CHAPTER - III

OXIDATION OF THE PENTACYCLO [5.4.0.$O^{2,6}O^{3,10}O^{5,9}$]UNDECANE-8,11-DIONE-4-SPIRO-1'-CYCLOPROPANE (27) AND PENTACYCLO [5.4.0.$O^{2,6}O^{3,10}O^{5,9}$] UNDECANE-8,11-DIONE-4-SPIRO-1'-CYCLOPENTANE (31) WITH CERIC (IV) ION

III.1 ABSTRACT

In this chapter of the thesis, transformation of two cage diones, pentacyclo [5.4.0.$0^{2,6}0^{3,10}.0^{5,9}$] undecane-8,11-dione-4-spiro-1'-cyclopropane (27) and pentacyclo [5.4.0.$0^{2,6}$.$0^{3,10}.0^{5,9}$] undecane-8,11-dione-4-spiro-1'-cyclopentane (31) with Ce(IV) ion is reported. Oxidation of each of the diones 27 and 31 furnished a mixture of three compounds which were separated by a careful chromatography of the product mixture on silica gel. The isomeric anhydrides 28, 29 followed by the lactone 30 from the oxidation of dione 27 and anhydrides 32, 33 followed by the lactone 34 were obtained from the dione 31 respectively. Structure of all these products (28-30 and 32-34) have been deduced from spectral data and a plausible mechanism has been advanced to explain the formation of various products.

III.2 INTRODUCTION

Ceric ion in various coordinated forms has been known as strong oxidizing agent for many decades.[1] However, early use of ceric ion in organic chemistry was primarily restricted to colorimetric and quantitative estimation[2] of alcohols. later studies revealed the ability of ceric ion to oxidise a variety of organic functional groups but these efforts are mostly devoted to the elucidation of reaction kinetics and little, if any, effort was expanded to the preparative aspects of these reactions.[1] Investigation during the last decade by Trahanovsky[3] and others[4] on ceric ammonium nitrate (CAN) and ceric ammonium sulphate (CAS) oxidation of a number

of organic compounds have drawn attention to the synthetic versatility of ceric ion in preparative organic chemistry.[4] Consequently, a great deal of promising methodology has been realised[4] employing ceric ions. As the results described in this chapter deals with oxidation of polycyclic ketones with ceric ion , it will be desirable to briefly discuss the oxidation of common organic functional groups with ceric reagents.

III. 2.1 Alcohols

Among various functional groups, alcohols are most readily oxidised by ceric ion and their reactions have been extensively studied. Thus benzylic[5] and cyclopropylcarbinyl[6] alcohols are oxidised to the corresponding aldehydes. Bridged bicyclic alcohols[7] and cyclobutanols[8] are oxidised with adjacent C-C bond fission. Simple cyclic alcohols like cyclopentanol and cyclohexanol as well as admantanol are oxidised[9] to the corresponding ketones in the presence of ceric ion. These reactions with typical illustrations are depicted in Scheme-III.1.

III.2.2 Carbonyl Compounds

Alicyclic ketones are rapidly consumed by ceric ammonium nitrate or ceric ammonium sulphate to furnish corresponding ω-nitrato carboxylic acids via a pathway involving α-cleavage.[10] Cyclopentanone, cyclohexanone and norbornanone (1) belongs to this category and furnish a mixture of ring opened carboxylic acids. (Scheme-III.2).

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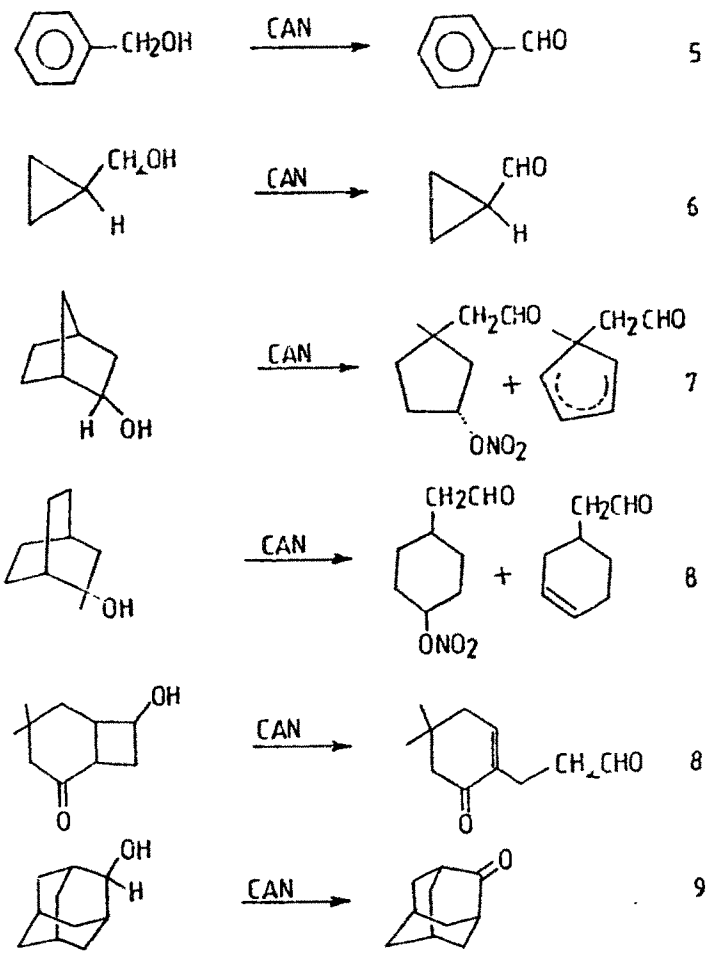

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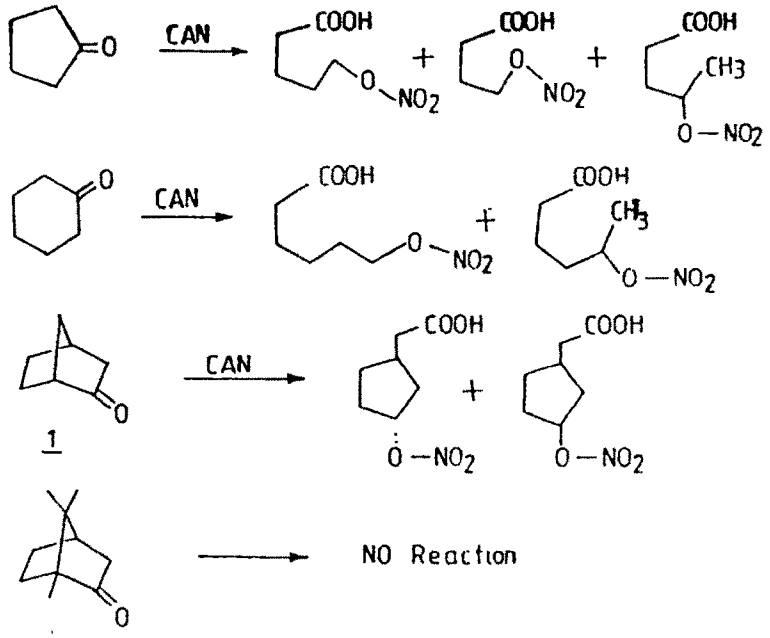

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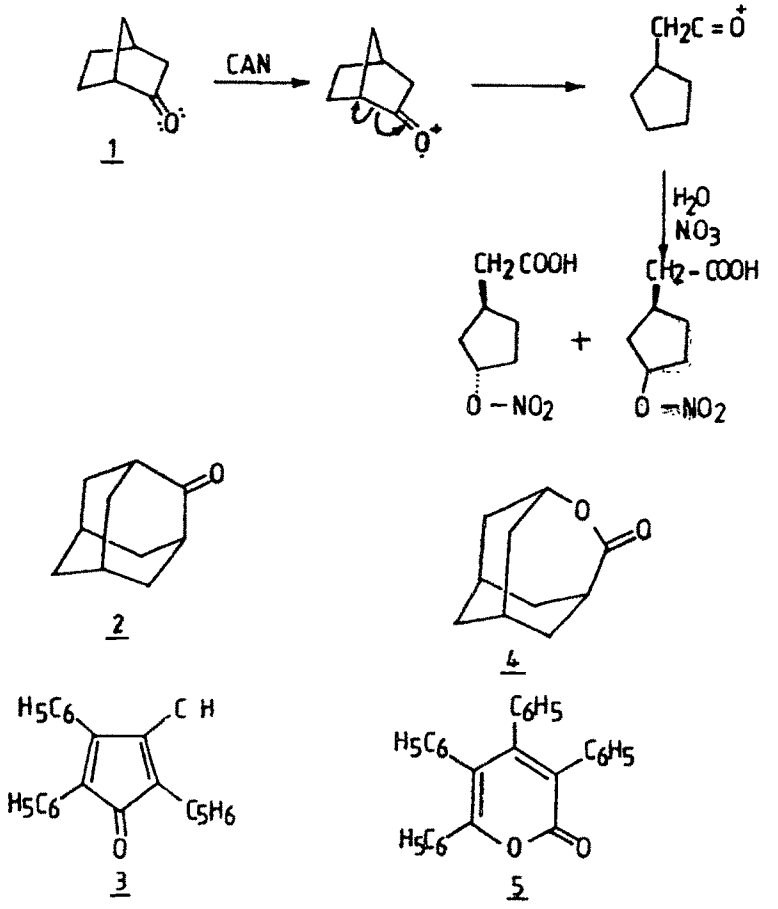
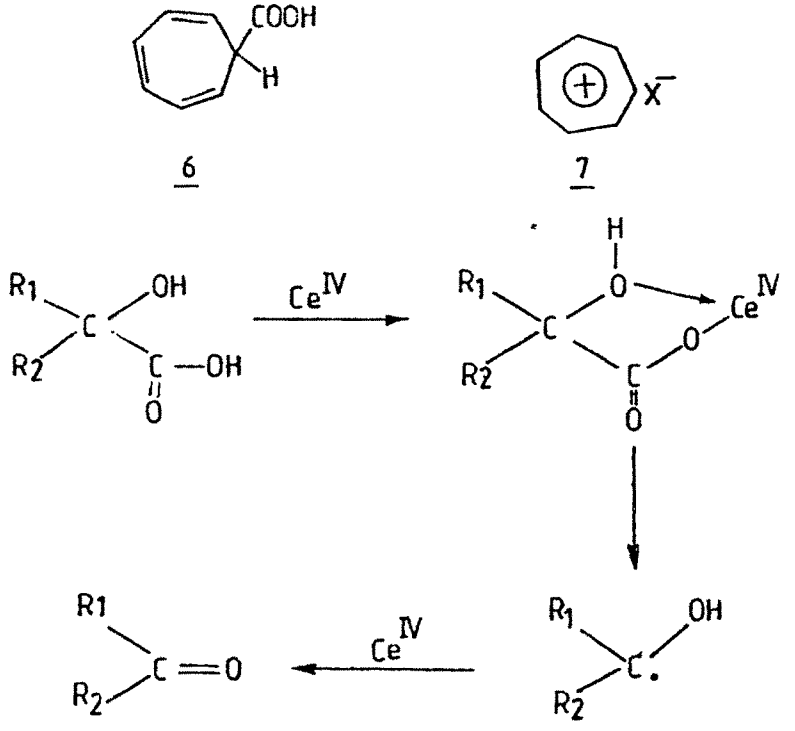
Surprisingly, camphor is inert towards CAN and this indicates that these oxidations require a close approach of the ketone and ceric ion, perhaps a complex formation is involved. Since Ce^{+4} is a bulky species in solution due to coordination with 8 to 12 atoms, its approach to camphor carbonyl is prohibited. Several mechanisms involving an enol intermediate[11] as well as α-hydrogen abstraction[12] have been formulated for ceric ion oxidation of ketones. The currently accepted mechanism[4,10] of ketone oxidation is illustrated for norbornanone (1) oxidation. Adamantanone (2) and Tetracyclone (3) exhibit unexpected behaviour towards CAN and undergo efficient Bayer-Villiger oxidation[10,13] to the lactone (4) and tetraphenyl α-pyrone (5) respectively (Scheme-III.3).



SCHEME-III.3

III. 2.3 Carboxylic acids

Simple aliphatic and aromatic carboxylic acids are usually stable towards ceric ion. However, oxalic acid[14] and malonic acid [15] are readily oxidised by ceric ion to carbon dioxide and water. The higher homologues of these dicarboxylic acids do not react with ceric ion. Cycloheptatriene carboxylic acid (6) is readily decarboxylated to tropilium salt (7) with CAN in 30% yield.[16] α-hydroxy carboxylic acids are degraded[17] to carbonyl compounds with the loss of a carbon atom by ceric ion and this constitutes a useful degradative method. (Scheme-III.4).



