

## 195. Carbon Magnetic Resonance Spectra of $\alpha, \beta, \gamma, \delta$ - and $\alpha, \beta, \alpha', \beta'$ -Unsaturated Ketones

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*Summary.* Carbon-13 spectra of a series of 26 unsaturated ketones (*ortho*- and *para*-cyclohexadienones and corresponding open-chain analogues) have been measured by *Fourier*-transform pulse spectroscopy. A complete analysis has been achieved by means of double resonance experiments using noise-modulated and coherent off-resonance proton irradiation and with the aid of non-decoupled spectra. Chemical shifts are interpreted in terms of charge distribution in the dienone system and of methyl substituent effects. Carbon chemical shifts were also obtained for O-protonated *ortho*- and *para*-cyclohexadienones. One-bond and long-range carbon-proton and carbon-fluorine spin coupling constants are reported for several compounds.

In two previous publications we have described and analysed proton spectra of a series of *ortho*- and *para*-cyclohexadienones [1a, b]. The chemical shifts and coupling constants obtained could be correlated with the electronic structure and chemical properties of the unsaturated ketones. We now make use of  $^{13}\text{C}$  resonance, which offers a range of chemical shifts an order of magnitude greater than proton spectroscopy and hence is sensitive to rather small structural changes.  $^{13}\text{C}$  spectra of saturated and  $\alpha, \beta$ -unsaturated carbonyl compounds have already been studied in detail [2a, b]. As a result of these investigations it was found that conjugation lowers the resonance frequency of the carbonyl carbon. Furthermore for cyclic saturated ketones a correlation between the C=O chemical shift and the energy of the  $n \rightarrow \pi^*$  transition in the electronic spectra was obtained [3].

In the present paper a complete analysis of the  $^{13}\text{C}$  spectra of linear- and cross-conjugated dienones of cyclic and acyclic structure is given. Spectra were obtained by *Fourier*-transform pulse spectroscopy under simultaneous proton noise-decoupling. To facilitate the assignment of the carbon singlets and to study carbon-proton coupling constants we also measured non-decoupled spectra and made extensive use of off-resonance coherent irradiation [4].

**1. Analysis of spectra.** – 1.1. *Linear-conjugated ketones.* – Sixteen compounds containing an  $\alpha, \beta, \gamma, \delta$ -unsaturated ketone fragment have been investigated in deuteriochloroform solution with tetramethylsilane as internal reference. As a typical example of the series of thirteen cyclic ketones we discuss the spectrum of 6-dichloromethyl-6-methyl-cyclohexa-2,4-diene-1-one (**1**). The proton noise-decoupled spectrum is illustrated in Figure 1a. Eight singlets are observed, whereby in this and the following compounds olefinic and carbonyl carbons appear at higher frequencies than the solvent triplet (77.0 ppm), alkyne and dichloromethyl carbons very close to it and aliphatic carbon atoms at lower frequencies. Assignment of the individual singlets is obtained from a partly decoupled spectrum which results from strong

coherent irradiation of the protons at a frequency corresponding approximately to the centre of the proton spectrum (off-resonance decoupling), Fig. 1b. Under these conditions carbon-proton coupling across more than one bond is eliminated for all carbon atoms and one bond coupling is reduced to an extent depending upon the difference between the proton chemical shift and the centre of irradiation [5]. The aliphatic region of the partly decoupled spectrum shows a quartet, a doublet and a singlet which correspond to the methyl, methine ( $\text{CHCl}_2$ ) and quaternary carbons

