CHAPTER - II

SYNTHESIS OF POLYCYCLIC CAGE DIONES

II.1.1 Abstract :

This chapter of the thesis describes the synthesis of novel polycyclic diones (22-27) via $\pi^{4s} + \pi^{2s}$ cycloaddition of dienes (7-10) with various quinones followed by intramolecular $\pi^{2s} + \pi^{2s}$ cycloaddition of the resulting endo Diels-Alder adducts (14-21). The Diels-Alder cycloaddition between dienes and quinones were studied in (i) conventional homogeneous medium by refluxing in toluene and (ii) in microheterogeneous micellar media at room temperature. A remarkable catalytic effect of cetyl trimethylammonium bromide (CTAB) micelle on all the $\pi^{4s} + \pi^{2s}$ cycloaddition has been observed.

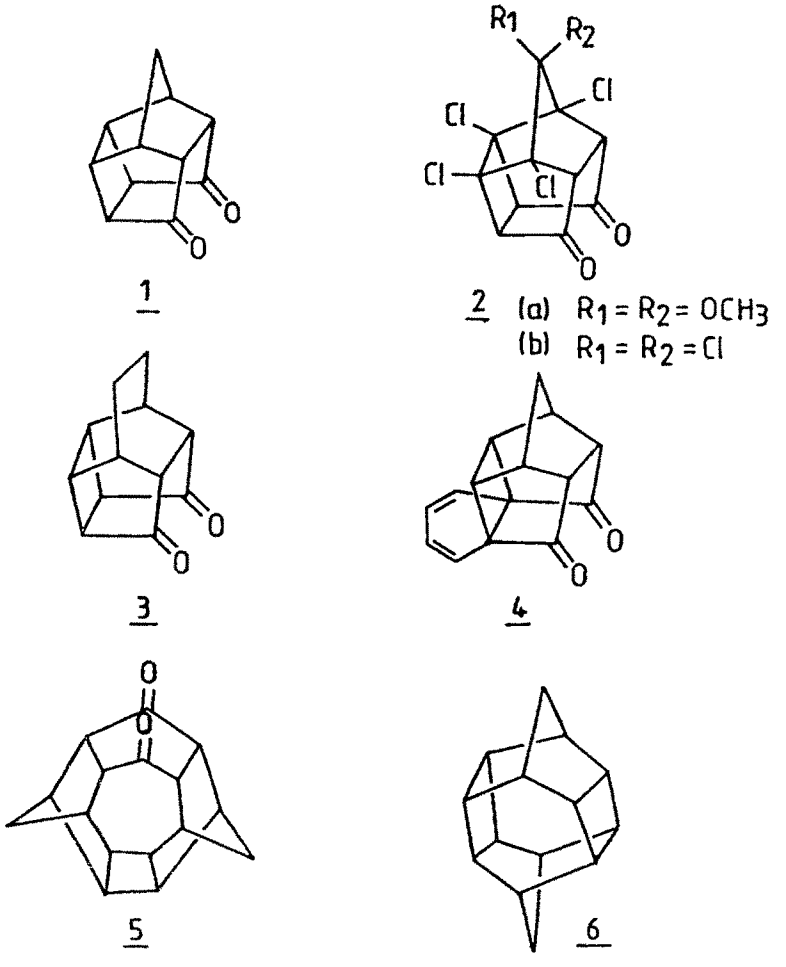
In the case of cycloaddition between spirohepta-1,3-diene (7) with benzoquinone, a bis adduct (28) was observed in aqueous medium containing higher amounts of CTAB. The extent of mono versus bis addition is found to be dependent upon surfactant concentration. The structure of the bis adduct has been determined by X-ray analysis.

In this context, we also developed a simple phase transfer method for the preparation of spirodienes required for the above objective, by bis alkylation of cyclopentadiene in the presence of aqueous base and a phase transfer catalyst.

II.1.2 Introduction

The polycyclic cage ketones continue to play an important

role in the development of various aspects of physical and synthetic organic chemistry.[1] The cage diketone (1) often referred to as Cookson's[2] dione, readily obtained by photo-isomerization of Diels - Alder adduct of cyclopentadiene benzoquinone has proved to be a versatile precursor for the synthesis of many novel carbocycles.[3,4] Similarly the caged diketone (2) has offered routes to pentaprismane[5] and many other ring systems.[6] Among many other diketones which have been studied[7-9] are the diones 3 and 4. (Scheme-II.1) obtained by photocyclisation of cyclohexadiene-benzoquinone and cyclopentadiene-naphthoquinone adducts respectively.



1

2 (a) $R_1 = R_2 = OCH_3$
(b) $R_1 = R_2 = Cl$

3

4

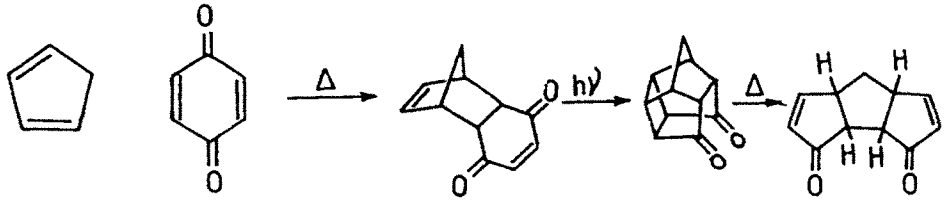
5

6

Scheme - II.1

Recently the heptacyclic dione 5 was synthesised and transformed into D_{2h} Bishomo [6] prismane (6) (Garudane).[10]

In most remarkable fashion, Mehta and his associates[11] have demonstrated that polycyclic cage diones of the type (1) offer novel and efficient route to a variety of functionalised cis : syn : cis triquinanes through olefin metathetic sequence (Scheme-II.2) and developed synthesis of many tricyclopentanoidal natural products such as corriolin,[12] hirsutene[13] and capnellane.[14]



Scheme-II.2

Strained polycyclic cage diones have also been suggested[15] to serve as good models for solar energy storage system. Since most of these ketones may also be prepared by irradiation of the corresponding Diels-Alder adduct in the sunlight[16] and the solar energy stored in the form of strain can be released through catalytic chemical reactions.[17]

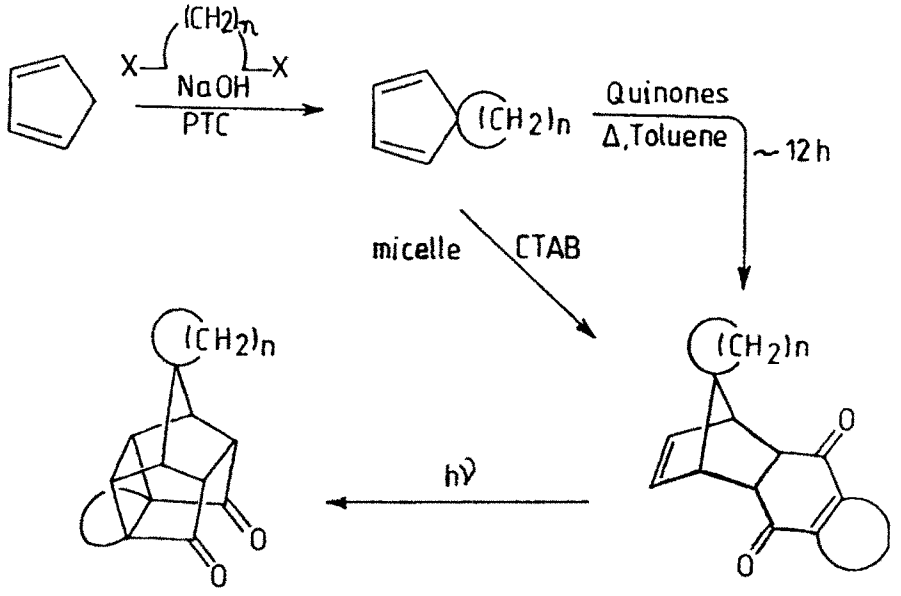
However most of the studies in this area have been done on the simple cage diones. We therefore initiated a programme towards synthesis of new polycyclic diones of type 22 and 25 (Scheme-II.4) having spiro ring substituent at the bridged methylene, inorder to exploit them as precursors for newer ring systems and also to study the effect of substitution on the various chemical reactions of these diones, it is known that even a minor change in the structure sometimes dramatically affects their behaviour towards chemical transformations.[18]

II.1.3 Present work:

The novel cage polycyclic diones (22-27) were synthesised via $\pi^{4s} + \pi^{2s}$ cycloaddition of the dienes (7-10) with quinones (11-13) followed by intramolecular $\pi^{2s} + \pi^{2s}$ photocyclisation of the resulting endo Diels-Alder adducts (14-19) as shown in the (Scheme-II.3).

The Diels-Alder addition was carried out in two ways (i) following the conventional method i.e. refluxing diene and dienophile in suitable solvent and (ii) in the micellar medium i.e. in aqueous solution of cetyltrimethylammonium bromide (CTAB) at room temperature.

Micellar cycloadditions were found to be remarkably

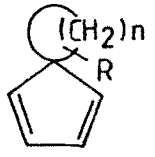


Scheme - II.3

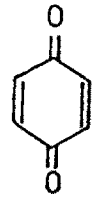
faster and furnished the adducts in good yields just after ~3 h of the reaction between diene and quinones at ambient temperature (~32°). However, both the methods gave endo adducts in all the cases. The micellar cycloaddition of spriohepta-1,3-diene (7) with benzoquinone was found to be dependent upon the surfactant concentration. It furnished the monoadduct (14) in aqueous solution of CTAB (0.068M), whereas a bis adduct (28) was obtained in 0.30 M solution of CTAB. The structure of the bis adduct has been determined by X-ray analysis (vide infra).

A simple phase transfer method was developed for the preparation of the requisite spirodienes (7-9) employed in the above objective.

The Diels-Alder adducts and the cage diones thus synthesised are listed in the (Scheme-II.4).



7 n = 2, R=H
8 n = 4, R=H
9 n = 2, R = CH_3
10 n = 0



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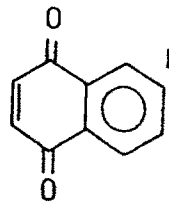

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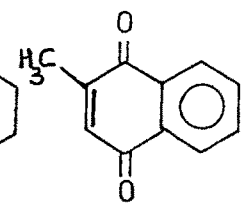

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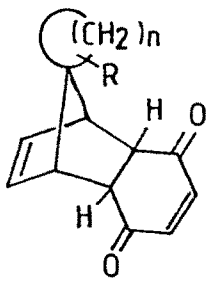
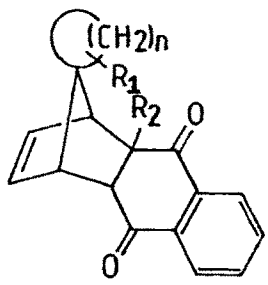
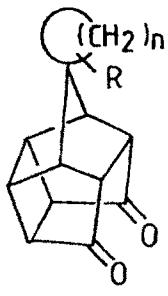


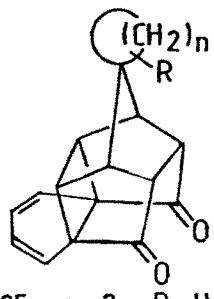
14 n = 2, R =H
15 n = 4, R=H
16 n = 2, R = CH_3



17 n=2, $R_1 = R_2 = H$
18 n=4, $R_1 = R_2 = H$
19 n=2, $R_1 = CH_3$, $R_2 = H$
20 n=0, $R_2 = H$
21 n=0, $R_2 = CH_3$



22 n = 2, R = H
23 n = 4, R = H
24 n = 2, R = CH_3



25 n = 2, R = H
26 n = 4, R = H
27 n = 2, R = CH_3

Scheme - II. 4

The preparation of the dienes (7-9), their Diels-Alder reaction with various quinones and photocyclization of the resulting endo Diels-Alder adducts is described in the following sections.

II.2 Preparation of the Spirodienes (7-9)

A large number of $\pi^{4s} + \pi^{2s}$ cycloadditions between a variety of dienes and dienophiles have been recorded in the literature.[19,20] Although a few cycloadditions between spirodienes (7-9) and reactive dienophiles such as maleic anhydride,[21] methylacrylate, dimethylacetylenedicarboxylate are known, the cycloaddition between spirodienes (7-9) and quinones has not yet been studied.

Though the spirohepta-1,3-diene (7) and spiro (4,4) nona- 1,3 -diene (8) have been prepared earlier, by alkylation of cyclopentadiene in the presence of very strong base such as sodium in liquid ammonia, the method[22] of preparation is tedious and cumbersome.

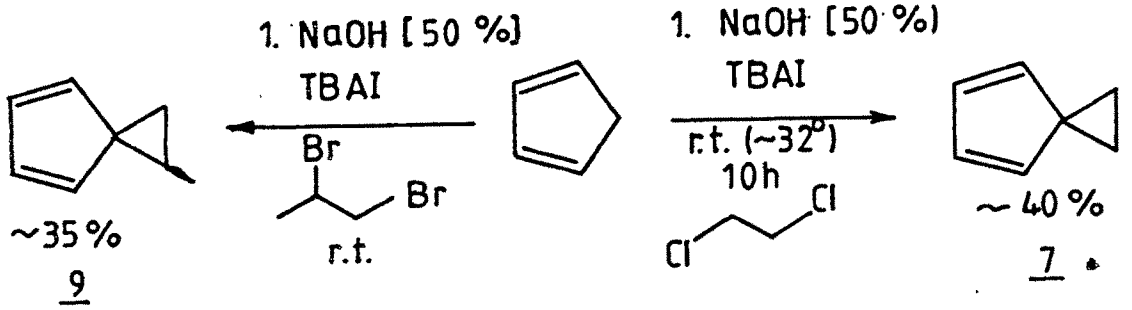
At the outset, therefore it was realised that a simple and convenient method for the preparation of the dienes (7-9) is necessary, if substantial quantities of the Diels-Alder adducts have to be generated which would in turn allow the synthesis of the desired polycyclic diones.

We therefore turned our attention towards phase transfer method[23] for alkylation of the cyclopentadiene since phase

transfer catalysis has proved to be an important synthetic method as it offers several advantages over conventional homogeneous reactions, such as simplicity, versatility, speed and selectivity.[24]

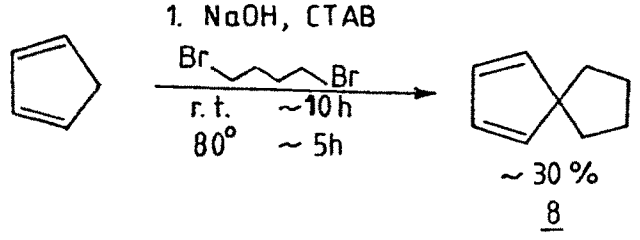
A quick literature survey on the phase transfer alkylation revealed that Makosza[25] has prepared one of the spirodienes, which we desire, the spiro (4,2) heptadiene, by bisalkylation of cyclopentadiene employing aqueous base in the presence of benzyltrimethylammonium chloride as a phase transfer catalyst. However, the details of his preparation was not available.

After considerable experimentation, we were able to prepare spiro (4,2) hepta-1,3-diene (7) and 1'-methylspiro-(4,2) hepta-4,6-diene (9) by alkylation of freshly cracked cyclopentadiene with appropriate halide in the presence of 50% aqueous sodium hydroxide and tetrabutylammonium iodide as a phase transfer catalyst (eq. II.1).



eq - II. 1

However, the bis alkylation of cyclopentadiene with 1,4-dibromobutane leading to spiro (4,4)- nonadiene (8) was not successful with tetrabutylammonium iodide as phase transfer catalyst. We therefore tried other phase transfer catalysts such as benzyltrimethylammonium chloride and CTAB for the above alkylation. It was satisfying to observe that bis-alkylation of cyclopentadiene occured in the presence of cetyltrimethylammonium bromide and aqueous alkali after stirring the reaction mixture for ~10 h at ambient temperature (32°) followed by heating at ~80° for ~4 h and furnished spiro (4,4) nona-1,3-diene (8) in ~30% yield. (Eq. II.2).



eq - II.2

The spirodienes (7-9) thus prepared were characterized through their cycloadducts with maleic anhydride and other physical properties. Since these dienes are prone to dimerisation at room temperature, they were prepared and immediately used in subsequent cycloaddition reaction.

Although our phase transfer method produces the spirodienes (7-9) in similar yields as those reported in the literature, it provides a much simpler and convenient method which does not require vigorous conditions, vigorously dried reagents and solvents. Moreover the phase transfer method permits repetitive preparation of the dienes routinely as and when desired.

After having developed the preparation of the required dienes we next turned to the cycloaddition reaction between the dienes and quinones which is described in the following sections.

II.3 $\pi^{4s} + \pi^{2s}$ Cycloaddition of dienes (7-10) with quinones (11-13) : Synthesis of Diels-Alder adducts

The Diels-Alder reaction[19] or $\pi^{4s} + \pi^{2s}$ cycloaddition[20] between a diene and dienophile is one of the most efficient and powerful methods for designing synthesis of polycyclic molecules with good regio and stereo control. The endo selectivity during cycloaddition provides opportunities for further manipulation/transformation of the adducts leading to novel carbocyclic systems which are not otherwise readily accessible.

The symmetry allowed[20] $\pi^{4s} + \pi^{2s}$ cycloaddition takes place easily, simply by mixing the components at room temperature or by gentle warming in a suitable solvent, although

in some cases with unreactive dienes or dienophiles more vigorous conditions may be necessary. The Diels-Alder reaction is reversible, and many adducts dissociate into their components at quite low temperatures. In such cases heating is disadvantageous and the forward reaction is facilitated and better yields are obtained by using an excess of one of the components, or a solvent from which the adduct separates readily. Many Diels-Alder reactions are accelerated by Lewis acid catalysis.[26] In a few cases high pressure have been used to facilitate reaction which otherwise takes place only slowly or not at all at room temperature.[27] More recently, the $\pi^{4s} + \pi^{2s}$ cycloadditions have also been accelerated in the presence of micelle.[28]

We first choose, the conventional method for preparation of the cycloadducts.

II-3.1 Conventional $\pi^{4s} + \pi^{2s}$ cycloaddition in refluxing Toluene :

Towards the preparation of the Diels-Alder adducts, we first treated an excess of freshly prepared and distilled spiro-(4,2)-hepta-1,3-diene (7) with freshly prepared and recrystallised benzoquinone in refluxing dry toluene for ~10 h, under nitrogen atmosphere. Removal of solvent and excess diene under vacuum followed by column chromatography of the residue over silica gel gave a crystalline adduct

(14) as yellow needles (m.p. 110°C) in 60% yield. The structure and stereochemistry of the adduct was deduced from its spectral characteristics and as well as by comparison with spectral data of the similar adducts known in the literature.[2] The IR spectra of the adduct showed absorption bands at 1680, 1665 and 1600 cm^{-1} suggesting the presence of a conjugated carbonyl group and olefinic linkage[29] in the compound. The NMR (90 MHz) spectrum of the adduct (14) showed following signals. A singlet at δ 6.55 (2H) characteristic of enone protons and a signal at 6.05 (dd, $J_1 = J_2 = 4Hz$) for olefinic proton. It further showed-multiplets at 3.35 (2H) and 2.90(2H) corresponding to bridgehead and ring junction protons respectively. Furthermore, two highly symmetrical multiplets at 0.58(2H) and 0.55(2H) suggested the presence of a cyclopropane ring in the adduct.[30,31] Mass spectrum of the Diels-Alder cycloadduct gave a molecular ion peak at 200(M^+) and analyzed correctly for $C_{13}H_{12}O_2$.

Above structural features were found similar to the endo adduct of cyclopentadiene and benzoquinone.[2] The endo stereochemistry of the adduct (14) was further proved through its conversion to cage diketone (22) upon photochemical irradiation (vide supra).

