CHAPTER - IV

NOVEL CARBOCYCLICS VIA SCHMIDT FRAGMENTATION OF THE SPIRO PENTACYCLIC DIONES (1) and (2)

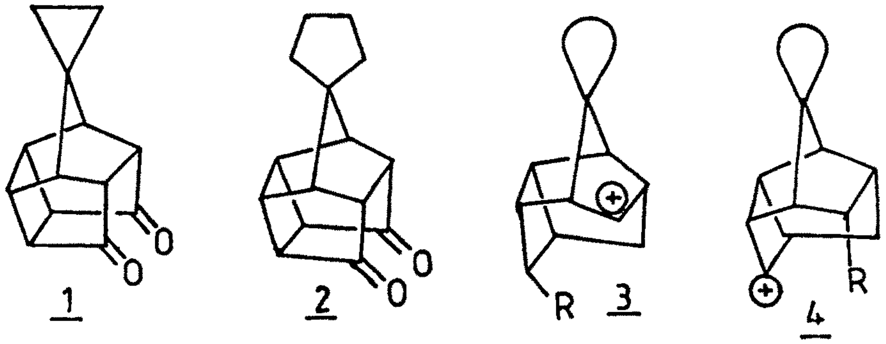
IV.1 Abstract

A novel one step rearrangement of pentacyclo [5.4.0.0^{2,6}0^{3,10}0^{5,9}] undecane-8,11-dione-4-spiro-1'-cyclopropane (1) & pentacyclo [5.4.0.0^{2,6}0^{3,10}0^{5,9}] undecane 8,11-dione-4-spiro-1'-cyclopentane (2) is reported. Reaction of diones (1 & 2) with sodium azide in methane sulphonic acid furnished four crystalline mesylates (39, 40 and 44, 45), which have been assigned structures on the basis of complementary spectral data (^{1}H NMR, ^{13}C NMR and IR). The close relationship between 39 & 40, 44 & 45 and their common genesis has been established through a facile conversion of 39 in to 40, 44 into 45 *via* solvolysis in methanesulphonic acid. A plausible mechanism for the formation of 39 & 40, 44 & 45 from 1 & 2 under Schmidt reaction conditions is proposed.

IV.2 Introduction

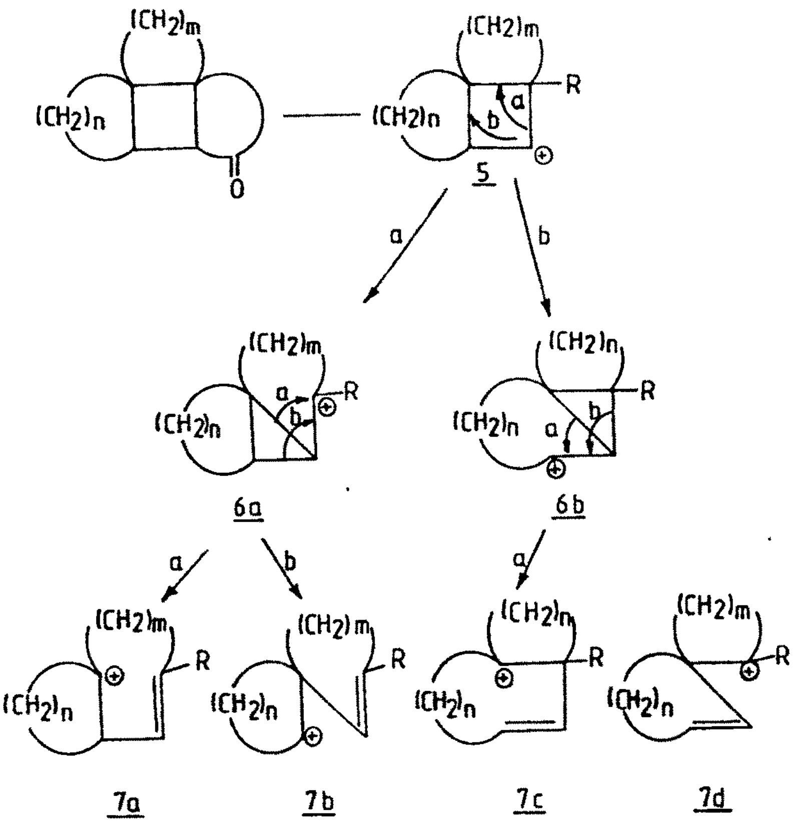
Skeletal bond reorganizations mediated through carbocations in polycyclic frameworks have played an important role in the development of mechanistic concepts in organic chemistry and also provided interesting routes to new carbocyclic systems which are otherwise not readily accessible.[1-4] The idea of the controversial non-classical carbonium ion[5-7] and the remarkable transformation of tetrahydrodicyclopentadiene into adamantane are some of the important examples among many others.[2,3,9,10]

The polycyclic caged diones (1 and 2) are endowed with structural features, such as a constrained cyclobutane ring, a spiro substituted bicyclo [2.2.1] moiety in a complex molecular framework, which make them as an attractive targets for the study of new skeletal reorganisations. In continuation[1] with our interest in the polycyclic diones (1 & 2) and the stimuli provided by the interesting results during Ce(IV) ion oxidation of these systems (Chapter-III), prompted us to explore the carbonium ion rearrangements of the spirodiones (1 and 2) during Schmidt reaction conditions which provide a simple method for generating carbonium ions from strained polycyclic ketones. (Scheme-IV.1).



SCHEME-IV.1

One of the objectives of our study was to find out, whether the Schmidt fragmentation of these diones leads regioselectivity to the carbocations of type 3 or carbonium ions of type 4 (Scheme-IV.1), and to unravel the fate of these carbonium ions. Furthermore, it was anticipated that the fused cyclobutylcarbonium ions of type 5 may rearrange to cyclopropyl-carbinyl carbonium ions 6a, b and/or homoallylic carbonium ions[11] 7a,b,c,d which will provide access to new and homologated carbocyclic frameworks. (Scheme-IV.2)



SCHEME - IV.2

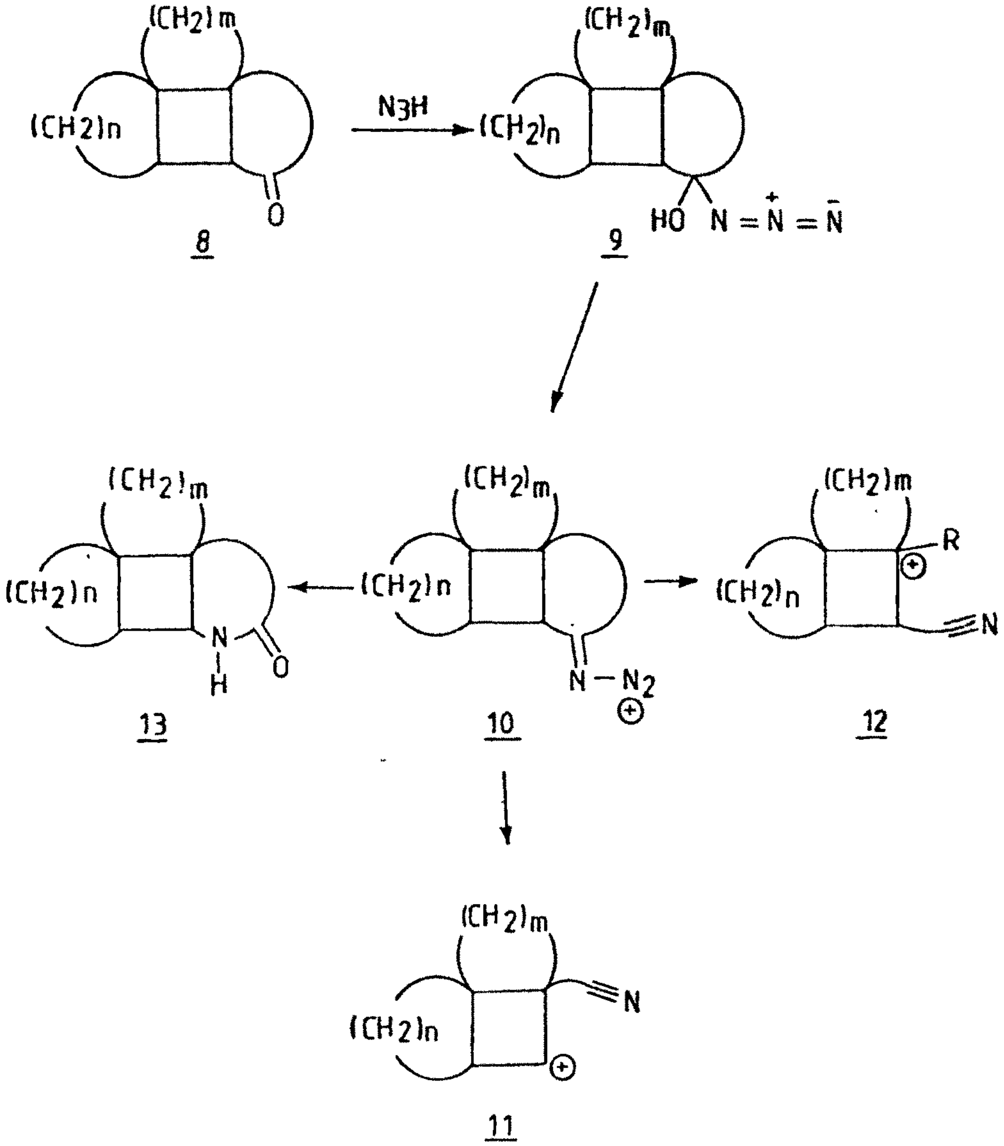
This offers an attractive synthetic strategy to a variety of polycycles, considering the fact that polycyclic cyclobutyl ketones like 8 are easily assembled through $\pi^{2s} + \pi^{2s}$ intramolecular photocycloadditions.

Among the various reactions by which the ketones of type 8 can be fragmented to various types of carbonium ions 11, 12 & 13 the Schmidt fragmentation is obviously the reaction of choice (Scheme-IV.3).