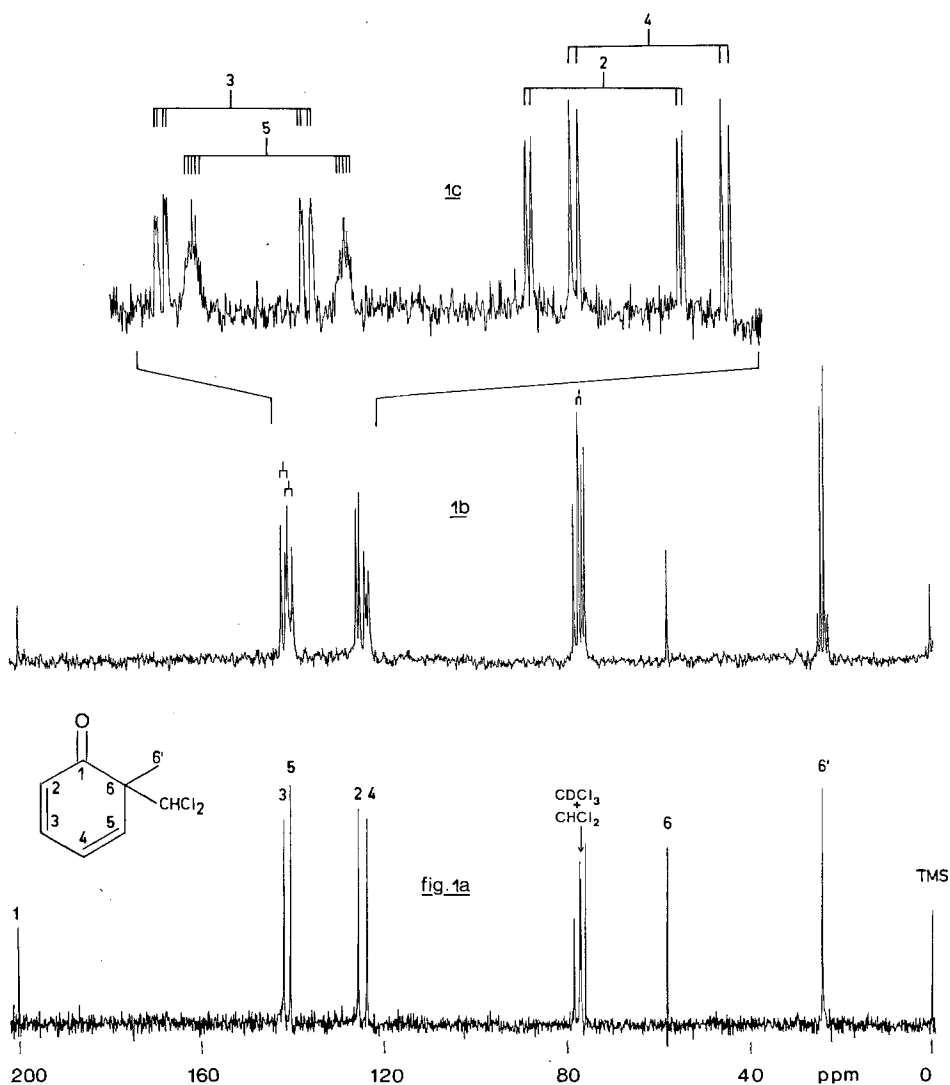


Fig. 1.  $^{13}\text{C}$ -NMR. spectra of 6-dichloromethyl-6-methylcyclohexa-2,4-diene-1-one (**1**) in  $\text{CDCl}_3$   
 a) Proton noise-decoupled (4000 transients); b) Partly decoupled; centre of coherent proton irradiation 4.00 ppm downfield of TMS; c) Non-decoupled, olefinic region (21000 transients)

respectively. The four doublets in the olefinic region can be grouped into C(5) and C(3) at high frequency and C(4) and C(2) at low frequency in analogy to the proton spectrum of **1** and other dienones [1a] [6]. The assignment within the two groups of signals is achieved by variation of the off-resonance conditions (centre of irradiation, amplitude of the irradiation frequency) leading to four different residual doublets. Thus making use of the known proton chemical shifts C(3) is found at higher frequency than C(5) and C(2) at higher frequency than C(4). This assignment is confirmed by decoupling experiments with selective proton irradiation. The carbonyl carbon resonance is always observed as a singlet at the high frequency end of the spectrum. A discussion of the chemical shifts is given in chapter 2.1.

To obtain quantitative information about carbon-proton spin coupling the spectrum has been measured without proton irradiation (Fig. 1c). Such spectra show a considerably higher multiplicity and are not intensity-enhanced by nuclear *Overhauser* effects. To achieve an acceptable signal-to-noise ratio the number of accumulated transients has to be increased about tenfold. Besides information about  $^1J_{\text{CH}}$  long-range coupling constants can be extracted from the fine structure of such multiplets (e.g. double doublets of the olefinic carbons). The coupling constants of compound **1** are discussed in chapter 2.2.

As an example for the analysis of methyl resonances we discuss the spectrum of the trimethyl-*ortho*-dienone **10** (Fig. 2a). The aliphatic region from 10 to 30 ppm contains four singlets arising from the three methyl carbons and the C(7) methylene group. The partly decoupled spectrum (Fig. 2b) reveals the high-frequency signal as arising from the methylene carbon (triplet). The methyl quartet with the largest residual splitting can be assigned to the methyl group at the saturated carbon atom C(6) since the corresponding proton signal has an offset of 3.81 ppm from the centre of irradiation whereas the offsets of the two other methyl proton signals are 3.14 and 3.08 ppm respectively. To distinguish between the two remaining methyl carbon signals, which is not possible by the above procedure, we make use of the non-decoupled spectrum (Fig. 2c) in which the quartet at low frequency shows a doublet fine structure and is assigned to  $\text{CH}_3\text{-C}(2)$  whereas the other quartet has a quartet fine structure and is assigned to  $\text{CH}_3\text{-C}(4)$ . This assignment parallels the sequence in compound **9**. In that case the identification could be achieved by off-resonance decoupling since the methyl proton signals are separated by 0,096 ppm.

1.2. *Cross-conjugated ketones*. – Using the experimental techniques described under 1.1. we have also analysed a series of six cyclic and four open-chain cross-conjugated ketones, a typical representative of which is 4-allyl-4-methyl-cyclohexa-2,5-dien-1-one (**18**) with the spectra illustrated in Fig. 3. Because of the  $C_s$  symmetry of the molecule the four olefinic carbon atoms exhibit only two resonances of increased intensity with respect to the intensity of the two other olefinic carbon atoms. Considering the established sequence of the  $^{13}\text{C}$  chemical shifts of the olefinic carbons in **1**, the proton chemical shifts of **18** and partial decoupling experiments the signal at 155.0 ppm must be assigned to C(3) and C(5) and the signal at 128.4 ppm to C(2) and C(6).

**2. Discussion.** – 2.1. *Chemical shifts.* – 2.1.1. *Linear-conjugated ketones.* – Chemical shift data of *ortho*-cyclohexadienones and open-chain ketones are summarized in

