been realised[42] to be useful intermediates in organic synthesis. Similarly, substituted 1,4-oxathianes apart from being important precursors are themselves useful fungicides and pesticides[43]. We, therefore, believe that heterocyclic compounds prepared by us should be useful in organic synthesis.

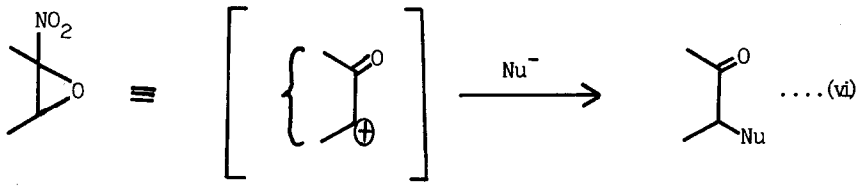
Finally, in order to assess the reactivity of the α-nitroepoxides under study towards carbon nucleophiles they were reacted with sodium salts of diethyl malonate and ethyl acetoacetate. The corresponding expected products **40**, **41**, **42** and **43** were obtained in 60%, 62%, 56% and 51% yields respectively (Scheme 7).

The above described study of the nucleophilic ring opening of α-nitroepoxides with a variety of nucleophiles appears to be useful



SCHEME 7

in synthesising a number of important intermediates. α-Nitroepoxides could thus be considered as α-keto carbocation equivalents (equation vi, below).



EXPERIMENTAL

General Methods : ^{1}H-NMR spectra were recorded on Varian EM 390, Jeol PMX 60 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 silica gel obtained from E.Merck. Acetone was dried from $KMnO_4$ followed by anhydrous K_2CO_3 and then stored over molecular sieves (4°A). Methanol and ethanol were dried from CaO and benzene was distilled from CaH_2. Sodium dried THF was distilled from $LiAlH_4$ prior to use. All the metal halides were dried in an oven at 120°C prior to use. Melting points are uncorrected. Boiling points were determined using Buchi's Kugelrhor distillation unit GKR-50 and they represent bath temperature.

α-Nitroepoxides **1**,2[2(i),2(ii)] and **15**[44] were prepared as reported in the literature. Likewise, the other α-nitroepoxides viz. **3-7** (cf. Table 1) and **16** and **17** (cf. Table 2) were also prepared from the corresponding nitroolefins following similar procedure.

2-Methyl-3-(4-methylphenyl)-2-nitro Oxirane 3 :

3 was obtained from 1-(4-methylphenyl)-2-nitropropene[45] in 65% yield. Oil; b.p. 65°C/0.2 mm. IR ($CHCl_3$) 1570 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 1.23 (br.s, 6H,-methyls), 4.8 (s, 1H, -CH<O>NO_2), 7.0-7.3 (m, 4H, aromatic). Anal. Calcd. for $C_{10}H_{11}NO_3$: C, 62.17; H, 5.69; N, 7.25. Found : C, 62.53; H, 5.61; N, 7.02.

3-(4-Methylphenyl)-2-nitro-2-phenyl Oxirane 4 :

2-(4-methylphenyl)-1-nitro-1-phenyl ethylene[46] gave 4, a white solid, in 85% yield. M.p. 95°C (from EtOH). IR (KBr) : 1550 cm^{-1};^{1}H-NMR ($CDCl_3$): δ 1.21 (s, 3H, $-CH_3$), 4.71 (s, 1H, -CH<O>NO_2), 6.9-7.3 (m, 9H, aromatic). Anal. Calcd. $C_{15}H_{13}NO_3$: C, 70.58; H, 5.09; N, 5.49. Found : C, 70.69; H, 5.46; N, 6.01.

3-Butyl-2-nitro-2-phenyl Oxirane 5 :

The nitroolefin i.e. 1-nitro-1-phenyl-hex-1-ene was prepared via Henry condensation[47] between phenylnitromethane and pentanal followed by dehydration[48]. Its b.p. was found to be 120°/0.2 mm. IR(thin film): 1515 cm^{-1}; ^{1}H-NMR (CCl_4) :δ 0.78-1.1 (m, 3H, $-CH_3$), 1.2-1.88 (m, 6H, CH_2s'), 7.0 (s, 1H, olefinic), 7.2-7.8 (m, 5H, aromatic). Anal. Calcd. for $C_{12}H_{15}NO_2$: C, 70.24; H, 7.31; N, 6.83. Found : C, 69.90; H, 7.76; N, 6.79 . The epoxide 5 was obtained as an oil in 92% yield. B.p. 160°C /0.2 mm. IR (thin film):1550 cm^{-1};^{1}H-NMR (CCl_4):δ 0.8-1.0 (m, 3H,$-CH_3$), 1.1-1.66 (m, 6H, CH_2s'), 3.2-3.7 (t, 1H, NO_2<O>H), 7.0-7.38 (m, 5H, aromatic). Anal. Calcd. for $C_{12}H_{15}NO_3$: C, 65.16; H, 6.78; N, 6.33. Found : C, 64.91; H, 6.26; N, 6.01.

For the synthesis of 1-nitrocyclopentene oxide 6 and 1-nitrocyclohexene oxide 7, a slightly modified procedure (as outlined below) was adopted. 1-Nitrocyclopentene and 1-nitrocyclohexene were prepared as described in the literature[50].