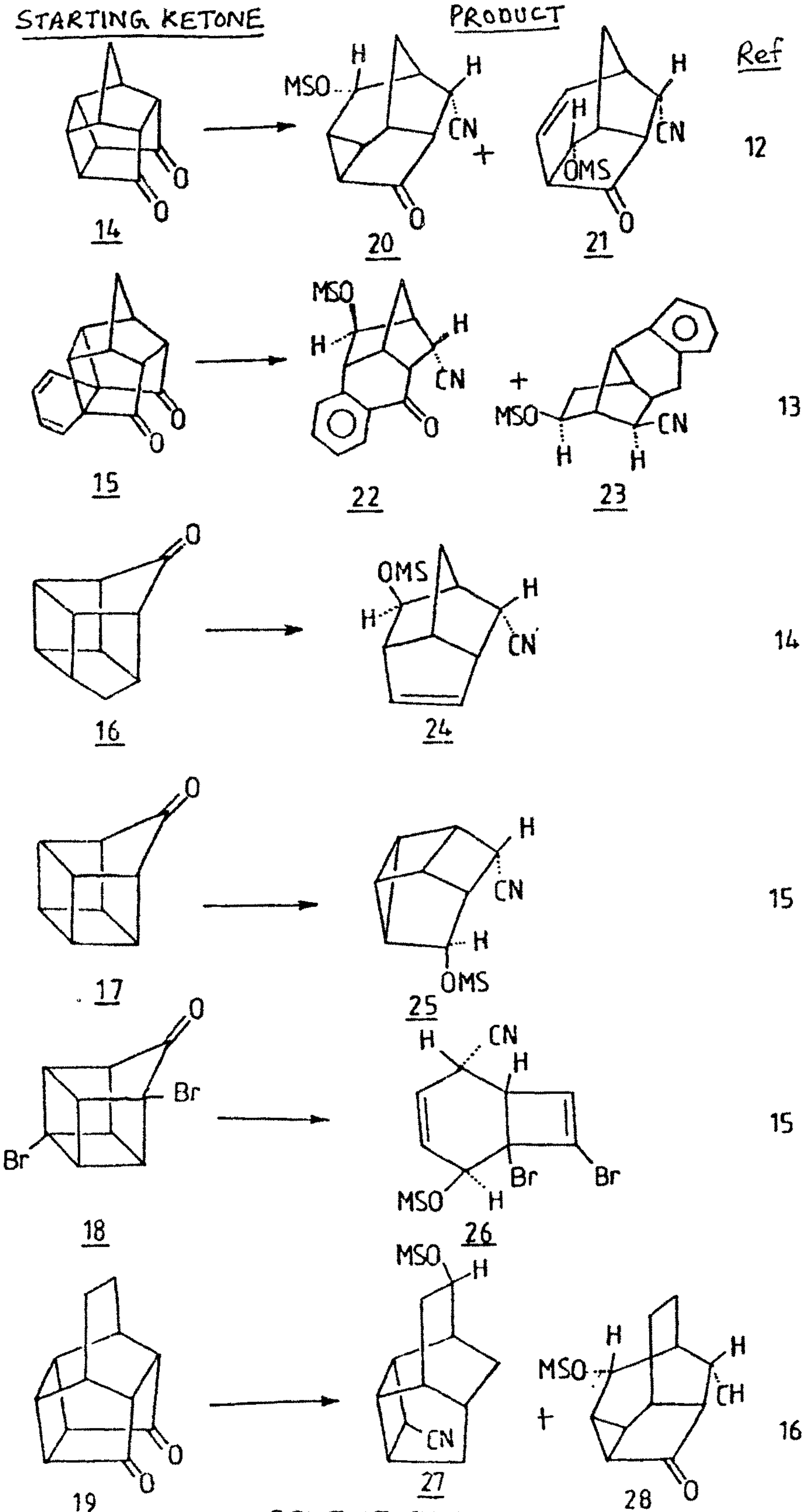
Since the formation of the carbonium ions of type 11 or 13 from Schmidt intermediate 10 involves substantial strain release within the polycyclic framework, it favours the fragmentation process (10 --> 11, and/or 10 --> 12) over the more often encountered rearrangement (10 --> 13) leading to the lactam formation.

Another aspect of the rearrangement of the carbonium ions especially of type 5 is the stereoelectronic control of cyclobutyl $\rightleftharpoons$ cyclopropylcarbinyl $\rightleftharpoons$ homoallylic carbonium ion rearrangements. In the fused polycyclic systems, the various carbonium ions will have different and discrete geometrical alignment of neighbouring bonds depending upon the size and shape of the carbocyclic framework.

Some of the interesting rearrangement of strained polycyclic ketones observed[12-16] under Schmidt reaction conditions are shown in Scheme-IV.4.



SCHEME-IV. 3


STARTING KETONE
PRODUCT
Ref
MSO
H
H
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14
20
+
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21
12
MSO
H
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18
26
15
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CN
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27
+
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MSO
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CH
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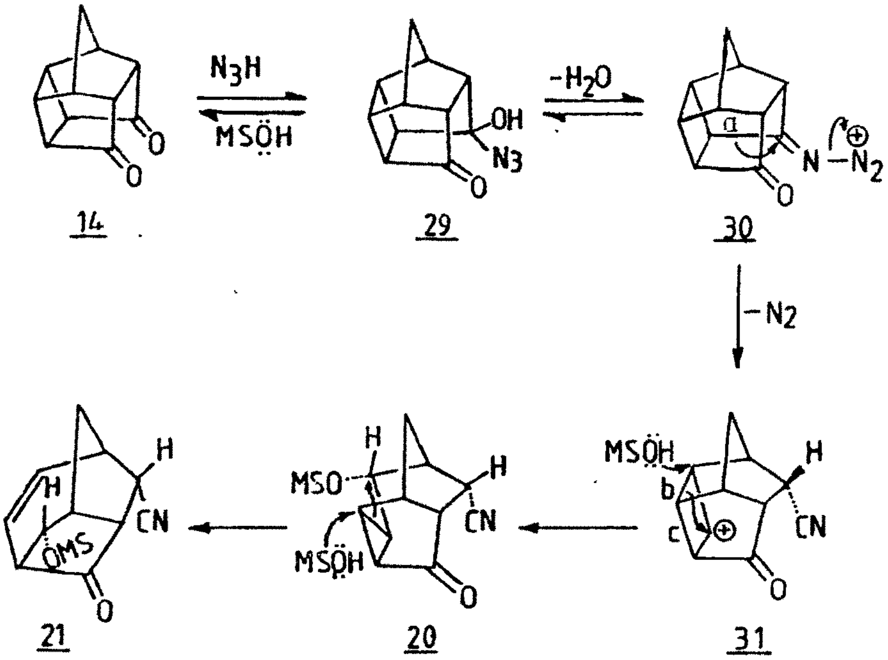
28
16

SCHEME-IV 4

In the case of the ketones 14-19, exclusive and regiospecific fragmentation occured and the cyclobutyl carbonium ion intermediate was produced. Further reorganisation of this carbonium ion led to the formation of the observed products. Since, the Schmidt fragmentation in all the cases was carried out in the nucleophilic medium of methane sulphonic acid (MsOH), the rearranged carbonium ions were trapped as the mesylate derivative.

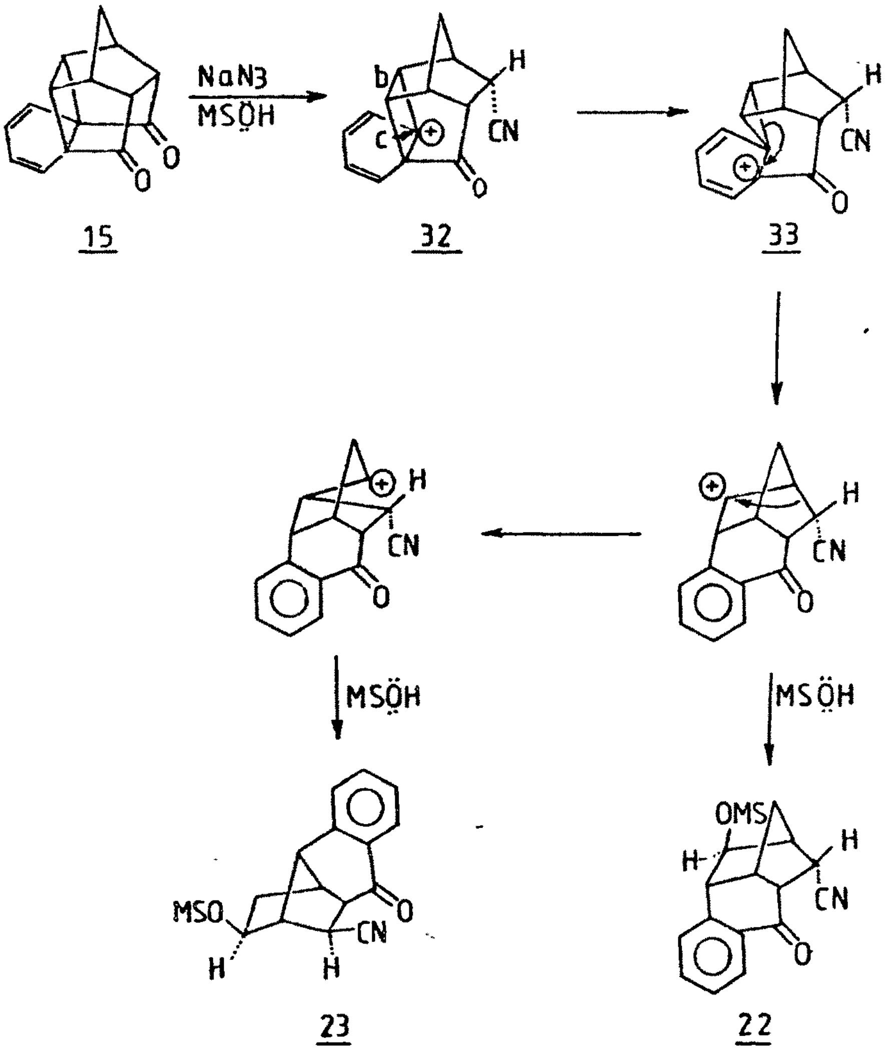
A representative mechanism for the formation of the carbocycles 20 and 21 from pentacyclic dione 14 is depicted in Scheme-IV.5.



SCHEME-IV.5

Regiospecific fragmentation of the bond 'a' from the intermediate (30) to cyclobutyl carbonium ion (31) and a stereospecific rearrangement to cyclopropyl-carbinyl system furnishes (20). A cyclopropyl carbinyl ---> homoallylic rearrangement accounts for the formation of 21.

The annulated polycyclic dione 15 underwent a deep seated skeletal bond reorganisation, when treated under Schmidt fragmentation condition and furnished benzoannulated bicyclic systems 22 and 23. The mechanism of the formation of 22 and 23 is shown in Scheme-IV.6.



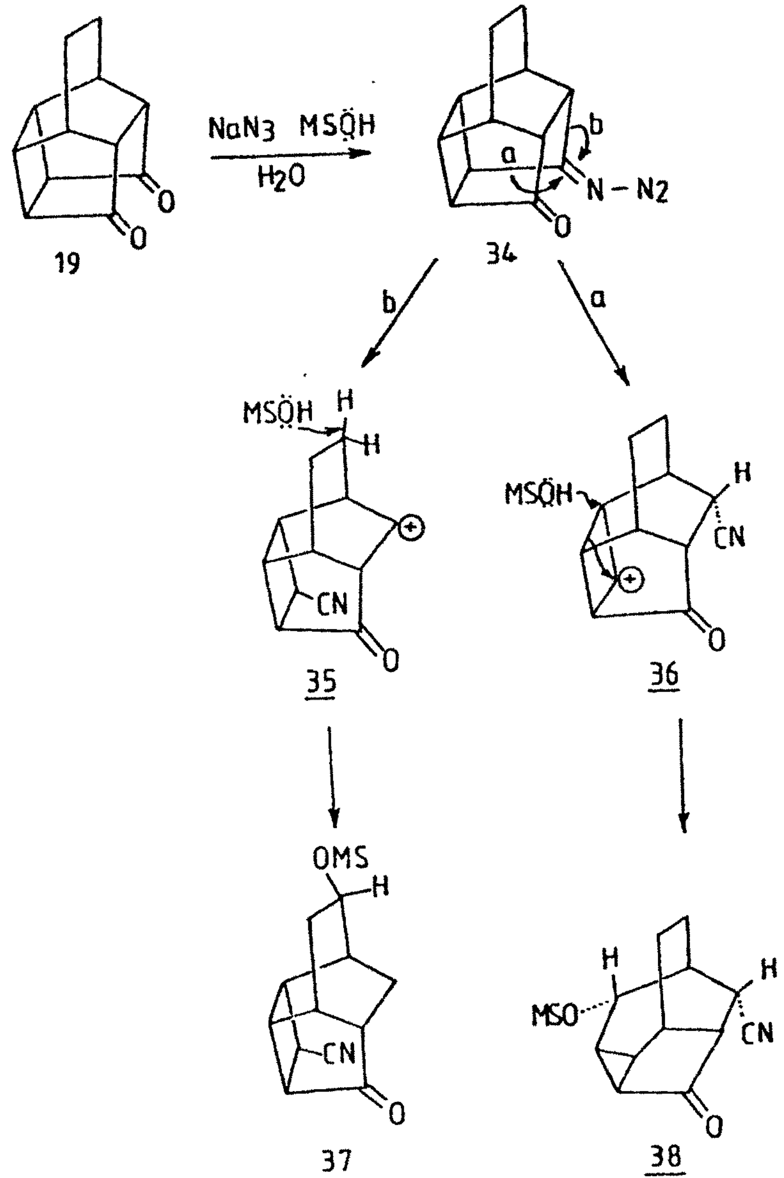
SCHEME - IV.6

It is interesting to note that the initially formed carbonium ion 32 rearranges to an unusual α-ketocarbonium ion 33, which is stabilized through π-delocalization and cyclopropyl conjugation. It is perhaps this stabilisation among other things, which directs the migration of bond 'C' in the ion 32 as against the migration bond 'b' in the rarrangement of pentacyclic dione 15.