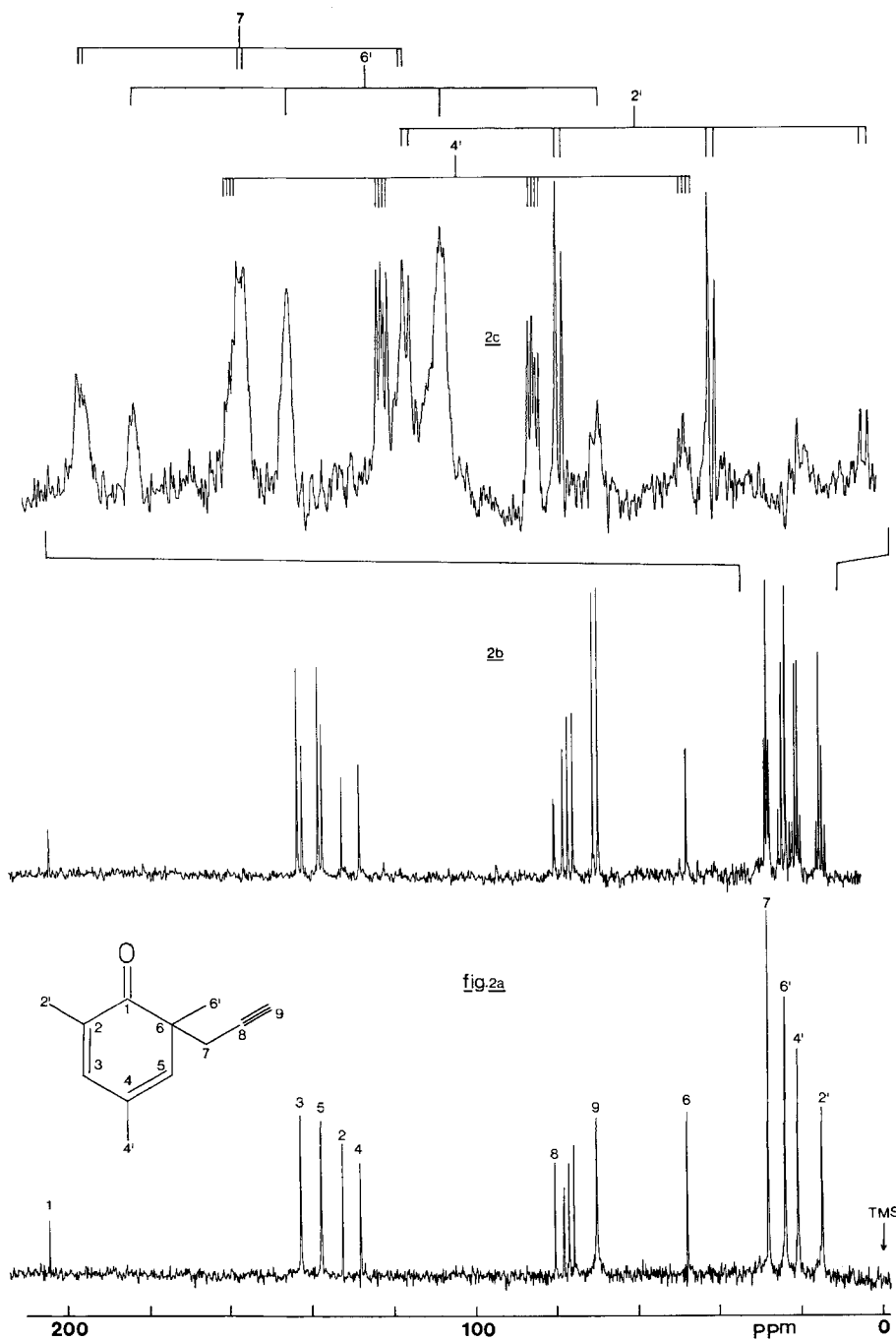


Fig. 2.  $^{13}\text{C}$ -NMR. spectra of 2,4,6-trimethyl-6-propargylcyclohexa-2,4-diene-1-one (10) in  $\text{CDCl}_3$   
 a) Proton noise-decoupled (3000 transients); b) Partly decoupled; centre of coherent proton irradiation 3.80 ppm downfield of TMS; c) Non-decoupled, 10–30 ppm region (35000 transients)

tables 1 and 3. The carbonyl carbon resonance in *ortho*-cyclohexadienones is observed between 201.4 and 205.8 ppm. In **1** the presence of a  $\text{CHCl}_2$  group leads to a shielding effect on  $\text{sp}^2$ -carbons  $\beta$ - to  $\text{CHCl}_2$  ( $=\text{C}-\text{C}-\text{CHCl}_2$ ). *Stothers & Lauterbur* [2a] reported a