1-Nitrocyclopentene Oxide 6 :

To a stirred solution of 1-nitrocyclopentene (904 mg, 8 mmol) in methanol (15 ml) at -10°C was added 15% H_2O_2 (0.24 ml, 10.6 mmol). After 4 min. a solution of 2N NaOH (2 ml, 4 mmol) was added dropwise over a period of 5 min. maintaining the temperature of the reaction mixture below 5°C. After stirring for another 5 min. at the same temperature, the reaction mixture was poured into cold water and extracted with ether (3 x 20 ml). Combined organic layers were washed with water (2 x 15 ml), brine (15 ml) and dried over anhydrous Na_2SO_4. Evaporation

of the solvent gave 1-nitrocyclopentene oxide 6 which was used as such further. Yield : 840 mg (81%). The product decomposed during attempted distillation. IR (neat) : 1550 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 1.32-2.86 (m, 6H, $3CH_2$s'), 3.92 - 4.21 (br.d, 1H, -CH-O-).

1-Nitrocyclohexene Oxide 7 :

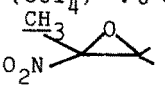
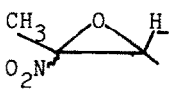
Following the procedure described above 7 was obtained in 70% yield (800 mg) from 1-nitrocyclohexene (1.016 g, 8 mmol), 15% H_2O_2 (0.24 ml, 10.6 mmol) and 2N NaOH (2 ml, 4 mmol). IR (neat) :1550 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 1.26 - 2.78 (m, 8H, 4 CH_2s'), 3.64-3.78 (br.s, 1H, -CH-O-).

3-Propyl-2-nitro-2-phenyl Oxirane 16 :

The nitroolefin viz. 1-nitro-1-phenyl-pent-1-ene i.e. the precursor for 16 was prepared in 91% yield using Henry condensation[47] between phenylnitromethane and butanal followed by dehydration[48]. Its b.p. was found to be 115°C/0.2 mm. IR (thin film) : 1515 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 0.8 - 1.1 (m, 3H, $-CH_3$), 1.2-1.8 (m, 4H, CH_2s'), 7.0 (s, 1H, olefinic), 7.2-7.8 (m, 5H, aromatic).

The epoxide 16 was obtained as an oil in 62% yield. IR (thin film) : 1550 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 0.8-1.0 (m, 3H, CH_3), 1.1-1.6 (m, 4H, CH_2s'), 3.2-3.7 (t, 1H, ), 7.01-7.36 (m, 3H, aromatic).

2-Methyl-2-nitro-3-pentyl Oxirane 17 :

Epoxidation of 2-nitrooctene[51] gave 17 as an oil in 70% yield. IR (thin film) : 1550 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 0.7-1.0 (m, 3H, $-CH_3$), 1.0-1.8(m, 8H, CH_2s'), 1.85 (s, 3H, ), 3.1-3.6 (br.t, 1H, ).

These nitroepoxides 6, 7, 16 and 17 were found to be relatively unstable and hence were used immediately after their preparation.

General procedure for the conversion of α-nitroepoxides 1 - 7 into α-diketones 8 - 14 using $Pd(PPh_3)_4$:

To a stirred solution of an α-nitroepoxide (0.41 mmol) in 3 ml of dry benzene were added $Pd(PPh_3)_4$ (23 mg, 0.02 mmol, 5 mol%) and triethylamine (0.06 ml, 0.41 mmol). The mixture was refluxed (see - Table 1 for time) under nitrogen atmosphere. It was cooled, neutralised

with dil. HCl[52] and then washed with water (2 x 5 ml) and brine (5 ml). After drying over anhydrous Na_2SO_4 the solvent was removed under vacuum to get crude product which was purified by distillation, recrystallisation or by chromatography. The products were then characterised by spectral and analytical means and literature comparison.

1-Nitro-1-phenyl-hexane-2-one 12 :

Thick oil. IR ($CHCl_3$) : 1550, 1700 cm^{-1}; ^{1}H-NMR ($CDCl_3$) : δ 0.9 (t, 3H, $-CH_3$), 1.2-1.9 (m, 4H, CH_2s'), 2.8-3.0 (t, 2H, $-\overset{O}{\overset{\|}{C}}-CH_2-$), 5.9 (s, 1H, $-CH-NO_2$), 7.2-8.1 (m, 5H, aromatic). Anal. Calcd. for $C_{12}H_{15}NO_3$: C, 65.16; H, 6.78; N, 6.33. Found : C, 65.31; H, 6.92; N, 6.81.

General procedures for the preparation of 1,2-diketones and α-iodoketones using $BF_3.Et_2O$ (or $ClSiMe_3$):

1,2-Diketones : A stirred mixture of α-nitroepoxide (1.6 mmol) in dry dimethyl sulfoxide (2 ml) and dichloromethane (0.5 ml) was treated with $ClSiMe_3$ (3.2 mmol) or $BF_3.Et_2O$ in dichloromethane (0.2 ml) at 0°C. The resultant mixture was stirred for an additional time (see Table 2) at the same temperature. Triethylamine (5 mmol) dissolved in dichloromethane was then added dropwise to the above reaction mixture at 0°C and stirring continued for an additional 1 hr. raising the temperature slowly to 30°C. The reaction mixture was poured in cold water, diluted with brine (5 ml) and extracted with ethyl acetate (5 x 15 ml). The combined organic layer upon drying over anhydrous Na_2SO_4 followed by evaporation gave a crude product which was purified by recrystallisation or preparative layer chromatography (PLC). [See Table 2 for yields].