The homologous pentacyclo $[6.2.2.0^{2,7}0^{4,10}0^{5,9}]$ dodecane-3,6-dione (19) having two bridged methylene groups provided yet another interesting carbocation rearrangement during which a novel hydride shift was also observed.[16] Thus the treatment of the dione (19) with NaN_3-MsOH gave the mesylates 37 and 38 as shown in the Scheme-IV.7.

In the light of these interesting rearrangements it was highly intriguing to study the carbonium ion rearrangements of the spiropentacyclic diones 1 and 2, which we had synthesised.

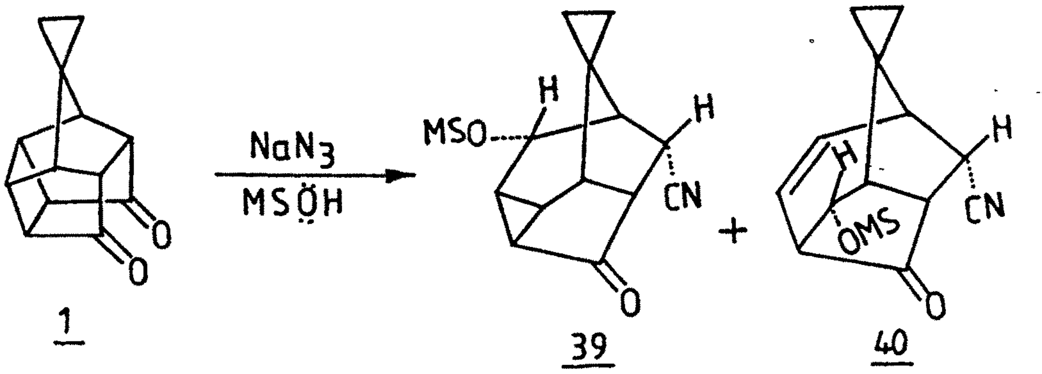
In this Chapter of the thesis we describe the formation of four novel carbocyclic systems (39, 40, 44 and 45) from 1 and 2 respectively under Schmidt reaction conditions.


NaN3 MSÖH
H2O
O
O
19
a
b
N – N2
O
34
b
a
MSÖH
H
H
CN
O
35
MSÖH
H
CN
O
36
OMS
H
CN
O
37
H
MSO
H
CN
O
38

SCHEME-IV.7

IV.3 Results and Discussion

Reaction of spirocyclic dione (1) with sodium azide (one equivalent) in methane sulphonic acid (1h, 0-5°) furnished a complex mixture of products (TLC), column chromatography on silica gel resulted in the isolation of two crystalline mesylates (39), m.p. 188° and (40), m.p. 183° in 18% and 8% yields respectively. (Scheme-IV.8)



SCHEME -IV. 8

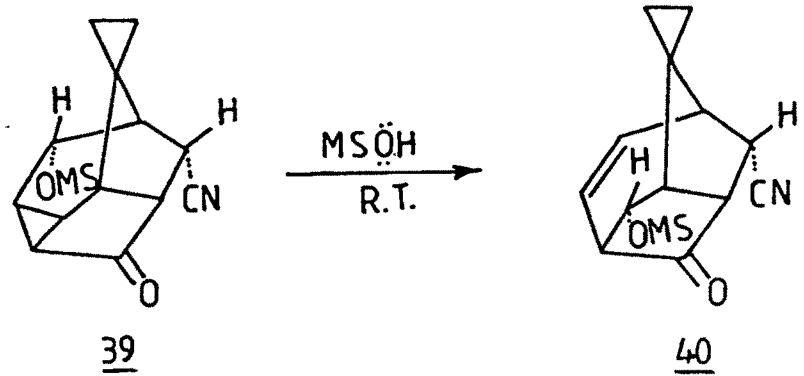
It is also observed that relative yields of 39 and 40 were markedly dependant on the reaction time. The stereo structures of these rearranged mesylates were elucidated with the aid of ^{13}C NMR spectra and high resolution spectra. We summarise below the complementary spectroscopic evidence that led to the formulation of 39 and 40 for the two mesylates obtained from 1.

The IR spectrum (Fig.IV.4) of 39, m.p. 188° was quite informative and revealed the nature of functional groups.

Thus the presence of a cyano group (2250 cm^{-1}) and a sulphonate ester group (1330 and 1175 cm^{-1}) was clearly indicated by diagnostic IR bands.[17] Furthermore, the carbonyl absorption at 1715 cm^{-1} was indicative of being either in a six membered ring or in a five membered ring in conjugation with a cyclopropyl group. The ^1H NMR spectrum (270 MHz, $CDCl_3$ - CD_3CN) (<u>Fig.IV.5</u>) confirmed the presence of a sulphonate ester functionality and exhibited signals at δ 3.12 (s, 3H) and δ 5.66 (t, 1H) due to the methyl group of the sulphonate ester and the proton adjacent to the methane sulphonoxy group respectively. The appearance of the proton attached to the mesyloxy group at δ 5.66 showed considerable deviation[18] from its normally encountered position around δ 5.0 indicating that it was attached to either an allylic or a cyclopropyl carbinyl carbon atom. The rest of the ^1H NMR spectrum showed signals at 2.91, 2.71, 2.39, 2.28, 2.12, 2.07, 1.98 and 0.68 and 0.48 (cyclopropane CH_2) due to the rest of the protons. The ^{13}C NMR ($CDCl_3$) spectrum (<u>Fig.IV.6</u>) displayed peaks at δ 209.8, 118.21, 89.0, 48.67, 46.03, 40.39, 37.83, 32.74, 31.99, 29.4, 28.50, 19.50, 10.29 and 3.52. The ^{13}C signals at δ 209.8, 118.21 and 89.0 could be readily assigned to the carbonyl carbon, cyanide carbon and carbon bearing mesylate functionality respectively. The presence of a characteristic signal at δ 19.5 appeared diagnostic of a cyclopropyl carbon conjugated with CO group. These structural features were found to be similar to the mesylate (20) obtained from the Schmidt fragmentation[13] of the Cookson's dione (14).

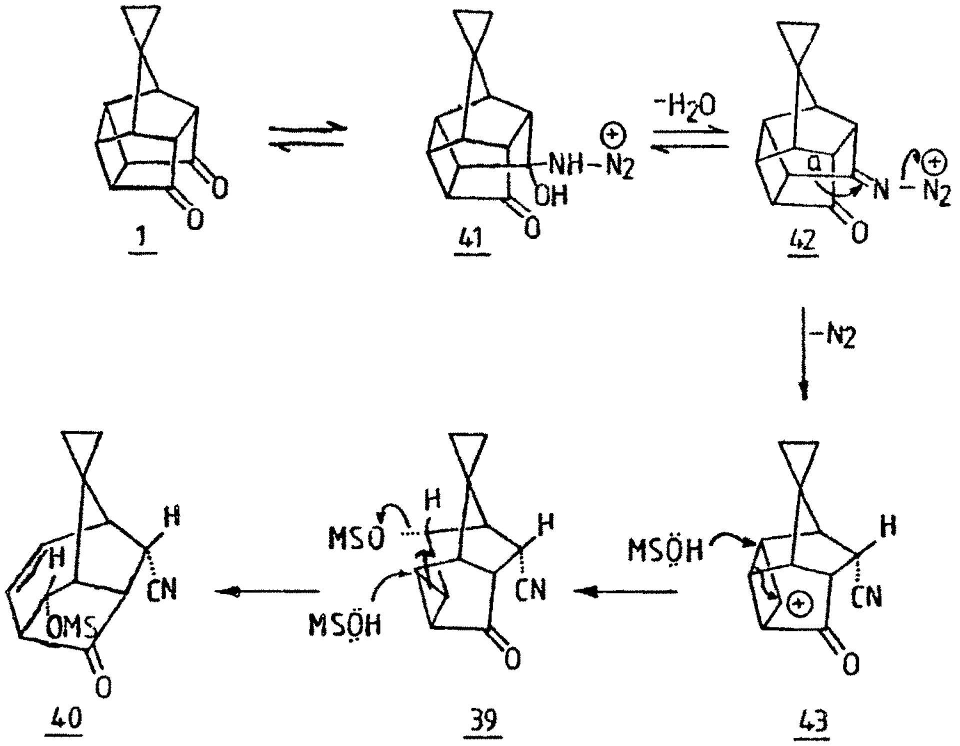
The less polar mesylate (40), m.p. 183° obtained during the Schmidt fragmentation reaction of 1 was assigned structure 40 on the basis of the following spectral data. The presence of diagnostic bands in the IR spectrum (Fig.IV.1) 2250, 1335 & 1175 cm^{-1} revealed the presence of cyano and the mesylate groups. Strong absorption bands at 1755 and 720 cm^{-1} could be readily attributed to a five membered cyclic ketone and cis-disubstituted olefinic linkage. The ^{1}H NMR ($CDCl_3$, 270 MHz) (Fig.IV.2) spectrum exhibits signals at δ 6.22 and 5.94 due to the presence of olefinic linkage, 5.00 (s, 1H) is due to the proton attached to the carbon bearing mesylate group. The signal at 3.04 (s, 3H) is due to the methyl group of mesylate ester. In conformity with these assignments, the ^{13}C NMR ($CDCl_3$) (Fig.IV.3) displayed signals at δ 206.48 (C=O), 135.92 and 122.93 ($\underline{C}=\underline{C}$), 116.32 ($\underline{C}\equiv N$), 89.09 ($\underline{C}-O-S-CH_3$), and 82.43, 55.19, 54.25, 52.02, 46.73, 42.86, 38.33, 32.63, 17.14 and 6.04 due to the rest of the carbons.

Further support for structure 40 was derived from the fact that it was almost quantitatively formed from 39 on solvolysis in methanesulphonic acid, the transformation representing a facile cyclopropylcarbinyl ---> homoallylic carbonium ion rearrangement (Scheme-IV.9).



SCHEME-IV.9

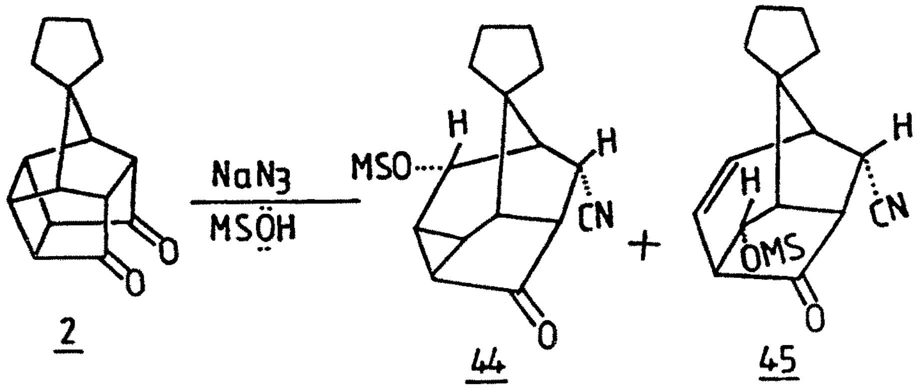
A reasonable mechanism for the formation of 39 and 40 from pentacyclic dione (1) during Schmidt reaction conditions (CH_3SO_2OH - NaN_3) is depicted in Scheme-IV.10.