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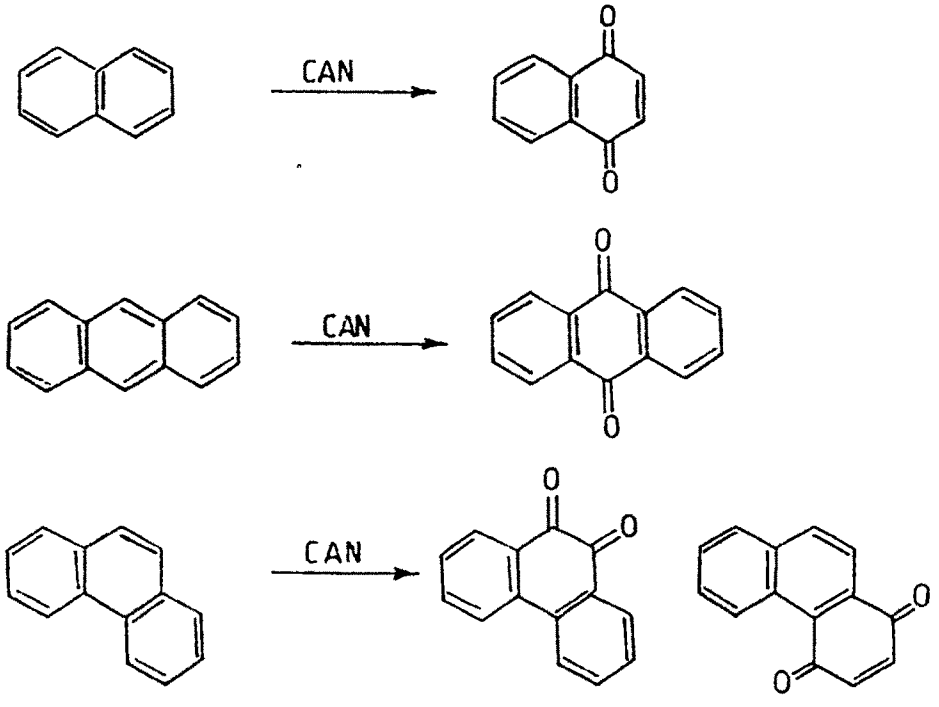
III.2.4 Hydrocarbons

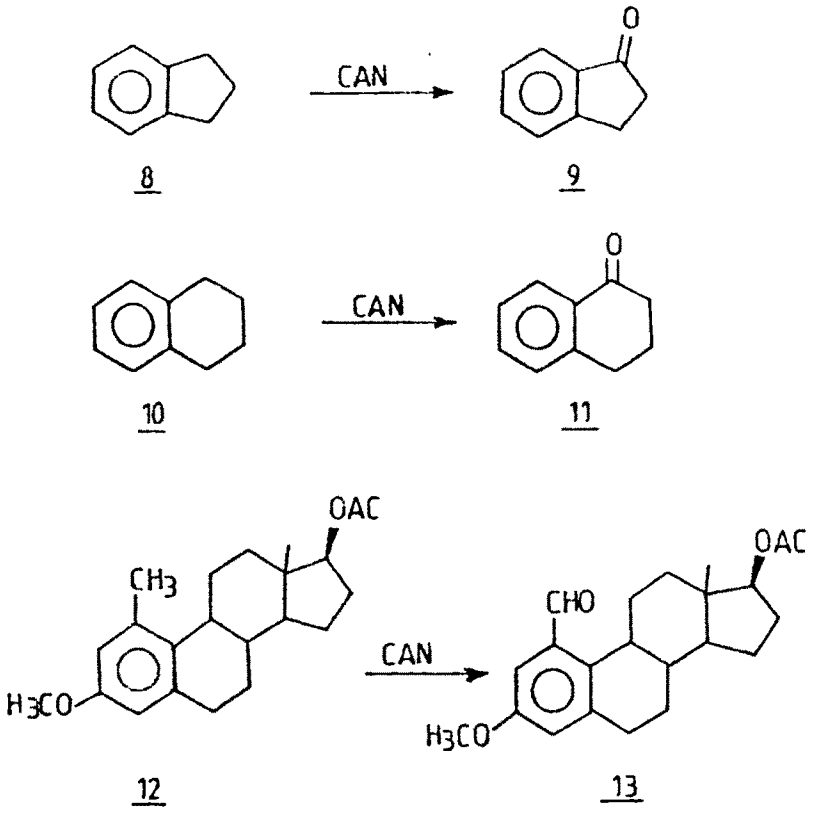
Aromatic hydrocarbons possessing benzylic, methyl and

methylene groups are rapidly oxidised to corresponding carbonyl function by CAN in acidic medium.[18] Thus, o- and p-xylenes are oxidised to 2- and 4-methyl benzaldehydes respectively in 100% yield.[18] Polynuclear hydrocarbons are directly oxidised[19] to quinones by CAN under mild conditions in reasonable yields (Scheme-III.5).



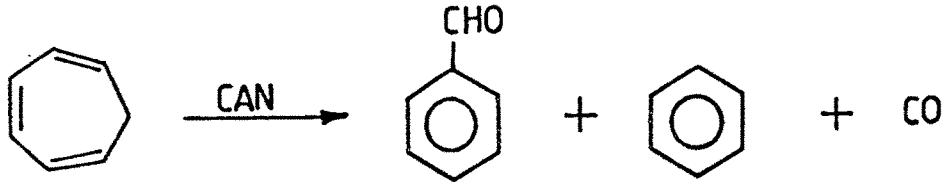
SCHEME-III.5

Efficient conversion of indane (8) to 1-indanone (9) tetralin (10) to 1-tetralone (11) and a steroidal substrate[20] 12 to 13 are useful examples of hydrocarbon oxidation. (Scheme-III.6).



SCHEME - III.6

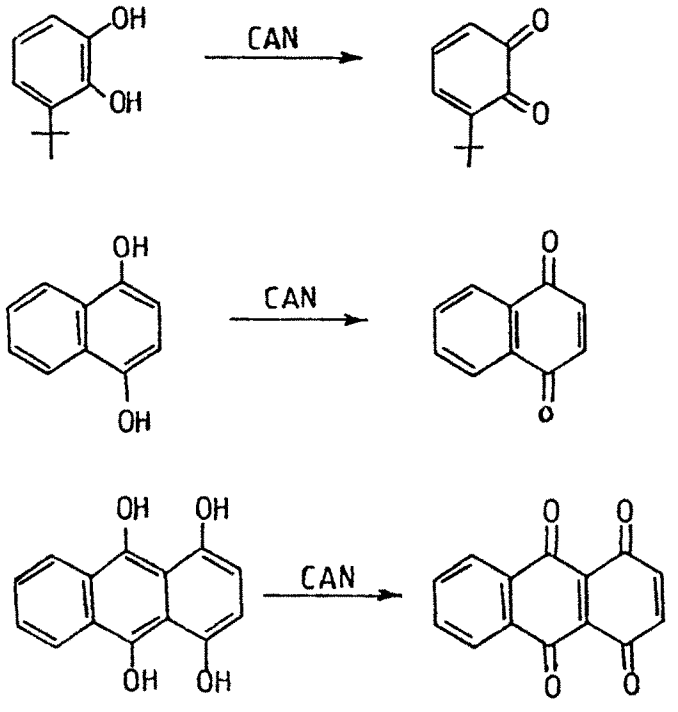
A mechanistically interesting example[21] of hydrocarbon oxidation is the oxidation of cycloheptatriene to benzaldehyde, benzene and carbon monoxide (Scheme-III.7).



SCHEME - III.7

III.2.5 Hydroquinones

Oxidation of hydroquinones to quinones can be effected with a variety of reagents but these reactions are generally messy and handicapped by low yields. However hydroquinones can be rapidly and efficiently oxidised to the corresponding quinones by CAN. This oxidation is applicable for the generation of ortho, para and diquinones. (Scheme-III.8)



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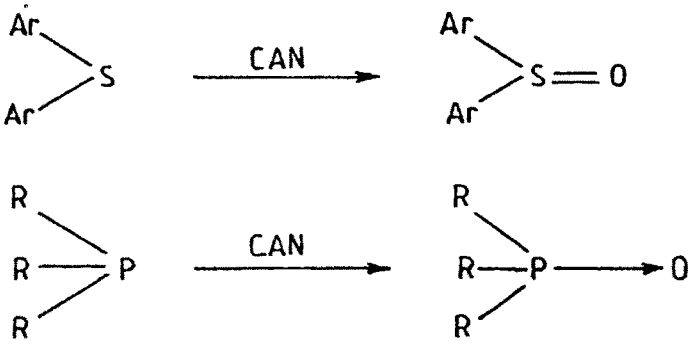
III.2.6 Oximes and Semicarbazones

In many synthetic operations, it is expedient to either protect or purify carbonyl compounds *via* their oxime and semicarbazone derivatives. Ceric ammonium nitrate regenerates[23] the parent ketone or aldehyde from oximes and semicarbazones at low temperature and in good yields. Thus providing

a superior and mild alternative to the conventionally used regeneration procedures.[23]

III.2.7 Miscellaneous

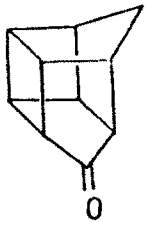
Diaryl sulphides are readily oxidised to the corresponding sulphoxides in high yield without any contamination of corresponding sulphones. Similarly, phosphines are quantitatively oxygenated[13] to phosphine oxides by ceric ion. (Scheme-III.9).



SCHEME - III.9

Among the various strained carbocyclic systems, the oxidation of only a few cage ketones (14-17) with Ce(IV) ion have been studied. (Scheme-III.10)

The unsymmetrical 1,3-bishomocubanone (14) has been reported to undergo an efficient regiospecific Bayer-Villiger type oxidation with ceric ammonium nitrate to yield the lactone (18) in good yield.[24] The observed regiospecificity



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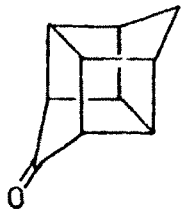

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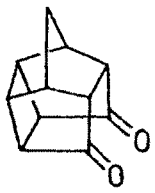

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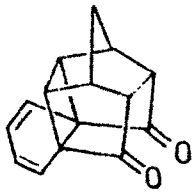

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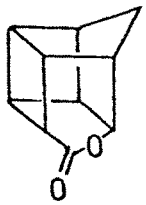

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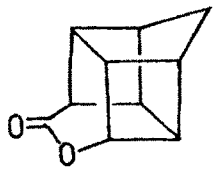

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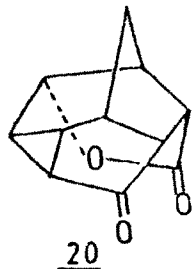

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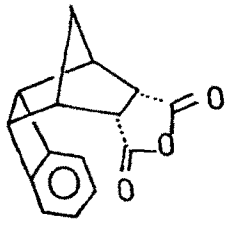

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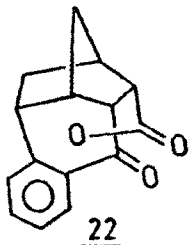

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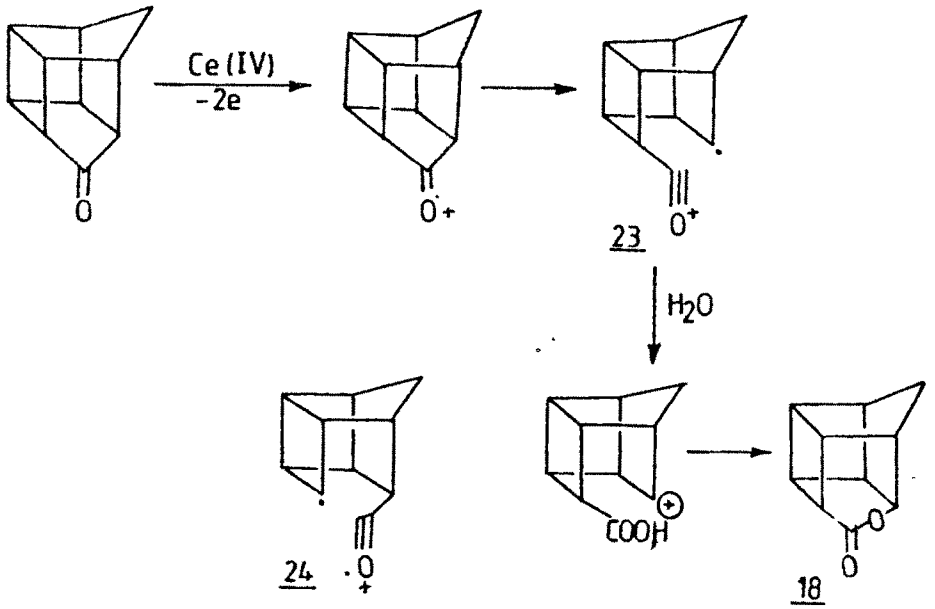
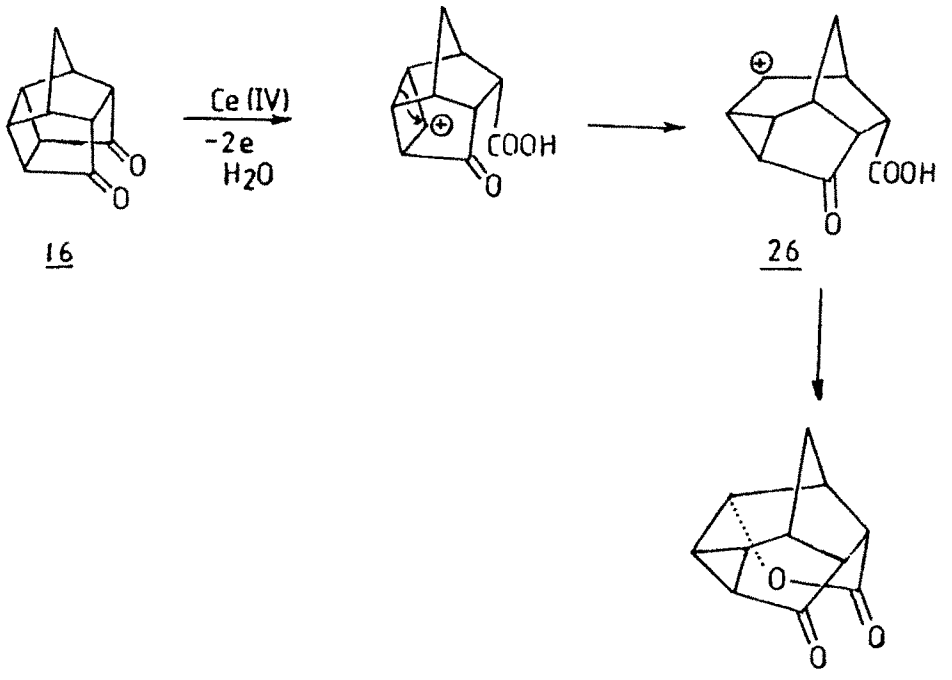
SCHEME-III.10

of this oxidation is apparently due to the greater stability of the cyclopentyl radical (23) over the cyclobutyl radical (24) which may result after α-cleavage (Scheme-III.11).