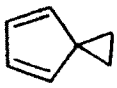
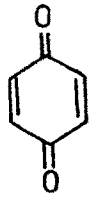
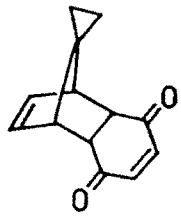
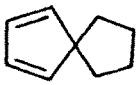
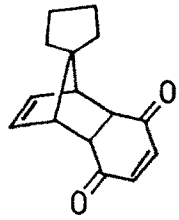
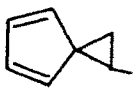
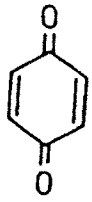
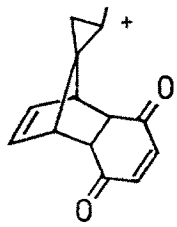
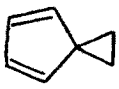
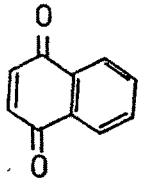
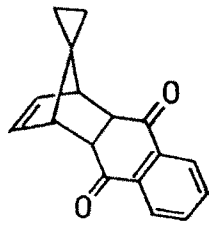
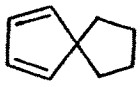
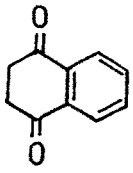
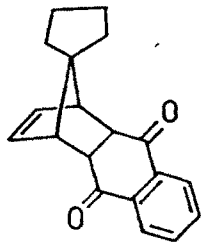
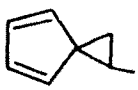
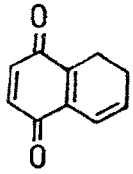
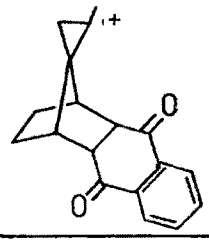
Following the above general procedure, other dienes and dienophiles were allowed to react which furnished the

corresponding adducts (15-21) whose spectral and analytical features were in agreement with their assigned structures. The reaction of cyclopentadiene with 2-methyl-naphthoquinone however, did not proceed even after reflux for ~30 h. The adducts thus synthesized are listed in Table-II.1.

Though the thermal $\pi^{4s} + \pi^{2s}$ cycloaddition of spirodienes (7-9) with quinones described above were satisfactory and could be routinely employed for the synthesis of the Diels-Alder adducts, we sought an alternate mode for conducting these cycloadditions with greater ease and efficiency. We however, refrained ourselves from employing Lewis acid catalysis for this purpose because of inherent problem of polymerisation of dienes during Lewis acid catalyzed Diels-Alder reactions.[26,32] Also we did not venture into high pressure technique for cycloaddition due to the requirement of specialized facility.

It occurred to us that the Diels-Alder reaction in aqueous micellar media would be a good alternative, to achieve our objective since micelles are known to be solubilize dissimilar solutes and organise them at the molecular level.[33] We envisaged that this characteristics of micelle might show a positive effect on the rate and stereochemical outcome of the $\pi^{4s} + \pi^{2s}$ cycloaddition because of the highly ordered nature of the transition state required for such cycloadditions.[20]

TABLE - II.1

S. No.	Diene	Dienophile	Adduct	Reaction time	% yield
1				10 h	60
2				10 h	45
3				12 h	45
4				12 h	53
5				12 h	62
6				12 h	40

+ May consist of stereoisomers

TABLE-II.1 : List of the adducts prepared through conventional Diels-Alder reaction

With this view, we therefore studied aforementioned cycloadditions in the aqueous micelle which is described in the following section.

II-3.2 Diels-Alder reaction in micellar media :

II.3.2.1 Introduction:

Surfactants or amphiphiles are molecules possessing both polar and nonpolar moieties.[34] A typical detergent/surfactant structure is represented byR-X, where R is a straight chain hydrocarbon of 8 to 18 carbon atoms or some other hydrophobic residue and X is a hydrophilic group. Depending upon the nature of X, the detergent may be classified as (a) non-ionic (b) cationic (R^+X^-) or (c) anionic. Such amphiphilic molecules having disimilar hydrophobic and hydrophilic regions exhibit a fascinating phenomenon of self organisation into a variety of molecular assemblies when they are exposed to environments ranging from non-polar to polar or mixed solvent system.[35]

Micelles are the structural entities of colloidal dimensions build up by spontaneous self association of detergent/surfactant molecules in aqueous solution.[33-35] It is commonly observed that there is relatively small range of concentrations below which micelles are absent and above which virtually all the detergent molecules exist as micelles. The narrow range of concentration of surfactant required for the micelle

formation is known as critical micelle concentration (or CMC), which may be determined from an experimental plot of some observable property such as density, surface tension, conductivity etc, versus detergent concentration.[33-36]

Structure of the micelles:

The Architecture of micellar agglomerate is such that hydrophilic head groups directed towards the aqueous phase and the hydrophobic hydrocarbon chains are directed away from the water. In the case of charged surfactants, a large fraction of the counter ions reside in the aqueous layer immediately in contact with the head groups (stern layer) and there is a diffuse double layer surrounding this and extending upto several hundred A°, which contains the remaining counter ions known as Guy-Chapman double layer (Fig. II.1). This is

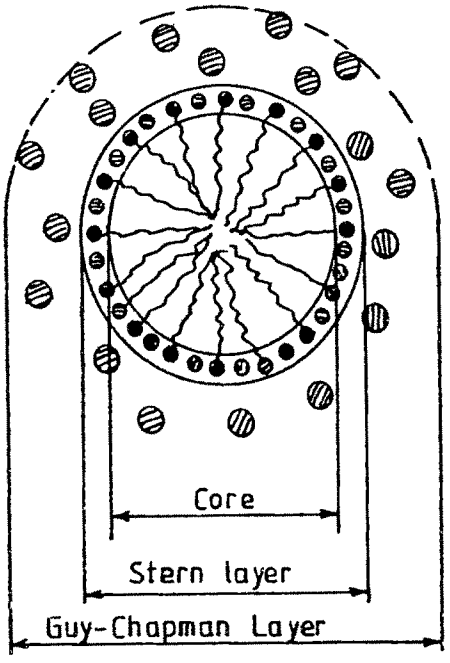


Fig. II.1

the most widely accepted model of the micelle, originally developed by Hartley,[37] which has been widely used in interpreting many phenomena observed with the micelle,[33-35] although more recent investigation[38] suggests that the micelle structure is much more open and less organised than previously suggested. Moreover, the shape of the micelle, may be roughly spherical, ellipsoidal, rod or disc like, depending upon the temperature, concentration and other experimental variables.[33,34] (Fig. II.2)

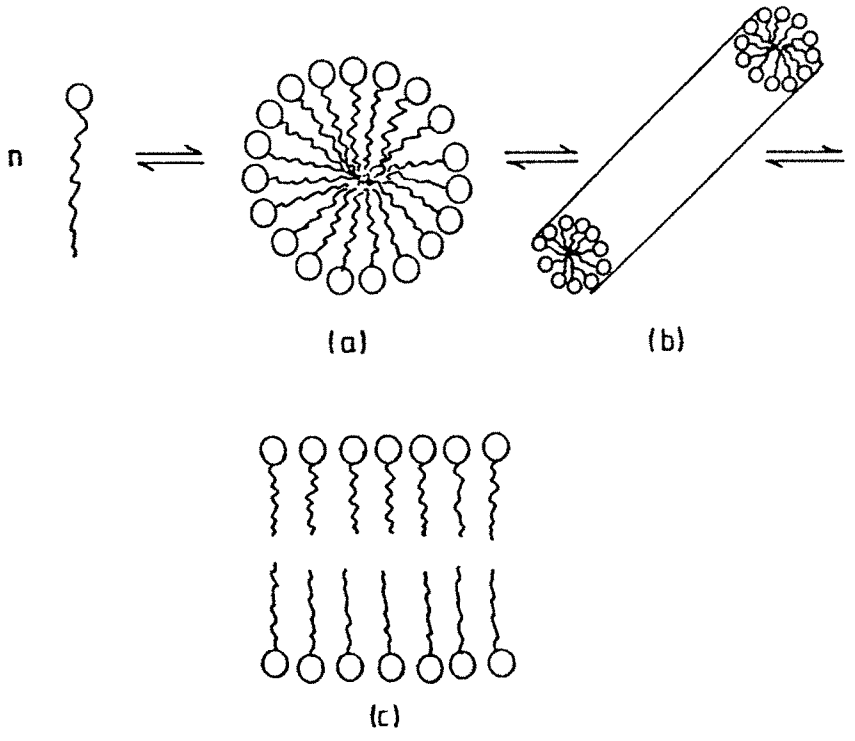


Fig. II.2

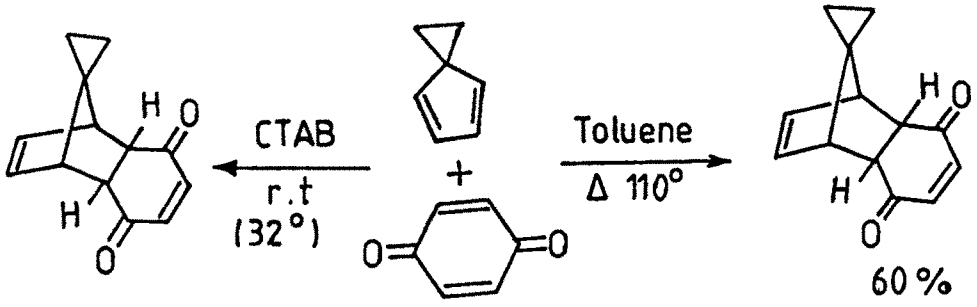
Because of the above structural features micelles are endowed with several unique characteristics. For instance their ability to solubilize and concentrate many dissimilar solutes have led to the occurrence of several organic reactions at accelerated rates compared to the homogeneous media, and in some cases even to the observation of reactions/products not otherwise obtainable.[39] Micelles have also been proposed as simple model system for a variety of important two phase systems such as monolayer, colloids, proteins, enzymes and membranes.[40] The importance of micelles in the transport and absorption of lipids as solubilizers in physiological systems have also been pointed out.

These properties of micelles have stimulated manifold interest in micelles and micellar reactions. Although many photochemical reactions have been studied [41] in micelle, especially to probe the micellar microenvironment, the cycloadditions in micellar media are rare and the Diels-Alder reaction between dienes with quinones were not recorded prior to our own observation.[28]

II-3.2.2 Results and Discussion:

In view of the unusual micellar effects on various chemical reactions and for the reasons stated earlier, we studied the cycloaddition of dienes (7-10) and quinones in cetyltrimethylammonium bromide (CTAB) micelle.

To this end, we first treated spirohepta-1,3-diene (7) with benzoquinone (11) solubilized in CTAB micelle, prepared by dissolving CTAB (0.025 g, 0.0686 mol) in distilled water (100 ml) at ambient temperature (~32°). It was indeed a surprise to observe that the reaction was remarkably faster and found to be complete (tlc) in less than 3 h, and furnished the cycloadduct in 66% yield, which was identical to the endo adduct (14) obtained by conventional reaction. (Eq. II.3)



eq - II. 3

It should be noted that the conventional reaction between the same diene and dienophile requires refluxing in toluene (~110°) for ~10 h to give the same adduct in 60% yield.

Encouraged by the above result, we carried out other cycloadditions in CTAB micelle. We observed that all the cycloadditions between the dienes (7-10) and quinones (11-13) are catalyzed by CTAB micelle, the reactions are remarkably

faster, found to be complete (tlc) within ~3 h at room temperature (~ 30°) and furnished the adducts (14-21) in better yields compared to the conventional Diels-Alder reaction in refluxing toluene for ~10-12 h.

It is interesting to note that the cycloaddition between cyclopentadiene and 2-methyl-naphthoquinone which does not occur even after reflux in toluene for ~30 h, gives the adduct (21) in 86% yield when conducted in CTAB micelle at ambient temperature for ~2 h.

However, both the micellar as well as conventional cycloaddition furnished the same endo adducts whose structures were established through spectral and analytical data. The adducts thus synthesized are recorded in Table-II.2 alongwith their yields from conventional and micellar cycloaddition.

The unusual rate enhancement in the micellar cycloaddition is not fully understood, however, it may be ascribed to the increased concentrations of the reactants in the core of micellar pseudophase where the reactants are more ordered compared to their homogeneous counterpart.[42] Similar rate enhancement in the Diels-Alder reaction has also been observed by Braun[43] and Grieco.[44] However, Breslow did not observe any such catalytic effect of surfactants during his study of cycloadditions.[45] Perhaps further studies are required

TABLE - II.2

List of the Diels-Alder adducts prepared by cycloaddition in CTAB micelle and homogeneous media

Sr.No.	Adduct	Yield[a]	Yield[b]
1	14	60[c]	66
2	15	45	78
3	16[d]	45	56
4	17	53	75
5	18	62	76
6	19[d]	40	46
7	20	50	68
8	21	nil[e]	86

a. Yield of the pure products from conventional Diels-Alder reaction.

b. Yield of the pure products from micellar reaction at ambient temperature.

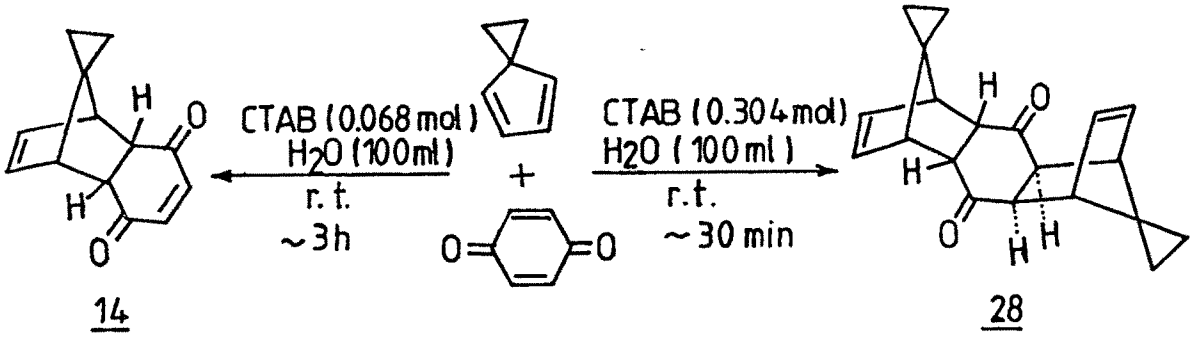
c. This cycloaddition was done in refluxing toluene for 10 h.

d. May consist of stereoisomers.

e. This reaction does not seem to occur even after reflux for 30 h.

to gain a deeper insight into the effect of surfactants on the $\pi^{4s} + \pi^{2s}$ cycloadditions, since hydrophobic acceleration on such reaction have been also noted.[46] In our case however, no reaction was observed either in the aqueous medium without surfactant or in the solution of any other quaternary ammonium salts such as tetrabutylammonium iodide which does not form micelles.

In addition to the micellar catalysis on the above cycloaddition, we also serendipitiously observed that in the case of spirohepta 1,3-diene (7) and benzoquinone (11) a stereospecific bis cycloaddition occured to give the novel adduct (28) in aqueous solution containing a very high concentration (much above CMC) of cetyltrimethylammonium bromide (CTAB, 0.304 mol/100 ml) (Eq. II.4). Such a bisaddition however, is not observed in the conventional reaction.



14 28

eq. - II.4

In addition to the unusally higher rate and stereospecificity of this bis cycloaddition, it is also remarkable to

note that the formation of mono (14) versus bis-adduct (28) is dependent upon concentration of the surfactant, the latter was found to increase with the increasing concentration of cetyltrimethylammonium bromide (CTAB) as shown graphically in Fig.II.3.

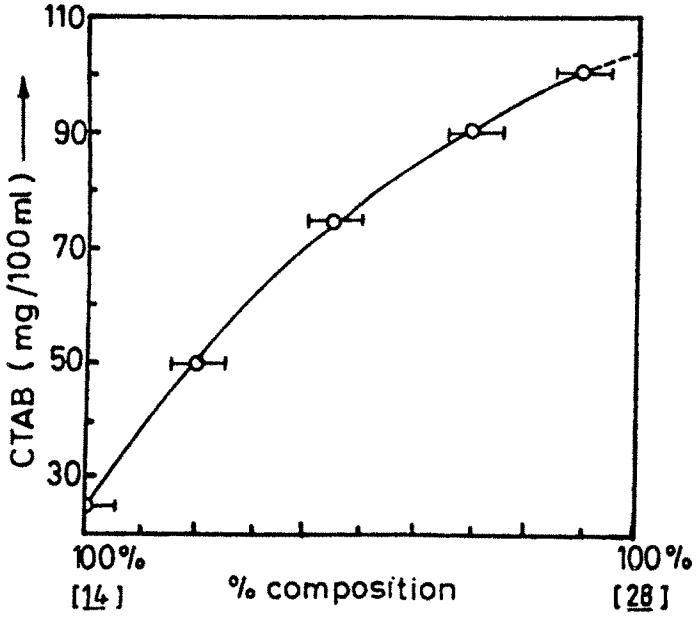


Fig. II.3. Effect of CTAB conc. on product distribution.

However, no bis cycloaddition of any type was observed during conventional homogeneous reaction in refluxing toluene for ~10 h. Although it is difficult to rationalize the modulation of the reactivity of spiroheptadiene (7) and benzoquinone (11) with the surfactant concentration and stereospecificity of the bis addition, it is probably a manifestation of the change in the nature e.g. shape and size of the

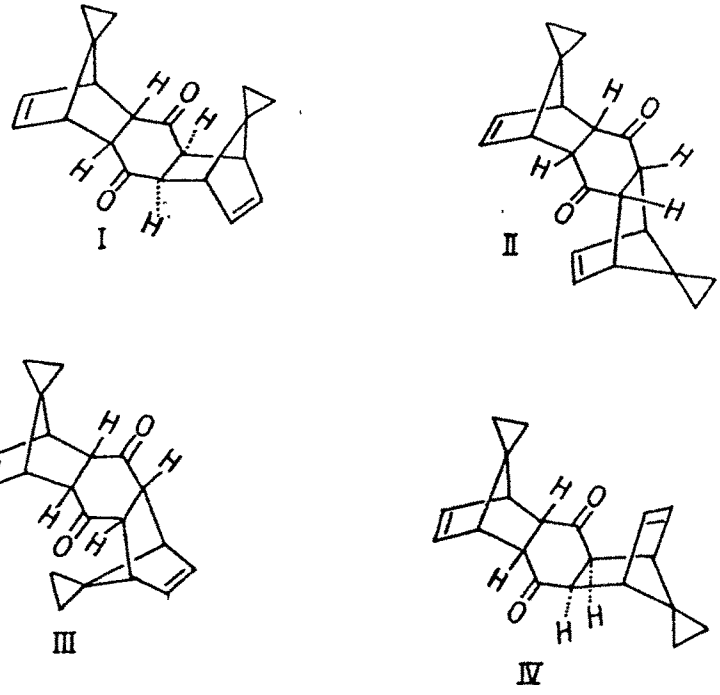
aggregate formed by dispersion of surfactants above their critical micelle concentration in aqueous media.[47]

While this unusual cycloaddition may serve as an interesting probe to gain further insight into the structure of micelles and post-micellar aggregates, it provides a simple avenue to prepare either monoadduct (14) and/or the bisadduct (28).

Structure of the bisadduct:

The gross structure of the bisadduct (28, m.p. 145°) was deduced from its spectral data as follows. The IR spectra showed absorption bands at 1705 and 1685 cm^{-1} and lacked any band for unsaturated carbonyl group. Proton NMR (270 MHz, $CDCl_3$) of the adduct gave the following signals (Fig. II.20) δ 6.35 (dd, $J_1=J_2=3Hz$, 4H, olefinic H), 3.1 (br s, 4H, methine H), 2.75 (d, J=7Hz, 4H ring junction H), 0.55 (m, 4H, cyclopropane H) and 0.42 (m, 4H, cyclopropane H). The ^{13}CNMR spectrum showed resonances at δ 213.3 (C=O), 136.42 (C=C), 53.94, 53.06, 45.0, 8.05 and 6.52 (cyclopropylcarbons). The absence of enone carbonyl and enone proton in its IR and ^1H-NMR spectra respectively suggested that two moles of diene (7) has added to the benzoquinone (11) leading to the bisadduct. The number of signals in its ^1H NMR and ^{13}CNMR[31] though indicated a highly ordered structure for the bisadduct, the exact stereochemical nature of the adduct was not easily discernible through

its physical data alone as there are four possible isomeric structures (I-IV) (Scheme-II.5) because of four different modes of approach of the second mole of diene during bis-addition.