SCHEME-IV.10

The key intermediate 41 for Schmidt fission is readily formed via nucleophilic addition of azide ion (N_3^-) to the protonated carbonyl of 1 to azidohydrin 42 followed by acid catalyzed dehydration. Loss of nitrogen and fragmentation of 41 leads to the cyclobutyl carbonium ion 43 which quickly rearranges to the cyclopropylcarbinyl carbonium ion with concomitant nucleophilic capture to furnish the endo-mesylate 39. The observed stereochemistry of 39 is in agreement with this process. The mesylate 39 undergoes, a methane sulphonic acid mediated stereospecific cyclopropyl carbinyl ----> homoallylic carbonium ion rearrangement. The observed stereochemistry of the mesylate group in 40 favours the concerted mechanism.

Similarly the spirocyclic dione (2) undergoes, Schmidt fragmentation in methanesulphonic acid with NaN_3 to give a mixture of two mesylates 44 and 45 in 20% and 9% respectively as shown in Scheme-IV.11.



SCHEME-IV.11

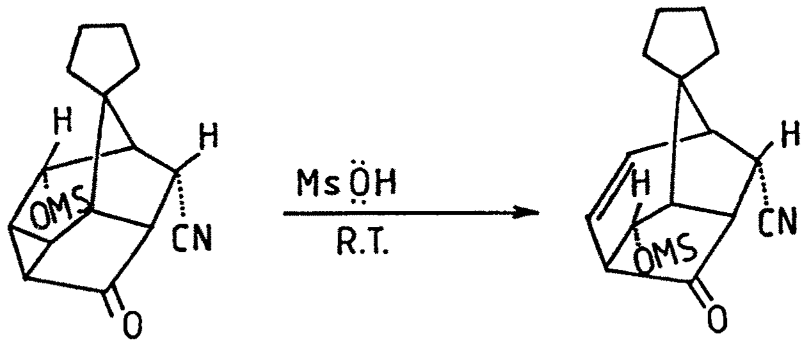
The stereo-structures of these mesylates were deduced from high rsolution ^{1}HNMR ($CDCl_3$, 270 MHz) and mass fragmentation pattern. We summarize below the spectroscopic evidence led to the formulation of 44 and 45 for the two mesylates obtained from 2.

The more polar mesylate 44, m.p. 175° showed IR absorption bands (Fig.IV.9) at 2250 (cyanogroup), 1365 & 1175 (methanesulphonoxy group) and 1715 cm^{-1} (carbonyl group) in its IR spectrum. The ^{1}HNMR ($CDCl_3$, 270 MHz) (Fig.IV.10) spectrum confirmed the presence of a sulphonate ester functionality and exhibited signal at δ 3.20 (s, 3H) for the methyl of the mesylate group and 5.75 (t, 1H) due to the proton attached to the carbon bearing mesylate group. The remaining peaks at δ 3.00, 2.9, 2.7, 2.6 were due to methine protons. 1.7 (s, 8H, cyclopentane CH_2). Mass spectrum shows peaks at (m/e) 321 (M^+), 293 (M^+-CO), 196, 182, 169, 145, 130, 117, 104, 91 ($C_7H_7^+$), 97 ($C_5H_3O^+$ or $C_6H_7^+$), 66 ($C_5H_6^+$) etc. These structural features were found to be similar with the mesylate 39.

The less polar mesylate 45, m.p. 169° has shown absorption bands in IR (KBr) spectrum (Fig.IV.7) at 2250 (cyano group), 1760 (carbonyl group), 1370 & 1175 (methane sulphonoxy group) and 710 cm^{-1} (in disubstituted olefin). The ^{1}HNMR ($CDCl_3$, 270 MHz) (Fig.IV.8) has showed signals at δ 6.18

(t, J=4.5Hz, 1H) and 5.98 (t, J=4.5Hz, 1H) were due to olefinic protons. 3.16 (d, J=6Hz, 1H, bridgehead proton), 3.06 (s, 3H, $CH_3-O-\overset{O}{\underset{O}{S}}-$). The rest of the signals were due to ring methine protons as the diagnostic resonances. The ^{13}CNMR spectrum (Fig. IV.9) displayed characteristic signals at δ 207.82 ($\underline{C}$=O), 135.0 and 122.17 ($\underline{C}$=$\underline{C}$), 117.52 ($\underline{C}\equiv N$), and 80.11 (H-$\underline{C}$-OMs) in addition to the signals at 60.12, 59.88, 55.51, 51.53, 48.04, 41.47, 40.94, 38.0, 32.09, 23.0 and 22.41 for other carbons. The mass spectrum has showed peaks at (m/e) 321 (M^+),254, 242, 225, 214, 196, 156, 145, 130, 117, 104, 91 ($C_7H_7^+$), 79 ($C_5H_3O^+$ or $C_6H_7^+$) 67 ($C_5H_7^+$) and 53.

Further support for structure 45 was derived from the fact that it was also formed from 44 on solvolysis in methane sulphonic acid, the transformation representing a facile cyclopropyl carbinyl ----> homoalylic carbonium ion rearrangement (Scheme-IV.12).

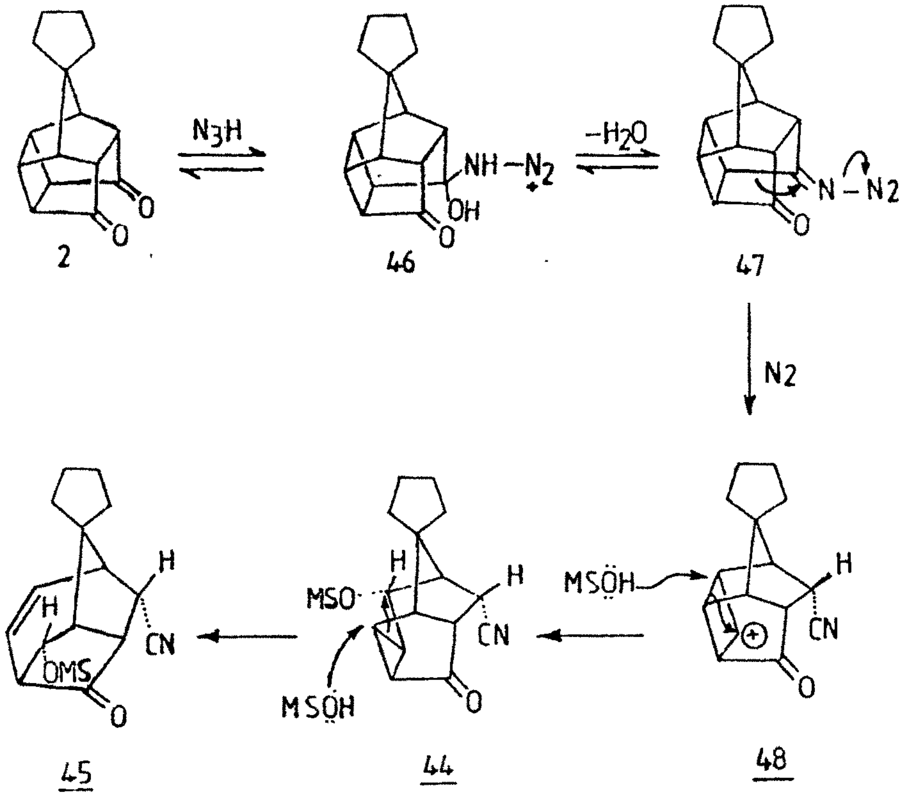


44

45

SCHEME - IV. 12

A plausible mechanism for the formation of mesylates 44 and 45 from the spirocyclic dione 2 during Schmidt fragmentation is depicted in Scheme-IV.13.



SCHEME - IV. 13

IV.4 EXPERIMENTAL

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

Schmidt reaction of pentacyclo $[5.4.0.0^{2,6}0^{3,10}0^{5,9}]$ undecane-8,11-dione-4-spiro-1'-cyclopropane (1)

A solution of the diketone 1 (1 g, 0.005 mol) in dichloromethane (25 ml) and methanesulphonic acid (6 ml) was cooled to 0-5° and sodium azide (NaN_3) (0.035 g) was slowly added pinch by pinch. After 1 h (tlc) it was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 50 ml). The organic layer was washed with $NaHCO_3$ solution, brine (2 x 15 ml) and water (2 x 10 ml) and dried over anhydrous sodium sulphate. Stripping off the solvent, under reduced pressure gave dark brown syrupy liquid, which was chromatographed over silica gel (Acme's) (60-120 mesh) using pet. ether - ethyl acetate mixture as eluent. Elution with pet. ether - ethyl acetate mixture (80:20) gave the less polar mesylate 40 (0.12 g) in 8% yield as white crystals, m.p. 183°, UV λ_{max}^{MeOH} : 209 nm, IR (KBr) ν_{max} (Fig. IV.1) : 2250 (C≡N), 1755 (C=O) 1355 and 1175 (CH_3-SO_3) and 710 cm^{-1} (cis C=C). ^{1}HNMR ($CDCl_3$, 270 MHz) : (Fig.IV.2) : δ 6.22 (t, J=10.5Hz, 1H, olefinic H), 5.94 (t, J=10.5Hz, 1H, olefinic H) 5.00 (s, 1H, H-C-OMs), 3.56 (q, J_1=11Hz, J_2=8Hz, 1H, H-C-CN), 3.37 (t, J=7Hz, 1H, methine H), 3.22 (d, J=5Hz, 1H, ring H), 3.04 (s, 3H, $CH_3-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O$), 2.78 (d, J=5Hz, 1H, ring H), 2.29 (t, J=8Hz, 1H, ring H) and 0.64 (m, 4H, cyclopropane (CH_2). ^{13}CNMR

($CDCl_3$) (Fig. IV.3) δ 206.48 (C=O) 135.92 and 122.9 (C=C), 118.3 (C≡N), 89.09, 82.43, 55.19, 54.23, 52.02, 46.73, 42.86, 38.33, 32.63, 17.14 (cyclopropyl-C-C=O) and 6.04 (cyclopropane CH_2). Analysis : Found C, 56.92 ; H, 4.96% : requires C, 57.33 ; H, 5.12% for $C_{14}H_{15}NO_4S$.

Further elution with pet. ether - ethyl acetate (60:40) gave the more polar mesylate 39 (0.265 g) in 18% yield as colourless crystals m.p. 188°, UVλ^{MeOH}_{max} : 206 nm, IR (KBr) : ν_{max} (Fig. IV.4) 2250 (C≡N), 1715 (C=O), 1330 and 1175 cm^{-1} (CH_3-SO_3 group). ^{1}HNMR ($CDCl_3$ + CD_3CN, 270 MHz) ; (Fig. IV.5) δ:5.66 (t, J=6Hz, 1H, H-C-OMs), 3.12 (s, 3H, $CH_3-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O$), 2.91 (m, 1H, ring H), 2.71 (q, J_1=7Hz, J_2=6Hz, 1H, ring H), 2.39 (t, 1H, ring H), 2.28 (t, 1H, methine H), 2.12 (s, 1H, ring H), 2.07 (s, 1H, ring H), 1.98 (s, 1H, methine H), 0.68 and 0.42 (m, 4H, cyclopropane CH_2). ^{13}CNMR ($CDCl_3$ + CD_3CN) (Fig. IV.6) δ 209.8 (C=O), 118.21 (C≡N), 89.0, 46.05, 40.93, 37.03, 32.74, 31.99, 29.46, 28.50, 19.50 (cyclopropyl C-CO), 10.29 and 3.52 (cyclopropyl CH_2). Analysis : Found C, 57.12 ; H, 4.82% : requires C, 53.33 ; H, 5.12% for $C_{14}H_{15}NO_4S$.