α-Iodoketones : A stirred mixture of sodium iodide (1.3 mmol) and α-nitroepoxide (1 mmol) in dry CH_3CN (2 ml) was treated with $BF_3.Et_2O$ (1.3 mmol) in CH_3CN (1 ml) at 0°C and the resultant mixture stirred at the same temperature till the reaction was complete (see Table 2). The reaction mixture was then poured in cold water (5 ml) and extracted with ether (3 x 15 ml). The combined ether layer was washed with 10% sodium thio sulphate solution (15 ml), water (2 x 15 ml), brine (15 ml) and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave crude product whichwas purified by PLC.

1,4-Dioxaspiro [4,5]decane-6,7-dione 18 :

M.p. 136°C. IR ($CHCl_3$) : 3400, 1680, 1620 cm^{-1}; ^{1}H-NMR ($CDCl_3$) : δ 1.4-2.8 (m, 4H, CH_2s'), 3.6-4.1 (m, 4H, ), 6.04 (t, 1H,

vinylic), 7.80 (s, 1H, OH). Anal. Calcd. for $C_8H_{10}O_4$: C, 56.47; H, 5.88. Found : C, 56.01; H, 5.80.

2-Iodo-1-phenyl-pentane-1-one 25 :

Thick oil. IR (thin film) : 1680 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 1.0 (t, 3H, CH_3), 2.08-2.18 (m, 4H, CH_2s'), 5.2 (t, 1H, -CHI), 7.3-7.6 (m, 3H, aromatic), 7.8-8.1 (m, 2H, aromatic); mass spectrum : m/e 288.

3-Iodo-octane-2-one 26 :

Oil. IR (thin film) : 1710 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 0.9 (t, 3H, $-CH_2\underline{CH_3}$), 1.3-1.8 (m, 8H, CH_2s'), 2.4 (s, 3H, $\underline{CH_3}-\overset{O}{\overset{\|}{C}}-$), 4.4 (t, 1H, CHI) ; mass spectrum : m/e 254.

General procedure for the preparation of α-haloketones 22, 23, 27 :

To a stirred solution of a metal halide (1.05 mmol) in dry acetone (4 ml) was added an α-nitroepoxide (1 mmol) at 0.5°C. After 5 min. acetone was removed under vacuum and the residue diluted with water (10 ml) and extracted with ether (3 x 15 ml). After washing the combined ethereal extracts with sodium thiosulphate (10 ml), water (2 x 5 ml) and brine (5 ml), it was dried over anhydrous Na_2SO_4. Removal of the solvent gave crude α-halocycloalkanone which was purified by vacuum distillation (Table 3). α-Halocycloalkanones so obtained were characterised by spectral means and compared with the literature values reported for them.

General procedure for the preparation of α-aminocycloalkanones 28 :

To a well stirred suspension of NaH (1.1 mmol) in dry THF (2 ml) was added a freshly distilled amine (1.1 mmol) dissolved in 2 ml THF at 0°C. After 45 min. an α-nitroepoxide (1 mmol) was added to the reaction mixture at 15°C. After stirring for another 10 min., the solvent was removed under vacuum and the residue diluted with water (10 ml) and extracted with ethyl acetate (3 x 15 ml). Usual work up gave a crude product which was purified by preparative layer chromatography (PLC) (eluent : benzene, acetone = 90, 10). Products were further purified by distillation and characterised by spectral and analytical means (Table 2).

28a : IR (neat) 3340, 1650 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 0.72-2.67 (m, 16H, 8 CH_2s'), 2.68-2.92 (m, 1H, -CH-NH-), 3.82-4.12 (m, 1H, -NH-: D_2O exchangeable), 5.10-5.24 (m, 1H, -NH-CH-C=O); mass spectrum, m/e 181; Anal. Calcd. for $C_{11}H_{19}NO$: C, 72.92; H, 10.49; N, 7.73. Found : C, 72.88; H, 10.52; N, 7.65.

28b : IR (neat) 1710 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 1.87-2.57 (m, 6H, ring 3 CH_2s'), 2.67-3.03 (m, 4H, -C<u>H</u>$_2$-N-C<u>H</u>$_2$-), 3.30-3.67 (m, 4H, -C<u>H</u>$_2$-O--C<u>H</u>$_2$), 5.97 (t, 1H, -C<u>H</u>-N-, J = 2 Hz); mass spectrum, m/e 170 $(M+1)^+$; Anal. Calcd. for $C_9H_{15}NO_2$: C, 63.90; H, 8. 87; N, 8.28. Found : C, 63.88; H, 8.80; N, 8.25.