SCHEME - III. 11

Oxidation of 1,4-bishomocubanone[24] with CAN furnished the lactone (19). The pentacyclic dione (16) however, gave a ketolactone[24,25] (20) as a sole product probably arising via the cyclobutyl-cyclopropylcarbinyl rearrangement of the initially formed carbonium ion followed by lactonization. (Scheme-III.12).



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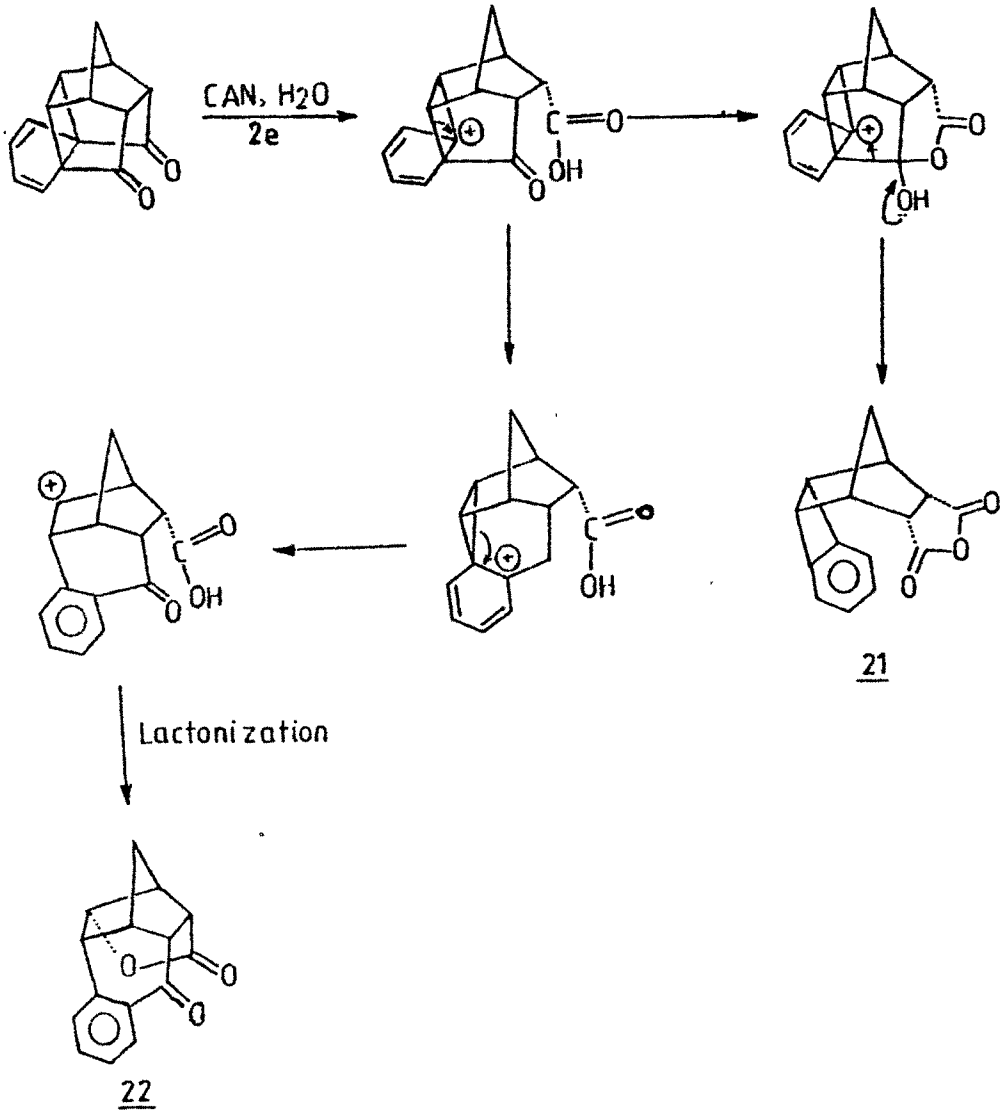
SCHEME - III. 12

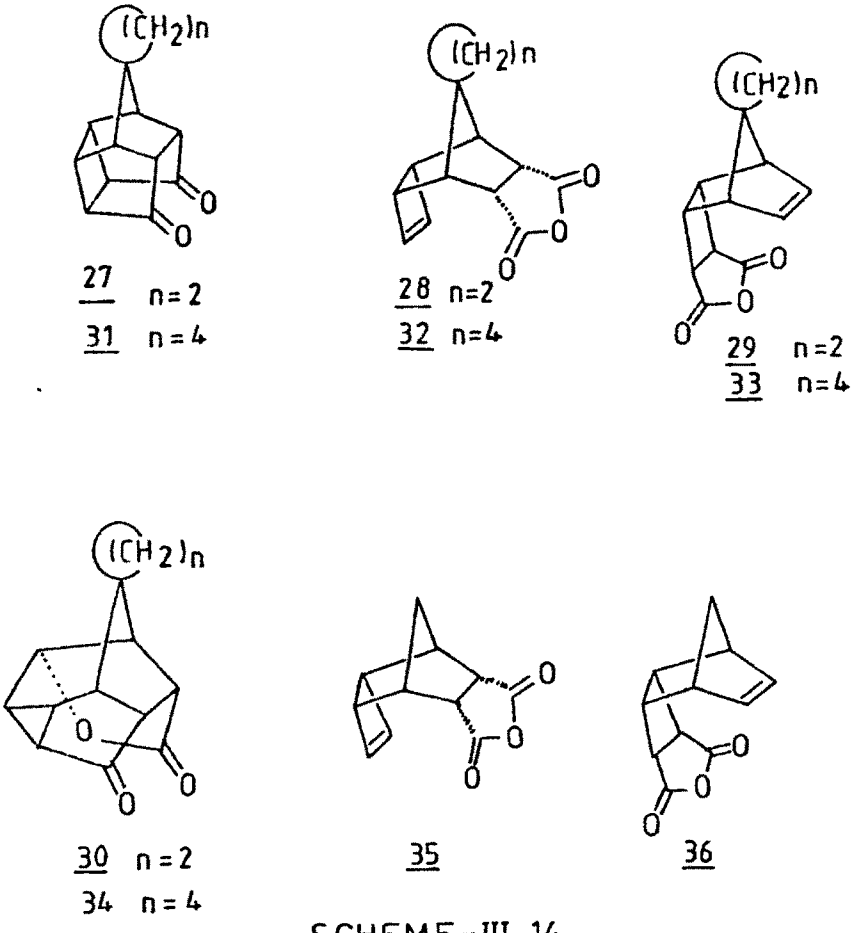
The hexacyclic dione (17), on the other hand took a slightly different course[26] upon its treatment with ceric ammonium nitrate and furnished the anhydride (21) in addition to the lactone (22). (Scheme-III.13).

In the light of these interesting and synthetically useful results, we have investigated the Ce(IV) ion oxidation of pentacyclo [5.4.0.$O^{2,6}O^{3,10}O^{5,9}$] undecane-8,11-dione-4-spiro-1'-cyclopropane (27) and its homologue, pentacyclo [5.4.0.$O^{2,6}O^{3,10}O^{5,9}$] undecane-8,11-dione-4-spiro-1'-cyclopentane (31) in order to explore the possibility of new routes to novel carbocyclics and to examine the effect of annulated spiro ring at the bridged methylene on the mode of oxidation.



SCHEME-III.13

In this section of the Chapter III of this thesis, we describe the formation and structure elucidation of three C_{13} and three C_{15} -novel carbocyclic systems (28-30) and (32-34) by Ce(IV) oxidation of (27) and (31) respectively. (Scheme-III.14)



SCHEME-III.14

III.3 Results and Discussion

The treatment of dione (27) (1 m mol) with ceric ammonium nitrate (CAN) (1.2 m mol) in aq. acetonitrile at ambient temperature (~32°, 1 h) and usual workup (vide

experimental) gave a mixture of compounds(tlc). A careful column chromatography of the product mixture over silica gel furnished three crystalline compounds, the isomeric anhydrides 28 (m.p. 218°), 29 (m.p. 178°) and the keto lactone 30 (m.p. 217°) in 5%, 10% and 50% respectively. The identity of these products were established as follows.

The infrared spectrum of 28 showed absorption bands (Fig.III.1) at 1850 and 1780 cm^{-1} clearly indicating the presence of anhydride moiety.[27] The proton nmr ($CDCl_3$, 100 MHz) (Fig.III.2) spectrum of 28 exhibited signals at δ 6.2 (s, 2H, olefinic H), 3.55 (m, 2H, methine H), 3.3 (m, 2H, methine H), 2.1 (br, 2 H) and 0.5 (m, 4H, cyclopropane CH_2). The olefinic singlet at δ 6.2 immediately suggested it to be a cyclobutene derivative. Since a C=C double bond in norbornane framework always appears as a triplet[29] and hence we formulated this anhydride as 28 which was further supported by other analytical data.

The anhydride 29 also showed absorption bands (Fig.III.3) 1790 cm^{-1}. Its proton nmr ($CDCl_3$, 100 MHz) spectra consisted of signals (Fig.III.4) at δ 6.4 (t, $J_1=J_2=2Hz$, 2H, olefinic H), 3.40 (m, 4H, methine H), 2.50 (br, s, 2H, methine H) and 0.45 (m, 4H, cyclopropane CH_2). In this case the olefinic signal at δ 6.4 appeared as a triplet ($J_1=J_2=2Hz$), characteristic of the double bond in the bicyclo [2.2.1]

framework.[29] We therefore assigned the structure 29 to this compound.

The structure of the ketolactone 30 was derived from the following spectral data and its similarity with the known ketolactone (20). The absorption bands (Fig.III.5) at 1770, 1715 cm^{-1} indicated the presence of lactone carbonyl and cyclopentanone. The mass spectral fragmentation (M^+ 216) of 30 with strong peaks at m/e 171 and 172 ($M^+ - CO_2$, $M^+ - CO_2H$) and 144 and 143 ($M^+ - CO_2$-COH), ($M^+ - CO_2$, CO) is in complete harmony with the ketolactone structure. Proton nmr spectra ($CDCl_3$, 90 MHz) displayed signals (Fig.III.6) at δ 5.11 (1H, t, J=7.5Hz, H-C-O-C), 3.00 (t, J=5Hz, methine H), 2.72 (m, 2H, methine H), 2.52 (m, 4H, ring H), 2.01 (d, 1H, $J_1 = J_2$ =4Hz, ring H) and 0.62 (m, 4H, cyclopropane CH_2). ^{13}C-NMR (DMSO-d_6) (Fig.III.7) δ 210.52 (C=O), 174.62, 76.04, 50.42, 49.38, 45.87, 42.62, 33.25, 31.82, 26.23, 20.51, 9.97, 2.42 (due to cyclopropyl carbon). The signal at 20.51 in the ^{13}cmr of the lactone 30 suggested[25] the presence of a cyclopropyl carbon conjugated with carbonyl group.

Similarly the reaction of the cage dione (31) (1 m mol) with ceric ammonium nitrate (1.2 m mol) in aq. acetonitrile furnished three compounds the isomeric anhydrides 32 (m.p. 162°), 33 (m.p. 156°) and the ketolactone 34 (m.p. 195°)in 7%, 11% and 40% yields respectively.

The anhydride 32 showed absorption bands (Fig.III.8)

at 1860 and 1780 cm^{-1} in its infra-red spectra. Proton nmr ($CDCl_3$, 90 MHz) (Fig.III.9) exhibited following resonances at δ 6.25 (s, 2H, olefinic H), 3.65 (br, s, 2H, methine H), 3.45 (br, s, 2H, methine H), 2.35 (m, 2H) and a broad signal at 1.7 (8H) for methylene proton of the spiroring substituent. Similarity of these spectral features with that of 28 and the characteristic singlet at 6.25 for the olefinic protons present in the cyclobutene ring suggested the structure 32 for this anhydride.

The anhydride 33 also showed bands (Fig.III.10) at 1850 and 1790 cm^{-1} in its IR spectrum and displayed an olefinic signal in its NMR ($CDCl_3$, 90 MHz) (Fig.III.11) spectrum at δ 6.40 as a triplet (J=3Hz) in addition to the resonances at 3.35 (br, 4H), 2.65 (br s, 2H, methine H), 1.7 (m, 6H, CH_2 proton) and 1.45 (m, 2H, methylene proton). The splitting of the methylene proton of the spiro ring substituent in two groups (one CH_2 appearing at 1.7 the other at 1.45) in the nmr spectrum also supports the formulation of 33 for this anhydride, since the protons syn to the double bond are known[29] to resonate at higher fields.