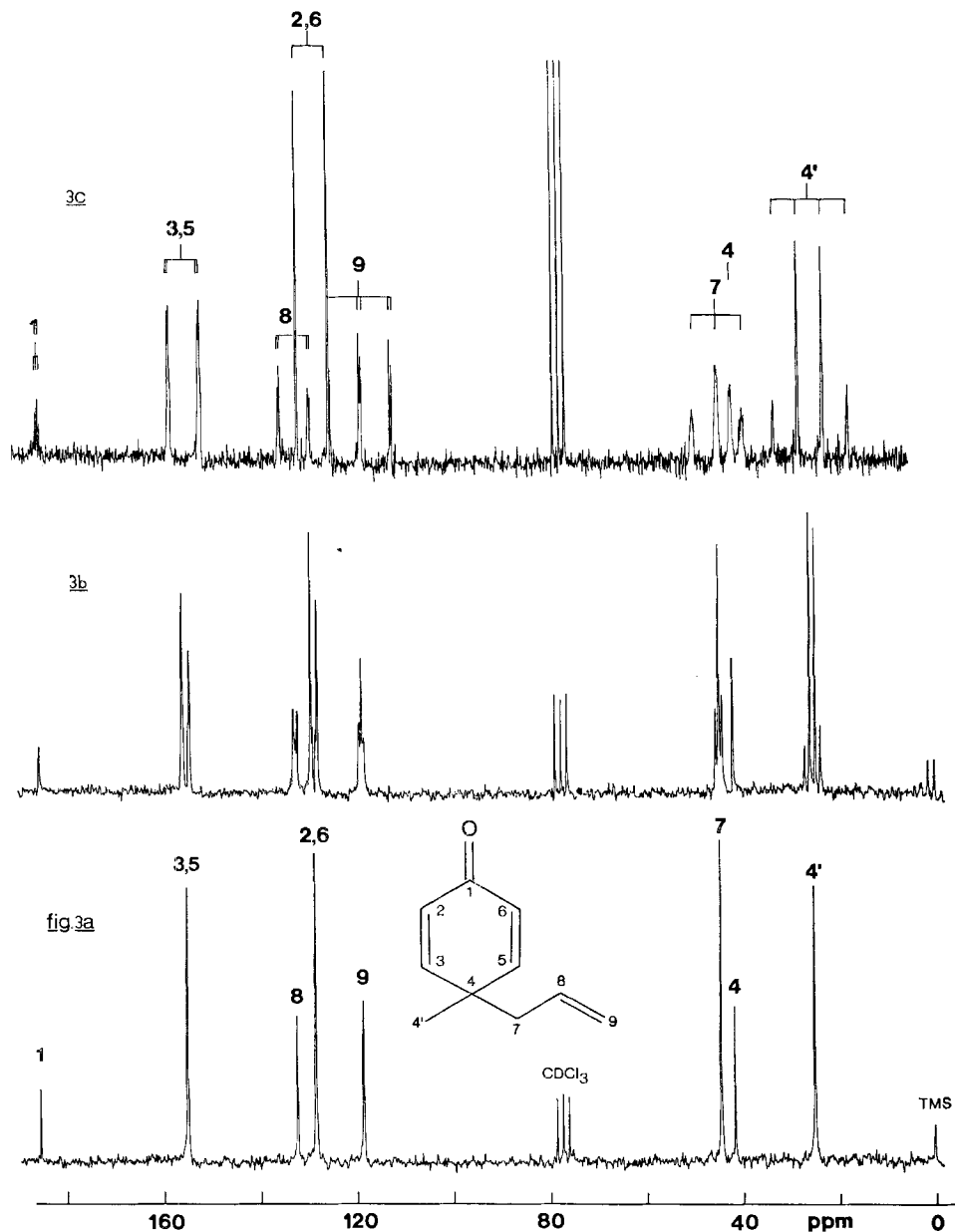


Fig. 3.  $^{13}\text{C}$ -NMR. spectra of 4-allyl-4-methyl-cyclohexa-2,5-diene-1-one (**18**) in  $\text{CDCl}_3$   
 a) Proton noise decoupled (3000 transients); b) Partly decoupled; centre of coherent proton irradiation 3.80 ppm downfield of TMS; c) Non-decoupled (21 000 transients)

similar effect on a carbonyl carbon  $\alpha$ - to  $\text{CHCl}_2$  ( $\text{CO}-\text{CHCl}_2$ ). They assumed that the electron-withdrawing power of the dichloromethyl group reduces the polarity of the attached double bond thus increasing the negative charge at the  $\alpha$ -carbon. If the  $-I$  effect of  $\text{CHCl}_2$  in dienones is also efficacious on the  $\beta$ -carbon, this explanation could account for the lower  $\delta$  value of the carbonyl carbon and the smaller chemical shift difference between C(5) and C(4) in **1** (16.7 ppm) than in **2** (26.8 ppm). Effects of similar magnitude are observed upon  $\text{CHCl}_2$ -substitution in *para*-cyclohexadienones (see 2.1.2). Hence the typical range of carbonyl-carbon absorption in linear-conjugated cyclohexadienones is  $204.5 \pm 1.5$  ppm (average of compounds **2** to **13**). This range lies in between the values for cyclohexanone (211.6 ppm) and cyclohexenone (199.2 ppm) and seems to indicate that conjugation over one more double bond reduces the polarity of the  $\text{C}=\text{O}$  bond. At the same time the polarity of the  $\alpha, \beta$  double bond is reduced, resulting in a smaller chemical shift difference between C(2) and C(3) in dienones. This observation has been made in enone-dienone pairs of different structures and suggests an electron-donating effect of the second double bond rather than reduced planarity in the conjugated system.

The chemical shifts of the olefinic carbons are spread over 45 ppm (115–160 ppm). The side chain  $\text{sp}^2$  carbons in **2**, **6**, **7**, **9** and **12** can be identified by examination of the spectra of **1**, **3**, **4**, **5**, **8**, **11** and **13** where the side chain is either propargyl, methyl or dichloromethyl, by the very constant shifts observed and by partial decoupling experiments. The terminal vinylic carbon always appears at the low-frequency end of the olefinic region.

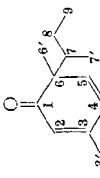
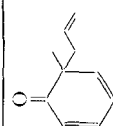
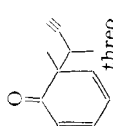
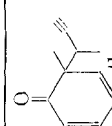
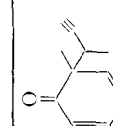
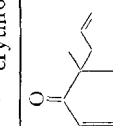
The sequence of the chemical shifts ( $\delta$ ) of the dienone ring carbons in **2** is  $\text{C}(5) > \text{C}(3) > \text{C}(2) > \text{C}(4)$  and does not parallel the reported sequence of proton chemical shifts ( $\delta$ )  $\text{H}-\text{C}(3) > \text{H}-\text{C}(5) > \text{H}-\text{C}(4) > \text{H}-\text{C}(2)$  which follows both the  $\pi$ -electron densities [1a] and total-charge distribution<sup>1)</sup> at the carbon atoms. The different sequence of the carbon chemical shifts for C(3) and C(5) originates from substituent effects at C(6). Reported  $^{13}\text{C}$  chemical shifts of hydrocarbons [7] and  $\alpha, \beta$ -unsaturated ketones [2b] indicate that introduction of alkyl substituents adjacent to  $\text{C}=\text{C}$  double bonds deshields the a-carbon and shields the b-carbon ( $\text{C}_b=\text{C}_a-\text{C}-\text{CH}_3$ ). The a- and b-carbons correspond to C(5) and C(4) in the dienone system. The opposite effect of the  $\text{CHCl}_2$  substituent on C(5) causes an overcrossing of the C(5) and C(3) resonances in **1**.

Upon replacement of hydrogen by methyl a deshielding effect on the directly bonded carbon is observed, which increases with the positive charge on the respective carbon. Thus  $\delta(\text{C}-\text{CH}_3)-\delta(\text{C}-\text{H})$  is about 12 ppm for C(3), 9 ppm for C(5), 7 ppm for C(2) and 6 ppm for C(4). The  $\text{sp}^2$  carbon  $\beta$  to the methyl carbon suffers a shielding effect, which may be the result of a  $-I$  effect transferred via the  $\sigma$ -skeleton and of a larger  $+M$  effect caused by hyperconjugation of the methyl group [2b] [8]. This concept is not generally accepted since it requires an electron withdrawing property of the methyl group, however, so far no better interpretation of the  $^{13}\text{C}$  chemical shifts has been given. The problem is discussed in [9].