Schmidt reaction of pentacyclo [5.40.$0^{2,6}0^{3,10}0^{5,9}$] undecane-8,11-dione-4-spdiro-1'-cyclopentane (2)

A solution of diketone 2 (1 g, 0.0043 mol) in dichloromethane (25 ml) and methanesulphonic acid (6 ml) was cooled to 0-5°. To the stirred mixture sodium azide (0.040 g) was added in small quantities. The mixture was stirred for about 1 h. (tlc). It was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 50 ml). The organic layer was washed with $NaHCO_3$ solution, water (2 x 20 ml) and brine (2 x 15 ml) and dried over anhydrous sodium sulphate. Stripping off the solvent gave a dark brown syrupy liquid, containing a mixture of two mesylates (tlc) $\underline{44}$ and $\underline{45}$. They were separated by column chromatography on silica gel (Acme, 60-120 mesh) using pet. ether ethylacetate mixture.

Elution with pet. ether - ethylacetate mixture (80:20) gave the less polar mesylate $\underline{45}$ (0.13 g) in 9% yield as colourless crystals, m.p. 169°. $UV\lambda_{max}^{MeOH}$: 208 nm, IR (KBr) ν_{max} (Fig. IV.7) 2250 (cyano) 1760 (carbonyl), 1370 and 1175 (methane sulphonoxy) and 710 cm^{-1} (cis disubstituted olefinic groups) ^{1}HNMR ($CDCl_3$, 270 MHz) (Fig. IV.8); δ 6.18 (t, J=4.5Hz, 1H, olefinic H), 5.98 (t, J=4.5Hz, 1H, olefinic H), 5.12 (s, 1H, $\underline{H}$-C-OMs), 3.50 (q, J_1=10Hz, J_2=8Hz, 1H, $\underline{H}$-C-CN), 3.25 (t, J=7Hz, 1H, bridgehead H), 3.16 (d, J=6Hz, 1H, bridgehead H), 3.08 (s, 3H, $\underline{CH}_3 - \overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}} - O$), 2.64 (t, J=7Hz, 1H, ring H) and 1.8-1.6 (m, 8H, cyclopentane CH_2). ^{13}CNMR ($CDCl_3$) (Fig-IV.9): δ207.82 ($\underline{C}$=O), 135.0 and 122.17 ($\underline{C}$=$\underline{C}$), 117.52 ($\underline{C}$=$\underline{N}$), 80.11 (H-$\underline{C}$-OMs), 60.12, 59.88, 55.51, 51.53, 48.04, 41.47, 40.94, 38.0, 32.09, 23.0, 22.41. Mass (m/e) : M^+ 321. Analysis : Found C, 59.50 ; H, 6.07% requires C, 59.81 ; H, 5.91% for $C_{16}H_{19}NO_4S$.

Further elution with pet. ether - ethylacetate mixture (60:40) gave the more polar mesylate 44 (0.28 g) in 20% yield as colourless crystals, m.p. 175°, UVλ_{max}^{MeOH} : 206 nm, IR (KBr)ν_{max} : (Fig. IV.10) 2250 (cyano) 1715 (carbonyl) 1360 and 1175 cm^{-1} (methanesulphonoxy group) ^{1}HNMR (CDCl$_3$, 270 MHz) (Fig. IV.11) δ 5.75 (t, J=6Hz, 1H, H-C-OMs), 3.18 (s, 3H, CH$_3$-S - O), 3.00 (q, J$_1$=8Hz, J$_2$=5Hz, 1H, H-CN), 2.90 (t, 1H, bridgehead H), 2.70 (t, 1H, bridgehead H), 2.62 (m, 1H, ring H), 2.14 (t, 1H, ring H), 2.04 (m, 1H, ring H), 1.94 (m, 1H, ring H) and 1.75-1.45 (m, 8H, cyclopentane CH$_2$). Mass (m/e) : M$^+$ 321. Analysis : Found C, 59.62 ; H, 6.14% requires C, 59.81 ; H, 5.91% for $C_{16}H_{19}NO_4S$.