The structure of the ketolactone (34) was similarly derived from its spectral data. The IR spectrum of the compound

showed absorption bands (Fig.III,12) at 1775 and 1720 cm^{-1} characteristic for a lactone carbonyl and cyclopentanone carbonyl group. The mass spectral fragmentation of 34 (M^+ 244) with peaks at m/e 200, 199 ($M^+ - CO_2$, $M^+ - CO_2H$) and 172, 171 ($M^+ - CO_2 - CO$, $M^+ - CO_2 - COH$) also suggested the ketolactone structure. The proton nmr ($CDCl_3$, 300 MHz) (Fig.III.13) spectra showed a triplet at δ 5.12 (t, J=7Hz), characteristic of a H-O-C=O functionality in addition to the signals at 2.9 (m, 1H), 2.85 (m, 2H), 2.7 (m, 1H), 2.6 (m, 1H), 1.95 (m, 2H), 1.9 (m, 1H), 1.7 (m, 5H), 1.35 (m, 2H). ^{13}C-NMR (DMSO-d_6) (Fig.III.14) spectra at δ 210.39 (C=O), 175.0, 76.17, 52.63, 52.24, 48.86, 44.44, 41.45, 36.50, 32.34, 31.82, 28.18, 24.28, 23.63, 20.25 (due to cyclopropyl carbon conjugated with C=O).

Similarity of these spectral features with the lactone (20) also supported the assigned structure to the lactone 34.

In view of these results, it is interesting to record that the Ce(IV) ion oxidation of the parent dione (16) gives only the ketolactone (20) none of the anhydrides of the type (35 or 36) have been observed.[24,25] However the oxidation of the annulated diketone (17) with Ce(IV) ion gave the anhydride 21 in addition to the lactone 22.[26]

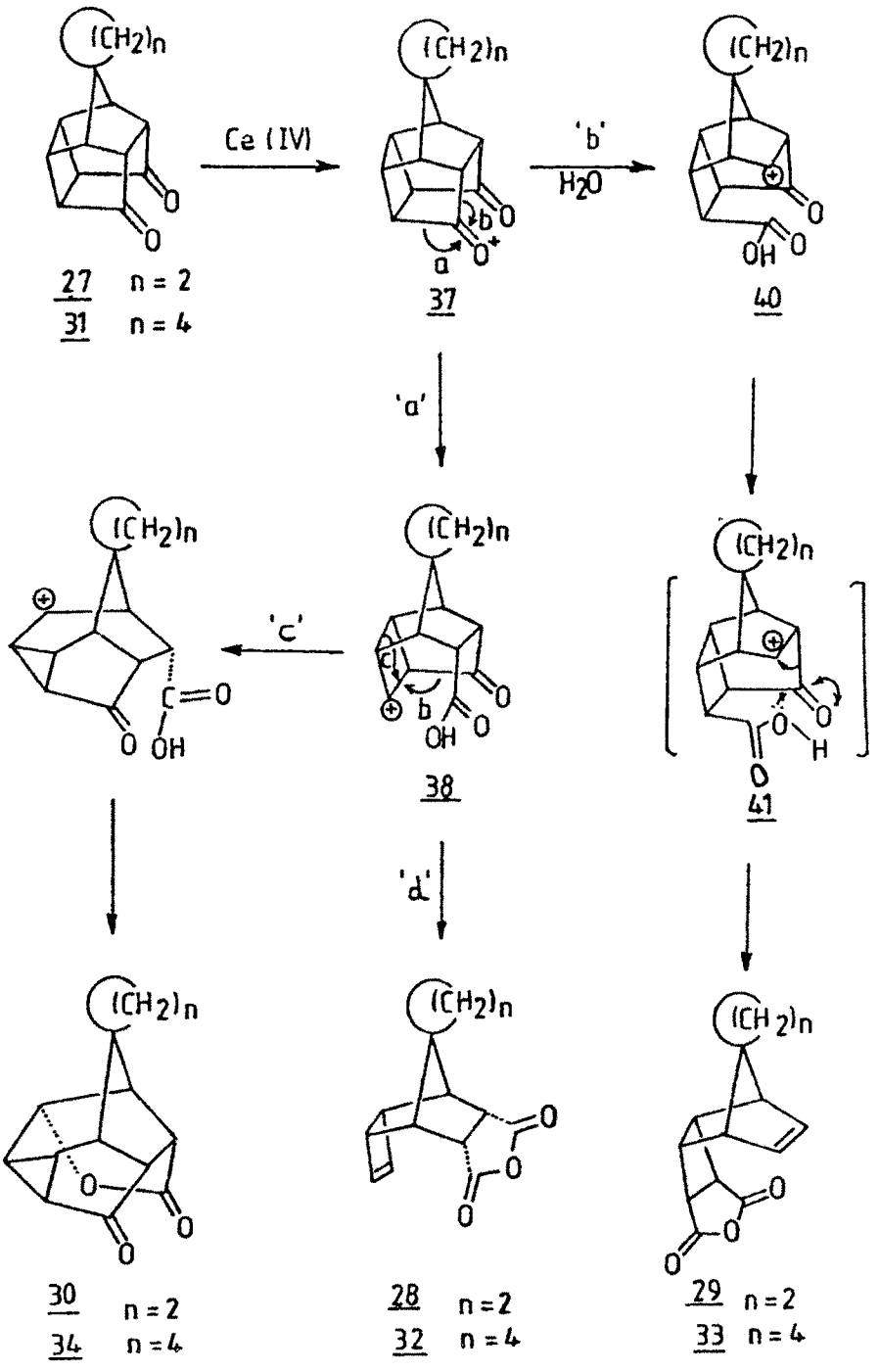
The results of oxidation of spirodiones (27 & 31) indicate that additional modes of fragmentation is competing

with the fragmentation mode observed[25] with 16. A plausible mechanism for the formation of the various products is outlined in the Scheme-III.15 and is in harmony with the currently accepted mechanism of ceric ion oxidation.

The formation of the cyclobutene anhydrides (28 & 32) and the ketolactones (30 & 34) can be rationalized through the formation of the cyclobutyl carbocation (38) via fragmentation of the bond 'a' in the species 37, which can either undergo cyclopropyl-carbinyl rearrangement (mode c) to 39 and lactonizes to give (30 & 34) or it may undergo 'α' cleavage (mode 'd') leading to the cyclobutyl anhydrides. (28 & 32) (Scheme-III.15)

On the other hand the genesis of the anhydrides (29 & 33) requires the formation of the norbornyl cation (40) which may result through alternate mode of α-cleavage in the intermediate (37) (mode 'b') subsequent carboxyl induced cleavage of 41 followed by anhydride formation results in the anhydrides (29 & 33) (Scheme-III.15).

In the absence of any other data regarding molecular parameters of the diones (27 & 31), it is rather difficult to rationalize the difference in the behaviour of the cage ketones 16, 17 and 27 & 31 towards ceric(IV) ion oxidation, especially the formation of the anhydrides 29 & 33 in the



SCHEME-III.15

latter case. Apparently, the spiroannulation also favours the alternate fragmentation (mode b) of the species 37, leading to the formation of norbornyl type cation 40 in addition to the usual fragmentation (mode 'a'). This competitive fragmentation (mode b) could be the result of the homoconjugative stabilization of incipient norbornyl type cation (40) through σ participation[31] of the carbon-carbon bond of the annulated rings. A cyclopropane ring is well known to assist the formation of a carbocation at β-position[32,33] through its interaction with the 'corner' in addition to its ability to stabilize a cation at adjacent centre through the 'edge'. However, not much is known about the σ-participation of other rings.

III.4 Experimental

General Remarks : Please refer Chapter-II, Section-5.

Oxidation of pentacyclo [5.4.0.$0^{2,6}0^{3,10}0^{5,9}$] undecane-8,11-dione-4-spiro-1'-cyclopropane (27) with Ce(IV) ion

To a slurry of ceric ammonium nitrate (6 g, 0.011 mol) in water (30 ml) was added a solution of spirocagedione (27) (1 g, 0.005 mol) in acetonitrile (20 ml). The reaction mixture was stirred at room temperature (32°) for about 1 h (tlc), it was diluted with water, extracted with dichloromethane (3 x 50 ml). The combined extract was washed with water (2 x 15 ml), brine (2 x 10 ml) and dried over anhydrous sodium sulphate. Stripping off the solvent gave a residue, which was chromatographed over silica gel (60 - 120 mesh). Elution with pet. ether - ethylacetate (95:5) mixture yielded the anhydride 28 (0.058 g, 5%), m.p. 218°, UV λ_{max}^{MeOH} : 208 nm, IR (KBr) ν_{max} : (Fig.III.1) 1850 (anhydride), 1780 ; 1290, 1220 cm^{-1}. ^{1}HNMR ($CDCl_3$ 100 MHz) : (Fig.III.2) δ 6.20 (s, 2H olefinic H), 3.55 (m, 2H, methine H), 3.3 (m, 2H, methine H), 2.1 (br m, 2H) and 0.52 (m, 4H, cyclopropane CH_2). Analysis : Found C, 71.78 ; H, 5.72% requires C, 72.22 ; H, 5.55% for $C_{13}H_{12}O_2$.

Further elution gave another anhydride (29) (0.116 g, 10%) m.p. 178°, UV λ_{max}^{MeOH} : 208 nm, IR (KBr) ν_{max} : (Fig. III.3) 1850 (anhydride), 1790, 930, 900 cm^{-1}. ^{1}HNMR ($CDCl_3$, 100 MHz)

(Fig.III.4) : δ 6.4 (t, $J_1=J_2=2Hz$, 2H, olefinic H), 3.40 (m, 4H, methine H), 2.50 (br s, 2H, methine H) and 0.45 (m, 4H, cyclopropane CH_2). Analysis : Found : C, 72.35 ; H, 6.00% requires : C, 72.22 ; H, 5.55% for $C_{13}H_{12}O_3$.

Continued elution with pet. ether - ethylacetate (80:20) mixture gave the ketolactone (30) (0.58 g, 50%) m.p. 217°, UV λ_{max}^{MeOH} : 206 nm, IR (KBr) ν_{max} : (Fig.III.5) 1770 (δ-lactone), 1715 (cyclopentanone) and 1120 cm^{-1}. ^1H NMR ($CDCl_3$ 90 MHz) (Fig. III.6) : δ 5.11 (t, J=7.5Hz, 1H, H-C-O-C-), 3.00 (t, J=5Hz, 1H, methine H), 2.72 (m, 2H, methine H), 2.52 (m, 4H, ring H), 2.01 (d, J=4Hz, 1H, ring H), and 0.62 (m, 4H, cyclopropane CH_2). ^{13}CNMR (DMSO-d_6) : (Fig. III.7) δ 210.52 (C=O), 174.62, 76.04, 50.42, 49.38, 45.87, 42.62, 33.25, 31.82, 26.23, 20.51, 9.97, 2.43 (due to cyclopropyl carbon). Mass : (m/e) 216 (M^+), 172 (M^+-CO_2), 171 ($M-CO_2H$), 144 (M^+-CO_2-CO), 143 (M^+-CO_2-COH), 91 ($C_7H_7^+$), 79 ($C_5H_3O^+$ or $C_6H_7^+$), 66 ($C_5H_6^+$). Analysis : Found C, 71.83 ; H, 5.66% requires : C, 72.22 ; H, 5.55% for $C_{13}H_{12}O_3$.

Oxidation of pentacyclo [5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]-undecane-8,11-dione-4-spiro-1'-cyclopentane (31) with ceric (IV) ion

To a slurry of ceric ammonium nitrate (6 g, 0.011 mol) in water (30 ml) was added a solution of spiro cage dione (31) (1 g, 0.0044 mol) in acetonitrile (20 ml). The reaction mixture was stirred at room temperature (~32°) for about 1h (tlc). The reaction mixture was diluted with water,

extracted with dichloromethane (3 x 50 ml) and the combined extract was washed with water (2 x 10 ml), brine (2 x 15 ml) and dried over anhydrous sodium sulphate. Removal of solvent gave a residue was chromatographed over silica gel (60-120 mesh). Elution with pet. ether - ethylacetate (95:5) mixture yielded, the fast moving anhydride 32 (0.075 g, 7%) m.p. 162°, UV λ_{max}^{MeOH} : 208 nm, IR (KBr) ν_{max} : (Fig.III. 8) : 1860 (anhydride), 1780 cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz) : (Fig.III.9) δ 6.25 (s, 2H, olefinic H), 3.65 (br s, 2H, methine H), 3.45 (br s, 2H, methine H), 2.35 (m, 2H) and 1.7 (br m, 8H, cyclopentane CH_2). Analysis : Found C, 73.37 ; H, 6.85% : requires L: H, 6.55% for $C_{15}H_{16}O_3$.

Further elution, gave the another anhydride (33) (0.118 g, 11%) m.p. 156°, UV λ_{max}^{MeOH} : 208 nm, IR (KBr) ν_{max} : (Fig. III.10) 1850 (anhydride), 1790, 930, 900 cm^{-1}. ^1H NMR ($CDCl_3$ 90 MHz) : (Fig.III.11) δ 6.40 (t, J=3Hz, 2H, olefinic H), 3.35 (br s, 4H), 2.65 (br s, 2H, methine H) and 1.7-1.4 (br m, 8H, cyclopentane CH_2). Analysis : Found C, 73.56 ; H, 6.58% ; requires C, 73.77 ; H, 6.55% for $C_{15}H_{16}O_3$.

Continued elution with pet. ether - ethyl acetate (80:20) gave the ketolactone (34) (0.43 g, 40%) m.p. 195°, UV λ_{max}^{MeOH} : 260 nm, IR (KBr) ν_{max} : (Fig.III.12) 1775 (δ-lactone) 1720 (cyclopentanone) and 1130 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) : (Fig.III.13) δ 5.12 (t, J=7.5Hz, 1H, H-C-O-C-), 2.9 (m, 1H), 2.85 (m, 2H), 2.7 (m, 1H), 2.6 (m, 1H), 1.95 (m, 2H), 1.9

(m, 1H), 1.7 (m, 5H), 1.35 (m, 2H) : ^{13}CNMR (DMSO-d_6) (Fig. III.14) : δ 210.39, 175.0, 76.17, 52.63, 52.24, 48.86, 44.44, 41.45, 36.50, 32.34, 31.82, 28.18, 24.28, 23.63, 20.25 (cyclopropyl carbon). Mass:(m/e) 244 (M^+), 200 (M^+-CO_2), 199 (M^+-CO_2H), 172 (M^+-CO_2-CO), 171 (H^+-CO_2-COH), 91 ($C_7H_7^+$), 79 (C_5H_3O + or $C_6H_7^+$), 65 ($C_5H_5^+$). Analysis : Found C, 73.47 ; H, 6.67% : requires : C, 73.77 ; H, 6.55% for $C_{15}H_{16}O_3$.