In order to rationalize the observed chemical shifts for the olefinic ring carbons we have worked out a set of additive substituent parameters which are summarized in Table 2.

<sup>1)</sup> Obtained from a CNDO calculation of 6,6-dimethylcyclohexadienone.

Table 1.  $^{13}\text{C}$  Chemical shifts  $\delta$ [ppm] of cyclic linear-conjugated dienones

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(2')	C(3')	C(4')	C(5')	C(6')	C(7')	Ref.
<b>1</b> 	201.4	125.3	141.5	123.3	140.0	57.9	76.8 <sup>a)</sup>							24.0		[15]
<b>2</b> 	204.6	125.7	141.2	120.2	147.0	50.7	44.2	132.8	117.6					24.0		[16]
<b>3</b> 	204.4	133.0	138.0	121.7	142.1	53.2	34.8	85.4	71.3	15.3				24.8	17.0	[17]
<b>4</b> 	203.4	123.5	153.7	125.6	143.8	52.2	34.4	85.3	71.5		22.7			24.8	17.1	[18]
<b>5</b> 	203.4	123.6	152.8	125.5	143.1	51.5	33.4	84.9	69.4		22.6			21.4	15.0	[18]
<b>6</b> 	205.2	125.4	145.6	127.7	141.2	50.3	44.6	133.1	117.6			20.8		24.5		b)

	b)	19.3	24.8	116.9	43.2	54.7	155.6	119.4	141.8	123.6	205.8
7											
	[19]	19.3	24.8	69.5	26.7	54.1	154.4	119.6	142.0	123.3	204.4
8											
	[16]	21.1	24.7	117.2	44.9	49.8	138.8	127.5	142.2	132.5	205.2
9											
	[18]	21.1	24.2	70.3	28.4	48.1	137.4	127.9	142.3	132.2	203.9
10											
	[20]	18.8	25.4	21.0	21.0	46.0	143.7	127.8	155.0	123.2	205.2
11											
	[21]	18.9	25.2	10.6	43.5	52.3	150.1	124.4	147.7	127.0	204.5
12											
	[22]	15.7	25.0	11.5	18.1	48.3	145.2	124.2	149.9	126.3	204.6
13											

a)  $\delta(\text{CHCl}_2)$ ; b) Prepared according to the procedure described in [16]



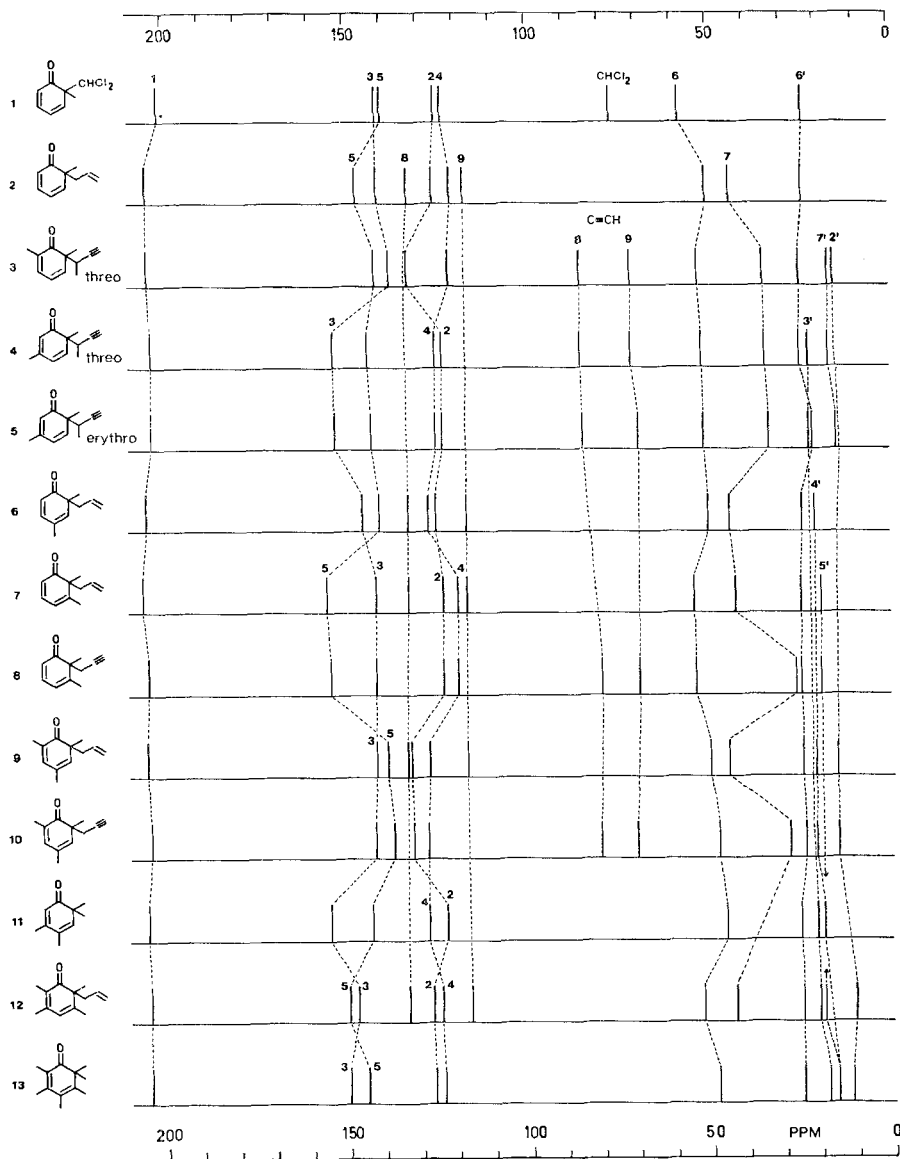
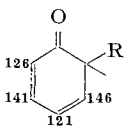


Fig. 4. Schematic spectra and  $^{13}\text{C}$ -chemical shift correlation of ortho-cyclohexadienones

With these increments 41 out of 52 shift data are reproduced within 1 ppm and 46 within 2 ppm. The agreement is poor for the dichloro compound **1** and compounds with vicinal methyl groups, **11**, **12**, **13**, except for C(2) the chemical shift of which is nicely predicted in all cases. It can be seen that by hyperconjugation negative charge may be transmitted over more than one double bond.

