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# NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF METAL CYCLOPENTADIENYLS
## I. PMR SPECTRA OF METHYLDICHLOROSILYLCYCLOPENTADIENE

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## SUMMARY

The PMR spectra of methyldichlorosilylcyclopentadiene show the presence of all three isomeric forms equilibrated through a prototropic rearrangement. The saturation transfer technique applied to the 5-isomer demonstrates this to undergo a fast metallotropic rearrangement. The signals are assigned to isomers or nuclei by double resonance. The spectrum of the main vinylic isomer has been analysed completely including the signs of the constants. With the assumption that $^3J(HH) > 0$ and $^4J(HH) < 0$, this isomer is shown to be 1-methyldichlorosilylcyclopentadiene. The spectrum of 2-methyldichlorosilylcyclopentadiene present at a concentration not greater than 5% has been partially analysed.

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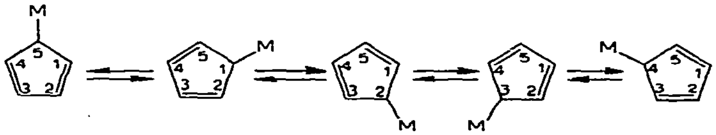
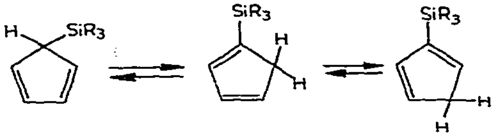
Dynamic molecular phenomena are a challenging problem of modern organic chemistry. This is especially true with stereochemically non-rigid molecules[1] capable of degenerated intramolecular rearrangements. Such rearrangements isomerize a molecule to the initial one, the activation energy being never in excess of 15 kcal·mole$^{-1}$. This is characteristic of certain hydrocarbons (homotropilidene, bullvalene[2], etc.) or arenonium[3], carbonium, and arylcarbonium ions[4]. These rearrangements often occur also in organometallic compounds containing an alkenyl (allyl[5], cyclopentadienyl[6], indenyl[7]) group, or with organometallic π-complexes (complexes of cyclooctatetraene[1], π-benzyl compounds). An understanding of such rearrangements, will give a better insight into the nature of chemical bonds.

Cyclopentadienyl compounds are convenient models for the phenomenon discussed. π-Cyclopentadienyl compounds of Si, Ge[6], Sn[6,9], Fe[10], Cr[11], Mo[12], Hg[13] and Cu[14] are known to undergo fast metallotropic rearrangements.



Earlier, we have stated that cyclopentadienyl compounds can enter a competing process; the prototropic rearrangement characteristic of cyclopentadiene[15] and alkylated cyclopentadienes[16]. An investigation of the compound $C_5H_5Si(CH_3)_3$ showed[17] that the rearrangement did occur but was much slower than the metal migration.



Degenerated intramolecular rearrangements are studied mainly by the nuclear magnetic resonance technique because the processes are characterized by rates readily adjustable to the NMR scale of time. In general, however, dynamic processes are rather difficult to analyse by NMR because indirect spin–spin coupling must be taken into account together with the many-sites exchange problem[18]. Such difficulties are inherent in the study of cyclopentadienyl compounds. A metal can migrate through either a 1,2- or 1,3-shift, or any superposition of the two mechanisms. This is the decisive point in constructing a theory of the phenomenon[19]. Literature data show that this or that migration course may be thought to be the true course depending on the calculation accuracy and, principally, on assignment of the spectrum lines to the nuclei[10,14]. So far, however, PMR spectra of compounds containing a cyclopentadienyl fragment have not been analysed in sufficient detail. We have, therefore, studied a number of $\sigma$-cyclopentadienyl derivatives of Si, Sn, Ge, and Au by PMR, $^{13}C$ NMR, or electronography[20]. In studying the proton resonance spectra we have tried to analyse them as completely as possible by using double resonance and computations. We hope that the results will give reliable criteria for the assignment of the PMR lines or for the determination of the migration types. This paper, which is the first part of a series, analyses the PMR spectrum of methyldichlorosilylcyclopentadiene.