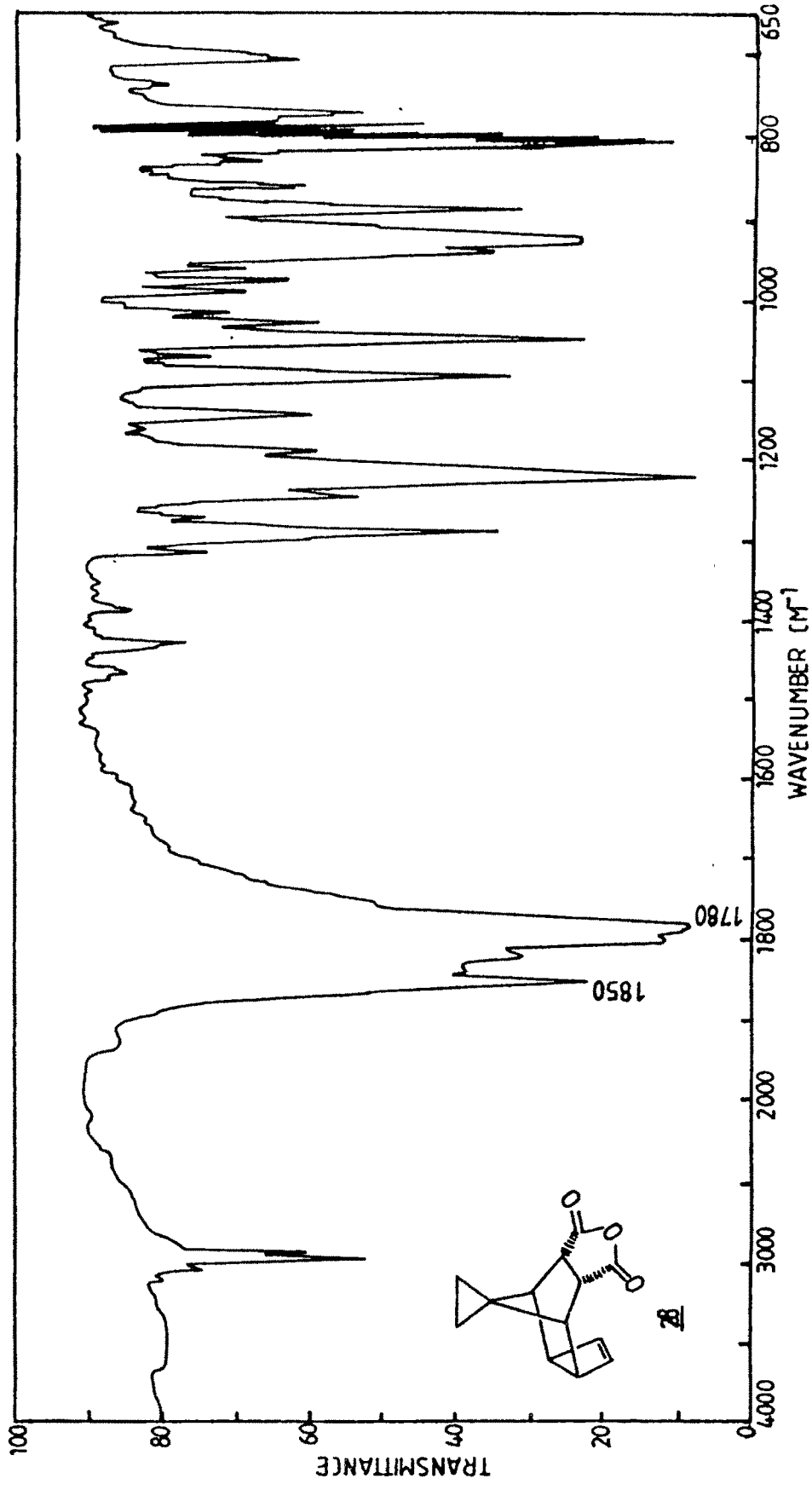


Fig. III.1 : IR (KBr) spectrum of compound 28

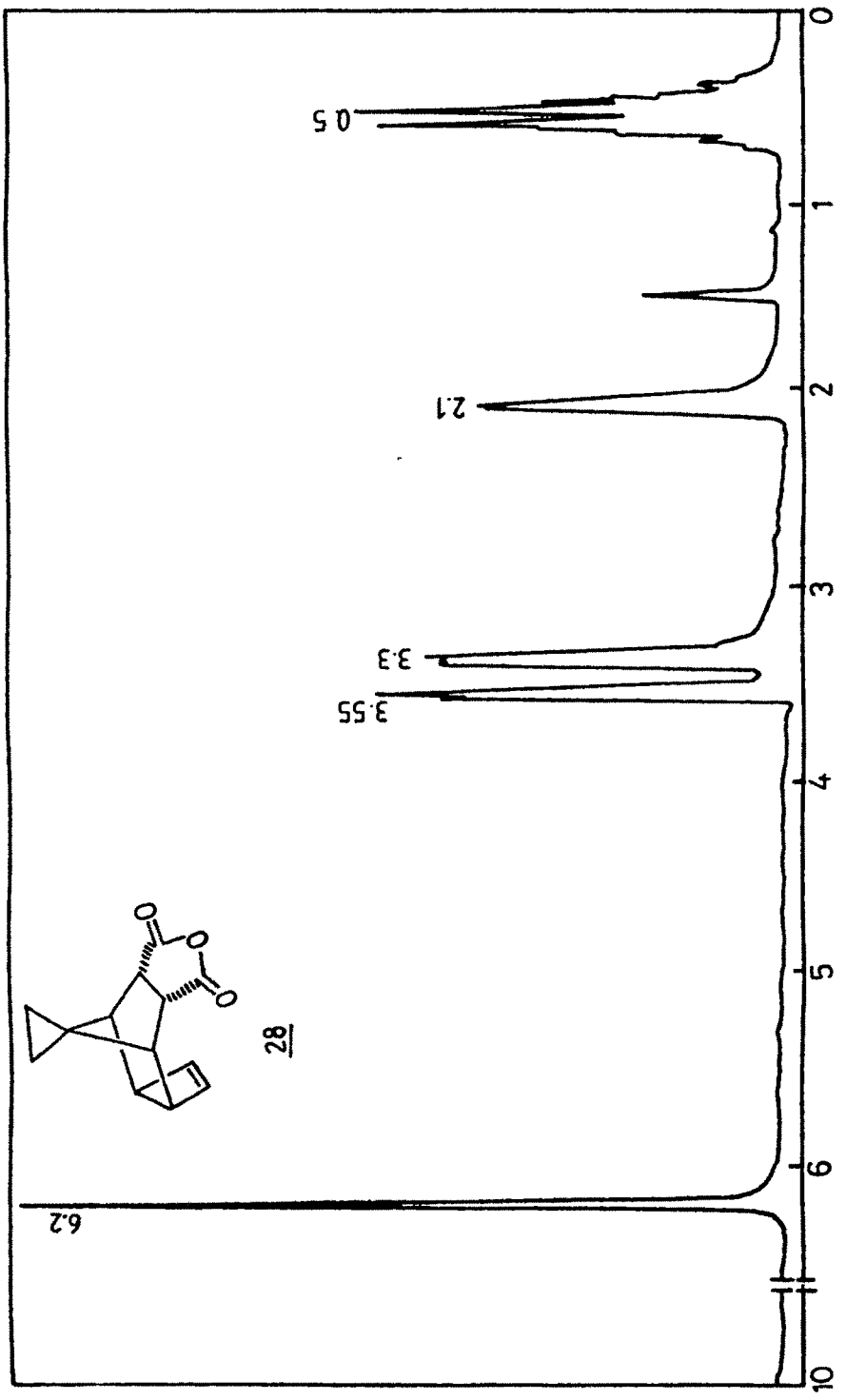


Fig. III.2 : NMR ($CDCl_3$, 100 MHz) spectrum of compound 28

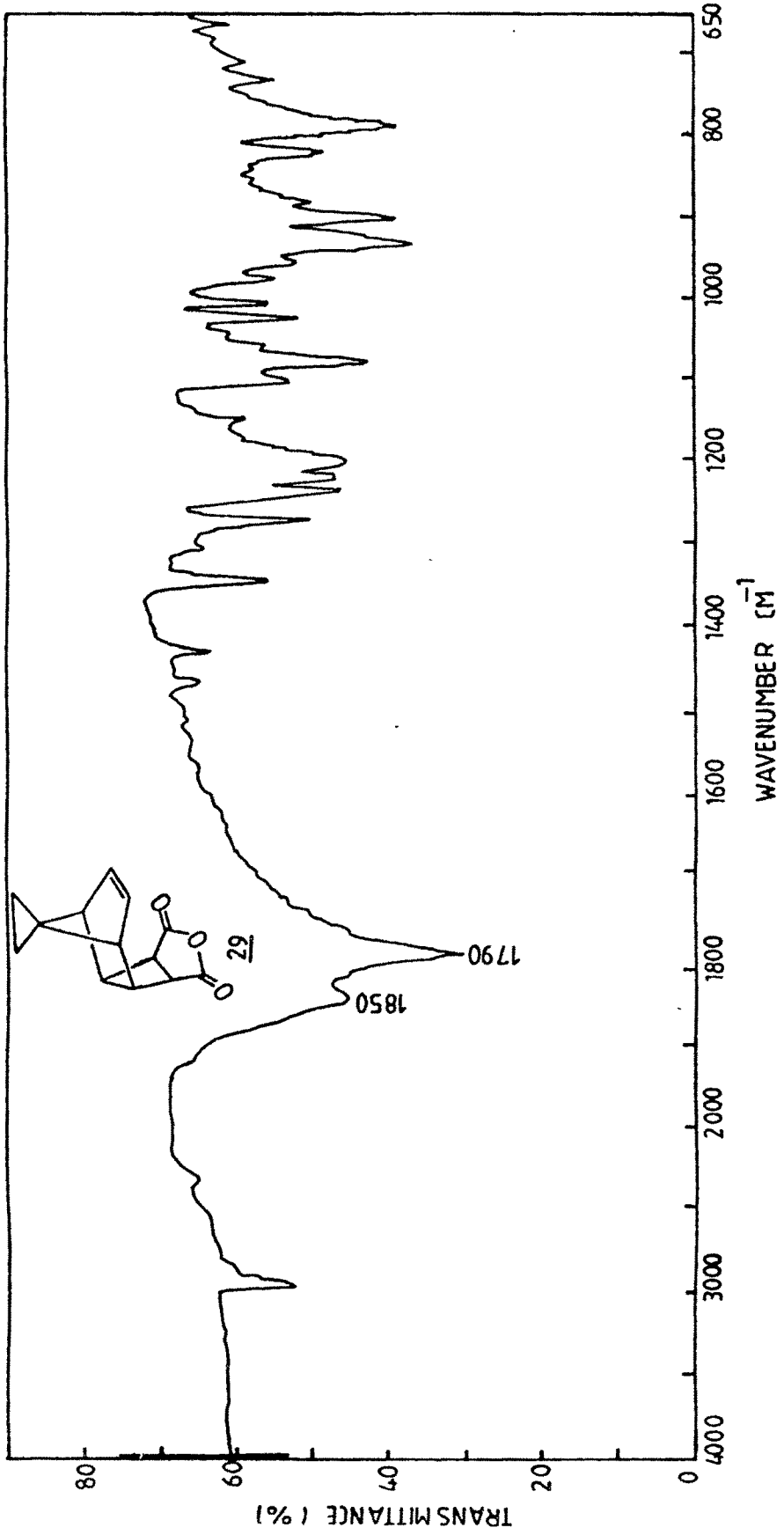


Fig. III.3 : IR (KBr) spectrum of compound 29

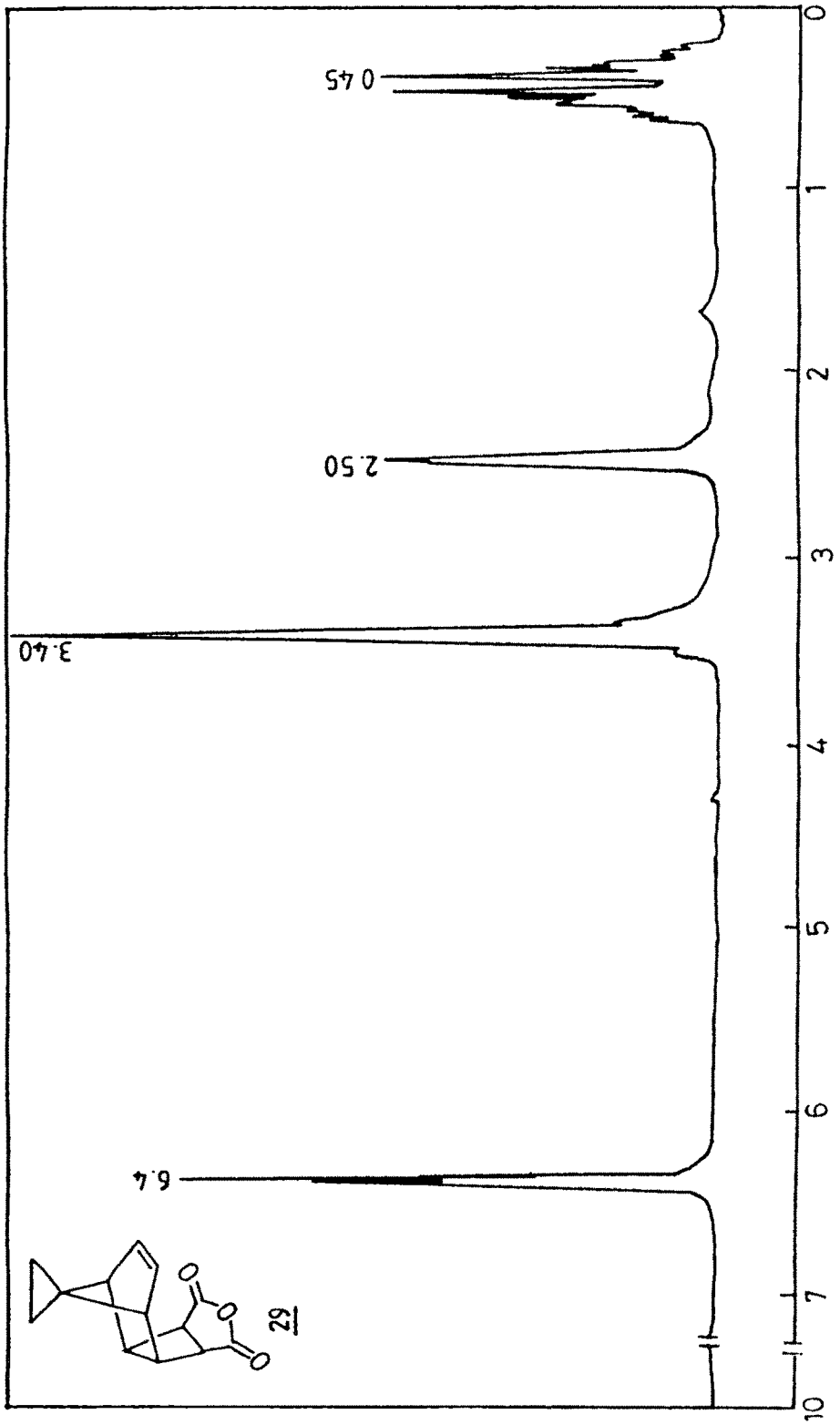