Deviations from additivity of substituent effects in polymethylated dienones may be due to competitive stabilizations and destabilizations of charge by inductive and

Table 2. Chemical shift increments  $\delta_M$  [ppm] for methyl-ortho-cyclohexadienones

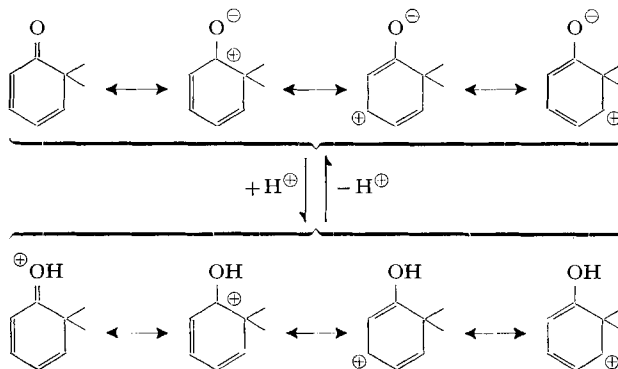
$\delta$ [ppm]	Methyl position	Chemical shift increment ( $\delta_M$ )			C(5) <sup>a)</sup>
		C(2)	C(3)	C(4)	
	C(2)	7	-2.5	0	-3
	C(3)	-2.5	12	4	0
	C(4)	0	4	6	-4
	C(5)	-3	1	-2	9.5

a) If  $R = \text{CH}_2-\text{C}=\text{CH}_2$  an additional increment of  $-1.5$  ppm must be added to all C(5) chemical shifts.

hyperconjugative effects and to steric interactions. These do not affect the  $\text{C}=\text{O}$  frequency but rather the data of the four diene carbons and the methyl carbons. The latter are shifted to lower frequency when vicinal methyl groups are present. Similar interactions leading to deviations from planarity have been reported for polymethoxybenzenes [10].

The sequence of methyl carbon shifts is  $\text{C}(3') > \text{C}(4') > \text{C}(5') > \text{C}(2')$  and does neither correspond to the sequence of the  $^1\text{H}-\text{CH}_3$  data nor to that of the carbons to which they are attached. For C(6') a very constant value of  $24.7 \pm 0.7$  ppm is observed. From the two diastereomeric 3-methyldienones **4** and **5** the *erythro* compound shows a different resonance position of C(6') (21.4 ppm), thus providing a possibility to distinguish between *erythro* and *threo* isomers in this series if both are available. C(7) is observed at  $44.1 \pm 1$  ppm for the allylic and at  $27.5 \pm 1$  ppm for the propargylic side chain. Methylation at C(7) in **3**, **4** and **5** shifts the resonance to  $34.0 \pm 1$  ppm. Fig. 4 shows schematic spectra of all *ortho*-cyclohexadienones investigated.

To study the influence of charge distribution on carbon chemical shifts we have also studied the spectrum of **1** in  $\text{D}_2\text{SO}_4$ . Under these conditions the dienone is deuterated on oxygen [6]. The changes in the carbon chemical shifts are expressed in  $\Delta\delta_{\text{CDCl}_3}^{\text{D}_2\text{SO}_4}$  values ( $\delta_{\text{D}_2\text{SO}_4} - \delta_{\text{CDCl}_3}$ ).<sup>2)</sup>



<sup>2)</sup> For  $\text{D}_2\text{SO}_4$  solutions tetramethylsilane was used as an external standard and  $\delta$  values are given without susceptibility correction.

The high-frequency shifts of C(1),  $\Delta\delta = +10.3$  ppm, C(3),  $\Delta\delta = +30.0$  ppm and C(5),  $\Delta\delta = +19.1$  ppm, are expected on the basis of resonance forms of the kation and parallel the results obtained from the proton spectrum in  $\text{H}_2\text{SO}_4$  [6].

The  $\Delta\delta$  values of C(4) and C(6) are  $+4.8$  ppm and  $+3.9$  ppm respectively, whereas the C(2) resonance is shifted to lower frequency,  $\Delta\delta = -4.5$  ppm. This leads to an overcrossing of the C(4) and C(2) resonances in going from  $\text{CDCl}_3$  to  $\text{D}_2\text{SO}_4$ . The assignment follows from partial decoupling experiments and is based on the established H-C(4) and H-C(2) proton chemical shifts. Moreover an analogous low-frequency shift of C(2) has been found in the  $\text{D}_2\text{SO}_4$  spectrum of the *para*-dienone **17** (see 2.1.2). The different behaviour of C(2) may be rationalized if one assumes that the chemical shift of this carbon in the neutral molecule is predominantly affected *via* inductive deshielding by the neighbouring positively charged carbonyl carbon. Probably this effect has a minor contribution to the chemical shift of C(2) in the protonated species where the positive charge is more effectively delocalized.

In our investigation we have also measured the three open-chain linear-conjugated dienones **14**, **15** and **16** (table 3).