Scheme-II.5

The chemical structure and stereochemistry of the bis-adduct was therefore determined by a direct single crystal X-ray analysis.[48] The monoclinic crystal of (IV) conform to space group P_{2_1}/a with a = 12.866(3), b = 275(2), c = 6.618(2)

A, β = 110.19(2), V = 741.2(6), A^3, Dx = 1.310 g cm^{-3}, Z = 2.F(000) = 312.0, λ(MoKα) = 0.71069A, μ(Mo Kα) = 0.89 cm^{-1}

A prismatic crystal (0.1 x 0.1 x 0.2 mm) was selected and mounted on a philips PW - 1100 four circle diffractometer. Unit cell parameters were determined from an automatic centring of 25 reflections($4 \leq \theta \leq 12$) and refined by least square method. A total of 827 reflections were measured in the range of $2 \leq \theta \leq 25$. Intensities were collected with graphite monochromatized Mo Kα radiation using the scan technique. The structure was solved by direct method using the SHELXS computer programme[49] and refined by full matrix least square method employing SHELX 76 computer programme.[50] The hydrogen atoms were located from different synthesis and refined with and overall isotropic temperature factors, while the remaining atoms were anisotropically refined. The final R factor was 0.046 (wR = 0.049) for all observed reflections. A perspective view of the molecule is shown in Fig. II.4. The bond length, bondangles and final atomic coordinates are given in Tables II.3 & II.4 respectively.

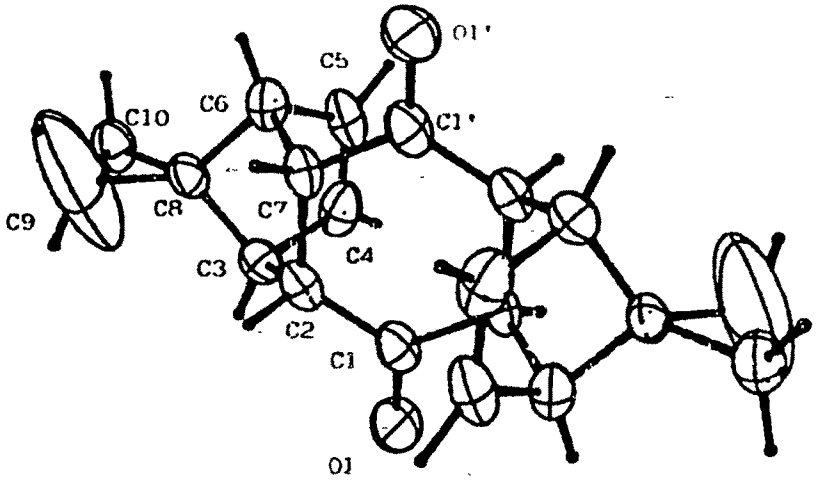


Fig.II.4 : Perspective view of 28

TABLE-II.3

Bond lengths (A°) and Angles (O°) for $C_{20}H_{20}O_2$ with e.s.d. in Parantheses

C(1)	- - - C(1)	1.227 (6)	C(5)	- - - C(4)	1.324 (7)
C(2)	- - - C(1)	1.518 (7)	C(6)	- - - C(5)	1.499 (7)
C(7)	- - - C(1)	1.497 (7)	C(7)	- - - C(6)	1.564 (7)
C(3)	- - - C(2)	1.579 (7)	C(8)	- - - C(6)	1.521 (7)
C(7)	- - - C(2)	1.557 (6)	C(9)	- - - C(8)	1.474 (8)
C(4)	- - - C(3)	1.505 (7)	C(10)	- - - C(9)	1.481 (7)
C(8)	- - - C(3)	1.517 (6)	C(10)	- - - C(9)	1.505 (8)

C(2)	-C(1)	-C(1)	118.2 (5)	C(8)	-C(6)	-C(7)	101.3(4)
C(7)i	-C(1)	-C(1)	119.9 (5)	C(6)	-C(7)	-C(2)	101.9(4)
C(7)i	-C(1)	-C(2)	122.0 (5)	C(1)i	-C(7)	-C(2)	119.1(4)
C(3)	-C(2)	-C(1)	112.1 (4)	C(1)i	-C(7)	-C(3)	110.9(5)
C(7)	-C(2)	-C(1)	118.7 (4)	C(6)	-C(8)	-C(3)	94.6(4)
C(7)	-C(2)	-C(3)	102.9 (4)	C(9)	-C(8)	-C(3)	125.2(5)
C(4)	-C(3)	-C(2)	106.4 (4)	C(9)	-C(8)	-C(6)	126.0(5)
C(8)	-C(3)	-C(2)	99.2 (4)	C(10)	-C(8)	-C(3)	124.3(4)
C(8)	-C(3)	-C(4)	99.6 (4)	C(10)	-C(8)	-C(6)	127.3(5)
C(5)	-C(4)	-C(3)	108.3 (5)	C(10)	-C(9)	-C(9)	61.3(4)
C(6)	-C(5)	-C(4)	106.9 (5)	C(10)	-C(8)	-C(8)	59.3(3)
C(7)	-C(6)	-C(5)	106.0 (4)	C(9)	-C(10)	-C(8)	59.2(4)
C(8)	-C(6)	-C(5)	100.3 (4)				

Symmetry code i = - x, 1 - y, 1 - z

TABLE-II.4

	X/A	Y/B	Z/C	BEQ
C(1)	1517 (4)	4772 (5)	2970 (7)	4.82 (25)
C(1)	814 (5)	4889 (6)	3834 (9)	2.97 (28)
C(2)	1073 (4)	4149 (6)	6033 (8)	2.62 (24)
C(3)	1157 (4)	2453 (6)	5936 (8)	3.10 (25)
C(4)	23 (5)	1925 (6)	4585 (9)	3.58 (29)
C(5)	-650 (5)	2112 (7)	5689 (10)	3.88 (29)
C(6)	20 (4)	2787 (6)	7793 (8)	3.03 (27)
C(7)	247 (5)	4373 (6)	7258 (8)	2.81 (26)
C(8)	1140 (4)	2087 (6)	8158 (8)	2.78 (24)
C(9)	1537 (5)	725 (7)	9313 (9)	3.59 (29)
C(10)	2125 (5)	2121 (7)	10149 (9)	3.86 (30)

II.4 Intramolecular $\pi^{2s} + \pi^{2s}$ or (2 + 2) and $\pi^{6s} + \pi^{2s}$ or (6 + 2) photocycloaddition of Diels-Alder adducts : Synthesis ofcage diones:

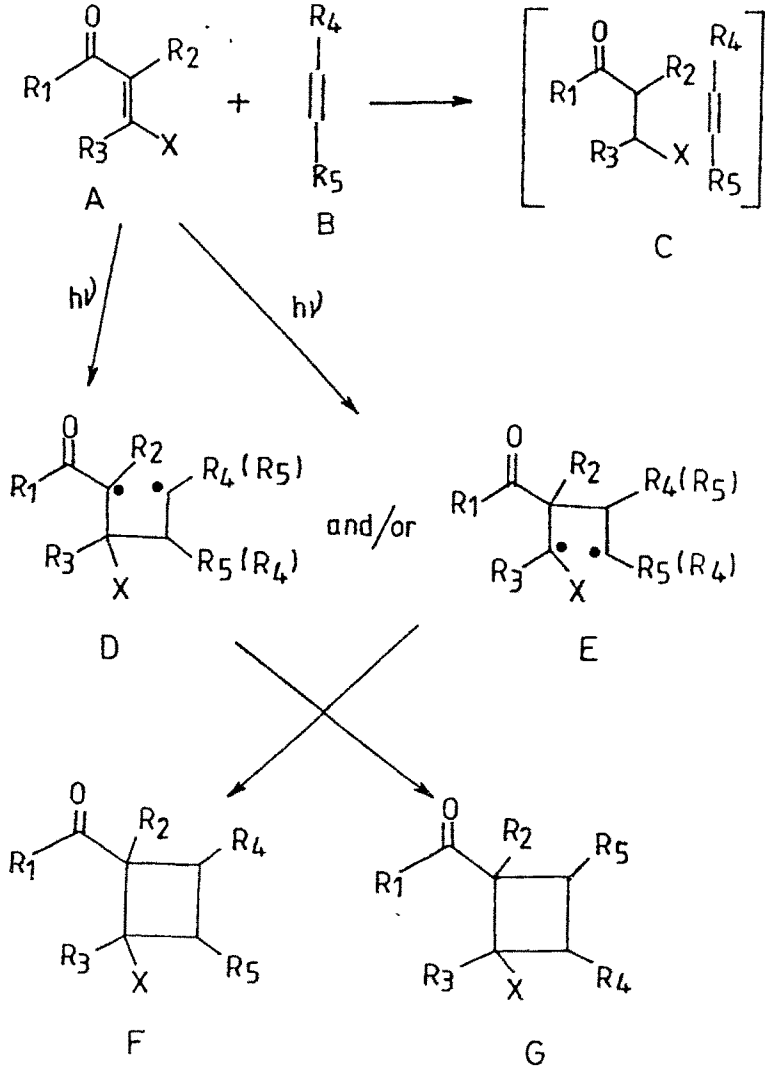
In this section of this chapter the transformation of Diels-Alder adducts (14-19) into polycyclic cage diones via intramolecular photochemical cycloaddition is described.

II.4.1 Introduction:

The intramolecular photoaddition of carvone to carvone-camphor was first described by Ciamician[51] in 1908, however no attention was paid to this type of reaction until 1954-58. Subsequently the reinvestigation of carvone photoisomerization by Buchi[52,53] and exemplary irradiation of cyclopentadiene-benzoquinone adduct by Cookson[2] led to the exploitation of the intramolecular enone olefin cycloaddition as an efficient route to various cage compounds.

In the early 1960's mechanistic and synthetic work, particularly in the laboratories of Corey,[54] Eaton[55] and de Mayo[56] focussed on intermolecular photo [2+2] addition of cyclic conjugated enones to olefins. Ever since, light induced [2+2] cycloaddition between enone and enone like chromophore has become one of the most widely employed photochemical reaction in organic synthesis. A large number of both inter and intra molecular [2+2] cycloaddition has been reported and several reviews dealing with synthesis[57] and

mechanistic[58] aspects have been published. Most of the mechanistic understanding of this cycloaddition emerged largely due to one of the earliest investigation of this reaction.[54] Experimental evidence suggested the formation of an initial oriented π complex 'C' which was later identified as exciplex,[59,60] between triplet excited enone A and the ground state olefin B. This short lived exciplex C then collapses to 1,4-diradicals D and/or E which can then cyclize to give the product F and G or revert to the starting materials A and B. (Scheme-II.6).



Scheme-II.6

The orientation of the reactants derives from the dipolar attraction of the ground state alkene and triplet excited enone which determines the orientation of the final adducts.

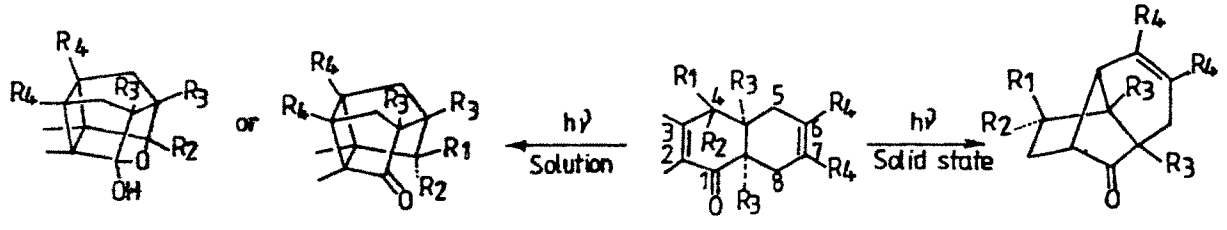
However, direct biradical formation without the intermediacy of a triplet exciplex C may also be operative in some cases.[61] In terms of conservation of orbital symmetry[20] the suprafacial addition of one 'π' component into another is the most favourable symmetry allowed pathway for the concerted photochemical [2+2] cycloaddition and hence such cycloadditions are also designated as $\pi^{2s} + \pi^{2s}$ cycloaddition reactions.

After the initial report[2] on the photoisomerisation of cyclopentadiene - benzoquinone adduct, Cookson further demonstrated[62] that intramolecular photocycloaddition, both in solution and solid state of endo Diels-Alder adduct of various dienes and quinones offer an efficient route to cage polycyclic diones. Thus the quinone adduct of hexachlorocyclopentadiene, cyclohexadiene, cyclooctatetraene, 1,1-dimethoxy tetrachlorocyclopentadiene have been smoothly converted into corresponding cage diones.[62] However the butadiene-benzoquinone adduct[62] did not undergo photoisomerisation to the corresponding cage dione.

The endo adduct of cyclopentadiene and naphthoquinone has also been reported[63] to undergo $\pi^{6s} + \pi^{2s}$ intramolecular

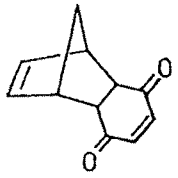
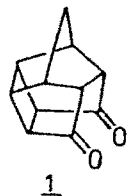
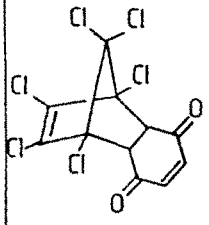
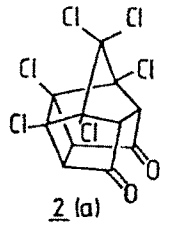
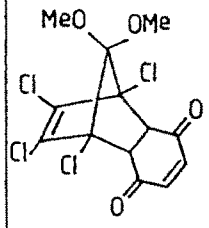
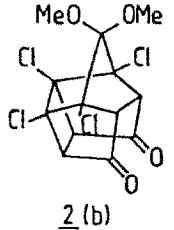
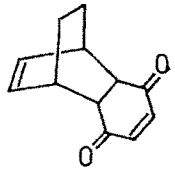
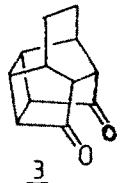
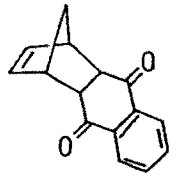
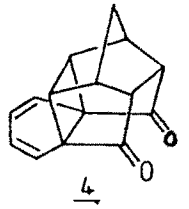
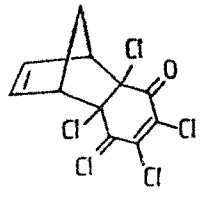
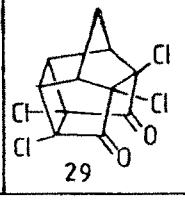
photocycloaddition, with destruction of aromaticity to give the corresponding cage dione (4) (Table-II.5). Though aromatic ring was known[64] to participate in $\pi^{6s} + \pi^{2s}$ cycloaddition, the aromaticity was conserved in the photoproducts. Some of the cage diones thus prepared are listed in the Table-II. 5.

John R. Scheffer, in his recent studies on unimolecular photoprocesses showed that photochemistry of the derivatives of various butadiene-benzoquinone adducts are medium dependent. He observed that hydroxy enones (36) undergo intramolecular [2+2] photocycloaddition to furnish cage ketones/or acetate in solution, whereas the irradiation in the solid states leads to the formation of rearranged products which are the result of intramolecular allylic hydrogen abstraction by enone 3-carbon followed by biradical collapse (Eq. II.5).

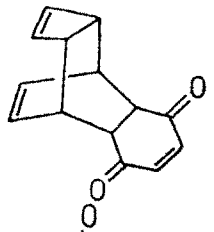
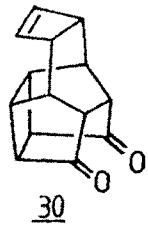
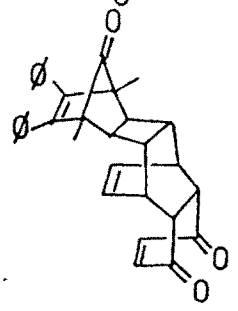
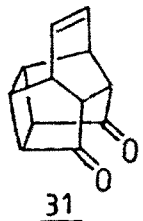
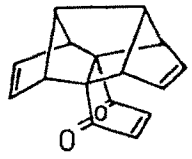
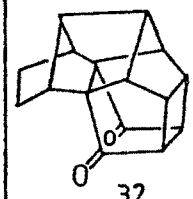
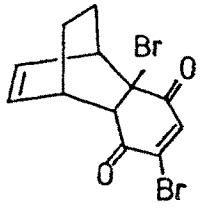
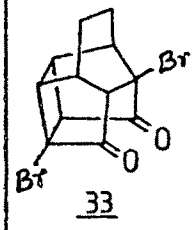
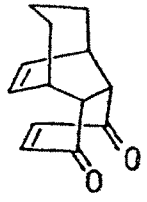
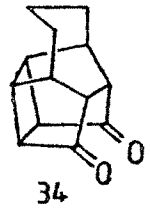
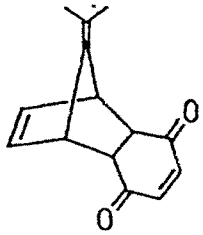
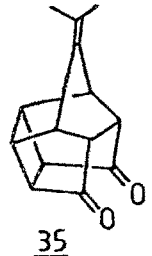


Eq.-II.5

TABLE -II 5

S No	Starting Substrate	Cagedione	Solvent	Yield, %	Ref
1		 1	EtOAc	90 %	2,62
2		 2 (a)	EtOAc	36 %	62
3		 2 (b)	EtOAc	65 %	62
4		 3	EtOAc	80 %	62
5		 4	C_6H_6	80 %	63
6		 29	EtOAc	54 %	62

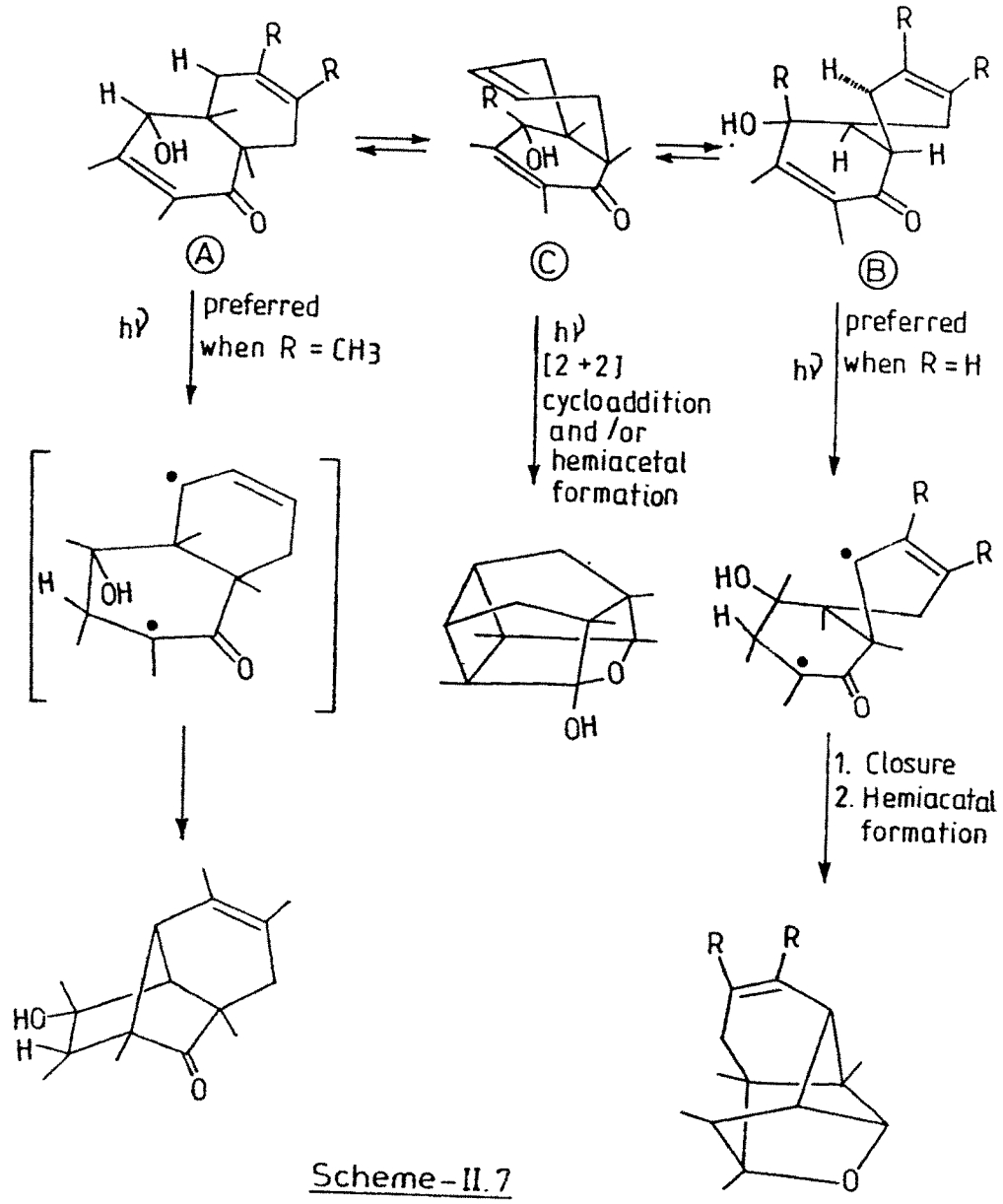
Contd

S. No.	Starting Substrate	Cagedione	Solvent	Yield, %	Ref.
7.		 30	EtOAc	90 %	62
8		 31	CH_3COCH_3	75 %	70
9		 32	C_6H_6	87 %	71
10		 33	C_6H_6	81 %	72
11		 34			73
12		 35			74

This highly interesting photochemical behaviour in the solution and solid state is probably the consequence of conformational control on the reaction. The X-ray structure of the starting cyclohexenones indicated that, they exist either in conformation A or B in the solid state which depends upon the nature of the substituent at C-4 and by the relative configuration at this centre. It further suggests that the [2+2] photochemical cycloaddition should be topochemically[65] forbidden in the solid state since the C(2) - C(3) and C(6) - C(7) double bonds are not only nonparallel but are too far apart to permit cycloaddition in any of the conformation A or B (Scheme-II.7). Specifically, the angle between C(2) - C(3) and C(6) - C(7) vector was found to be very close to 50° in each case and the double bond separation were all > 4.4 A°. Thus cycloaddition in the solid state would have to be accompanied by a substantial conformational change and is not permitted. It is well established concept that intermolecular [2+2] photocycloaddition in the solid state requires a parallel double bond orientation with a separation of approximately 4.1 A°.[67] Surprisingly not much is known about the geometric and distance requirements for the intramolecular process.[68] X-ray crystal structure data of the 1,3-cyclohexadiene-benzoquinone adduct,[69] which undergoes efficient [2+2] intramolecular photocycloaddition in the solid state to give 3, shows that its carbon-carbon double bonds are infact parallel. The ene-dione ring is very nearly planar. The double bond centre to centre distance is ~3.53 A°.