28c : IR (neat) 3360, 1660 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 0.67-2.60 (m, 18H, 9 CH_2s'), 2.62-3.0 (m, 1H, -C<u>H</u>-NH-), 3.77-4.10 (m, 1H, -NH- : D_2O exchangeable), 5.0-5.2 (m, 1H, -C<u>H</u>-C=O); mass spectrum, m/e 195; Anal. Calcd. for $C_{12}H_{21}NO$: C, 73.84; H, 10.76; N, 7.18. Found: C, 73.81, H, 10.81; N, 7.12.

28d : IR (neat) 1720 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 1.40-2.73 (m, 12H, 4 ring CH_2s' and -C<u>H</u>$_2$-N-C<u>H</u>$_2$-), 3.6 (t, 4H, -C<u>H</u>$_2$-O-C<u>H</u>$_2$-, J = 4 Hz), 6.53 -(t, 1H, -C<u>H</u>-N-, J = 4 Hz); mass spectrum, m/e 184 $(M+1)^+$; Anal. Calcd. for $C_{10}H_{17}NO_2$: C, 65.57; H, 9.29; N, 7.65. Found : C, 65.46; H, 9.32; N, 7.60.

General procedure for the preparation of α-alkoxycycloalkanones 29 :

Sodium alkoxide (1 mmol) dissolved in the corresponding alcohol (2 ml) was treated with the α-nitroepoxide (1 mmol) at room temperature. After stirring for another 2 min. excess of the alkanol was removed under vacuum and the residue was diluted with water (10 ml) and extracted with ether (3 x 15 ml). Usual work up gave a crude product which was purified by distillation or by PLC to obtain pure products (Table 5). The purified products were characterised by spectral and analytical means and compared with the data reported in the literature.

29c : IR (neat) 1735 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 0.83-2.80 (m, 14H, ring 4 CH_2s' and 2 CH_3s'), 3.20-3.55 (m, 1H, -O-C<u>H</u>-), 3.57-4.10 (m, 1H, -O-CH-C=O); mass spectrum, m/e 157 $(M + 1)^+$; Anal. Calcd. for $C_9H_{16}O_2$: C, 69.23; H, 10.25. Found : C, 69.10; H, 10.30.

29d : IR (neat) 1725 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 1.03-2.50(m,8H,ring 4CH_2s'), 3.7-4.2 (m, 1H, -CO-CH-O-), 4.72-6.07 (m, 5H, -C<u>H</u>=C<u>H</u>$_2$ and -O-C<u>H</u>$_2$-), mass spectrum, m/e 155 $(M + 1)^+$; Anal. Calcd. for $C_9H_{14}O_2$: C, 70.12; H, 9.09. Found : C, 70.02; H, 9.02.

Preparation of 2-(phenylthio)cyclopentanone 30 :

A stirred solution of NaOMe (54 mg, 1 mmol) in dry methanol (2 ml) at 0°C was treated with thiophenol (111 mg, 1.01 mmol) by adding it dropwise over a period of 10 min. After 30 min. α-nitroepoxide **6** (129 mg, 1 mmol) in dry methanol (2 ml) was also added dropwise at room temperature. After additional stirring for 5 min. methanol was removed under vacuum, the residue was diluted with water (10 ml) and

extracted with ether (3 x 15 ml). Further usual work up gave a crude product which was purified by PLC (eluent : benzene, acetone = 95,5) followed by distillation to obtain 173 mg (90%) of **30**. B.P.104-106°C /0.03 mm (lit.[53] b.p. 102-105°C/0.03).

Preparation of 2-(phenylthio)cyclohexanone 31 :

Following the procedure as described above **31** was prepared in 89% yield (184 mg) from α-nitroepoxide **7** (143 mg, 1 mmol) and sodium thiophenolate (132 mg, 1 mmol). B.P. 104-106°C/0.03 mm, (lit.[53]b.p. 101-105°C /0.03 mm).

Preparation of 2-[(carbethoxy)methylthio]cyclopentanone 32 :

Ethyl 2-mercaptoacetate (120 mg, 1 mmol) dissolved in 1 ml ethanol was added dropwise at 0°C to a stirred solution of NaOEt (68mg,1mmol). After 30 min., a solution of **6** (129 mg, 1 mmol) in dry ethanol (1 ml) was added to the above reaction mixture at room temperature. It was stirred for additional 5 min. and solvent was removed under vacuum. The residue was diluted with water (10 ml) and extracted with ether (3 x 15 ml). Usual work up thereafter led to a crude product whose purification by PLC (eluent:benzene, acetone = 95,5) gave 164 mg of **32**. Yield : 81%. IR (neat) 1720, 1740 cm^{-1}; ^{1}H-NMR (CCl_4): δ 1.2(t, 3H, $-OCH_2\underline{CH}_3$, J = 7 Hz), 1.50-2.73 (m, 6H, ring 3 CH_2s'), 3.10 (s, 2H, $-S-\underline{CH}_2-C=O$), 3.03-3.43 (m, 1H, methine), 4.06 (q, 2H, $-O-\underline{CH}_2CH_3$, J = 7 Hz); mass spectrum, m/e 202.