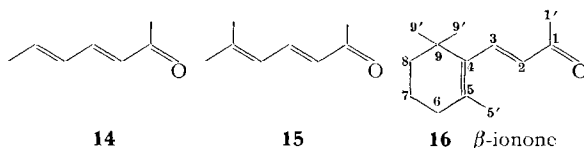


Table 3.  $^{13}\text{C}$  chemical shifts  $\delta$ [ppm] of open-chain linear-conjugated dienones

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(1')	C(5')	C(9')	Ref.
<b>14</b>	197.7	128.3	143.3	130.0	139.7	18.3				26.7			[23]
<b>15</b>	198.5	128.0	139.4	124.1	147.5	26.6				27.4	19.0		[24]
<b>16</b>	197.9	131.3	142.7	135.6	135.6	33.3	18.7	39.6	33.9	27.0	21.5	28.6	

The chemical shifts obtained for  $\beta$ -ionone are within experimental error the same as those reported by *Roberts et al.* [11]. However, the assignments of C(2) and C(3) given by these authors must be exchanged. The same applies for the corresponding resonances in  $\alpha$ -ionone. Our assignment with C(3) at higher frequency is based upon partial off-resonance decoupling making use of the established assignment of H-C(3) at higher frequency than H-C(2) in the proton spectrum.

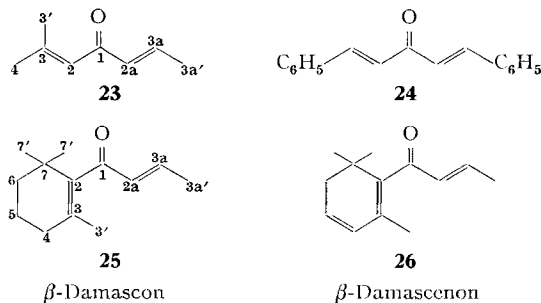
The carbonyl chemical shift of the open-chain dienones lies in the range of  $\alpha,\beta$ -unsaturated methyl ketones and is not affected by the second double bond. The extension of conjugation is only perceptible in the smaller chemical shift difference between C(2) and C(3). The identical shifts of C(4) and C(5) in  $\beta$ -ionone are in agreement with the known fact that the two carbon-carbon double bonds cannot form a completely coplanar dienone system because of steric hindrance [12].

**2.1.2. Cross-conjugated ketones.** – The C=O, C( $\alpha$ ) and C( $\beta$ ) chemical shifts of 2,6-dimethylhepta-2,5-dien-4-one (phorone) and 6-isopropylidene-3-methylcyclohex-2-en-1-one (piperitenone) have been reported [2b]. Recently a complete analysis of the four stereoisomers of santonin has been published [13].

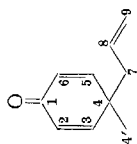
The *para*-cyclohexadienones (**17**, **18**, **21**, **22**) exhibit a carbonyl resonance at  $185 \pm 1$  ppm. This value is 14 ppm lower than for cyclohexenone and 27 ppm lower than for cyclohexanone. Thus the introduction of a second double bond into  $\alpha,\beta$ -unsaturated ketones leading to cross-conjugated dienones doubles the deshielding effect of the first double bond, whereas linear conjugation leading to  $\alpha,\beta,\gamma,\delta$ -unsaturated ketones reduces the effect of the first double bond. The two types of olefinic ring carbons are observed at  $129 \pm 2$  ppm (C(2) and C(6)) and  $152 \pm 5$  ppm (C(3) and C(5)). The chiral dienone **22** yields four signals for the two pairs of diastereotopic dienone carbons C(2), C(6) and C(3), C(5) respectively. The diastereotopic effect decreases with increasing distance from the chiral centre,  $\Delta\delta_{C(5)}^{C(3)} > \Delta\delta_{C(6)}^{C(2)}$ . A comparison of the spectra of **17** and **18** shows a shielding of all carbons  $\beta$  to  $\text{CHCl}_2$  and a deshielding of C(4) in **17** (see 2.1.1).

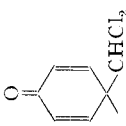
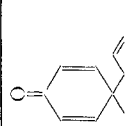
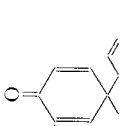
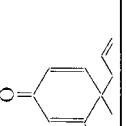
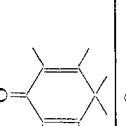
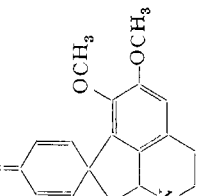
It follows from the spectra of **19** and **20** that the C=O resonance is shifted to higher frequency by fluorine substitution on C(3) (187.9 ppm, **20**) and to lower frequency in a 2-fluorodienone (178.3 ppm, **19**). The carbon atom directly attached to fluorine shows a large high-frequency shift, whereas the olefinic carbon  $\beta$  to fluorine is shifted to lower frequency. The first shift can be explained by the  $-I$  effect and the second one by the  $+M$  effect of the fluorine atom. Chemical shift data of *para*-cyclohexadienones are given in table 4.

Protonation of the *para*-cyclohexadienone **17** causes analogous effects on the chemical shifts as described for the protonated *ortho*-cyclohexadienone **1**. The observed relative chemical shifts  $\delta_{\text{D}_2\text{SO}_4} - \delta_{\text{CDCl}_3}$  are +8.3 ppm for C(1), +27.4 ppm for C(3) and C(5), +9.2 ppm for C(4) and  $-5.0$  ppm for C(2) and C(6). The C(4') and  $\text{CHCl}_2$  resonances are shifted by  $-1.2$  ppm and  $-3.0$  ppm respectively.



Four open-chain cross-conjugated ketones **23–26** have been investigated. The chemical shifts of this series are summarized in table 5. Since the chemical shifts of the olefinic carbons in the cyclic and acyclic series are strongly influenced by substituent effects the discussion is restricted to the carbonyl frequencies. Whereas the carbonyl resonance in *para*-cyclohexadienones is observed at  $185 \pm 1$  ppm (**17**, **18**, **21**, **22**), the corresponding value for **23**, **24** and phorone is  $189 \pm 1$  ppm. Although data are limited the high-frequency shift of the C=O resonance may reflect the conformational change at the C(1)–C(2) bond from *s-trans* in cyclohexadienones to *s-cis* in the acyclic series. The carbonyl frequency of **25** and **26** ( $201 \pm 1$  ppm) is close to the value of  $\alpha,\beta$ -unsaturated ketones supporting the accepted non-planarity of the C=O and C(2)–C(3) double bonds in these compounds [12].