Fig. III.4 : NMR ($CDCl_3$, 100 MHz) spectrum of compound 29

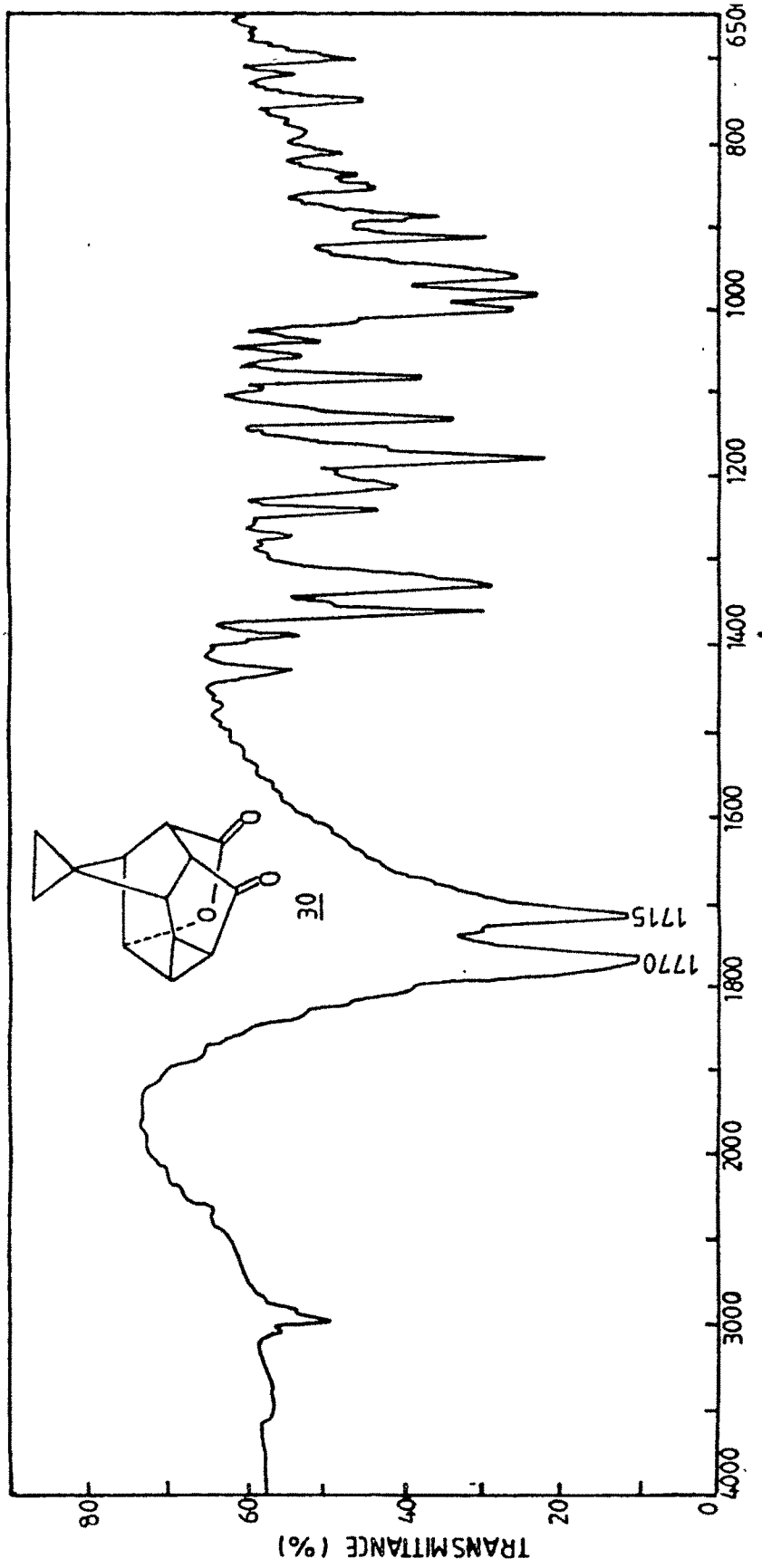


Fig. III.5 : IR (KBr) spectrum of compound 30

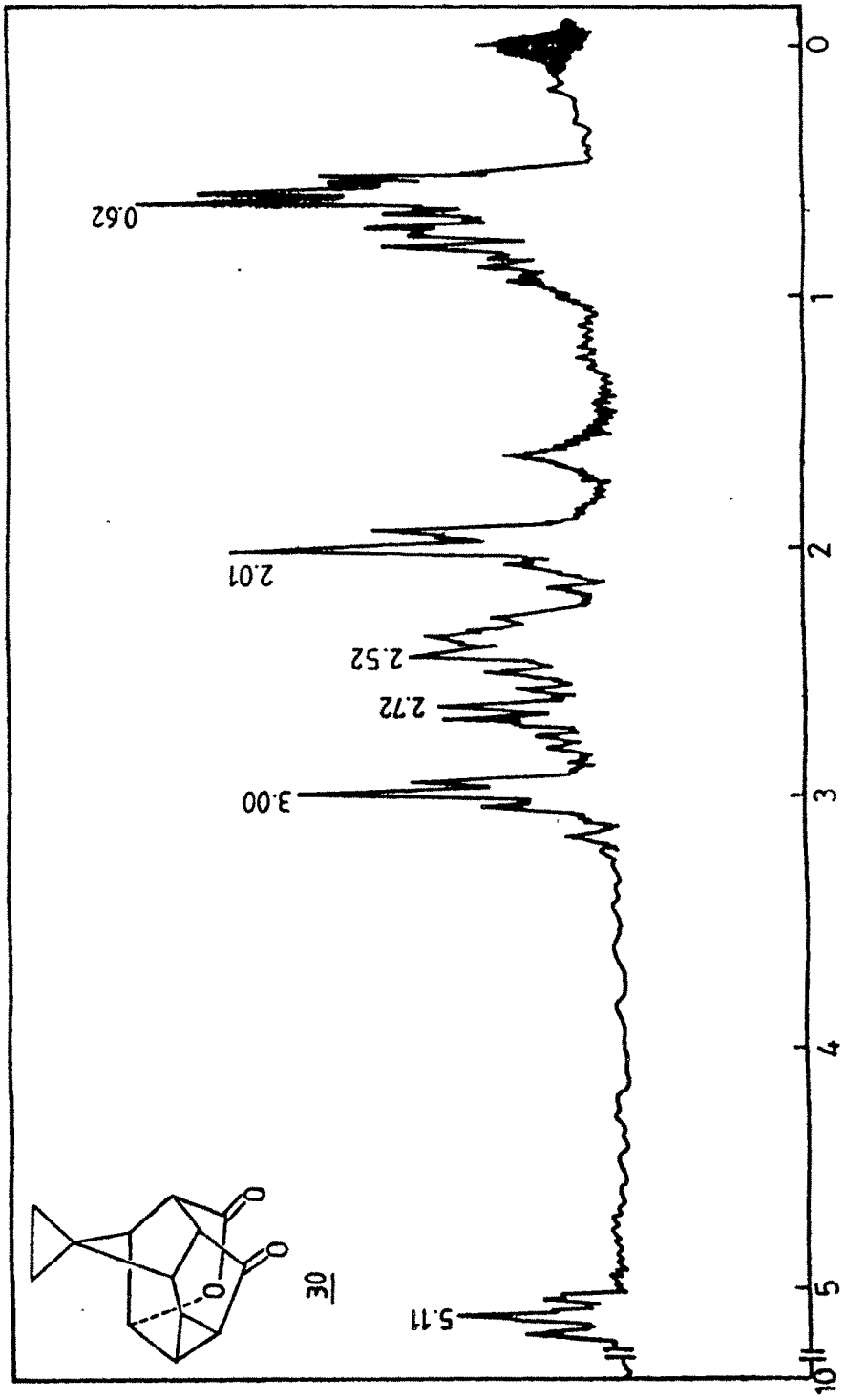


Fig. III.6 : NMR ($CDCl_3$, 90 MHz) spectrum of compound 30

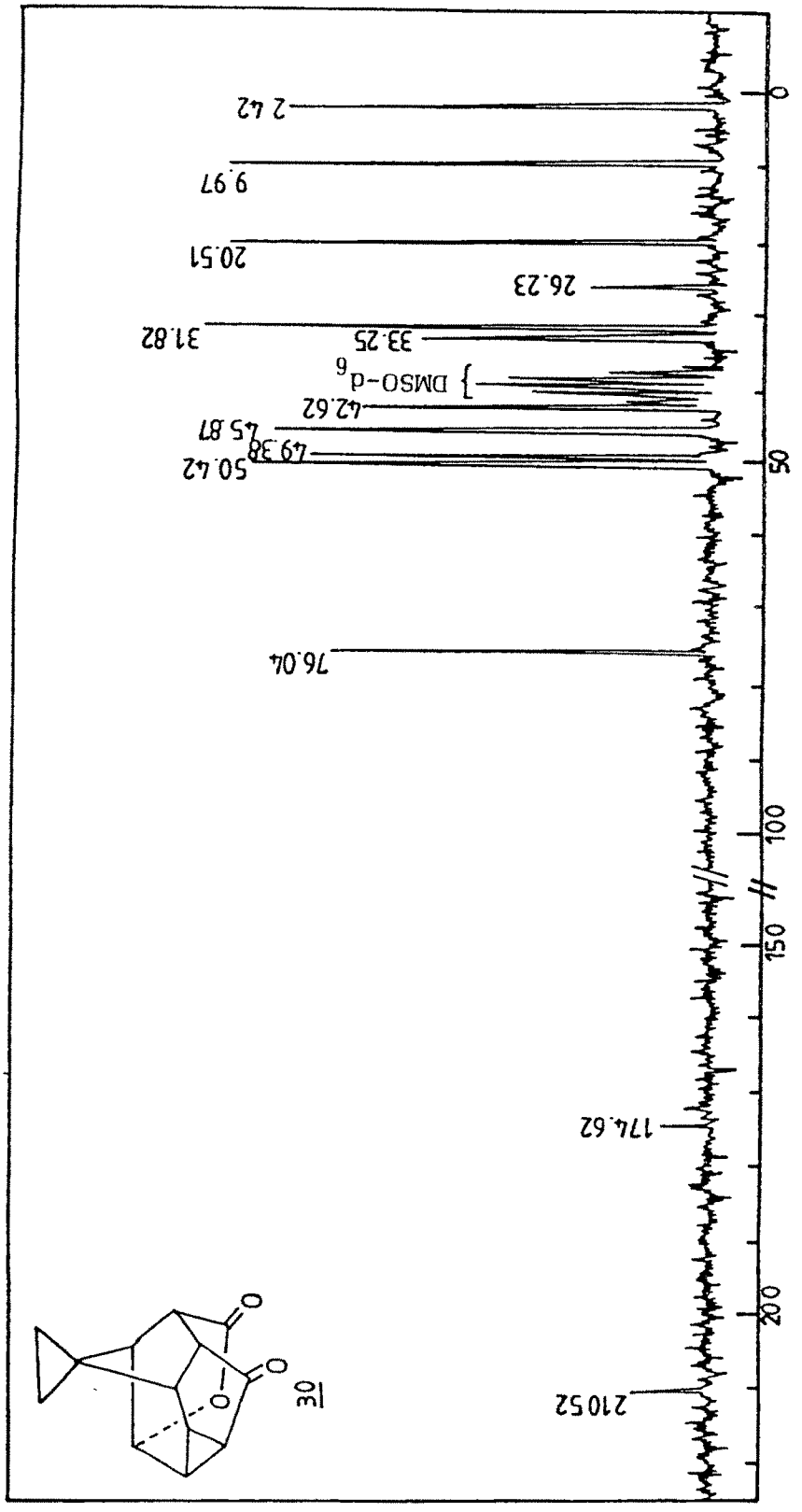


Fig.III.7 : ^{13}CNMR 9dmso-d_6) spectrum of compound 30

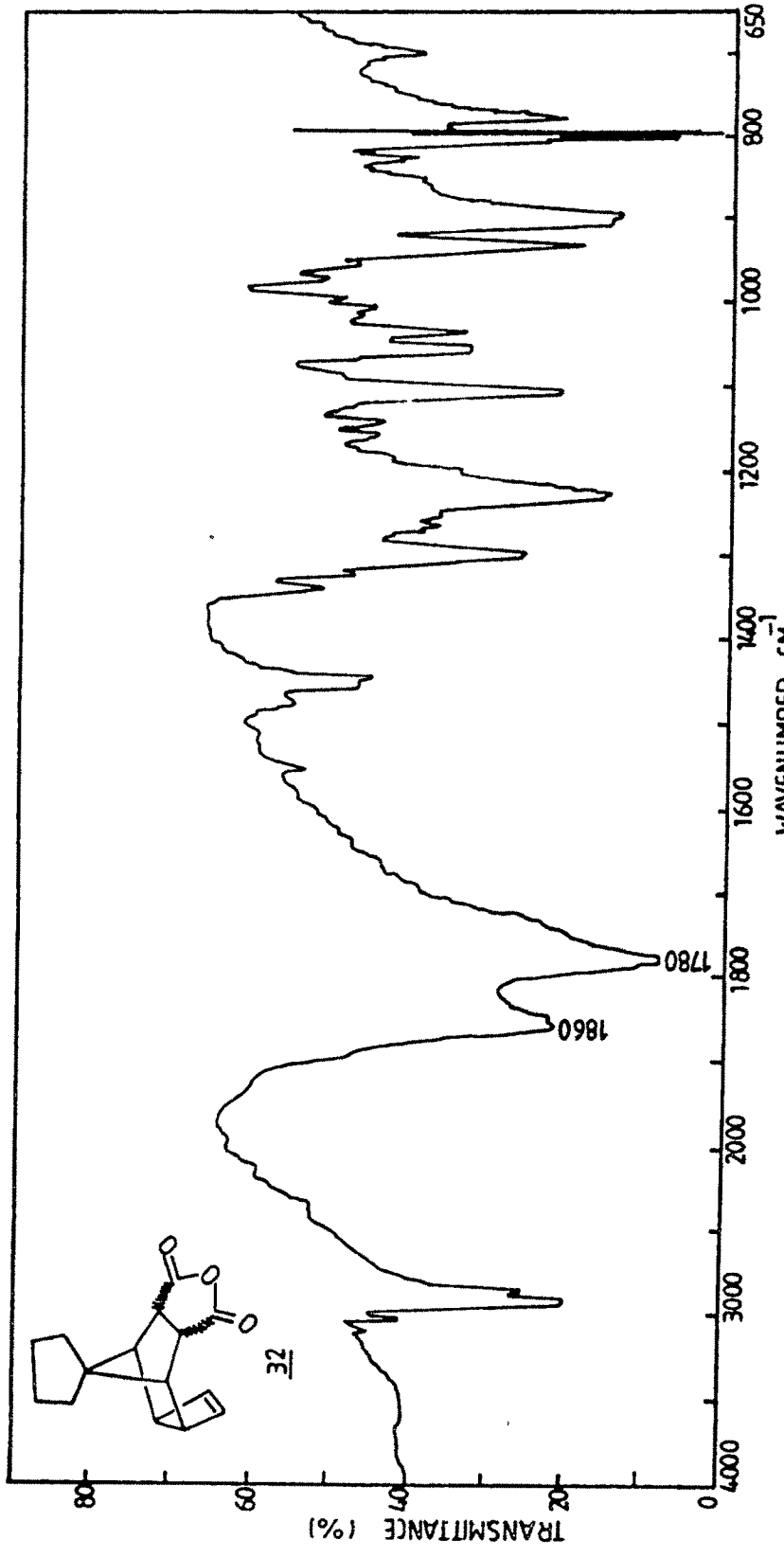