Thus with [2+2] photocycloaddition forbidden for both conformers A and B in the solid state, intramolecular hydrogen abstraction is observed instead.

These results suggest that [2+2] cycloaddition occurs from a different conformation C in solution (Scheme-II.7). This



Scheme-II.7

conformation C would be expected to be of higher energy than conformer A and B hence it must be minor conformational isomer since conformers A and B will be preferred in solution as well as in the solid states.

Although there is not much known about the excited state conformational behaviour nor the reactive or absolute activation energies for the various photochemical processes, it appears that conformational equilibrium is established during the life time of the excited state and the photoproduct composition depends only upon the relative photochemical activation energies.

Therefore, it appears from the above that the endo geometry of the adducts though necessary but not the sufficient condition for the intramolecular [2+2] photocycloaddition to occur. There are some subtle structural features which also governs this process.

II-4.2 Results and Discussion

The spirodienes-benzoquinone adducts (14-16) were dissolved in ethylacetate and irradiated by a mercury vapour lamp (250W, Bajaj) in a quartz immersion well under nitrogen atmosphere. All the adducts were smoothly transformed into the corresponding polycyclic cage diones (22-24) in very good yields.

Similarly the diene-naphthoquinone adducts (17-19) were

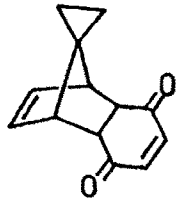
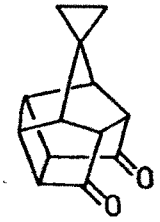
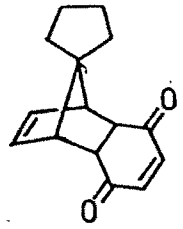
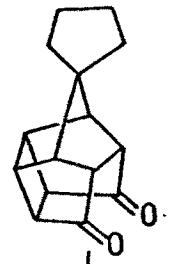
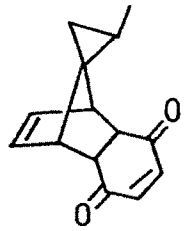
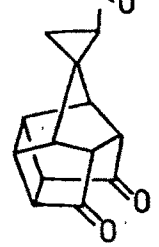
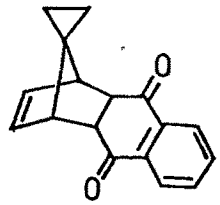
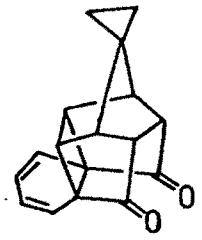
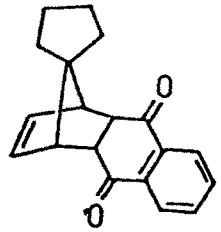
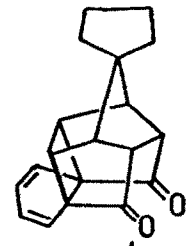
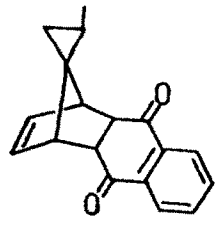
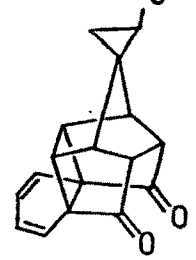
irradiated in benzene solution until most of adducts were consumed (TLC). Removal of the solvent under reduced pressure followed by chromatography over silica gel furnished the photo-adducts (25-27) in good yields.

The caged diones thus prepared are listed in the Table-II.6 along with experimental conditions, yields etc., the structure of the diones were deduced through their spectral and analytical data.

Thus the photoisomer (22) obtained from irradiation of spiroheptadiene-benzoquinone adduct (14) exhibited following spectral characteristics. The infra-red spectrum of 22 lacked any absorption band for enone carbonyl and showed bands at ν_{max} 1755, 1735 cm^{-1} which are characteristic of carbonyl groups of caged system.[62] Similarly the proton nmr spectrum (90 MHz, $CDCl_3$) (Fig. II.13) did not show signal for enone protons and displayed following resonances. δ 3.3 (br 2H), 2.85 (br, s, 4H), 2.25 (m, 2H) and 0.7 (br, s, 4H, cyclopropane H). These spectral features which were found similar to known cage diones, clearly suggested that intramolecular [2+2] photo-cycloaddition of (14) had occurred to give the cage dione (22). It was further confirmed by its mass spectrum (M/e) : 200(M^+) and its analytical data.

Similarly the structures of other photoadducts (23-27) were also deduced from their spectral and analytical data.

TABLE - II.6

S. No.	Starting adduct	cage dione	Irradiation time	Solvent	% of Yield
1			4h	EtOAc	87%
2			5h	EtOAc	70%
3			4h	EtOAc	82%
4			4h	C_6H_6	70%
5			4h	C_6H_6	68%
6			4h	C_6H_6	60%

II.5 EXPERIMENTAL

General remarks

All the melting points and boiling points are uncorrected. Petroleum ether fraction refers to the fraction of 60-80°. Solvent ether was dried over sodium wire. Methanol was dried over magnesium methoxide. Acetone was refluxed over $KMnO_4$ and then distilled from anhydrous potassium carbonate (K_2CO_3). Benzene was refluxed over anhydrous calcium chloride ($CaCl_2$), distilled and dried over sodium wire. Ethylacetate was distilled and dried over molecular sieve (5A°). All the solvent extracts were finally washed with brine, water and dried over anhydrous sodium sulphate (Na_2SO_4).

The following instruments were used, unless otherwise stated, for spectral/analytical data : Shimadzu Infrared Spetrophotometer, IR-408 ; Shimadzu Spectrohotometer UV - 240; Perkin-Elmer R-32 (90 MHz) Spectrometer (PMR) : Microanalyses were performed on Coleman instrument. While citing NMR data, the following abbreviations have been used ; s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad).

Silica gel for column chromatography was 60-120 mesh (Acme's) and used as such. T.L.C. plates were of 0.25 mm thickness and silica gel G (Acme's) containing 13% $CaSO_4$ was used to make the plates. T.L.C. spots were visualised on exposure to iodine vapour.

Spiro [4,2] hepta-1,3-diene (7)

To a stirred solution of tetrabutylammonium iodide (TBAI) (1.0 g, 0.003 mol) in water (30 ml) was added freshly cracked cyclopentadiene (16 ml) and sodium hydroxide (aq. 50%, 14 ml). The reaction mixture was cooled in an ice bath (0-5°) and 1,2-dichloroethane (12.5 g, 0.125 mol) was added dropwise and it was further stirred for 10 h. at ambient temperature (~30°). Water (30 ml) was then added into the reaction mixture and it was extracted with solvent ether (3 x 50 ml). The combined organic extract was washed with water (2 x 20 ml), brine (2 x 15 ml) and dried over anhydrous sodium sulphate. Removal of the solvent under reduced pressure gave a residue which was distilled under vacuum to give spiroheptadiene 7 as a pale liquid (11.2 g, 40%), b.p. 53-55°/10 mm (literature[22] records, b.p. 55°/10 mm). A small portion of this diene was allowed to react with maleic anhydride to give an adduct, m.p. 78°, (literature records same melting point).

Spiro [4,4] nona-1,3-diene (8)

To a stirred suspension of cyclopentadiene (6.5 g, 0.1 mol), aqueous sodium hydroxide (10 ml, 50%) and CTAB (1.0 g, 2.7 m mol) was added 1,4-Dibromobutane (21.6 g, 0.01 mol) dropwise at 5°C within half an hour. The reaction mixture was brought upto room temperature (~30°) and stirred for 10 h followed by heating at 60-80° for 5 h. It was diluted

with water and extracted with solvent ether (3 x 50 ml). The organic layer was washed with water (3 x 15 ml), brine (2 x 15 ml) and dried over anhydrous sodium sulphate. Removal of the solvent gave an orange liquid, which was distilled under reduced pressure to furnish the diene (8) (3.1 g, 30%), b.p. 50°/10 mm. [Literature records[22] b.p. 52°/10 mm].

1-Methyl spiro [4,2] hepta-4,6-diene (9)

To a stirred solution of TBAI (1 g, 0.003 mol) in water (30 ml) was added freshly cracked cyclopentadiene (16 ml) and NaOH (aq. 50%, 14 ml). The mixture was cooled in an ice bath (0-5°) and 1,2-dichloropropane (11.56 g, 0.102 mol) was added dropwise. The reaction mixture was stirred for additional 12 h at room temperature (~30°), and finally heated at 60° for 2 h. It was allowed to cool to room temperature (~30°). Water (30 ml) was then added and the reaction mixture was extracted with solvent ether (3 x 50 ml). The combined organic extract was washed with water, brine and dried over anhydrous sodium sulphate. Solvent ether was stripped off and the residue (~ 20 ml) was distilled under reduced pressure to give methyl spiroheptadiene (9) or colourless liquid (9 g, 35%), b.p. 62°/10 mm (literature records[25] b.p. 65°/10 mm)

Synthesis of 1,4,5a,8a-Tetrahydro-1,4-methanonaphthalene-5,8-dione-9-spiro-1'-cyclopropane (14)

i) Thermal cycloaddition

To a solution of p-benzoquinone (11) (2.8 g, 0.026 mol)

in dry toluene was added spiroheptadiene (7) (4 g, 0.047 mol) and refluxed for 10 h. Removal of solvent followed by column chromatography gave the adduct (14) (3.1 g, 60%) as yellow needles, m.p. 110°, IR (KBr) ν_{max} : 1680, 1665, 1600 and 1020 cm^{-1}, UV λ_{max}^{MeOH} : 333.3, 278 nm, NMR (90 MHz, $CDCl_3$) (Fig.II.5) : δ 6.55 (s, 2H, enone H), 6.05 (dd, 2H, $J_1=J_2=4Hz$, olefinic H), 3.35 (m, 2H, bridgehead H), 2.9 (m, 2H, ring junction H), and 0.6 (m, 4H, cyclopropane H), Mass (m/e) : 200 (M^+), Analysis : Found C, 77.89 ; H, 6.07% requires C, 78.0 ; H, 6.0% for $C_{13}H_{12}O_2$.

ii) Micellar Cycloaddition

The spiroheptadiene (7) (1.5 g, 0.016 mol) was added with stirring to p-benzoquinone (11) (1.0 g, 0.009 mol) solubilised in CTAB micelle, prepared by dissolving CTAB (0.025 g, 0.0686 m mol) in water (100 ml). The reaction mixture was stirred for 3 h. at room temperature ($\sim$ 30°). It was extracted with solvent ether (3 x 25 ml). The combined organic extract was washed with water (2 x 15 ml), brine (2 x 10 ml) and dried over anhydrous sodium sulphate. Removal of solvent followed by recrystallization (3.4 g) gave the adduct (14) in 66% yield, having identical physical and spectral properties with the sample obtained from thermal addition.

Synthesis of 1,4,5a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione-9-spiro-1'-cyclopentane (15)

i) Thermal Cycloaddition

A solution of p-benzoquinone (11) (2.0 g, 0.018 mol) and

spirononadiene (8) (4.0 g, 0.032 mol) in dry toluene (40 ml) was refluxed for 10 h. Removal of the solvent followed by column chromatography of the residue gave the endoadduct (15) (1.8 g, 45%), which was recrystallised from pet. ether-ethylacetate mixture to give yellow needles, m.p. 97° IR (KBr) ν_{max} : 2950, 1670, 1600 cm^{-1}, UV λ_{max}^{MeOH} : 303 nm, NMR (90 MHz, $CDCl_3$) (Fig. II.6) ; δ 6.45 (s, 2H, enone H), 5.95 (dd, $J_1=J_2=$ 3Hz, 2H, olefinic H), 3.23 (br, 2H, bridgehead H), 3.05 (m, 2H, ring junction H), 1.50 (br, s, 8H, cyclopentane H) ; Analysis : Found C, 78.62 ; H, 7.02% : requires C, 78.96 ; H, 7.01% for $C_{15}H_{16}O_2$.

ii) Micellar cycloaddition

The spirononadiene (8) (1.5 g, 0.0125 mol) was added with stirring to p-benzoquinone (11) (0.5 g, 45 m mol) solubilized in CTAB micelle, prepared by dissolving CTAB, (0.025 g, 0.0686 m mol) in water (100 ml). The reaction mixture was further stirred for 4 h. at room temperature (~30°). It was extracted with ether (3 x 25 ml). The combined organic extract was washed with water (2 x 15 ml) and brine (2 x 20 ml). Drying and removal of solvent followed by recrystallization furnished the adduct (15) (0.858 g, 78%), which was identical with the sample obtained from thermal cycloaddition.

Preparation of 1,4,5a,8a-Tetrahydro-1,4-methanonaphthalene-5,8-dione-9-spiro-1'-(2'-methyl) cyclopropane (16)

i) Thermal Cycloaddition

A solution of p-benzoquinone (11) (1.0 g, 0.009 mol)

and 1-methyl spiro (4,2) hepta 4,6-diene (9) (2.0 g, 0.018 mol, excess) in dry toluene (40 ml) was refluxed for 12 h. Solvent was removed under vacuum and the residue was chromatographed over silica gel to furnish the endo adduct (16) (1.98 g, 45%) as yellow crystals, m.p. 106°, IR (KBr) ν_{max} 2950, 1660, 1600 cm^{-1}, UV λ_{max}^{MeOH} : 223 nm, NMR (90 MHz $CDCl_3$) (Fig. II.7) : δ 6.50 (s, 2H, enone H), 6.15 (superimposed dd, $J_1=J_2=2.5$Hz, 2H, olefinic H), 3.5 (m, 2H, bridgehead H), 3.1 (m, 1H, ring junction H), 2.85 (m, 1H, ring junction H), 1.00 (d, J=3Hz, superimposed with another signal 4H, CH_3 and 1H of cyclopropane), 0.70 (m, 2H, cyclopropane CH_2). Analysis : Found C, 78.41 ; H, 6.20% requires C, 78.50 ; H, 6.54% for $C_{14}H_{14}O_2$.

ii) Micellar Cycloaddition

1-Methyl spiro (4,2) hepta 4,6-diene (9) (2 g, 0.018 mol excess) was added with stirring to p-benzoquinone (11) (1 g, 0.009 mol) solubilized in CTAB micelle, prepared by dissolving CTAB (0.03 g, 0.082 m mol) in water (100 ml). The reaction mixture was stirred for 3 h. at room temperature ($\sim$30°). It was extracted with solvent ether (3 x 25 ml), the organic layer was washed with water (2 x 20 ml), brine (20 ml) and dried over anhydrous sodium sulphate. Removal of solvent followed by recrystallization of the residue gave the adduct (16) (1.1 g, 56%) as yellow needles, which was found to have identical physical and spectral properties with the sample obtained from thermal cycloaddition.

Synthesis of 1,4,4a,9a-Tetrahydro-9,10-dioxo-1,4-methanoanthracene-11-spiro-1'-cyclopropane (17)

i) Thermal Cycloaddition

A solution of 1,4-naphthoquinone (12) (1 g, 6.3 m mol) in dry toluene (40 ml) and spiro (4,2) hepta-1,3-diene (7) (4 g, 0.047 mol) was refluxed for 12 h. Removal of solvent followed by column chromatography yielded the adduct (17) (0.85 g, 53% as white crystals, m.p. 152-3° . IR (KBr) ν_{max} ; 2950, 1680, 1585 cm^{-1}, UV λ_{max}^{MeOH} 310, 303 nm, NMR (90 MHz, $CDCl_3$) (Fig. II.8) : δ 8.0 (m, 2H, aromatic H), 7.7 (m, 2H, aromatic H), 6.05 (superimposed dd, $J_1=J_2=4Hz$, 2H, olefinic H), 3.65 (superimposed dd, $J_1=J_2=4Hz$, 2H, bridgehead H), 3.00 (br,d, J=5Hz, 2H, ring junction H) and 0.60 (br, s,4H, cyclopropane CH_2). Analysis : Found C, 81.3 ; H, 5.7% requires C, 81.6 ; H, 5.6% for $C_{17}H_{14}O_2$.

ii) Micellar Cycloaddition

Spiro (4,2) hepta-1,3-diene (7) (1.5 g, 0.016 mol), was added with stirring to 1,4-naphthoquinone (12) (0.4 g, 2.5 m mol), solubilized in CTAB micelle, prepared by dissolving CTAB (0.1 g, 0.27 mmol) in water (100 ml). The reaction mixture was further stirred for 3 h. at room temperature ($\sim$30°). It was extracted with ether (3 x 25 ml). The combined organic extract was washed with water (2 x 10 ml) , brine (2 x 15 ml). Drying and removal of solvent followed by recrystallization furnished the adduct (17) (0.47 g, 75%), which was identical to the sample obtained from thermal cycloaddition.

Synthesis of 1,4,4a,9a-Tetrahydro-9,10-dioxo-1,4-methanoanthracene-11-spiro-1'-cyclopentane (18)

i) Thermal Cycloaddition

A solution of 1,4-naphthoquinone (12) (0.5 g, 3.15 m mol) in dry toluene (40 ml) and spiro (4,4) nona 1,3-diene (8) (1.5 g, 0.0125 mol) were refluxed for 12 h. Removal of solvent followed by column chromatography furnished the adduct (18) (0.55 g, 62%), m.p. 149°. IR (KBr) ν_{max} : 2950, 1675, 1595, 1270, 710 cm^{-1}. UV λ_{max}^{MeOH} : 308, 300 nm ; NMR (90 MHz, $CDCl_3$) (Fig. II.9) : δ 8.00 (m, 2H, aromatic, H), 7.70 (m, 2H, aromtic H), 6.00 (superimposed dd, $J_1=J_2=4.5$Hz, 2H, olefinic H), 3.55 (brd, 2H, bridgehead H), 3.25 (brd, 2H, ring junction H) and 1.6 (br s, 8H, cyclopentane CH_2) Analysis : Found C, 81.7 ; H, 6.13% requires C, 82.0 ; H, 6.47% for $C_{19}H_{18}O_2$.

ii) Micellar Cycloaddition

Spiro (4,4) nona-1,3-diene (8) (1.5 g, 0.0125 mol) was added with stirring to 1,4-naphthoquinone (12) (0.5 g, 3.15 mmol), solubilized in CTAB micelle, prepared by dissolving CTAB (0.1 g, 0.27 mmol) in water (100 ml). The reaction mixture was further stirred for 3 h. at room temperature ($\sim$30°). It was extracted with solvent ether (3 x25 ml). The combined organic extract was washed with water (2 x 10 ml) and brine (2 x 15 ml). Drying and removal of solvent followed by recrystallization from pet. ether - ethylacetate

mixture (70:30) gave the adduct (18) (0.662 g, 70%), which was found to have identical physical and spectral properties to the sample obtained from thermal cycloaddition.