Preparation of 2-[(carbethoxy)methylthio]cyclohexanone 33 :

Following the procedure described for **32**, compound **33** was prepared from the sodium salt of ethyl 2-mercaptoacetate (142 mg, 1 mmol) and α-nitroepoxide **7** (143 mg, 1 mmol) in 80% yield (173 mg). IR (neat) 1720, 1735 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 1.23 (t, 3H, $-O-CH_2-\underline{CH}_3$, J = 7 Hz), 1.4-3.0 (m, 8H, 4 CH_2s'), 3.07 (s, 2H,$-S-\underline{CH}_2-$), 3.33-3.60 (m, 1H,$-CO-\underline{CH}-S-$), 4.06 (q, 2H, $-O-\underline{CH}_2-CH_3$, J = 7 Hz); mass spectrum, m/e 216.

Reduction of 32 and 33 with $NaBH_4$:

The keto ester **32** (202 mg, 1 mmol) or **33** (216 mg, 1 mmol) dissolved in 95% ethanol (2 ml) was treated with $NaBH_4$ (38 mg, 1 mmol). After stirring for 30 min., ethanol was removed under vacuum and the reaction mixture diluted with brine (5 ml) and extracted with CH_2Cl_2 (4 x 25 ml). Further work up gave a crude product which was purified by PLC (eluent : benzene, acetone = 95,5) to obtain thick oils. **34** : 180 mg (88%) and **35** : 197 mg (91%).

Preparation of trans-2-acetoxycyclopentyl(carbethoxy)methyl sulphide 36 :

A mixture of the hydroxy ester 34 (204 mg, 1 mmol) and acetic anhydride (204 mg, 2 mmol) in 1 ml of anhydrous pyridine was stirred at room temperature for 8 hr. It was then poured into ice cold water (5 ml) and extracted with ether (3 x 10 ml). After usual work up and purification of the crude product by PLC (eluent : benzene, acetone = 85, 15). Yield : 236 mg (96%); m.p. 58-60°C. IR (CCl_4) 1735 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 1.24 (t, 3H, $-OCH_2\underline{CH}_3$, J = 7 Hz), 1.34-2.08 (m, 6H, $3CH_2$s'), 2.02 (s, 3H, $-OCOCH_3$), 2.89-3.14 (m, 1H, -CH-S-), 3.06 (d, 2H, $-S-CH_2-$, J = 5.2 Hz), 4.05 (q, 2H, $-OC\underline{H}_2CH_3$, J = 7 Hz), 4.84-5.12 (m, 1H, -CHOAc); mass spectrum, m/e 246; Anal. Calcd. for $C_{11}H_{18}O_4S$: C, 53.66; H, 7.31; S, 13.00. Found : C, 53.64; H, 7.29; S, 12.96.

Preparation of trans-2-acetoxycyclohexyl(carbethoxy)methyl sulphide 37 :

Following the procedure as above from the hydroxy ester 35 (218 mg, 1 mmol), acetic anhydride (204 mg, 2 mmol) and pyridine (1 ml) was obtained 37. Yield : 247 mg (95%); m.p. 69-72°C. IR (CCl_4) : 1740 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 1.26 (t, 3H, $-OCH_2\underline{CH}_3$, J = 7Hz), 1.33-2.13 (m, 8H, ring 4 CH_2s'), 2.0 (s, 3H, $-OCOCH_3$), 2.93-3.16 (m, 1H, -C<u>H</u>-S-), 3.06 (d, 2H, $-S-C\underline{H}_2-$, J = 5Hz), 4.06 (q, 2H, $-OC\underline{H}_2CH_3$, J = 7Hz), 4.83-5.10 (m, 1H, -C<u>H</u>-OAc); mass spectrum, m/e 260; Anal. Calcd. for $C_{12}H_{20}O_4S$: C, 55.38; H, 7.69; S, 12.30. Found : C, 55.42; H, 7.72; S, 12.28.

Preparation of trans-2-hydroxycyclopentyl(carbethoxy)methyl sulphide 34 and trans-2-hydroxycyclohexyl(carbethoxy)methyl sulphide 35 via baker's yeast reduction :

To the keto ester 32 (1.01g, 5 mmol) was added fermented baker's yeast prepared form sucrose (2g) and baker's yeast (1.5g) and water (4ml) and stirred for 24 hr. The reaction mixture was filtered through a pad of celite and the celite cake washed thoroughly with ethyl acetate (3x15 ml). The combined organic extracts were washed with water (2x10 ml) and with brine (10 ml) and dried over anhydrous Na_2SO_4. Evaporation of the solvent yielded a crude product whose purification by column chromatography yielded a pure product 164 mg (16%). IR (neat): 3400, 1740 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 1.21 (t, 3H, $-OCH_2\underline{CH}_3$, J = 7 Hz), 1.42-2.40 (m, 6H, ring 3 CH_2s'), 2.82-3.10 (br.s, 1H, -OH), 3.12 (d, 2H, $-SCH_2-$, J = 3Hz), 3.71-3.82 (m, 1H, -CH-S-), 3.83-4.02 (q, 2H, $-OC\underline{H}_2CH_3$, J = 7 Hz), 4.48-4.9 (m, 1H, -C<u>H</u>-OH); mass spectrum, m/e 204.