Fig. III.8 : IR (KBr) spectrum of compound 32

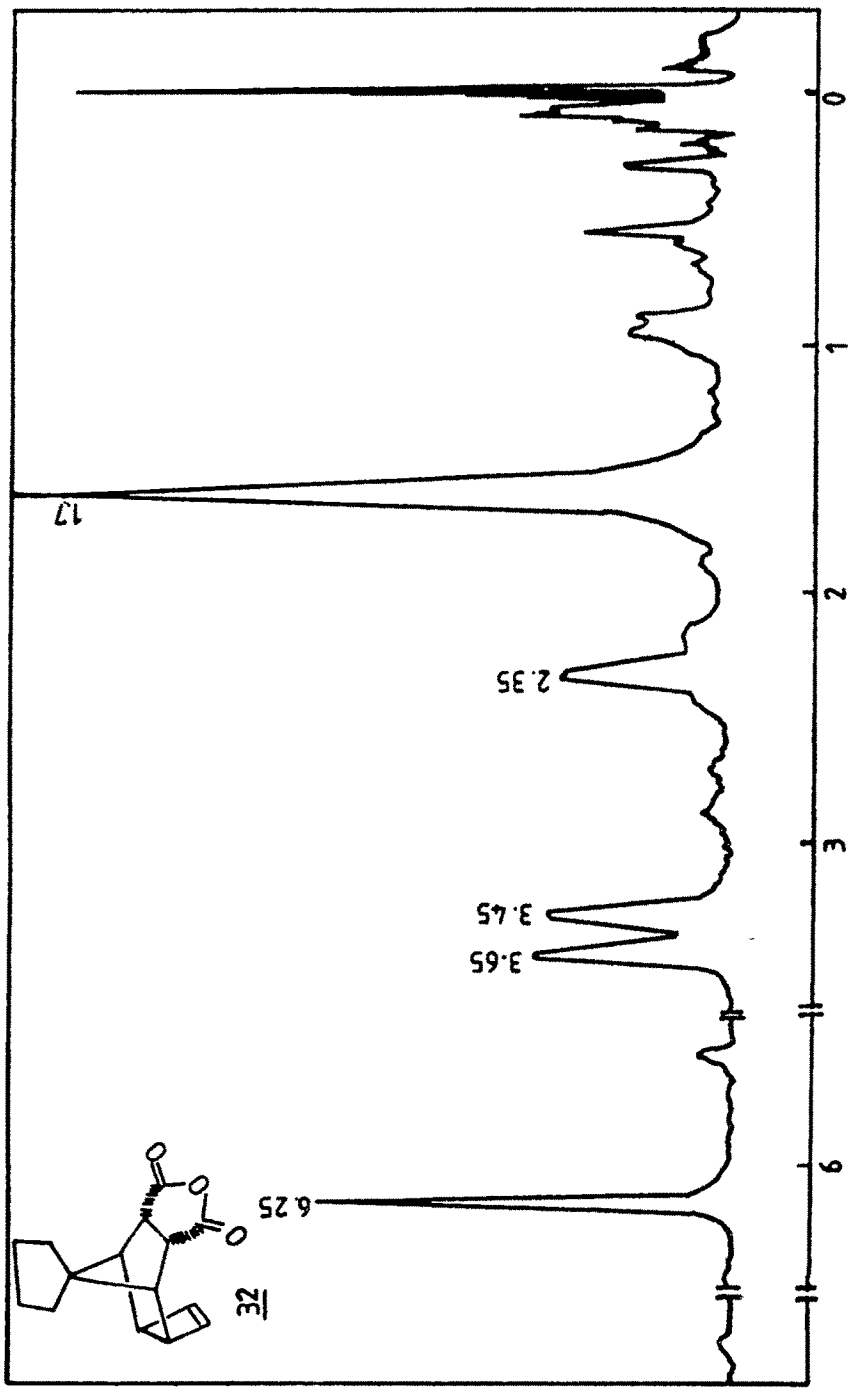


Fig. III. 9 : NMR ($CDCl_3$, 90 MHz) spectrum of compound 32

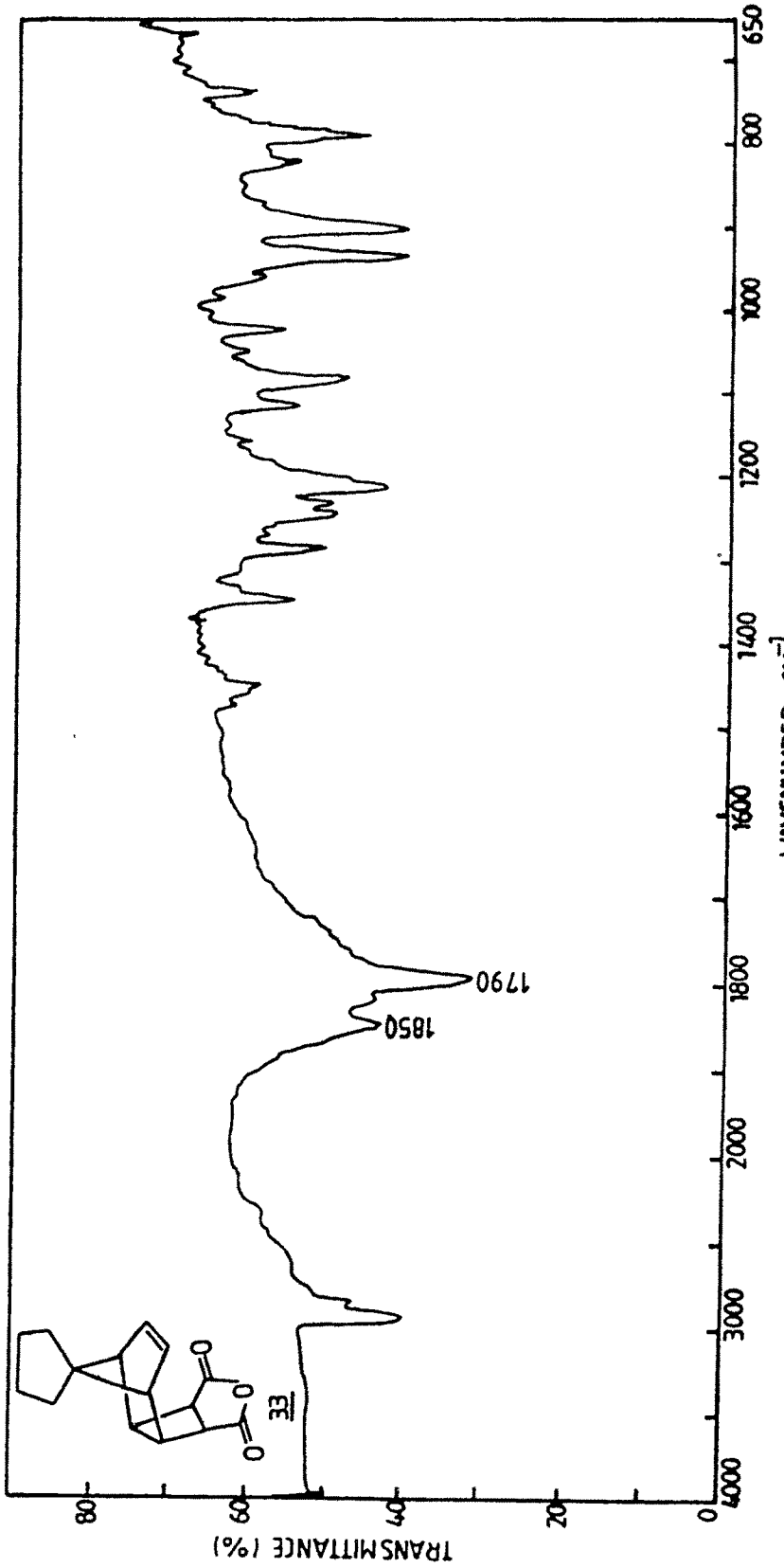


Fig. III. 10 : IR (KBr) spectrum of compound 33

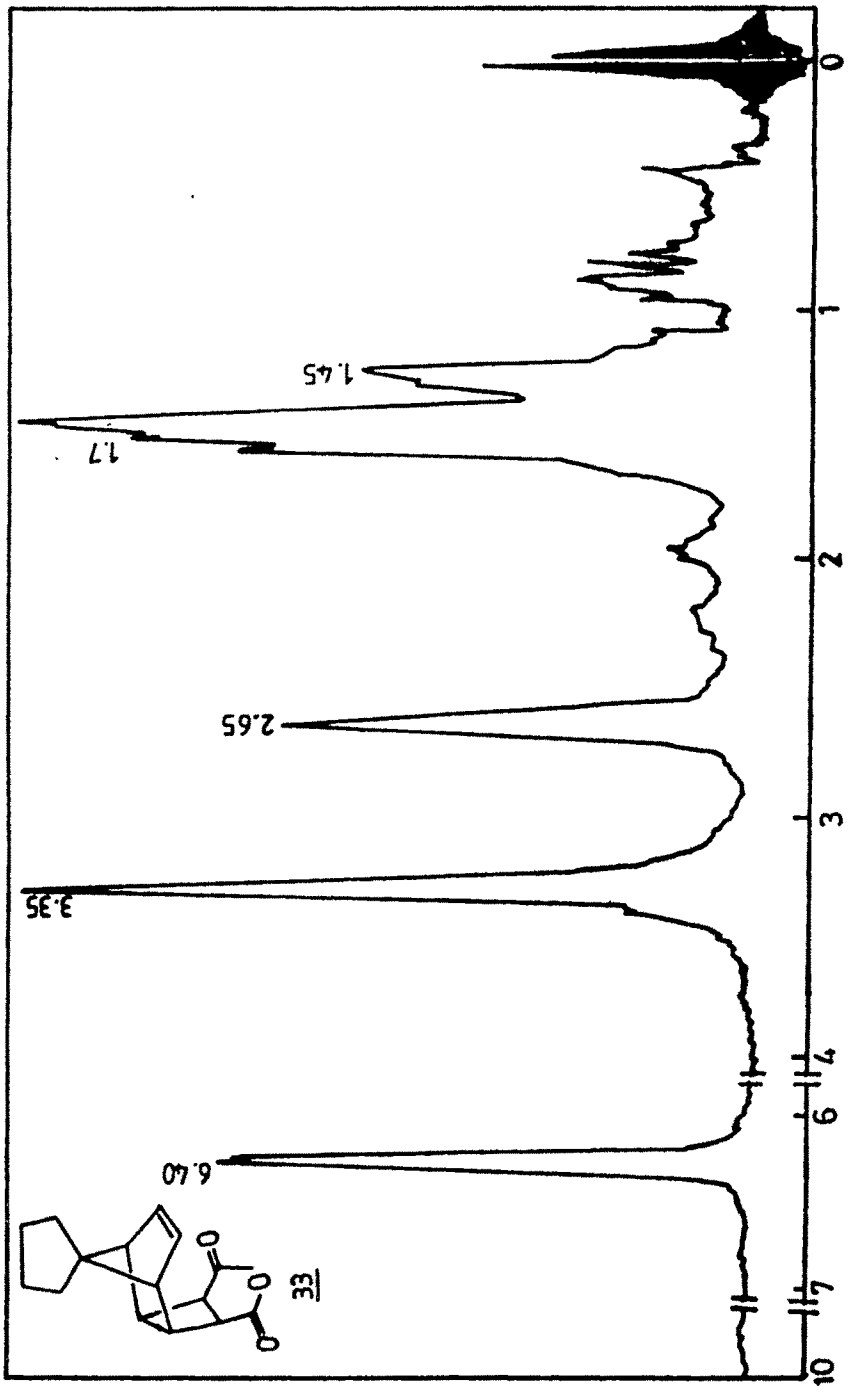


Fig. III. 11 : NMR ($CDCl_3$, 90 MHz) spectrum of compound 33