Preparation of 1,4,4a,9a-Tetrahydro-9,10-dioxo-1,4-methanoanthracene-11-spiro-1'-(2'-methyl) cyclopropane (19)

i) Thermal Cycloaddition

A solution of 1,4-naphthoquinone (12) (0.5 g, 3.15 m mol) in dry toluene (40 ml) and 1-methyl spiro (4,2) hepta 4,6-diene (9) (2 g, 0.018 mol) were refluxed for 12 h. Removal of solvent followed by column chromatography furnished the adduct (19) (0.33 g, 40%), m.p. 140°, IR (KBr) ν_{max} : 3000, 1690, 1590 cm^{-1}, UV λ_{max}^{MeOH}: 226, 257 nm, NMR (90 MHz, $CDCl_3$) (Fig. II.10) : δ 8.0 (m, 2H, aromatic H), 7.7 (m, 2H, aromatic H), 6.00 (superimposed dd, $J_1=J_2=2.5$Hz, 2H, olefinic H), 3.6 (m, 2H, bridgehead H), 3.25 (m, 1H ring junction H), 3.0 (m, 1H, ring junction H), 1.0 (d, J=4Hz, superimposed with another signal total 4H, CH_3 and 1H of cyclopropane ring) and 0.65 (m, 2H, cyclopropane CH_2). Analysis : Found C, 82.20 ; H, 5.97% requires C, 81.81 ; H, 6.06% for $C_{18}H_{16}O_2$.

ii) Micellar Cycloaddition

1-Methyl spiro (4,2) hepta-4,6-diene (9) (2 g, 0.018 mol) was added to 1,4-naphthoquinone (12) (1 g, 6.3 m mol) in CTAB micelle, prepared by dissolving CTAB (0.05 g, 0.137 m

mol) in water (100 ml). The reaction mixture was stirred for 3 h. at room temperature (~30°). It was extracted with ether (3 x 25 ml). The extract was washed with water (2 x 10 ml) and brine (2 x 15 ml). Drying and removal of solvent followed by recrystallization from pet. ether - ethyl acetate (60:40) gave the adduct (19) (0.38 g, 46%) which was found to be identical to the corresponding adduct obtained by thermal cycloaddition.

Synthesis of 1,4,4a,9a-Tetrahydro-9,10-dioxo-1,4-methanoanthracene (20)

i) Micellar Cycloaddition

A freshly cracked cyclopentadiene (10) (2.46 g, 37 m mol) was added to 1,4-naphthoquinone (12) (1.2 g, 7.6 m mol) solubilized in CTAB micelle, prepared by dissolving CTAB 90.05 g, 0.0137 m mol) in water (100 ml). The reaction mixture was stirred for 3 h. at room temperature (~ 30°). It was extracted with solvent ether (3 x 25 ml) and the extract was washed with water (2 x 20 ml) and brine (2 x 15 ml). Drying and removal of solvent followed by recrystallization from pet. ether - ethyl acetate (70:30) gave the known adduct (20) (1.15 g, 68%), m.p. 114°, (Literature[63] records m.p. 115°). IR (KBr) ν_{max} : 2950, 1675, 1580 cm^{-1}, UV λ_{max}^{MeOH} : 224, 257 nm ; NMR (90 MHz, $CDCl_3$) (Fig.II.11) : δ 7.85 (m, 2H, aromatic H), 7.55 (m, 2H, aromatic H), 5.95 (superimposed dd, $J_1=J_2=2.5Hz$, 2H, olefinic H), 3.55 (m, 2H, bridgehead H), 3.40 (m, 2H, ring junction H), 1.55 (s, with structure, 2H, methylenic H), Analysis : Found C, 80.03 ; H, 5.21% requires C, 80.35 ; H, 5.35% for $C_{15}H_{12}O_2$.

Synthesis of 1,4,4a-Trihydro-9a-methyl-9,10-dioxo-1,4-methano-anthracene (21)

Micellar Cycloaddition

Freshly cracked cyclopentadiene (10) (1.6 g, 19 m mol) was added to a solution of 2-methyl naphthoquinone (13) (1.7 g, 9.8 m mol) dissolved in CTAB micelle, prepared by dissolving CTAB (0.1 g, 0.274 m mol) in water (100 ml). The reaction mixture was stirred for 3 h. at room temperature (30°). It was extracted with ether (3 x 25 ml). The combined extract was washed with water (2 x 20 ml) and brine (2 x 15 ml). Drying and removal of solvent followed by recrystallisation from pet. ether - ethylacetate mixture (70:30) gave the adduct (21) (2.1 g, 86%), m.p. 96°, IR (KBr) ν_{max} : 2950, 1670, 1590 cm^{-1}, NMR (90 MHz, $CDCl_3$) (Fig. II.12): δ 7.90 (m, 2H, aromatic H), 7.55 (m, 2H, aromatic H), 6.00 (dd, J_1=5Hz, J_2=3Hz, 1H, olefinic H), 5.90 (dd, J_1=5Hz, J_2=3Hz, 1H olefinic H), 3.5 (m, 1H, methine H), 3.2 (m, 1H, methine H), 3.05 (d, J=4.5Hz, 1H, ring junction H), 1.65 (AB quartet, J=9Hz, 2H, bridge methylene H) and 1.55 (s, 3H, CH_3). Analysis Found C, 79.77 ; H, 5.91% requires C, 80.00 ; H, 5.83% for $C_{16}H_{14}O_2$.

Thermal Cycloaddition

The reaction between the diene 10 with 2-methyl naphthoquinone (13) did not occur even after refluxing for 30 h. (tlc).

Pentacyclo ($5.4.0.0^{2,6}0^{3,10}0^{5,9}$) undecane-8,11-dione-4-spiro-1'-cyclopropane (22)

The cycloadduct (14) (2.5 g, 0.0125 mol) was dissolved in ethylacetate (500 ml) and irradiated in a quartz immersion well by UV lamp(250 W, Bajaj) for 3-4 h. under nitrogen atmosphere. The solvent was removed under reduced pressure and the residue was chromatographed over silica gel. Elution with pet. ether - ethylacetate mixture (50:50) furnished the dione (22) (2.1 g, 87.4%), m.p. 152°. IR (KBr) ν_{max}: 1755, 1735, 1020 cm^{-1}, UV λ_{max}^{MeOH} : 285 nm, NMR (90 MHz, $CDCl_3$) (Fig. II.13) : δ 3.3 (br, s, 2H), 2.85 (br, s, 4H), 2.25 (m, 2H) and 0.7 (br, s, 4H, cyclopropane CH_2). Mass (m/e) : 200 (M^+), 157, 144, 129, 115, 91. Analysis : Found C, 78.16 ; H, 6.11% requires C, 78.0 ; H, 6.0% for $C_{13}H_{12}O_2$.

Pentacyclo ($5.4.0.0^{2,6}0^{3,10}0^{5,9}$) undecane-8,11-dione-4-spiro-1'-cyclopentane (23)

The cycloadduct (15) (2.5 g, 0.011 mol) was dissolved in ethylactate (300 ml) and irradiated in a pyrex immersion well by UV lamp (250 W, Bajaj) under nitrogen atmosphere for 5 h. The solvent was removed in vacuo and the residue was chromatographed over silica gel to furnish the cage dione (23) (1.75 g, 70%), m.p. 182°, IR (KBr) ν_{max} : 2950, 2850, 1755 and 1730 cm^{-1}, UV λ_{max}^{MeOH} : 286 nm, NMR (90 MHz, $CDCl_3$) (Fig. II.14) : δ 3.30 (br m, 2H), 2.80 (d, with st., 4H), 2.45 (m, 2H) and 1.65 (br s, 8H) cyclopentane CH_2). ^{13}CNMR ($CDCl_3$) (Fig.II.15): δ 211.74 (C=O), 64.51, 54.41, 52.24, 43.70 38.68, 32.31, 28.15, 25.41. Analysis : Found C, 78.56 ; H, 7.02% requires C, 78.96 ; H, 7.01% for $C_{15}H_{16}O_2$.

Pentacyclo ($5.4.0.0^{2,6}0^{3,10}0^{5,9}$) undecane-8,11-4-spiro-1'-methyl cyclopropane (24)

The cycloadduct (16) (2.0 g, 0.009 mol) was dissolved in ethylacetate (500 ml) and irradiated in a quartz immersion well by UV lamp (250 W, Bajaj) for 3-4 h. The solvent was removed under vacuo and the residue was chromatographed over silica gel to furnish the cage dione (24) (1.65 g, 82%), m.p. 154°, IR (KBr) ν_{max} : 2950, 1755, 1735 and 1020 cm^{-1} UV λ_{max}^{MeOH} : 286 nm, NMR (90 MHz, $CDCl_3$) (Fig. II.16) : δ 3.3 (br s, 2H), 2.9 (br s, 2H), 2.5 (br m, 1H), 2.2 (br m, 1H), 1.1 (d, J=3Hz, superimposed with another signal total 4H, CH_3 and 1H of cyclopropane) and 0.5 (m, 2H, cyclopropane CH_2). Analysis : Found c, 78.90 ; H, 6.55% requires C 78.50 ; H, 6.54% for $C_{14}H_{14}O_2$.

Hexacyclo ($7.4.2.0^{1,9}0^{3,7}0^{4,14}0^{6,15}$) pentadeca-10,12-diene-2,8-dione-5-spiro-1'-cyclopropane (25)

The adduct (17) (1 g, 0.004 mol) was dissolved in dry benzene (250 ml) and irradiated by UV lamp (250 W, Bajaj) for 4 h (tlc) in a pyrex immersion well under nitrogen atmosphere. Removal of solvent in vacuo, followed by chromatography of the residue over silica gel furnished the spiro dione (25) (0.7 g, 70%), m.p. 174°, IR (KBr) ν_{max} : 2950, 1755, 1730, 1580 cm^{-1}. UV λ_{max}^{MeOH} : 286 nm, NMR (90 MHz, $CDCl_3$) (Fig. II.17) : δ 6.0 and 5.35 (a symmetrical set of multi-

plets, 4H, olefinic H), 3.55 (br s, with St., 2H), 3.0 (br s, 2H), 2.30 (br m, 2H) and 0.60 (br s, 4H, cyclopropane CH_2). Analysis : Found C, 81.9 ; H, 5.44% requires C, 81.6 ; H, 5.6% for $C_{17}H_{14}O_2$.

Hexacyclo (7.4.2.$O^{1,9}O^{3,7}O^{4,14}O^{6,15}$) penta deca-10,12-diene-2,8-dione-5-spiro-1'-cyclopentane (26)

The endo adduct (18) (1 g, 0.0036 mol) was dissolved in dry benzene (250 ml) and irradiated by UV lamp (250 W, Bajaj) in a pyrex immersion well under nitrogen atmosphere for 4 h. (tlc). Removal of solvent in vacuo, followed by chromatography of the residue over silica gel gave the cage dione (26) (0.68 g, 68%), m.p. 186°, IR (KBr) ν_{max} : 2950, 1755, 1730, 1580 cm^{-1}, UV λ_{max}^{MeOH} : 289 nm. NMR (90 MHz, $CDCl_3$) (Fig. II.18) : δ 6.00 and 5.4 (symmetrical m, 4H, olefinic H), 3.45 (br dd, 2H), 2.9 (br dd, 2H), 2.50 (d, J=3Hz, 2H) and 1.60 (br s, 8H, cyclopentane CH). Analysis : Found C, 81.70 ; H, 6.47% requires C, 82.01 ; H, 6.46% for $C_{19}H_{18}O_2$.

Hexacyclo (7.4.2.$O^{1,9}O^{3,7}O^{4,14}O^{6,15}$) pentadeca-10,12-diene-2,8-dione-5-spiro-1'-methyl cyclopropane (27)

The endo adduct (19) (0.5 g, 0.0019 mol) was dissolved in dry benzene (250 ml) and irradiated by UV lamp (250W, Bajaj) in a pyrex immersion well for 4 h (tlc) under nitrogen atmosphere. Removal of solvent in vacuo, followed by chroma-

tography of the residue over silica gel furnished the cage dione (27) (0.3 g, 60%), m.p. 100°, IR (KBr) ν_{max} : 2950, 1755, 1730 and 1585 cm^{-1}, UV λ_{max}^{MeOH} : 287 nm, NMR (90 MHz, $CDCl_3$) (Fig. II.19) : δ 6.00 and 5.5 (symmetrical m, 4H, olefinic H), 3.5 (br dd, 2H), 3.00 (br dd, 2H), 2.56 (br m, 1H), 2.3 (b m, 1H), 1.15 (d, J=3Hz, superimposed with another signal total 4H, CH_3 and 1H of cyclopropane) and 0.75 (m, 2H, cyclopropane CH_2). Analysis : Found C, 82.21 ; H, 5.89% requires C, 81.81 ; H, 6.06% for $C_{18}H_{16}O_2$.

Preparation of 1,4,4a,5,8,8a,10a-octahydro-9,10-dioxo-1,4 : 5,8-dimethanoanthraene-11,12-dispiro-1',1'-dicyclopropane (28) (Bisadduct)

Micellar Cycloaddition

The spiroheptadiene (7) (1.5 g, 16 m mol) was added to p-benzoquinone (11) (10 g, 9 m mol) solubilized in CTAB micelle, prepared by dissolving CTAB (0.304 m mol) in water (100 ml). The reaction mixture was stirred for 3 h at ambient temperature (~32°). It was extracted with solvent ether (3 x 25 ml) and the combined extract was washed with water (3 x 20 ml), brine (2 x 10 ml), and dried over anhydrous sodium sulphate. Removal of solvent followed by column chromatography of the residue gave a bis-adduct (28) (2.1 g, 80%), m.p. 145°, IR (KBr) ν_{max}: 1705, 1685 cm^{-1} , UV λ_{max}^{MeOH} 278 nm ; NMR (270 MHz, $CDCl_3$), (Fig. II.20) : δ 6.35 (superimposed dd, $J_1=J_2=3Hz$, 4H, olefinic H), 3.1 (br s, 4H, methine

H), 2.75 (d, J=7Hz, 4H, ring junction H), 0.55 (m, 4H, cyclopropane H)and 0.42 (m, 4H, cyclopropane H). ^{13}CNMR ($CDCl_3$) (Fig. II.21) : δ 212.3 (C=O), 136.42 (C=C), 53.94, 53.06, 45.0, 8.05 and 6.52 (cyclopropyl carbons), Analysis : Found C, 82.69 ; H, 6.74% requires C, 82.19 ; H, 6.85% for $C_{20}H_{20}O_2$.