Following the above described procedure 35 was prepared from the ketoester 33 (1.08g, 5 mmol) and baker's yeast (amount as above). Yield: 185 mg(17%). IR (neat) : 3420, 1735 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 1.23 (t, 3H,

$-OCH_2\underline{CH}_3$, J = 7 Hz), 1.40-2.36 (m, 8H, ring 4 CH_2s'), 2.76-3.06 (br.s, 1H, -OH), 3.1 (d, 2H, $-SCH_2-$, J = 2 Hz), 3.63-3.86 (m, 1H, -CH-S-), 3.96-4.06 (q, 2H, $-O\underline{CH}_2CH_3$, J = 7 Hz), 4.46-4.86 (m, 1H, -CHOH) ; mass spectrum, m/e 218.

Preparation of 1-oxa-4-thiahydrindan-2-one 38 :

The hydroxy ester **34**, obtained via baker's yeast reduction,(204 mg, 1 mmol) was refluxed in dry benzene (5 ml) with p-toluenesulphohic acid monohydrate (9 mg) for 15 min.; while benzene-ethanol azeotrope was slowly removed. After cooling, the acid catalyst was neutralised by adding 10% aqueous $NaHCO_3$ solution dropwise. The reaction mixture was diluted with ethyl acetate (15 ml), washed with water (2 x 10 ml), brine (10 ml) and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a crude product which was purified by PLC (eluent : benzene) to obtain **38**. Yield : 152 mg (96%); m.p. 63-65°C. IR ($CHCl_3$) : 1740 cm^{-1}; ^{1}H-NMR (CCl_4) :δ 1.5-2.3 (m, 6H, ring 3 CH_2s'), 2.7 (d, 1H, $-S-C\underline{H}_c-CH_d$——COO-, J = 15 Hz), 3.3 (d, 1H, $-S-CH_c-C\underline{H}_d-COO-$, J = 15 Hz), 3.10-3.42 (m, 1H, -CH-S-), 4.40-4.83 (m, 1H, -CH-O-); mass spectrum, m/e 158; optical rotation $[\alpha]_D^{25}$: -122° (c, 0.5, $CHCl_3$).

Preparation of trans-heptahydro-1,4-benzoxathian-2-one 39 :

Following the procedure as detailed above, the hydroxy ester **35** (218 mg, 1 mmol) on lactonisation gave the lactone **39** as a white solid. Yield : 167 mg (97%); m.p. 89-91°C (lit.[40] m.p. 87-89°C). IR ($CHCl_3$) : 1744 cm^{-1}; ^{1}H-NMR (CCl_4) :δ 1.07-2.3 (m, 8H, ring 4 CH_2s'), 2.73 (d, 1H, $-S-C\underline{H}_c-CH_d-COO-$, J = 14 Hz), 3.33 (d, 1H, $-S-CH_c-C\underline{H}_d-COO-$,J =14Hz), 3.0-3.42 (m, 1H, $-C\underline{H}-S-CH_2-$), 4.43-4.72 (m, 1H, -CH-O-CO-); mass spectrum, m/e 172; optical rotation $[\alpha]_D^{25}$: -122°(c, 1, $CHCl_3$).

Preparation of diethyl 2-oxocyclopentyl malonate 40 and diethyl 2-oxocyclohexyl malonate 41 :

Freshly distilled diethyl malonate (160 mg, 1 mmol) in dry THF (2 ml) was added to a well stirred suspension of NaH (50 mg, 1.05 mmol) at 0°C. After stirring for 45 min. at 0-15°C, α-nitroepoxide **6** (129 mg, 1 mmol) was added dropwise to the reaction mixture at 10-15°C. After further 5 min. stirring, THF was removed under vacuum and the reaction mixture diluted with water (10 ml) and extracted with ether (3 x 15 ml). Usual further work up gave a crude product which was purified by distillation. Yield : 145 mg (60%); b.p. 101-103°C/ 1 mm. IR (neat) : 1720, 1750 cm^{-1}; ^{1}H-NMR (CCl_4) :δ 1.26 (t, 6H, 2 x $-OCH_2C\underline{H}_3$, J = 7 Hz), 1.66-2.86 (m, 7H, 3 CH_2s', -CH-CO-), 3.61 (d, 1H, $-C\underline{H}(COOEt)_2$, J = 5 Hz), 4.10 (q, 4H, 2 x $-O-C\underline{H}_2CH_3$, J = 7 Hz); mass spectrum, m/e

242; Anal. Calcd. for $C_{12}H_{18}O_5$: C, 59.5; H, 7.44. Found : C, 59.55; H, 7.50.

Following the procedure as described above **41** was obtained from α -nitroepoxide **7** (143 mg, 1 mmol) and sodiodiethyl malonate (182 mg, 1 mmol) in 62% yield (159 mg); b.p. 108-112°C/1 mm (lit.[54] b.p. 109-110°C/1 mm).

Preparation of ethyl 2-oxocyclopentyl(α -acetyl)acetate 42 and ethyl 2-oxocyclohexyl(α -acetyl)acetate 43 :

To a stirred suspension of NaH (53 mg, 1.1 mmol) in dry THF (3 ml) was added ethyl acetoacetate (130 mg, 1 mmol) in THF (2 ml) dropwise at 0°C. After 45 min. α -nitroepoxide **6** (129 mg, 1 mmol) was added dropwise at 15°C. After stirring for further 5 min. THF was removed under vacuum, the reaction mixture diluted with water (10 ml) and extracted with ether (3 x 15 ml). Usual work up then gave a crude product which upon distillation gave a colourless liquid **42**. Yield : 119 mg (56%); b.p. 142-143°C/5 mm (lit.[55] b.p. 138-140°C/5 mm).