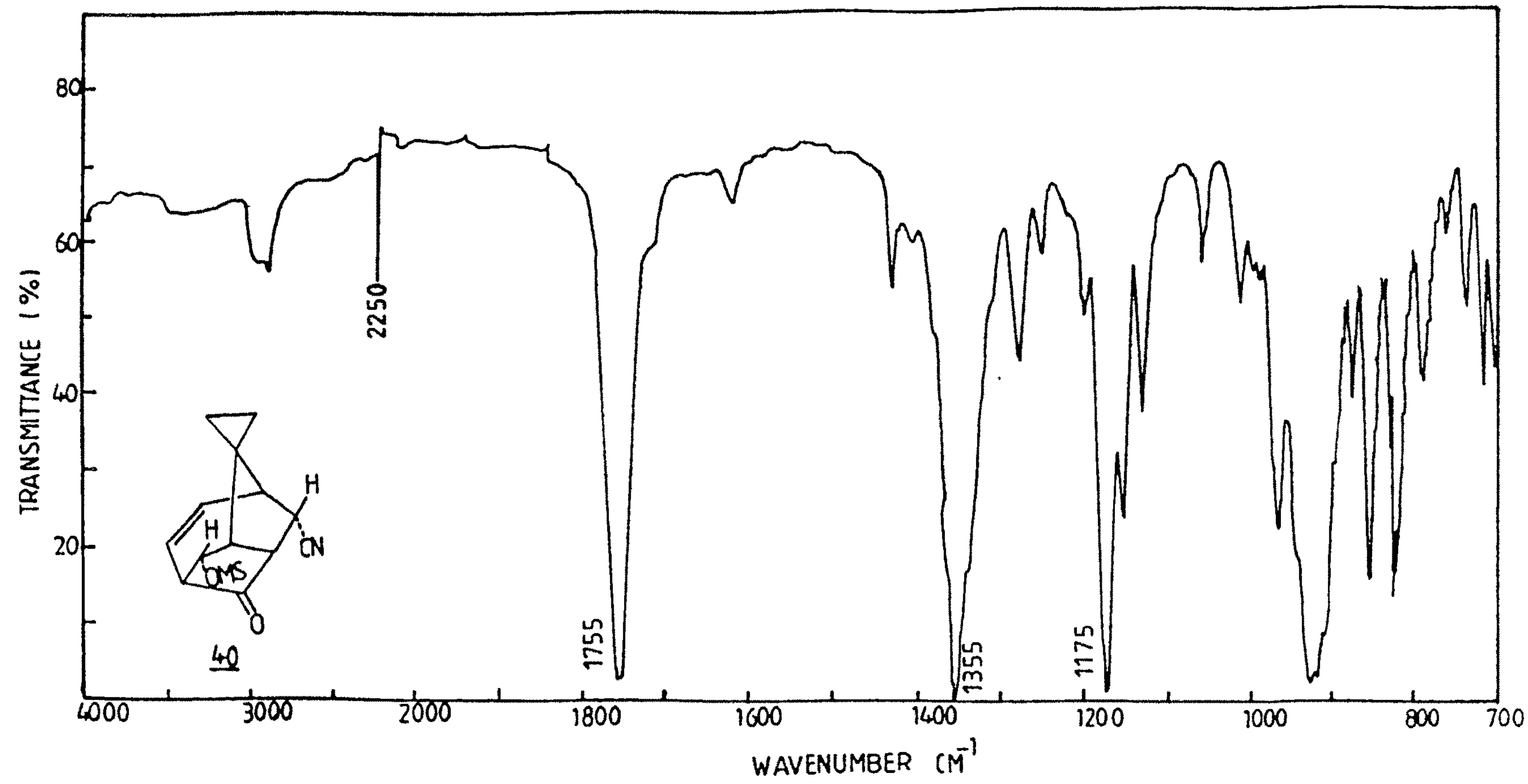


Fig. IV.1 : IR (KBr) spectrum of compound 40

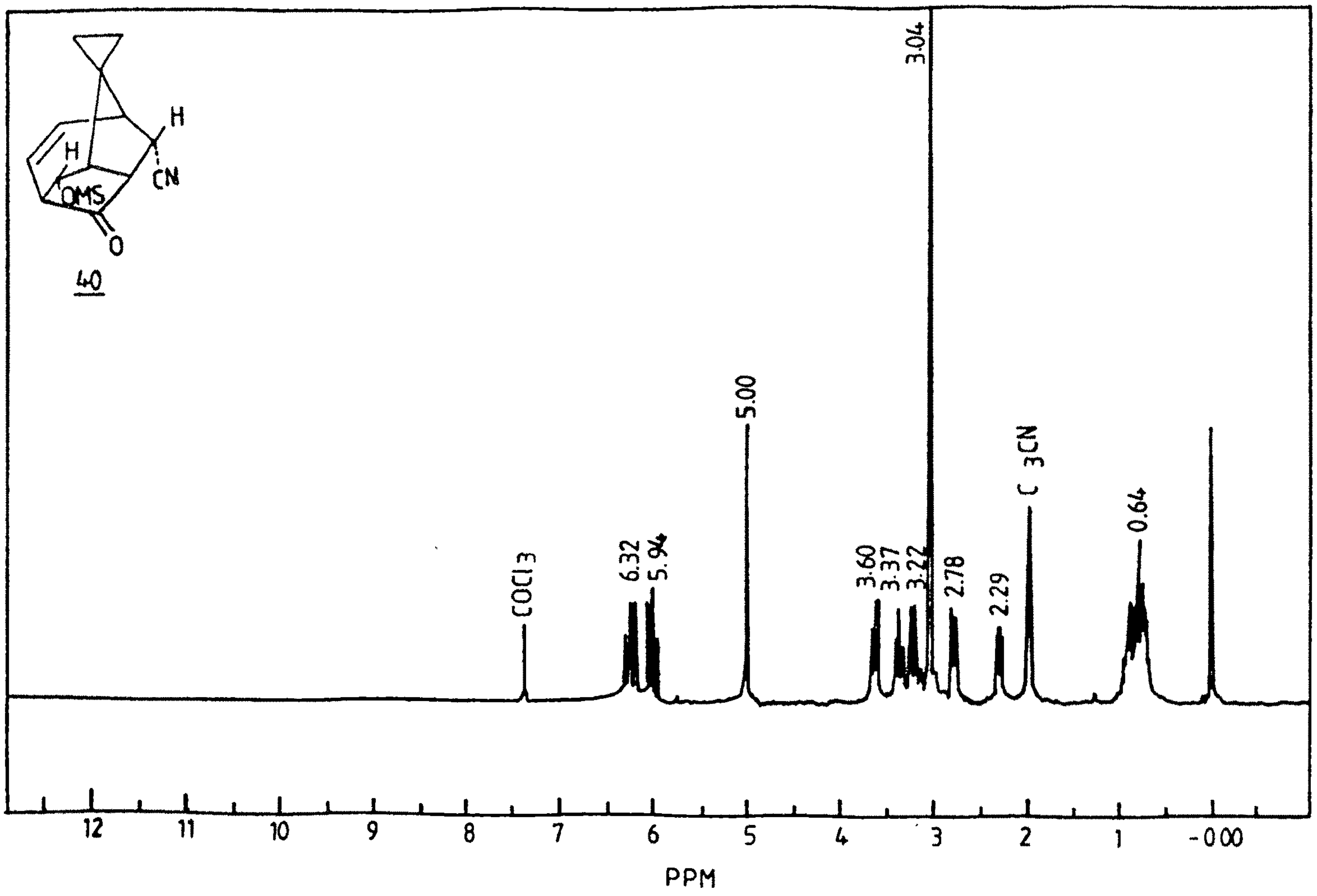


Fig. IV.2 : NMR ($CDCl_3$, 270 MHz) spectrum of compound 40

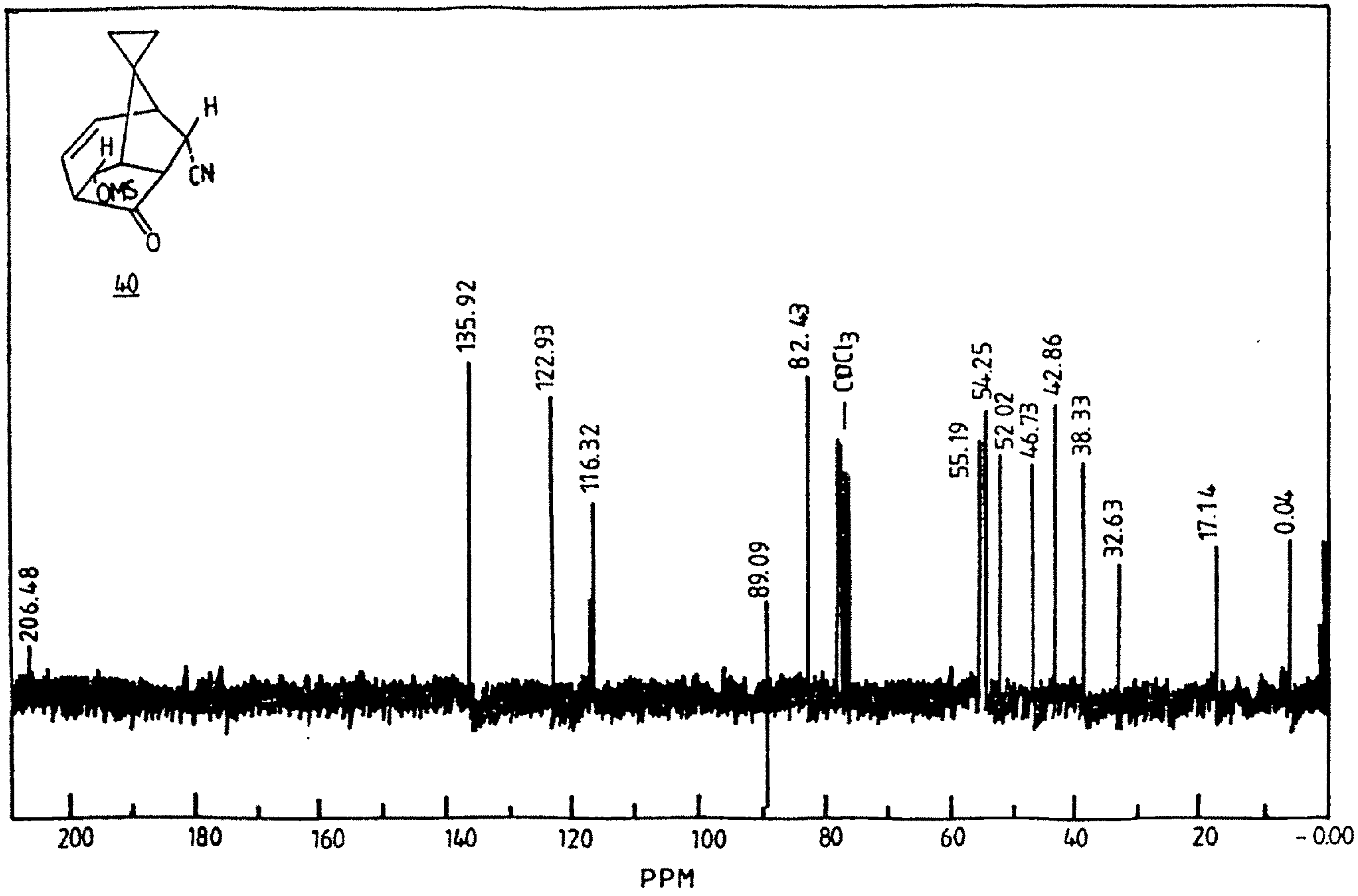


Fig. IV.3 : ^{13}CNMR ($CDCl_3$) spectrum of compound 40

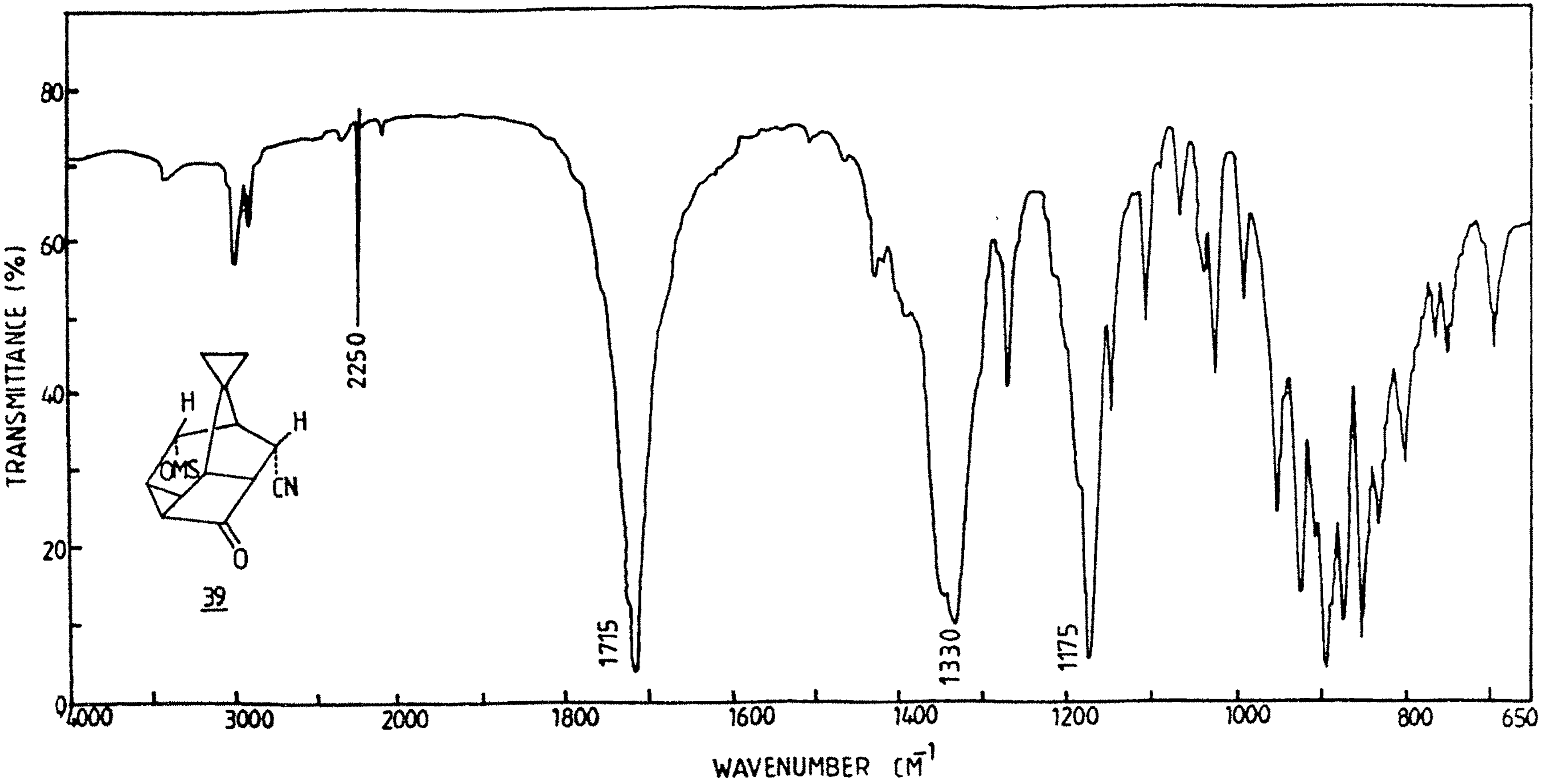