Table 4. <sup>13</sup>C chemical shifts δ [ppm] of cyclic cross-conjugated dienones

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(2')	C(3')	C(4')	Ref.
	184.4	130.6	148.4	48.1	148.4	130.6	76.6 <sup>a)</sup>					22.7	[25]
<b>17</b>													
	185.7	128.4	155.0	41.5	155.0	128.4	48.4	132.3	118.5			25.0	[1b]
<b>18</b>													
	178.3	152.1	129.8	42.9	155.6	127.8	44.6	131.7	119.2			25.1	[1b]
<b>19</b>													
	187.9	109.7	180.0	43.3	150.0	128.0	41.7	131.2	119.2			22.9	[1b]
<b>20</b>													
	184.7	129.6	157.1	42.3	157.1	129.6				11.6	16.5	24.3	[26]
<b>21</b>													
	185.8	127.3 or 128.1	153.3 or 149.8	51.2	153.3 or 149.8	127.3 or 128.1							[27]
<b>22</b>													

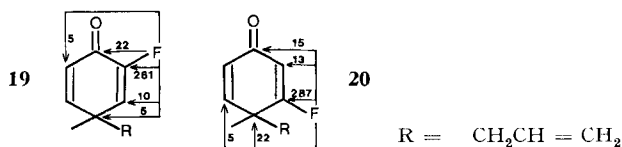
<sup>a)</sup> δ(CHCl<sub>2</sub>)

Table 5.  $^{13}\text{C}$  chemical shifts  $\delta$ [ppm] of open-chain cross-conjugated dienones

	C(1)	C(2)	C(2a)	C(3)	C(3a)	C(4)	C(5)	C(6)	C(7)	C(7')	C(3')	C(3a')	C(7')	Ref.
<b>23</b>	189.8	122.5	133.3	154.9	141.1	27.5					17.9	20.6		
<b>24</b>	188.4	125.2	125.2	142.9	142.9									
<b>25</b>	201.9	130.3	134.6	140.2	145.5	31.2	19.0	38.0	33.4	18.3	21.3	28.8		[29]
														[29]
<b>26</b>	200.6	127.9	134.4	139.2	145.8	127.1	127.9	39.4	33.8	18.3	19.4	26.3		[30]

2.2. *Coupling constants.* – Quantitative information about carbon-proton spin coupling can only be obtained from non-decoupled spectra. Such spectra were recorded for a limited number of compounds when sufficient material was available. The data will be discussed in terms of one-bond ( $^1J_{\text{CH}}$ ), two-bond ( $^2J_{\text{CH}}$ ) and three-bond ( $^3J_{\text{CH}}$ ) coupling.  $^1J_{\text{CH}}$  values are found in the range of 154 to 170 Hz. A correlation between  $^1J_{\text{CH}}$  and the chemical shift of the respective carbon atom is not apparent. All C–H coupling constants across more than one bond are smaller than 11 Hz and are responsible for the observed fine structure of the non-decoupled spectra (Fig. 1c, 2c, 3c). The well-resolved doublet fine structure in the C(2)-, C(3)- and C(4) signals of **1** (fig. 1c) may be interpreted in terms of geminal  $^2J_{\text{CH}}$  or vicinal  $^3J_{\text{CH}}$  coupling. In several cases (4-oxo-3,4-dihydropyrimidines [14a] and 2,4-dioxo-1,2,3,4-tetrahydropyrimidines [14b]) it has been observed that transoid vicinal coupling in  $-\text{HC}=\text{CH}-\text{CH}=\text{}$  systems is larger than geminal coupling. Therefore we prefer the following assignment for the splittings in the spectrum of **1** mentioned above:  $J_{2,\text{H}(4)} = 6$  Hz,  $J_{3,\text{H}(5)} = 10$  Hz,  $J_{4,\text{H}(2)} = 9$  Hz and  $J_{5,\text{H}(3)} = 8-9$  Hz. Additional long-range coupling constants are discernible in the C(3) and C(5) signals. Applying the same concept to the non-decoupled spectrum of **18** (Fig. 3c) the triplet fine structure of the carbonyl resonance results from transoid vicinal coupling with the two protons at C(3) and C(5). Further double resonance experiments are required to decide between vicinal and geminal carbon-proton coupling in each case. Cisoid  $^3J_{\text{CH}}$  coupling constants of 3–6 Hz are observed in the methylresonances of the trimethyl-*ortho*-dienone **10** and were used for the assignment of  $\text{CH}_3-\text{C}(2)$  and  $\text{CH}_3-\text{C}(4)$  (Fig. 2c).

A number of different C, F long-range couplings has been resolved in the spectra of two fluoro-substituted *para*-dienones **19** and **20**. The two formulae illustrate these interactions and give values for the C, F coupling constants in Hz.



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**3. Experimental Part.** - The majority of the compounds studied has been described in the literature and the respective references are given in the last column of Tables 1, 3, 4 and 5. All compounds gave correct proton spectra. The carbon spectra were measured in deuteriochloroform solution with tetramethylsilane as an internal reference. Typical concentrations were 50-100 mg/ml.

A Varian XL-100-15 spectrometer was used equipped with a pulse unit and a 620i-8k on-line computer system. Sample tubes of 12 mm diameter required a typical sample volume of 2 ml. The deuterium resonance of the solvent was used as an internal field-frequency lock signal. The probe temperature under condition of proton high-power decoupling was about 32°. Typical parameters for the pulse-experiments were as follows: spectral width 5500 (5000) Hz, acquisition time 0.3 (0.4) sec, pulse width 20 to 25  $\mu$ sec, pulse delay 0.2 sec. Under these conditions carbon chemical shift data may be reproduced within  $\pm 0.3$  ppm and carbon-proton coupling constants obtained from expanded spectra with an accuracy of  $\pm 1-2$  Hz.

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