The above described procedure was also followed to prepare **43** from α-nitroepoxide **7** (143 mg, 1 mmol) sodio ethyl acetoacetate (167 mg, 1.1 mmol) in dry THF. The crude product, upon distillation, gave a colourless liquid. Yield : 116 mg (51%), b.p. 119-121°C/1 mm. IR (neat) : 1720, 1740 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 1.26 (t, 3H, $-OCH_2\underline{CH}_3$, J = 7 Hz), 1.30-3.23 (m, 9H, 4 CH_2s' and $-\underline{CH}-C=O$), 2.26 (s, 3H, $O=\overset{|}{C}-CH_3$), 3.37 (d, 1H, $-CH(CO_2Et)_2$, J = 9 Hz), 4.1 (q, 2H, $-O\underline{CH}_2CH_3$, J = 7 Hz) ; mass spectrum, m/e 226; Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.72; H, 7.96. Found : C, 63.70; H, 7.90).

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

References and Notes

1. This paper is to be considered as part 5 in the series "Chemistry of Nitro Compounds". For part 4, see : ref. 44. For part 3 : see ref. 15. For part 2 : see ref. 5, and for part 1 : see Vankar, Y.D. and Bawa, A. Synthetic Commun. **1985**, 1253.

2. (i) Newman, H. and Angier, R.B. J. Chem. Soc. Chem. Comm. **1969**, 369.
   (ii) idem. Tetrahedron **1970**, 26, 825.

3. (i) Saito, I.; Takami, M.; Kanoike, T. and Matsura, T. Tetrahedron

Lett. **1972**, 13, 2689.
(ii) idem. Bull. Chem. Soc., Japan **1973**, 46, 3198.
(iii) Sokolov, N.A.; Chernov, Yu. G. and Glazkov, Yu. V. J. Org. Chem., USSR **1972**, 8, 2371.
(iv) Sokolov, N.A.; Chernov, Yu. G. and Mikhal'chuk ibid **1974**, 10, 2466.
(v) Sokolov, N.A.; Tischenko, I.G. and Kovganko, N.V. ibid **1978**, 14, 478.
(vi) idem, ibid, **1980**, 16, 248.
(vii) Fischer, R.H. and Weitz, H.M. Synthesis **1976**, 53.
(viii) Baer, H.H.; Madumelu, C.B.; Hanna, Z.S. and Potvin, P.G. Carbohydr. Res. **1979**, 76, 141 and references cited therein.
(ix) Nakagawa, T. and Sakakibara, T. ibid **1987**, 163, 227 and references cited therein.
(x) Miyashita, M.; Suzuki, T. and Yoshikoshi, A. Chemistry Lett. **1987**, 285.

4. (i) Ashwell, M. and Jackson, R.F.W. J. Chem. Soc. Chem. Comm. **1988**, 282.
(ii) Ashwell, M.; Jackson, R.F.W. and Kirk, J.M. Tetrahedron **1990**, 46, 7429.

5. Vankar, Y.D. and Singh, S.P. Chemistry Lett. **1986**, 1939.

6. (i) Suzuki, M.; Watanabe, A. and Noyori, R. J. Am. Chem. Soc. **1980**, 102, 2095.
(ii) idem. Recl. Trav. Chim. Pays-Bas **1988**, 107, 230.

7. Suzuki, M.; Oda, Y. and Noyori, R. J. Am. Chem. Soc. **1979**, 101, 1623.

8. A saturated nitro compound e.g. nitrocyclohexane, however, was not found to form cyclohexanone under the present reaction conditions. Hence the presence of a ketone adjacent to the nitro group is essential to form a diketone.

9. Russel, G.A. and Mikol, G.J. J. Am. Chem. Soc. **1966**, 88, 5498.

10. Dictionary of Organic Compounds, 4th Ed., Oxford University Press, New York, **1965**.

11. Bratchansku, P.E.; Komissarova, G.G. and Esipov, G.V. Zh.Org.Khim. **1985**, 21, 2143, C.A. **1986**, 104, 1677764C.

12. Anders, E.; Clark, T. and Gassner, T. Chem. Ber. **1986**, 119, 1350.

13. Rao, D.V.; Stuber, F.A. and Ulrich, H. J. Org. Chem. **1979**, 44, 456.

14. (i) Trost, B.M. and Massiot, G.S. J. Am. Chem. Soc. **1977**, 99, 4405.
(ii) Carre, M. and Caubere, P. Tetrahedron Lett. **1985**, 26, 3103 and references cited therein.

15. For a preliminary account see : Vankar, Y.D.; Saksena, R.K. and Bawa, A. Chemistry Lett. **1989**, 1241.

16. Shah, K., Ph.D. Thesis, **1990**, IIT Kanpur, India.

17. Davis, F.A.; Vishwakarma, L.C. and Billmers, J.M. J. Org. Chem. **1984**, 49, 3241.

18. Josephson, D.B.; Lindsay, R.C. and Stuiber, D.A. Can. Inst. Food Sci. Technol., J. **1984**, 17, 178.

19. Piskunova, Zh.P.; Popov, A.F. and Matvienko, N.N. Org. React. (Tartu) **1984**, 21, 428, C.A. **1986**, 104, 108930h.