Fig. IV.4 : IR (KBr) spectrum of compound 39

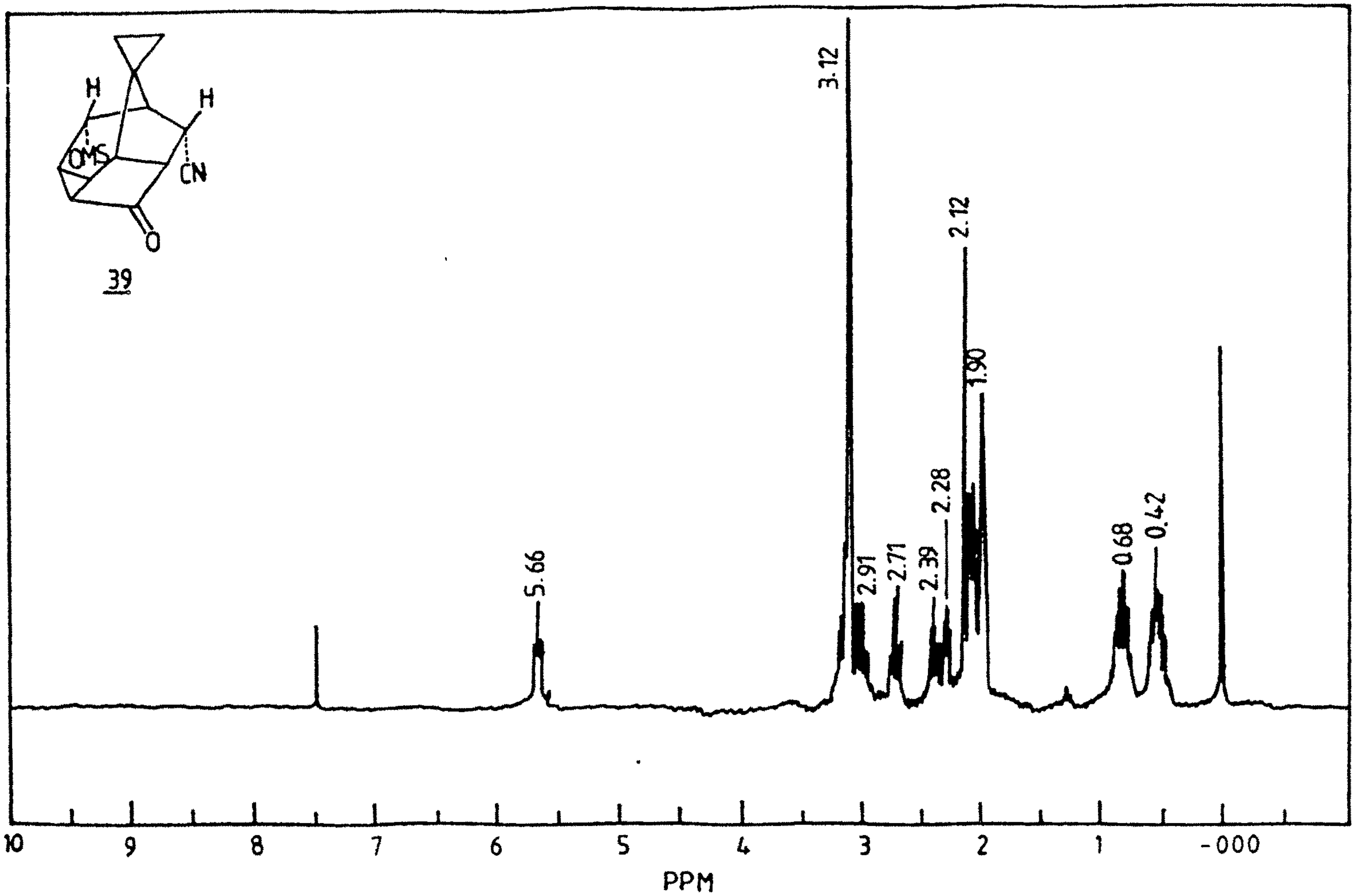


Fig. IV.5 : NMR ($CDCl_3$ + CD_3CN, 270 MHz) spectrum of compound 39

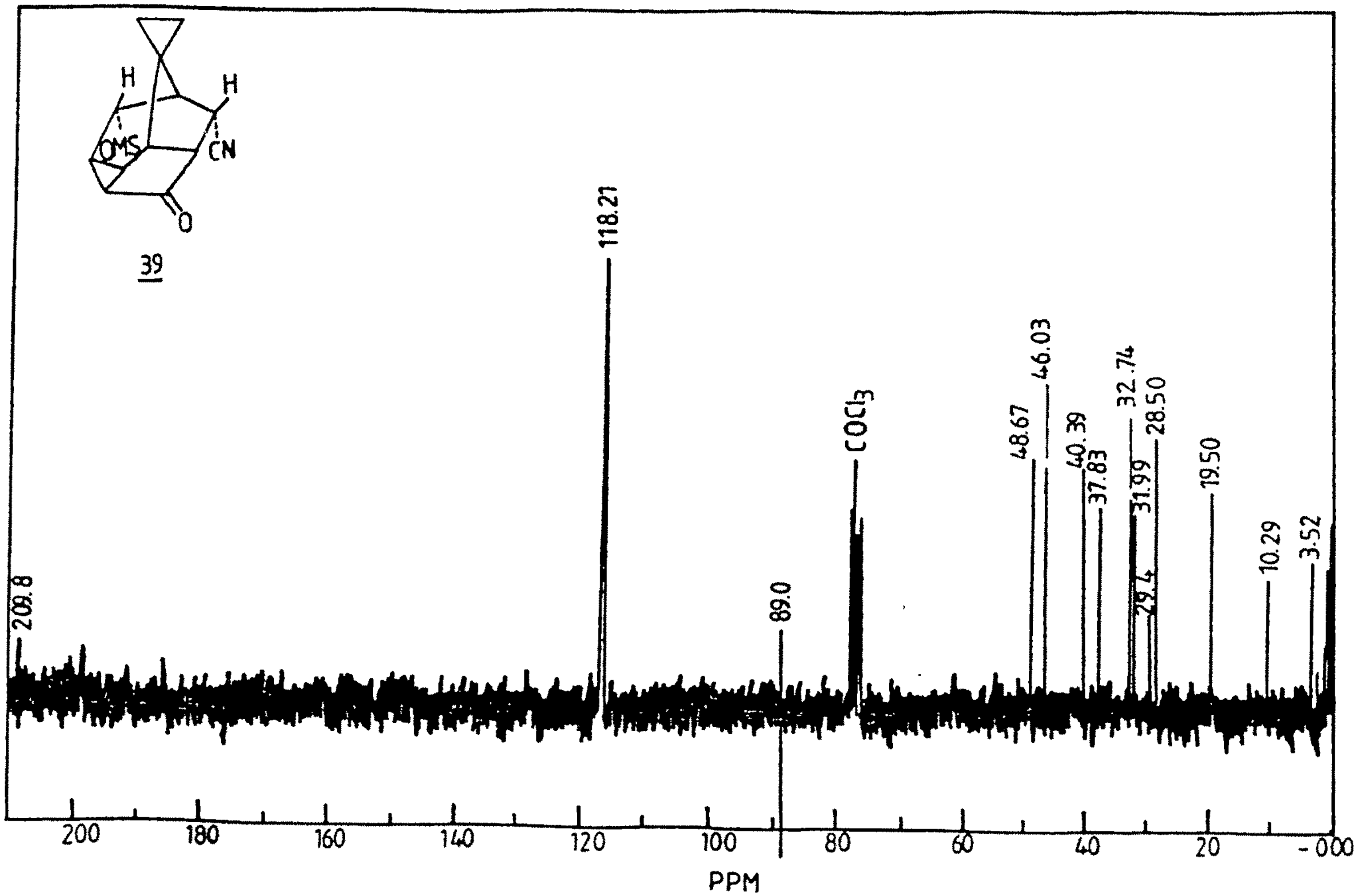


Fig.IV.6 : ^{13}CNMR (CDCl$_3$ + CD$_3$CN) spectrum of compound 39

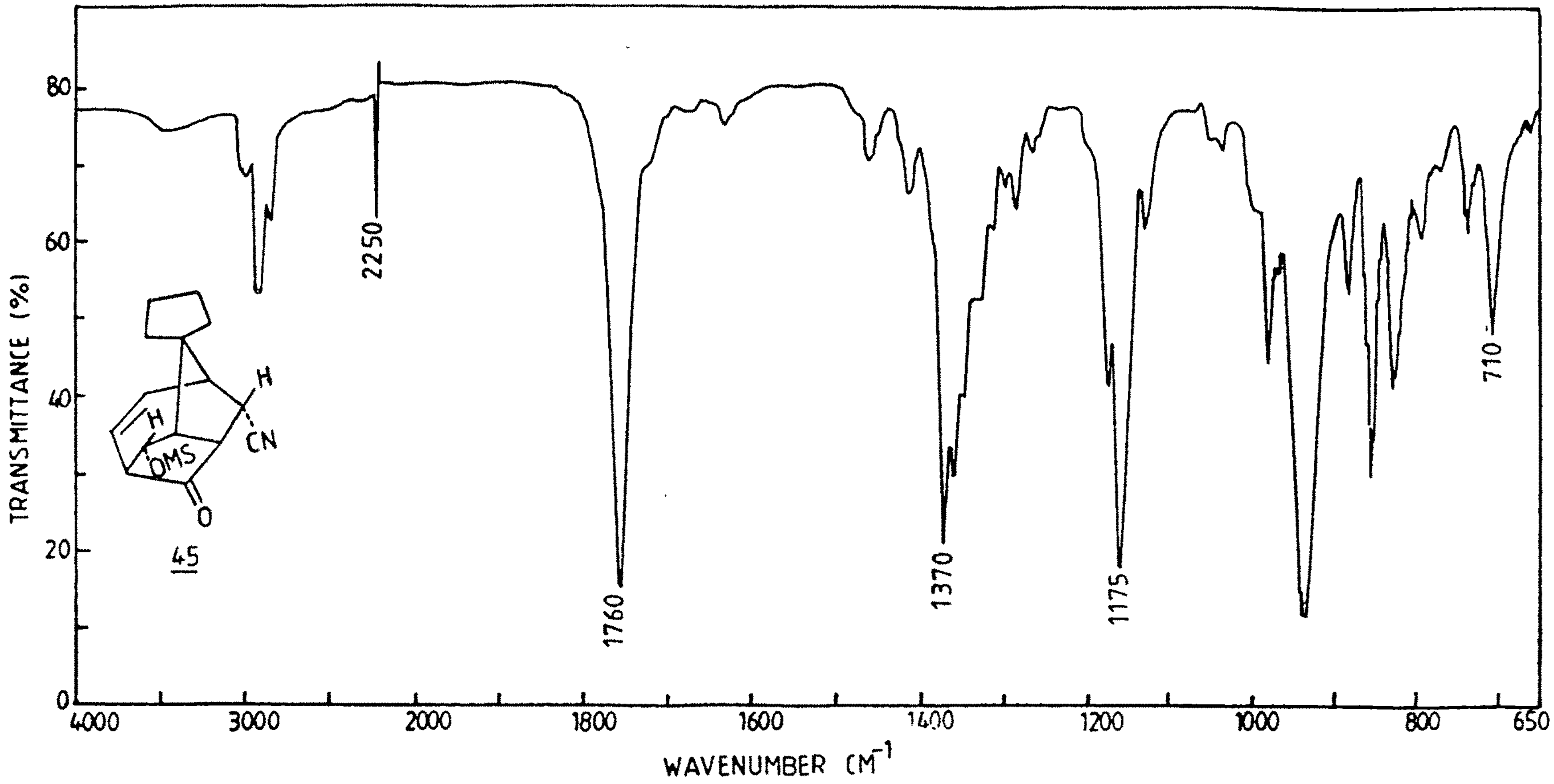
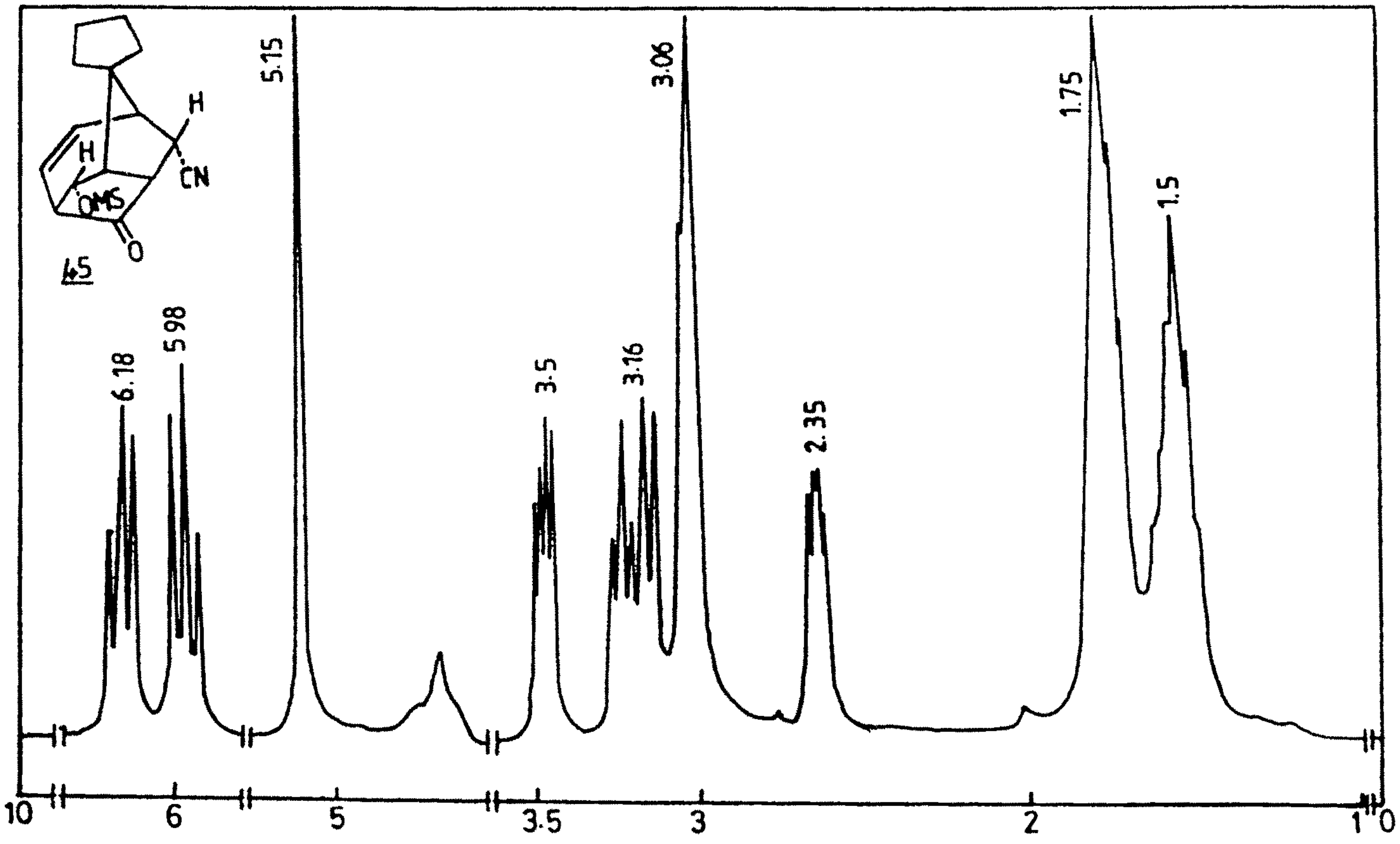