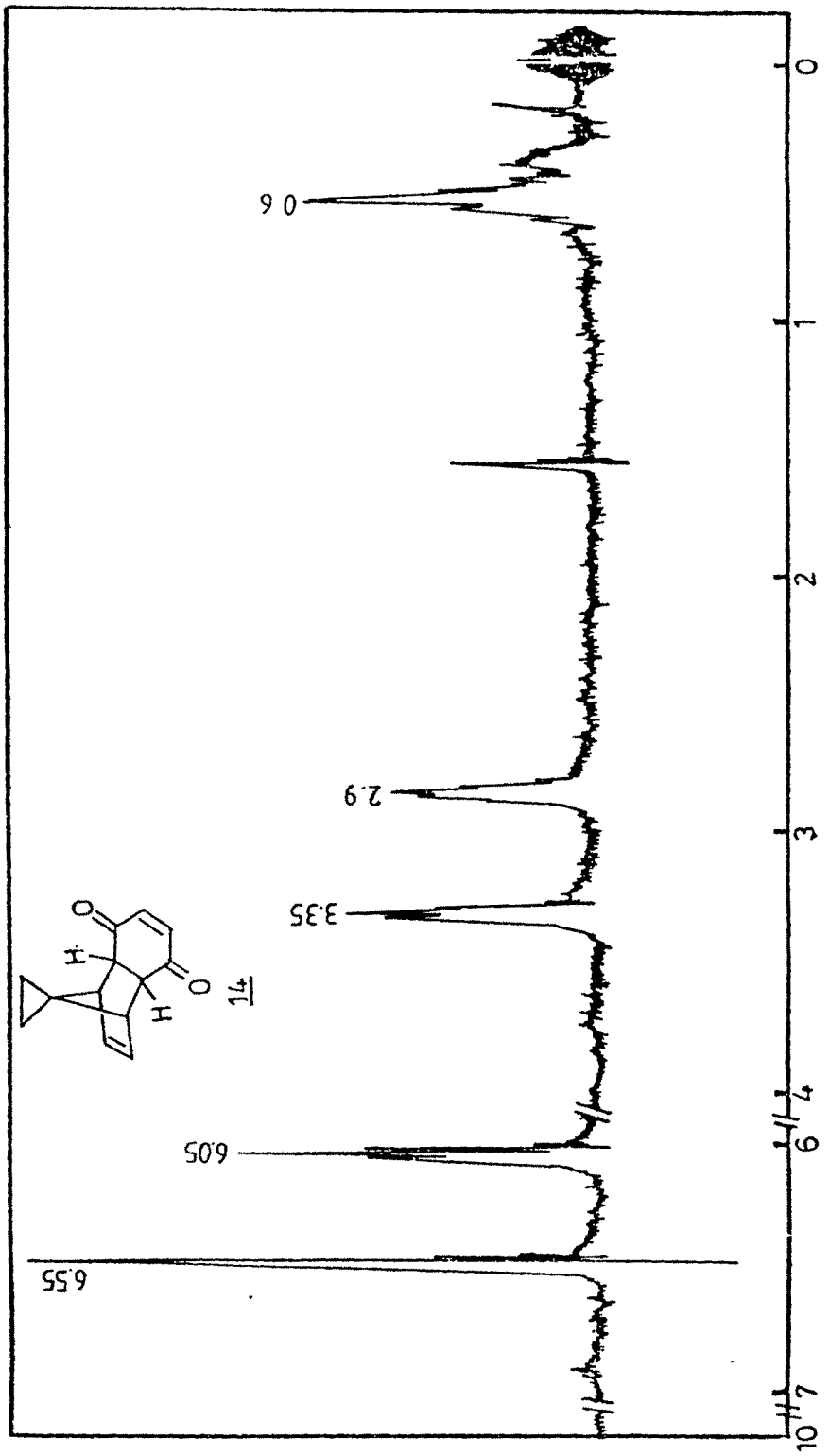


Fig. II.5 : NMR ($CDCl_3$, 90 MHz) spectrum of compound 14

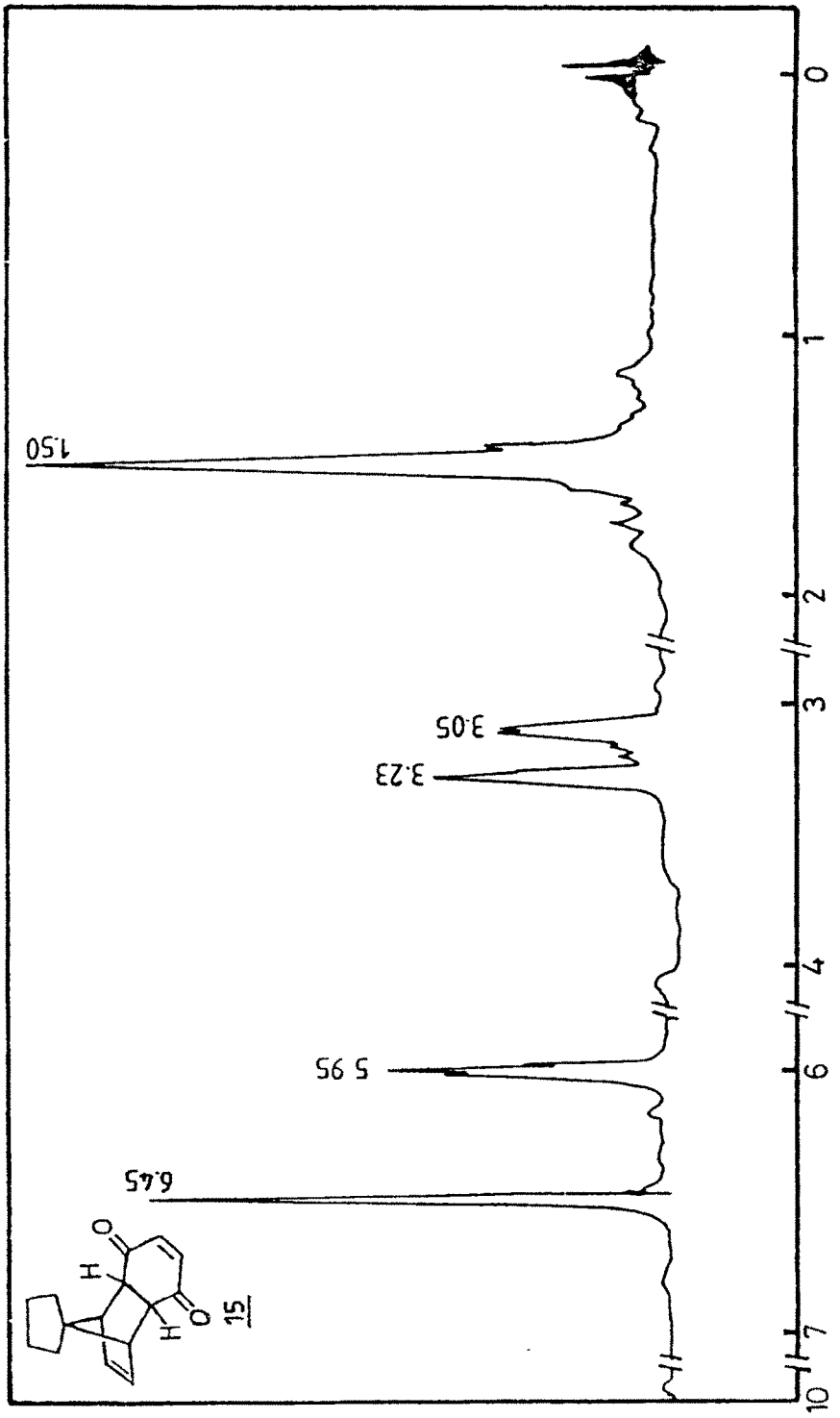


Fig. II.6 : NMR ($CDCl_3$, 90 MHz) spectrum of compound 15

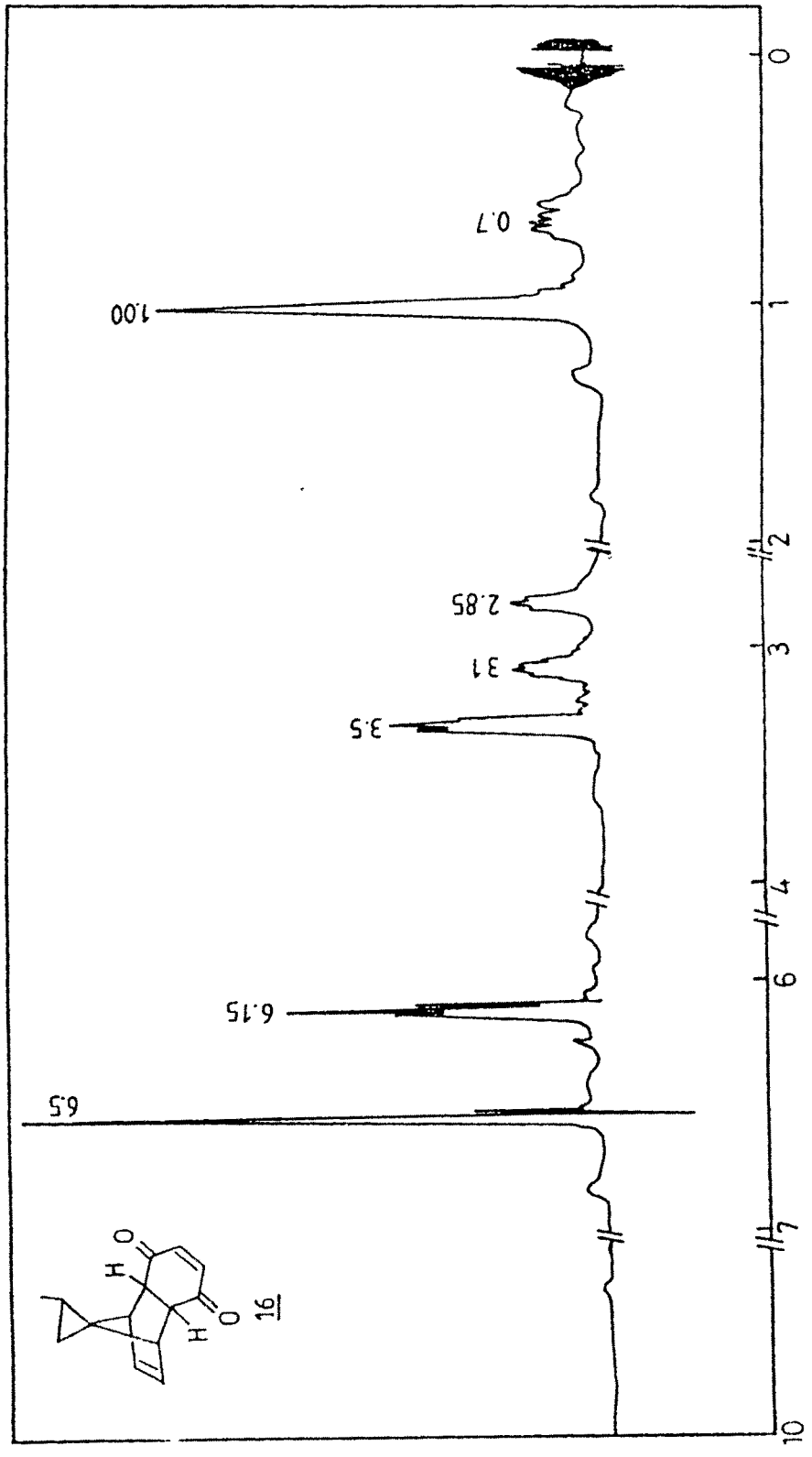


Fig. II.7 : NMR ($CDCl_3$, 90 MHz) spectrum of compound 16

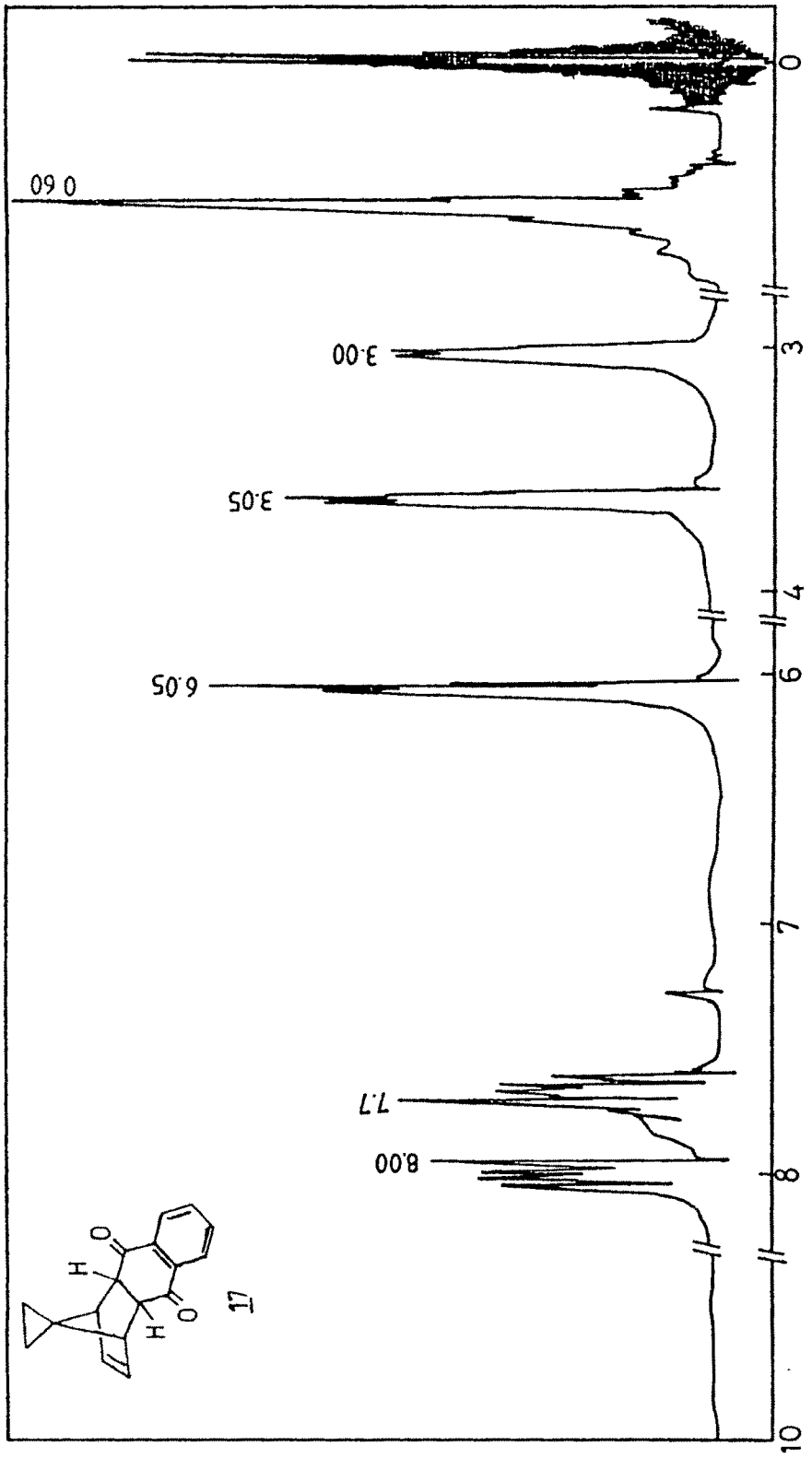


Fig. II.8 : NMR ($CDCl_3$, 90 MHz) spectrum of compound 17

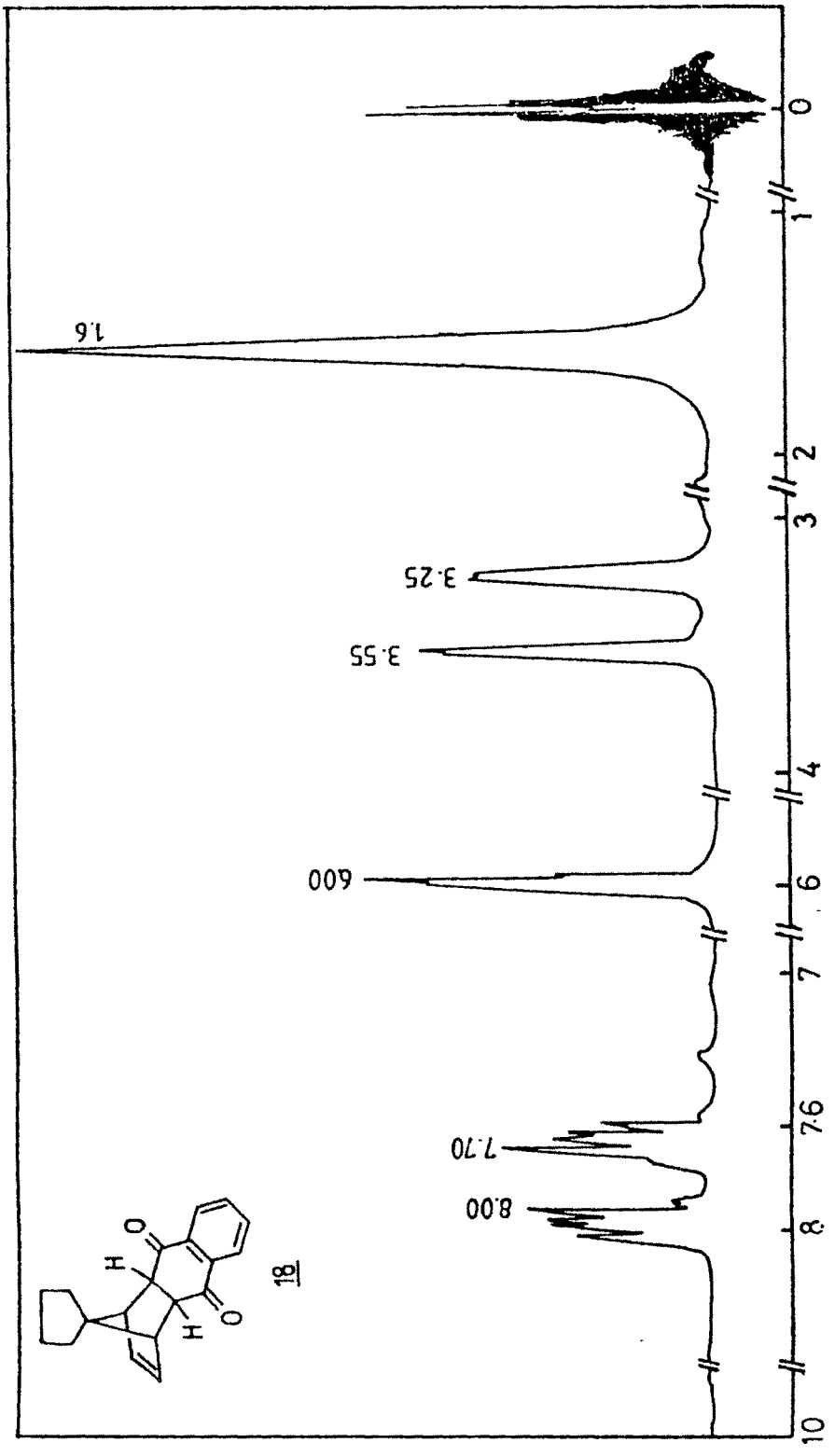


Fig. II.9 : NMR ($CDCl_3$, 90 MHz) spectrum of compound 18

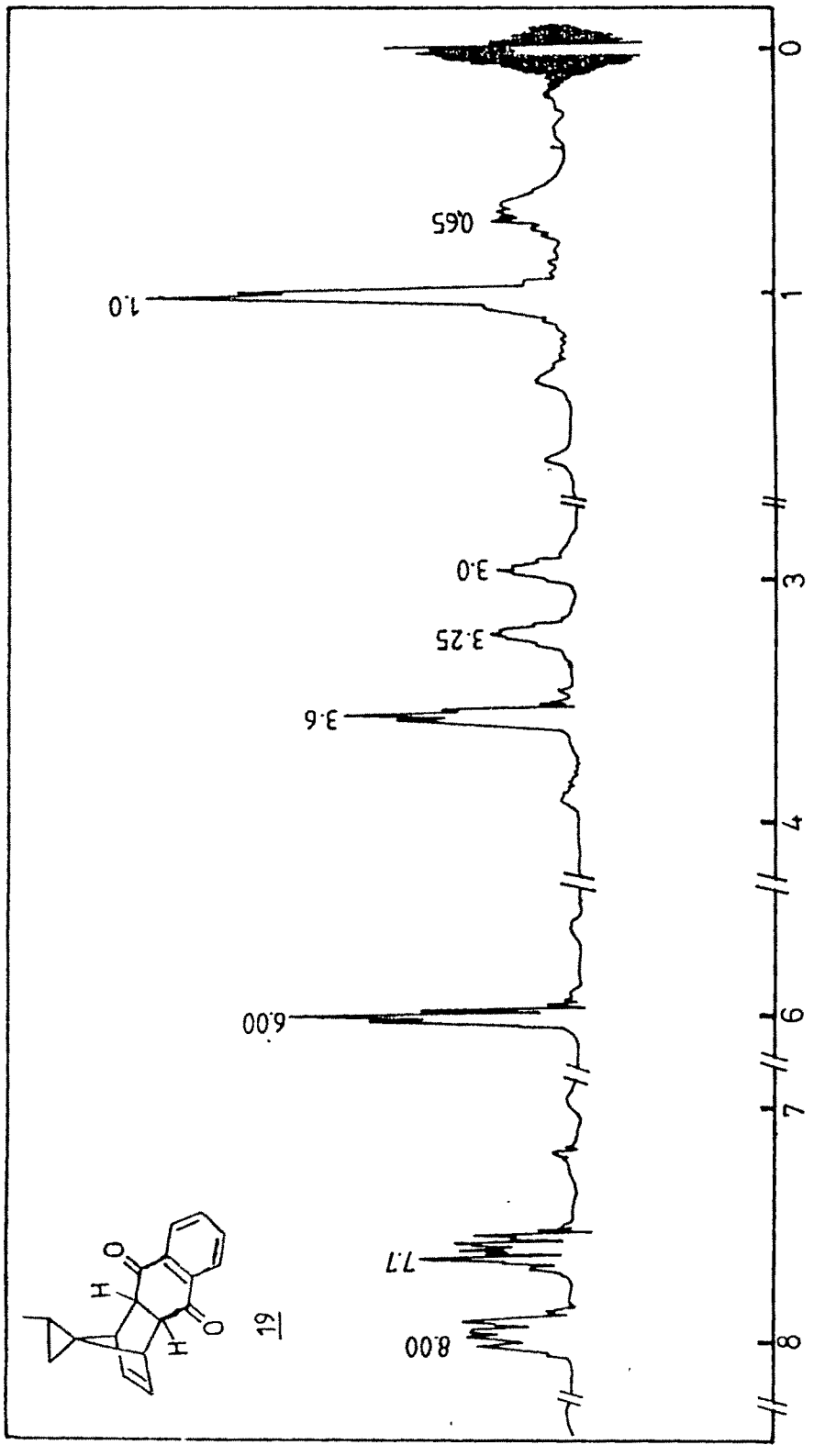


Fig. II.10 : NMR ($CDCl_3$, 90 MHz) spectrum of compound 19