20. Rubottom, G. M. and Mort, R.C., ibid **1979**, 44, 1731.

21. Cardillo, G. and Shimuzu, M. J. Org. Chem. **1977**, 42, 4268.

22. Product formation was indicated by the IR spectrum and TLC analysis of the crude reaction mixture. However, the reaction was very slow and the product was found to decompose during purification.

23. (i) For somewhat similar studies with other α-nitroepoxides see ref. 3 (vi).
(ii) We thank the referee for bringing the references 3 (iv), 3(v) and 3(vi) to our attention.

24. Corey, E.J., J. Am. Chem. Soc. **1953**, 75, 2301.

25. Mousseron, M.; Jacquier, R. and Fontaine, A. Bull. Chem. Soc. Jpn. **1952**, 767.

26. Satoh, T.; Sugimoto, A. and Yamakawa, K. Chem. Pharm. Bull. **1987**, 35, 4632 and references cited therein.

27. Satoh, T.; Kaneko, Y.; Sakata, K. and Yamakawa, K. ibid **1986**, 59, 457 and references cited therein.

28. Banfi, L.; Bernardi, A.; Colombo, C.; Gernari, C. and Scolastico, C. J. Org. Chem. **1984**, 49, 3784 and references cited therein.

29. Desmaele, D. and d'Angelo, J. Tetrahedron Lett. **1989**, 30, 345.

30. Ogma, K. and Tsuchihasi, G. ibid **1977**, 13, 2681.

31. Dunbeck, H.W.; Frischkorn, C.G.B. and Hilpert, K. Tetrahedron **1971**, 27, 2927.

32. Deyrup, J.A. and Moye, U.V. J. Org. Chem. **1969**, 34, 1835.

33. Bokker, B.H.; van Ramesdonk, H.J.; Steinberg, H. and deBoer, Th.J. Rec. Trav. Chim. Pays. Bas **1975**, 94, 64.

34. Kabalka, G.W. and Varma, R.S. Synthetic Commun. **1985**, 15, 443.

35. Hwu, J.R. and Wang, N. J. Chem. Soc. Chem. Comm. **1987**, 427.

36. Palmo, C.; Oiarbide, M. and Aizpurua, J.M. Tetrahedron Lett. **1987**, 28, 5361.

37. Begley, M.J.; Ladlow, M. and Pattenden, G. J. Chem. Soc. Perkin Trans. I **1988**, 1095.

38. (i) Trost, B.M. Chem. Revs. **1978**, 78, 363
(ii) Satoh, T.; Kumagawa, T. and Yamakawa, K. Bull. Chem. Soc. Jpn. **1985**, 58, 2849 and references cited therein.

39. Cocker, W. and Hopkins, L.O. J. Chem. Soc. **1961**, 4721.

40. Barry, C.N.; Baumrucker, S.J.; Andrews, R.C. and Evans, Jr. S.A. J. Org. Chem. **1982**, 47, 3980.

41. Servi, S. Synthesis, **1990**, 1.

42. Kozikowski, A.P. and Murage, B.B. J. Org. Chem. **1989**, 54, 2274.

43. King, R.R.; Greenhalgh, R. and Marshall, W.D. ibid **1978**, 43, 1262.

44. Vankar, Y.D.; Bawa, A. and Kumaravel, G. Tetrahedron **1991**, 47, 2027.

45. Boberg, F.; Garburg, K. -H.; Gorlich, K. -J.; Pipereit, E. and Ruhr, M. Liebigs Ann. Chem. **1985**, 239.

46. Ono, N.; Kamimura, A.; Kawai, S. and Kaji, A. Nippon Kagaku Kaishi **1987**, 1338, C.A. **1988**, 108, 131212 s. .

47. Schecter, H.; Ley, D.E. and Robertson, Jr. E.B. J. Am. Chem. Soc. **1956**, 78, 4978.

48. Melton, J. and McMurry, J.E. J. Org. Chem. **1975**, 40, 2138.

49. Seebach, D. and Knochel, P. Synthesis **1982**, 1017.

50. Corey, E.J. and Estreicher, H. J. Am. Chem. Soc. **1978**, 100, 6294.

51. Seebach, D.; Calderari, G. and Knochel, P. Tetrahedron **1985**, 41, 4861.

52. In case of **6** and **7**, after neutralisation with dil. HCl, the mixture was treated with NaCl and extracted with ethyl acetate and the products purified by distillation.

53. Posner, G.H. and Chapdelaine, M.J. Tetrahedron Lett. **1977**, 17, 3227.

54. Berlin, Yu. A.; Volkov, P.; Koslov, M.N.; Ovchinnikov, Yu. A.; Ta'o, chen and Shemyakin, M.M. Zh. Obshch. Khim. **1964**, 34, 790.

55. Machinskaya, I.V.; Smirova, G.P. and Barkhash, V.A. ibid **1962**, 32, 1248.