Fig. IV.7 : IR (KBr) spectrum of compound 45



<u>Fig. IV.8</u> : NMR ($CDCl_3$, 270 MHz) spectrum of compound <u>45</u>

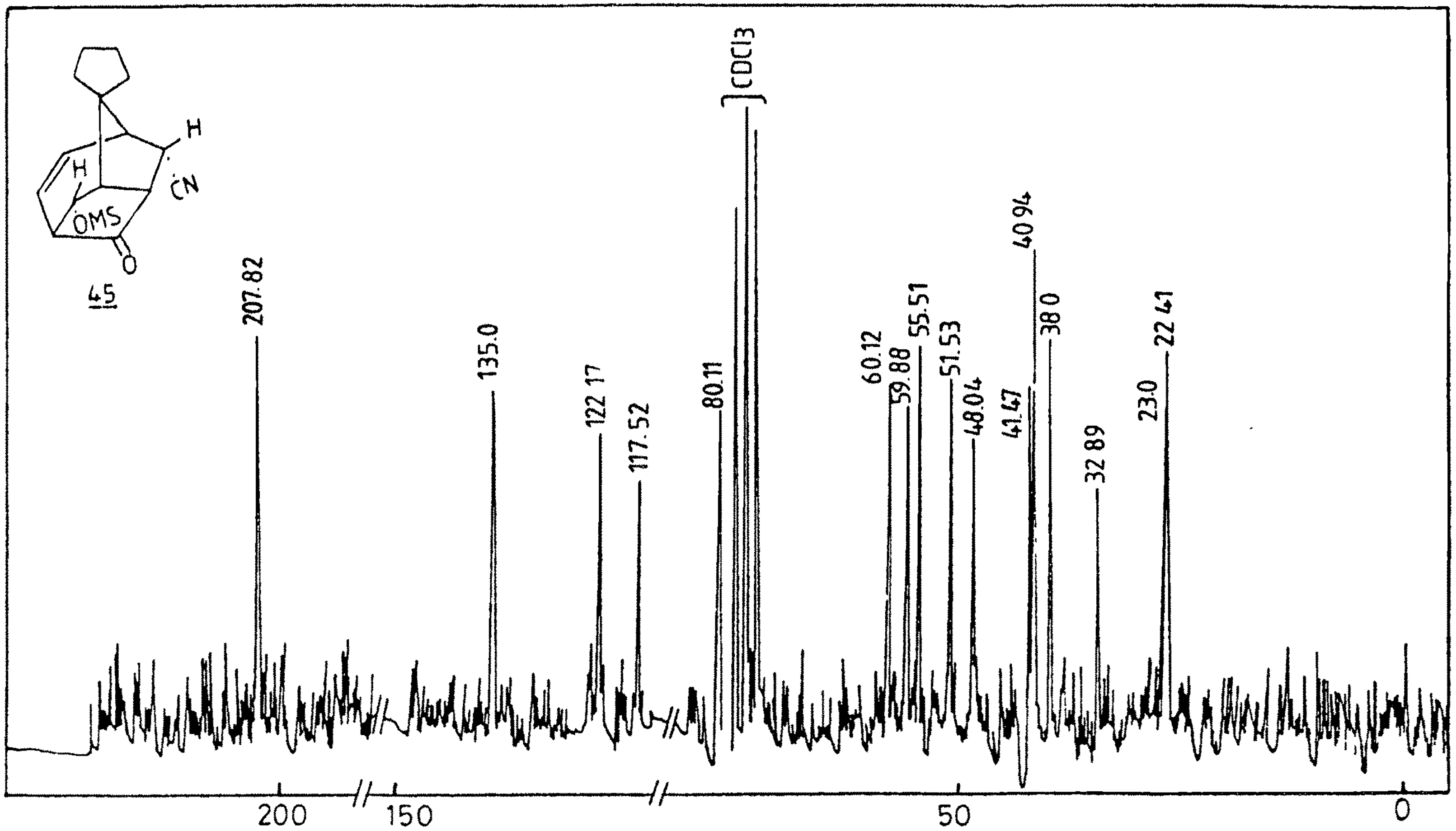


Fig IV.9 : ^{13}CNMR ($CDCl_3$) spectrum of compound 45

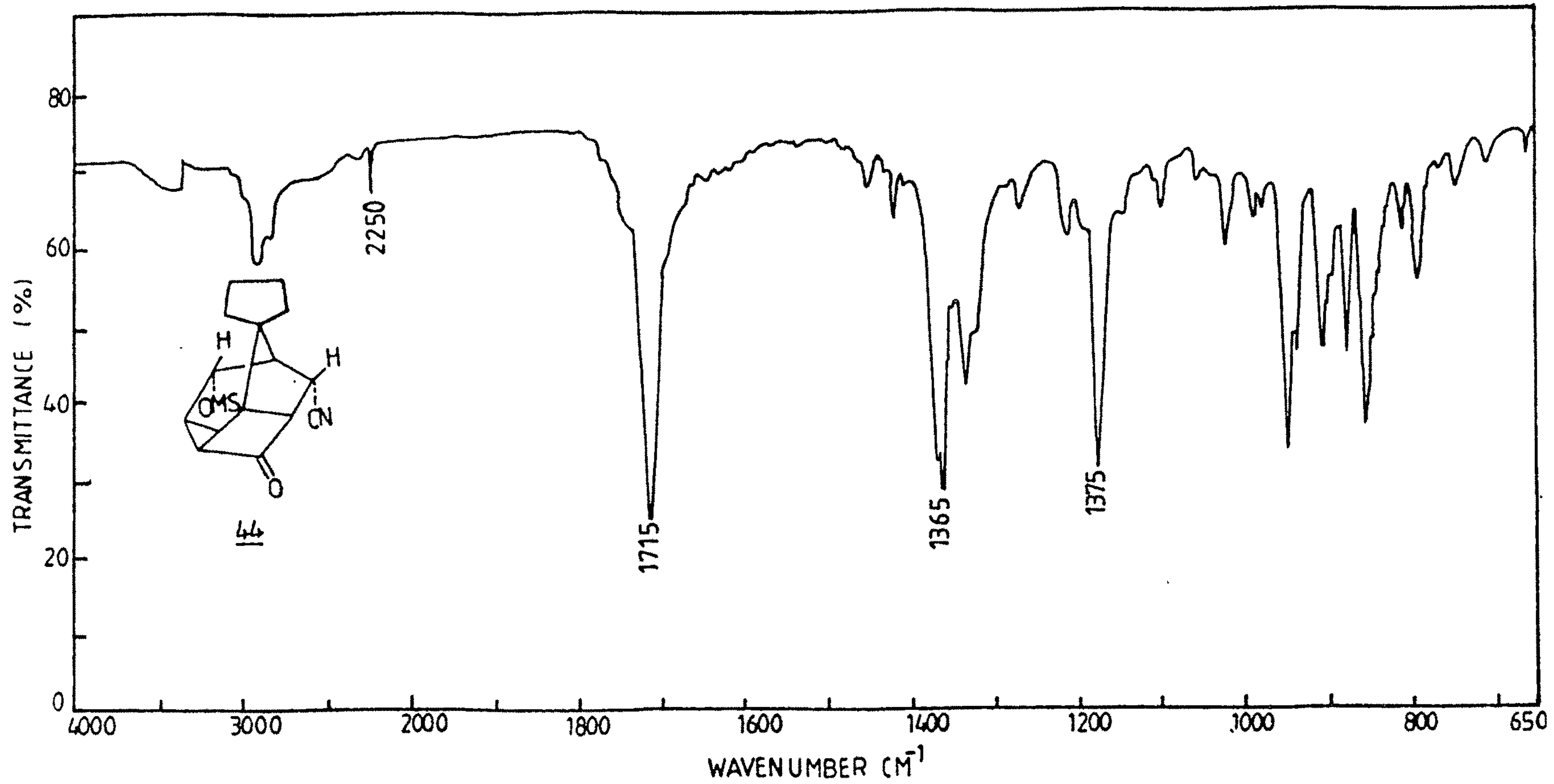


Fig IV.10 : IR (KBr) spectrum of compound 44

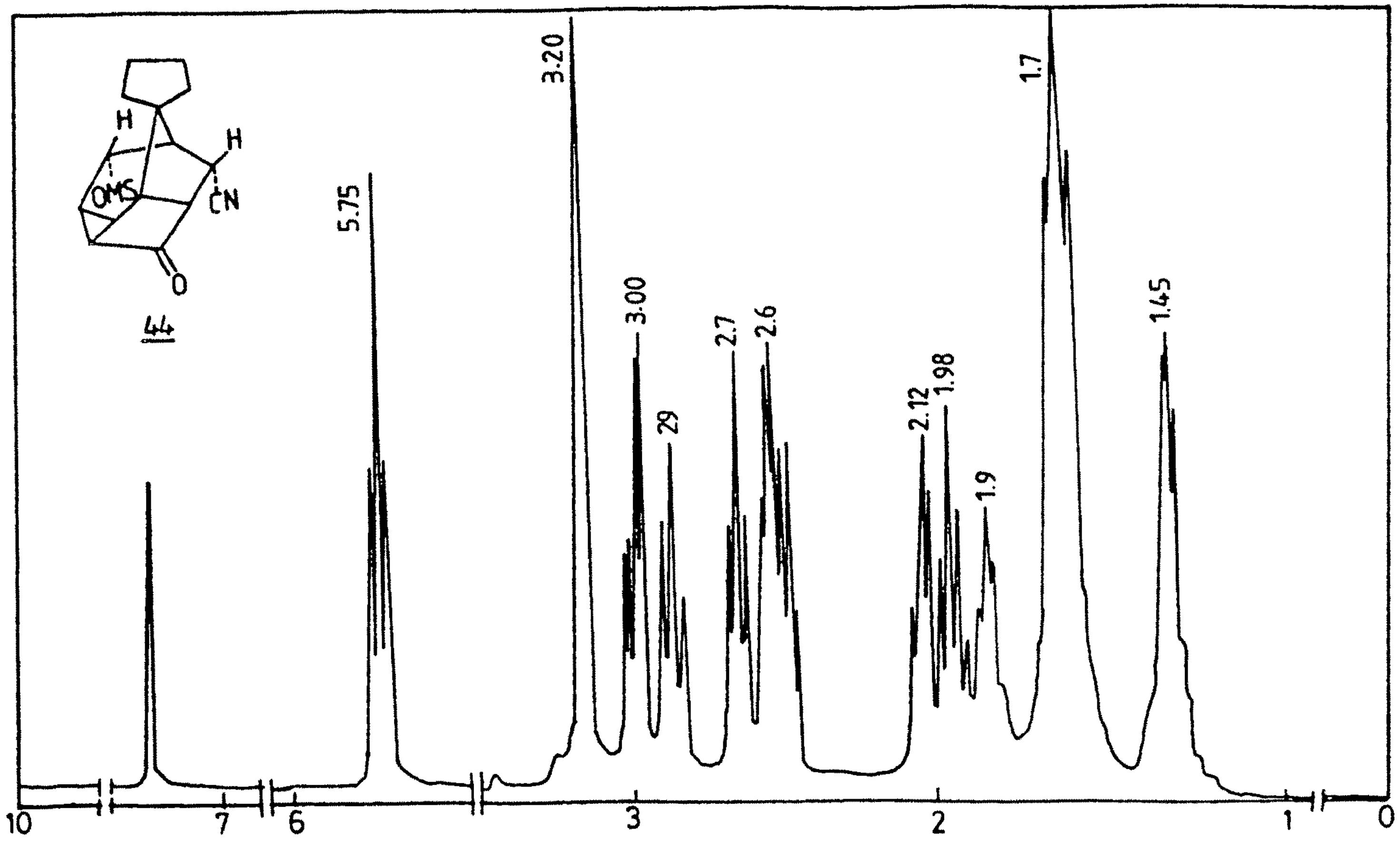


Fig-IV.11 : NMR ($CDCl_3$, 270 MHz) spectrum of compound 44

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