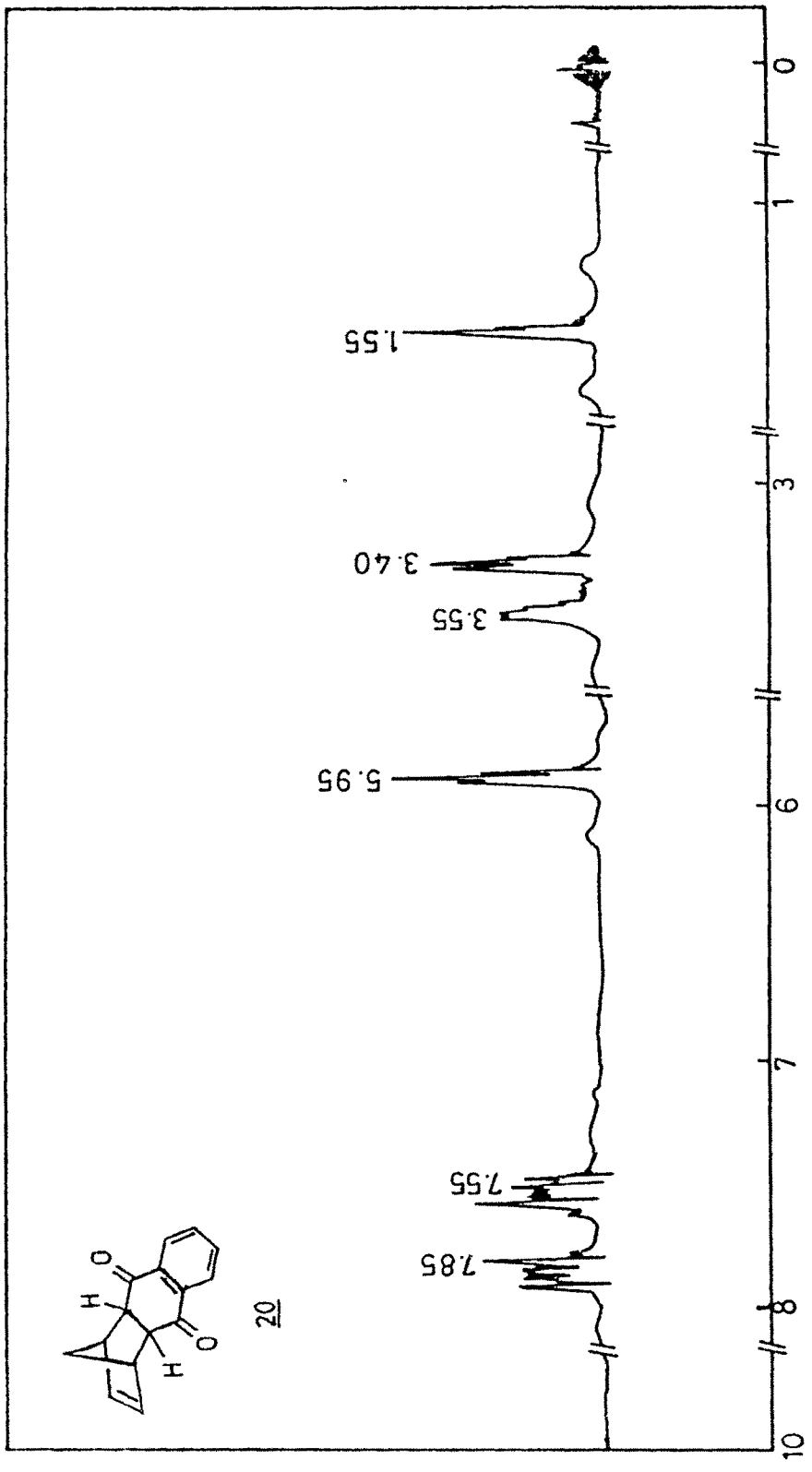


Fig. II.11 : NMR ($CDCl_3$, 90 MHz) spectrum of compound 20

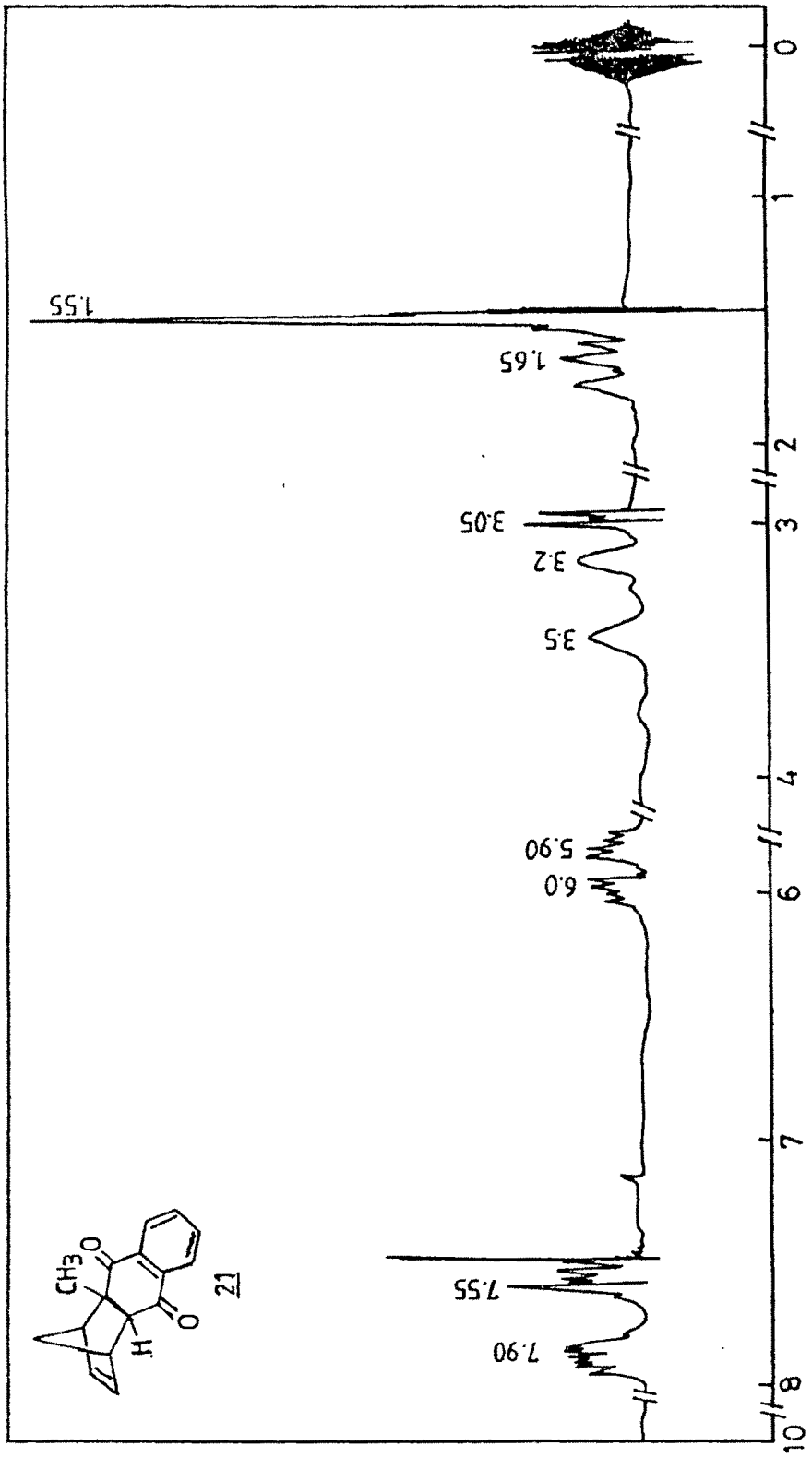


Fig. II.12 : NMR ($CDCl_3$, 90 MHz) spectrum of compound 21

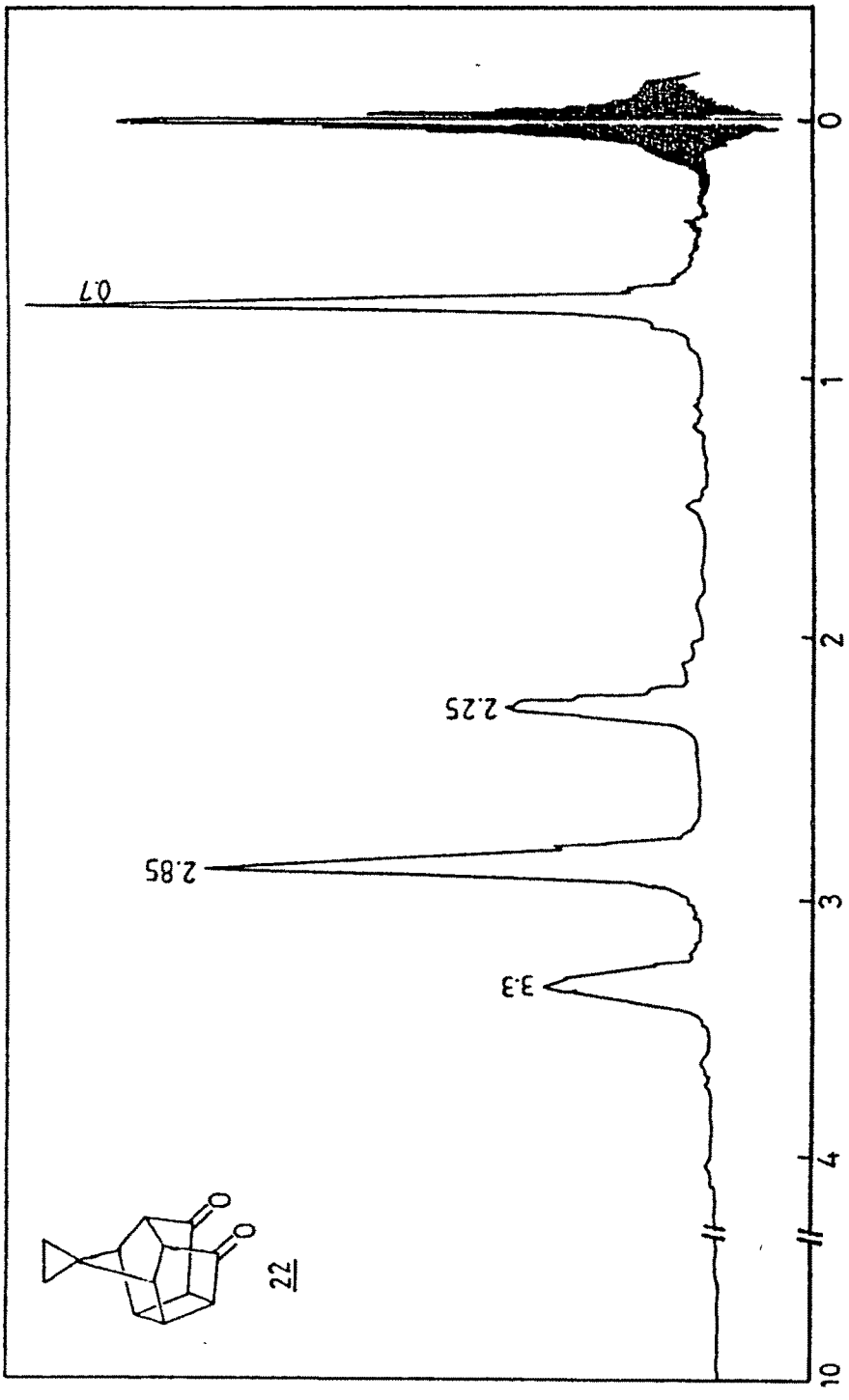


Fig. II.13 : NMR ($CDCl_3$, 90 MHz) spectrum of compound 22

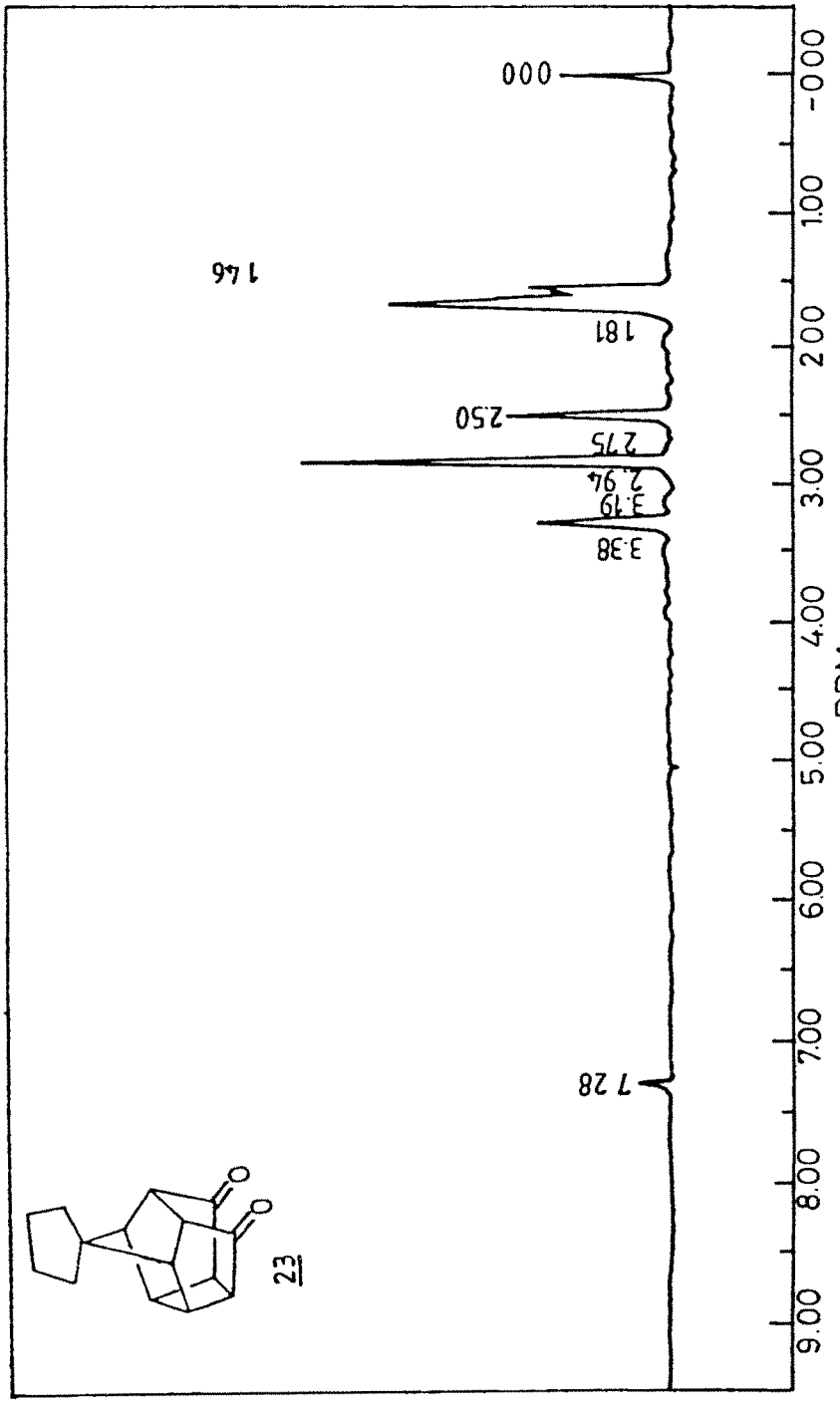


Fig. II.14 : NMR ($CDCl_3$, 300 MHz) spectrum of compound 23

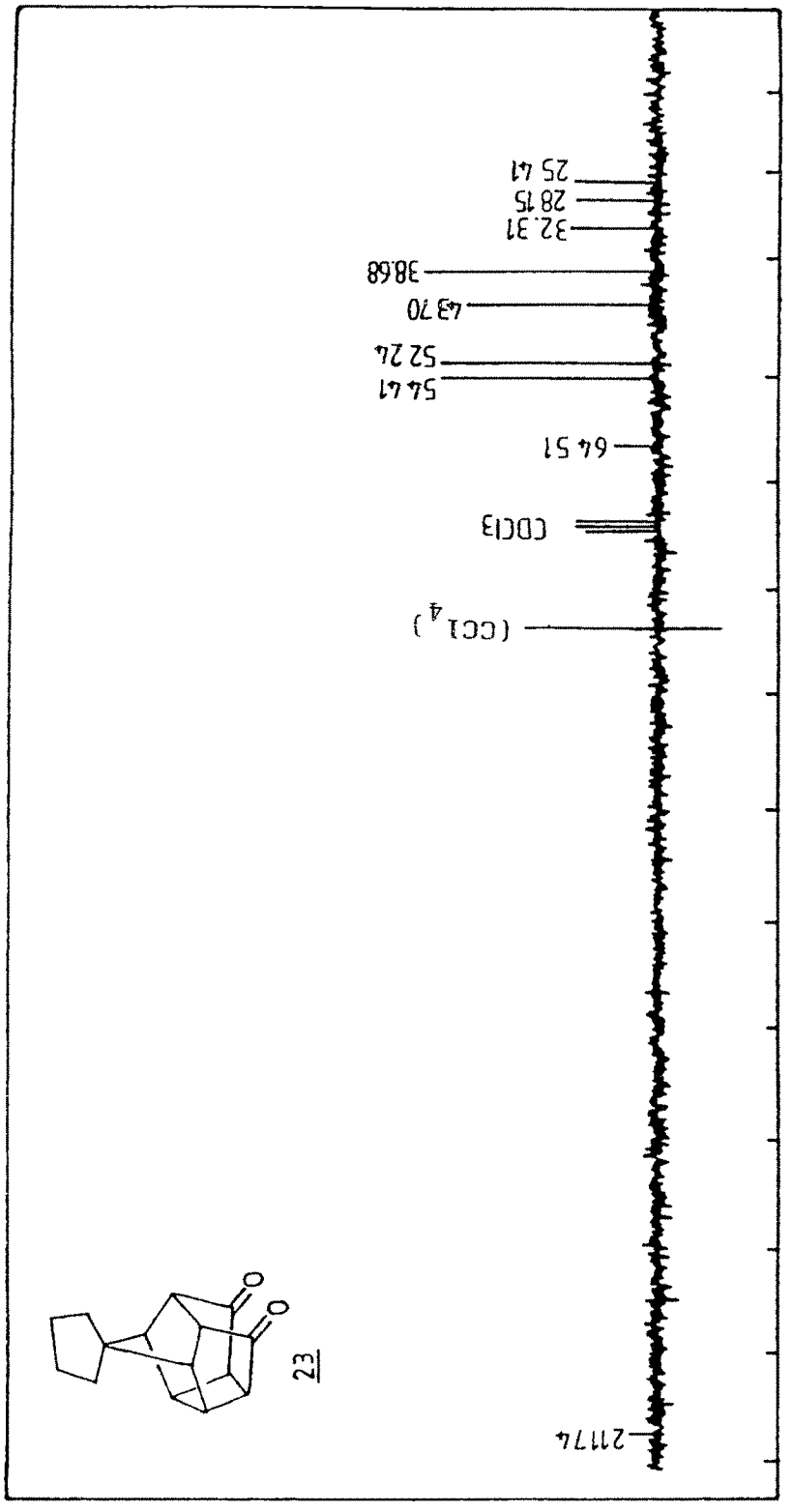


Fig.II.15 : ^{13}CNMR ($CDCl_3$) spectrum of compound 23

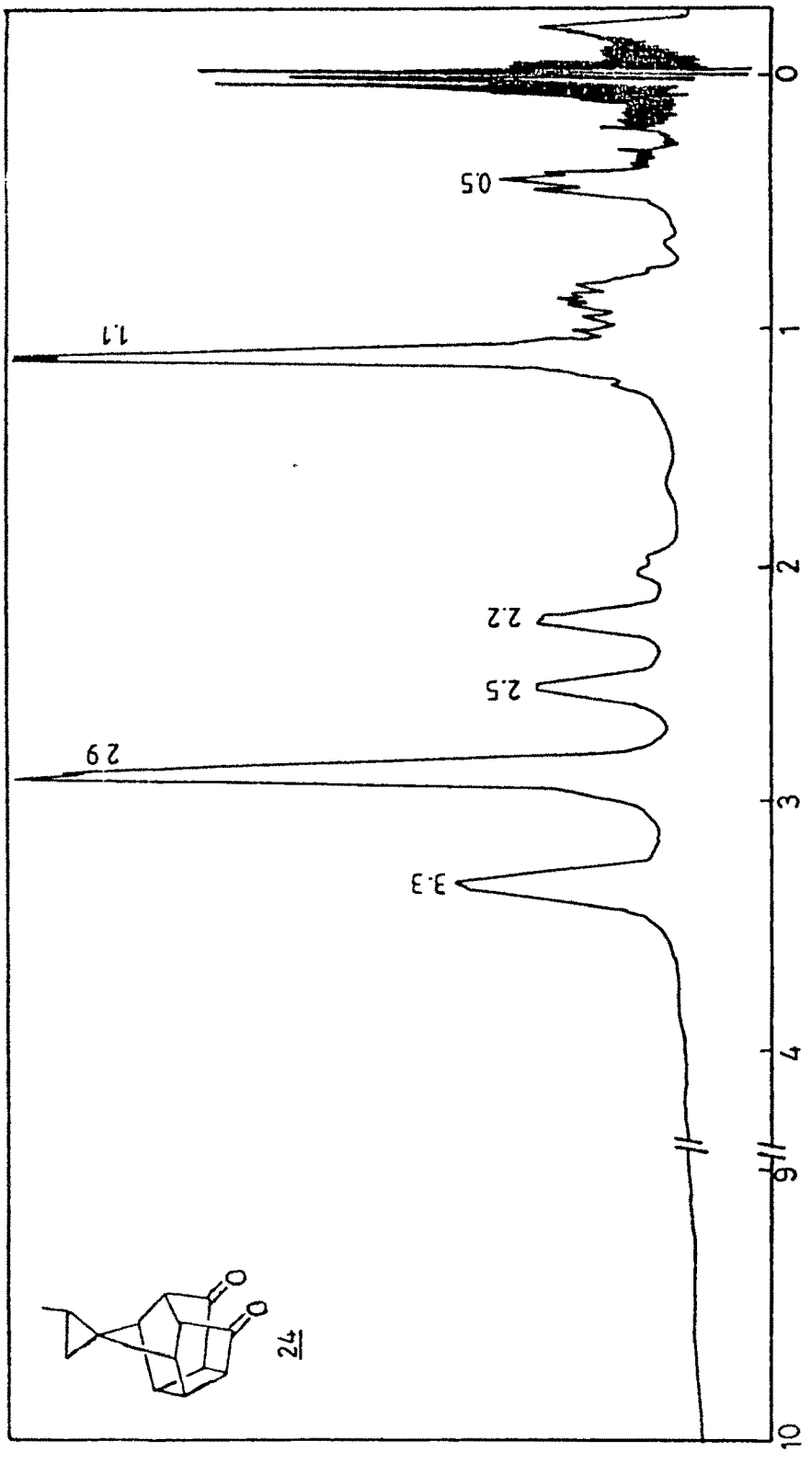