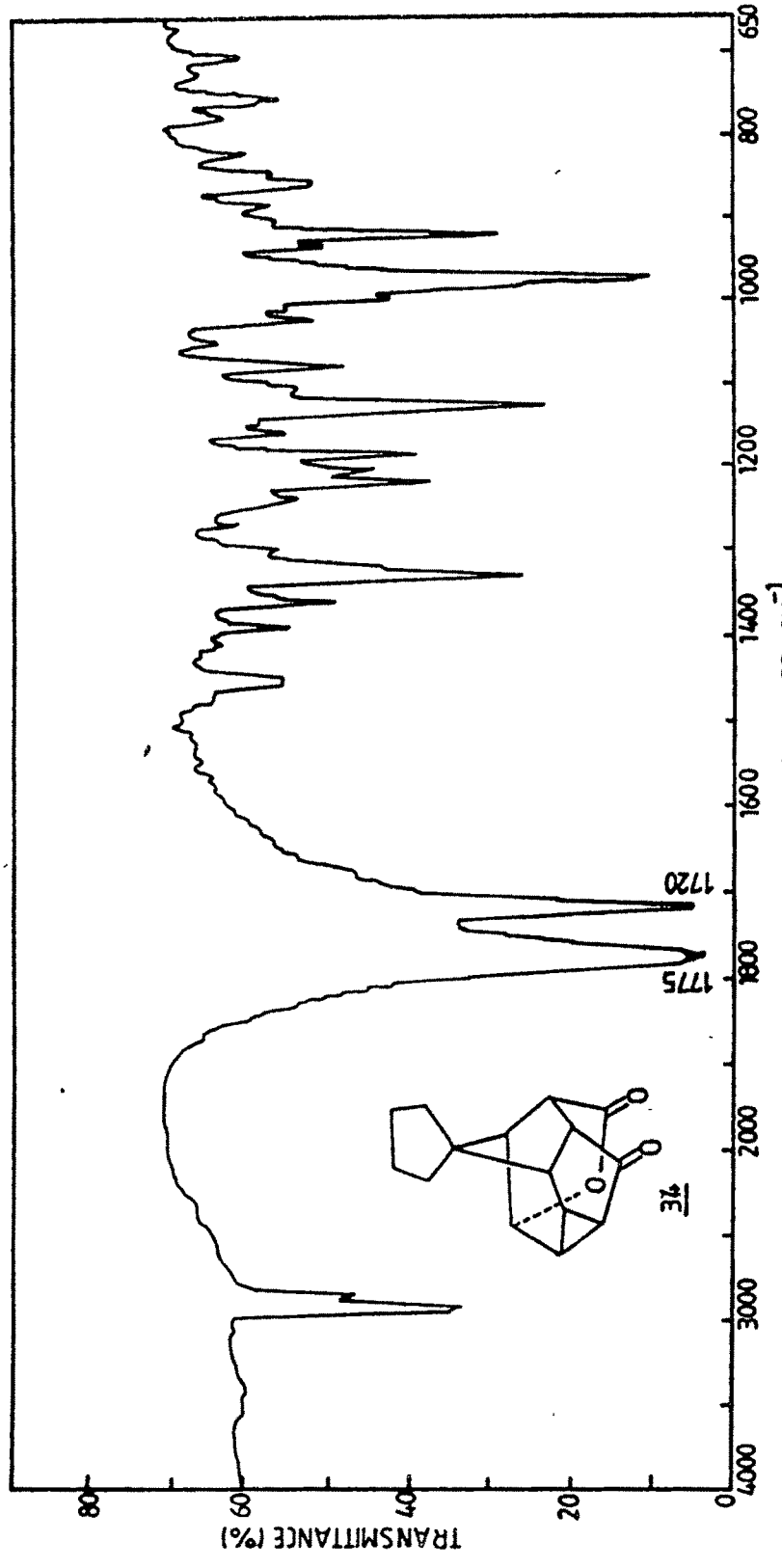


Fig. III. 12 : IR (KBr) spectrum of compound 34

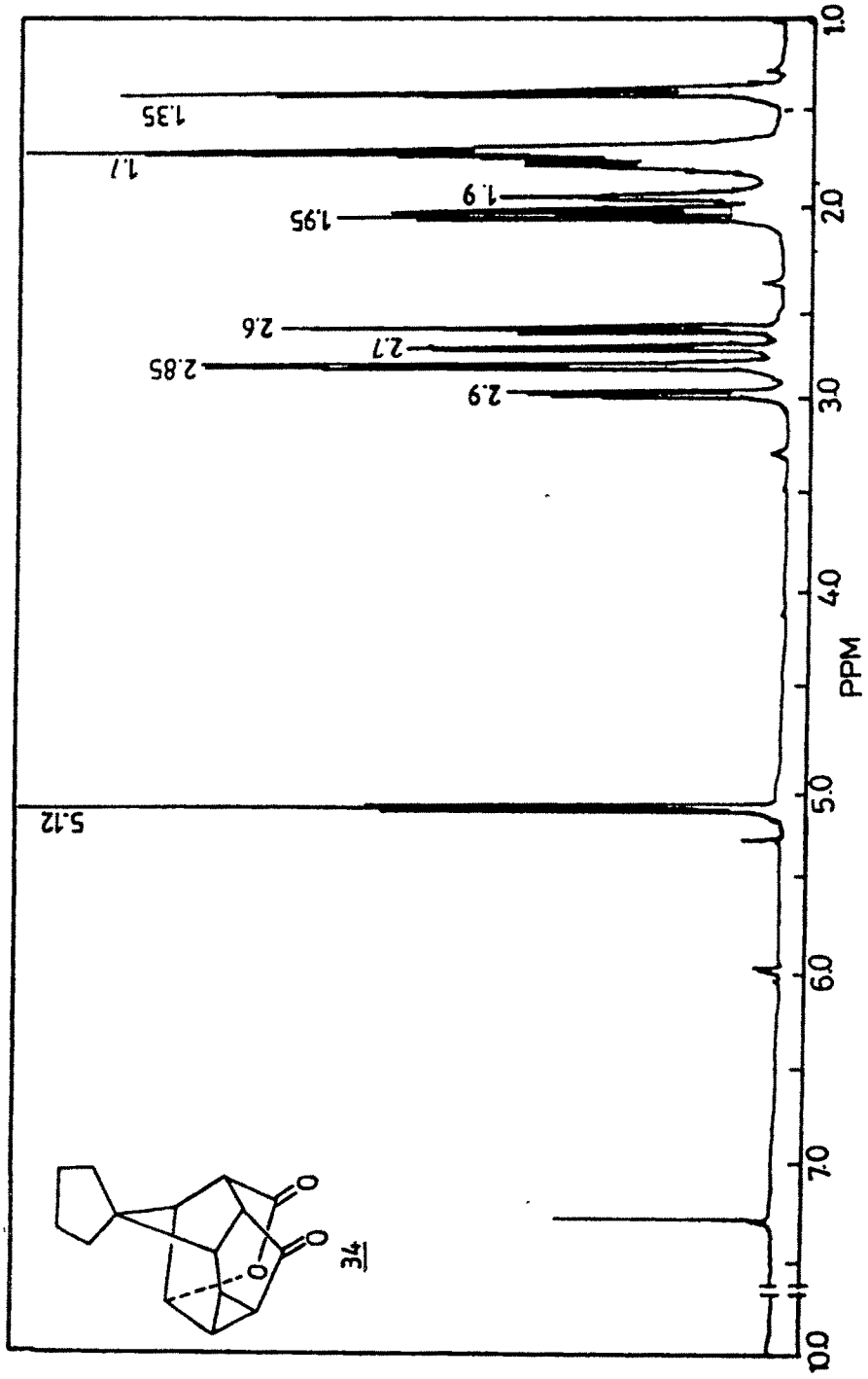


Fig. III.13 : NMR ($CDCl_3$, 300 MHz) spectrum of compound 34

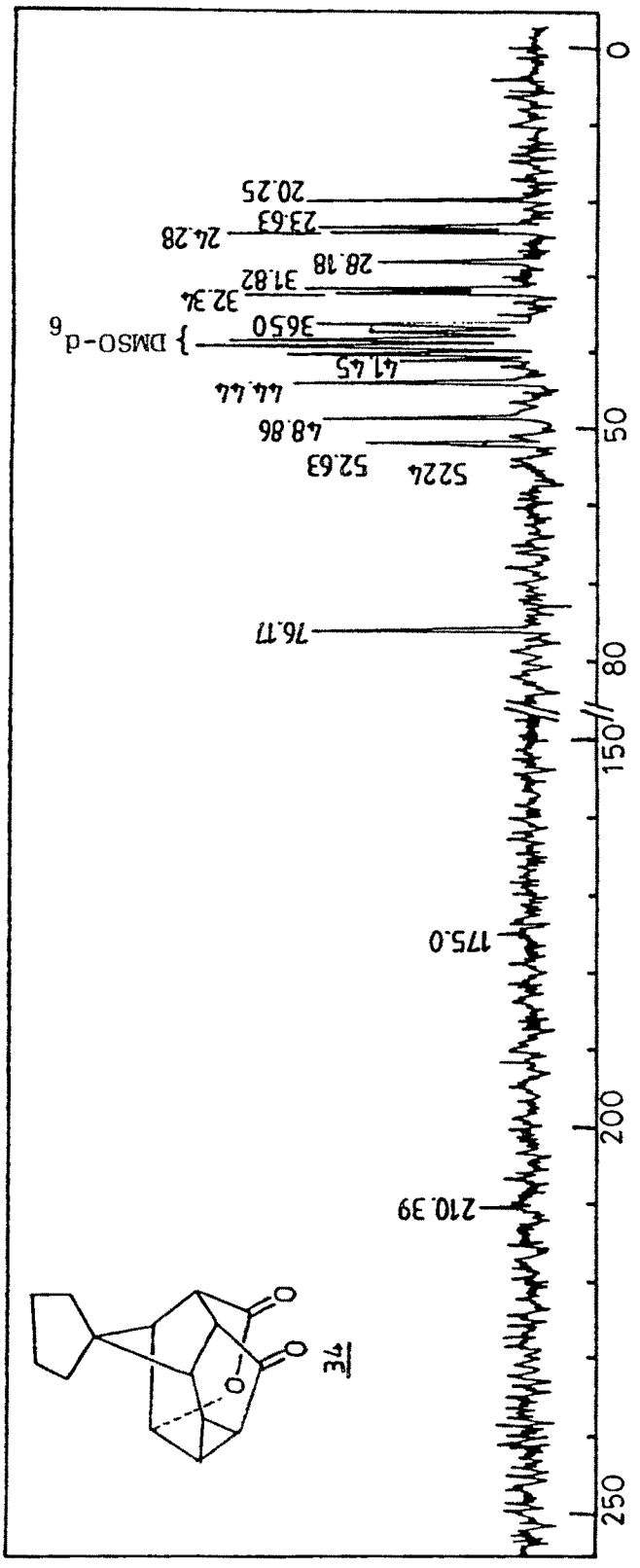


Fig.III.14 : ^{13}CNMR (DMSO-d_6) spectrum of compound 34

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