Fig. II.16 : NMR ($CDCl_3$, 90 MHz) spectrum of compound 24

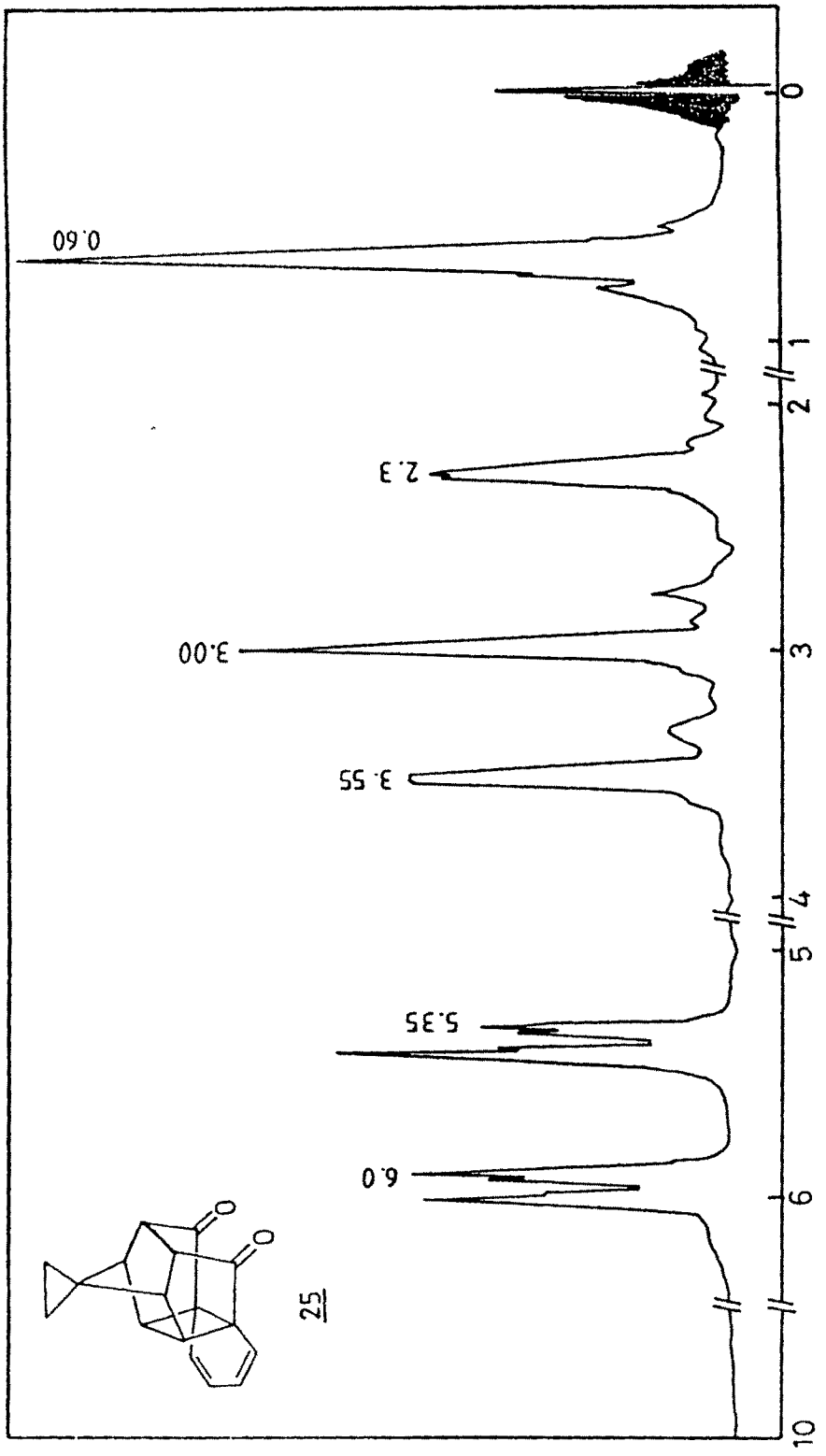


Fig. II.17 : NMR ($CDCl_3$, 90 MHz) spectrum of compound 25

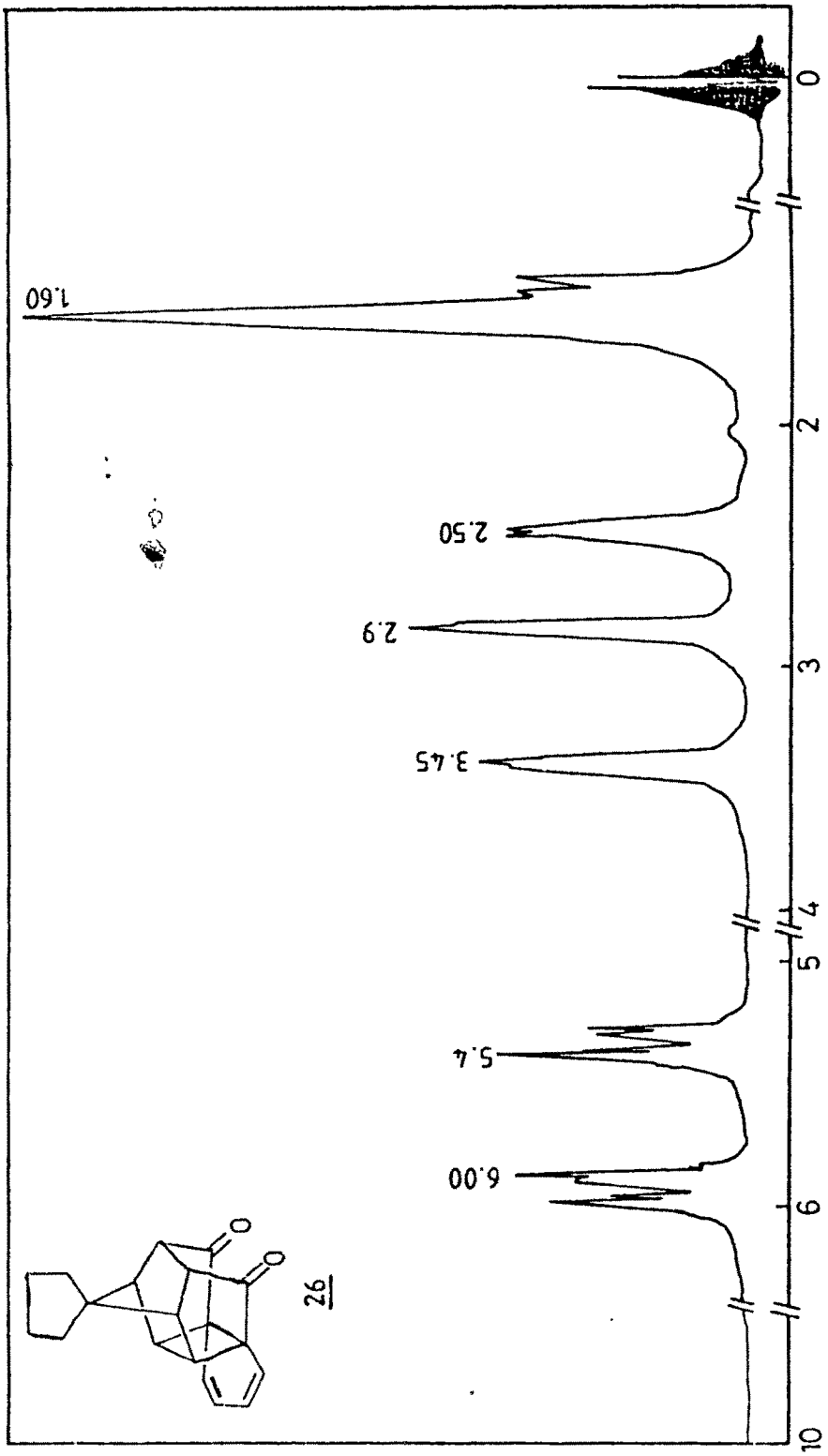


Fig. II.18 : NMR ($CDCl_3$, 90 MHz) spectrum of compound 26

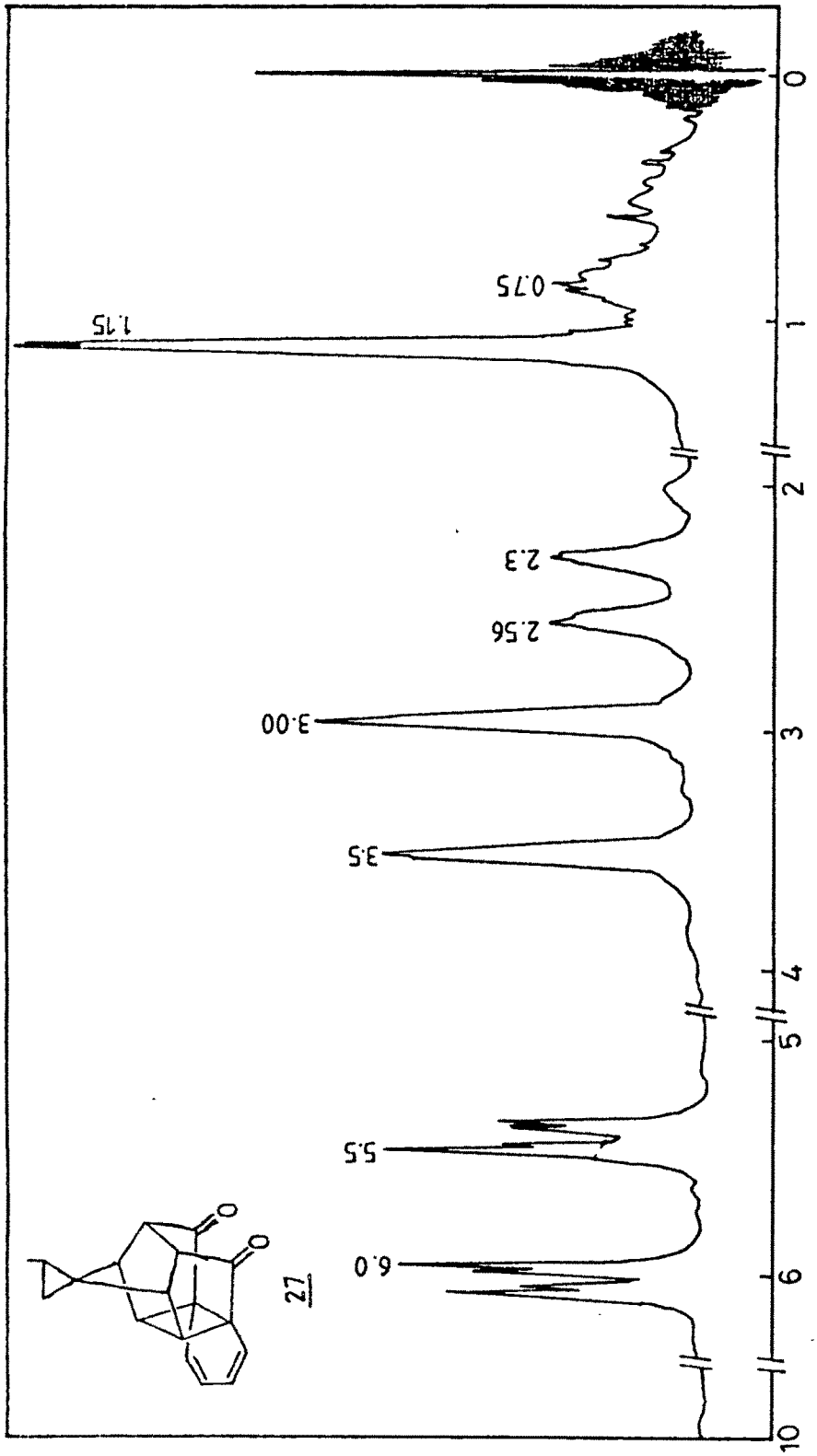


Fig. II.19 : NMR ($CDCl_3$, 90 MHz) spectrum of compound 27

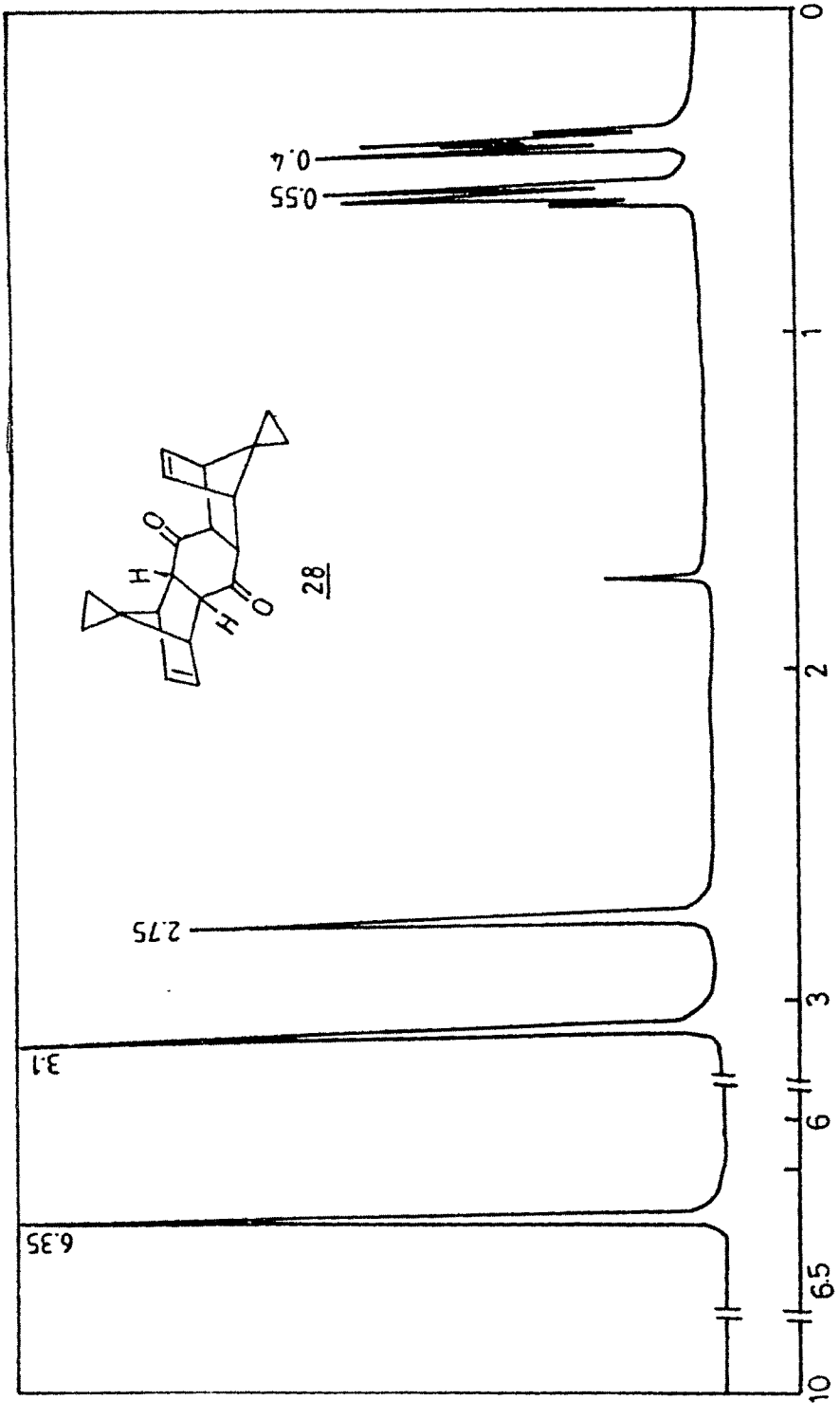


Fig. II.20 : NMR ($CDCl_3$, 270 MHz) spectrum of compound 28

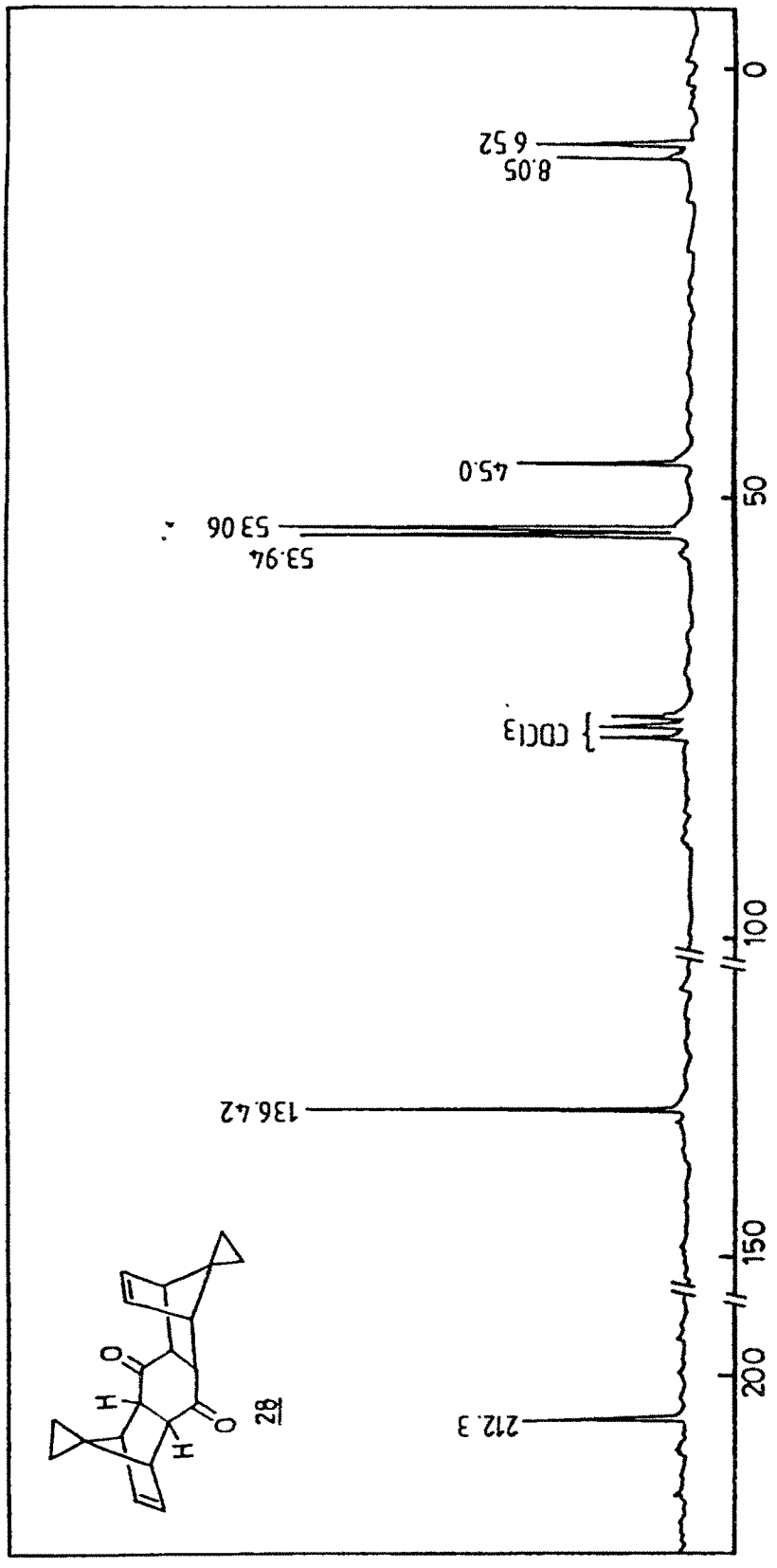


Fig-II.21 : ^{13}CNMR ($CDCl_3$) spectrum of compound 28

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