## I. TYPES OF PMR SPECTRA, AND CLASSIFICATION OF METAL CYCLOPENTADIENYLS

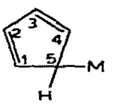
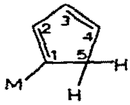
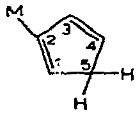
We limit ourselves to compounds containing only one metal atom (element) bonded to the cyclopentadienyl ring which contains no other substituents. We neglect here the effects that can be traced to magnetic isotopes of carbon ($^{13}C$) or other elements ($^{29}Si$, $^{117/119}Sn$, etc.), although these effects might be very helpful in studying the structures or dynamic processes characteristic of the compounds. In other words, we will discuss the spectra possible with the five protons of the cyclopentadienyl fragment.

Earlier data yielded three types of PMR spectra, see Table 1. Future work may reveal new types because the structure of the cyclopentadienyl fragment may decline significantly from the planar one. Non-coplanarity was found recently[20–22] with $\sigma$-cyclopentadienyl compounds of Si, Ge and Sn, but so far, however, it has not been found to affect the PMR spectra.

The classification given in Table 1 concerns stereochemically rigid systems, not those characterized by dynamic effects which could distort the symmetry of the molecule, *e.g.*, migration of a metal in the compound whose spectrum is structured as AA'BB'X will transform this to spectrum $A_5$. In the same system, prototropic rearrangement will give spectrum $AMXY_2$. The exchange in systems characterized by

TABLE 1

TYPES OF PMR SPECTRA OF METAL CYCLOPENTADIENYLS, $C_5H_5$–M

| *Spectrum type* | $A_5$ | AA'BB'X | $AMXY_2$ or $ABCX_2$ |
|---|---|---|---|
| *Structural notation* | <br> |  |  |
| *Symmetry group* | $C_{5v}$ | $C_{2v}$ | $C_s$ (2) |
| *Linguistic notation* | π-complexes,<br>ionic or central σ-bonded | σ-bonded 5-isomers | σ-bonded 1- or 2-isomers |
| *Examples* | $Fe(C_5H_5)_2$<br>Ferrocene<br>$(C_5H_5)_2Sn$<br>$C_5H_5Na$ | $C_5H_5Ge(CH_3)_3$ | $C_5H_5Si(CH_3)_3$ |

indirect spin–spin coupling was developed with the simplest examples only[18]; hence at intermediate rates of exchange, the problem so far yields only to qualitative analysis of the line shapes[23].

Thus, there are only three spectrum types which reflect the four structure types proposed by Fritz[24] to classify organometallic derivatives of cyclopentadiene: ionic compounds, compounds containing a central-symmetric σ-bond, normal σ-compounds, and π-complexes. The Fritz classification is rather arbitrary because there are many compounds which cannot be definitely ascribed to any of these classes. Therefore, chemical shifts of protons of the cyclopentadienyl nucleus are not characteristic and Table 1 suggests that σ-compounds can only be discerned by PMR spectra if their metallotropic rearrangement is sufficiently slow. Other types of the compounds give, as a rule, spectra $A_5$, so that further evidence is needed to confirm their structure (analysis of $^{13}C$ satellites, analysis of $^{13}C$ chemical shifts, or of the nature of $^1H$ chemical shift). These data will be discussed in other papers of this series.

## II. EXPERIMENTAL

Methyldichlorosilylcyclopentadiene, $C_5H_5Si(CH_3)Cl_2$, was obtained by a published method[25]. The compound was recorded immediately after a double distillation (b.p. 51° at 10 mm) in an argon atmosphere. (Found: C, 40.78; H, 4.57; Si, 15.57; Cl, 39.08. Calcd.: C, 40.20; H, 4.47; Si, 15.69; Cl, 39.64%.)

The spectra were measured on a C6OHL spectrometer (JEOL), operating frequency 60 Mc, maximal resolution 0.2 cps. Slow passage used internal lock. Line frequencies were measured by a JNM-SD-30 counter, accuracy ±0.1 cps. The double resonance experiments used external lock if spin decoupling was applied. The tickling experiments used internal lock. Frequency sweep was always used with the double resonance. The frequency was set by a JNM-SD-30 spin decoupler, accuracy ±0.1 cps. The triple resonance used a frequency generator (4 kc/sec) fitted to the C6OHL spectrometer. This paper discusses the spectra obtained at room temperature. Chemical shifts were measured from a TMS internal reference.

## III. SINGLE RESONANCE SPECTRA

Figure 1 shows the spectrum of a neat compound, $C_5H_5(CH_3)Cl_2$, at room temperature. Qualitative assignment of the signals was carried out by means of published data[6,17]. The spectrum shows all the three isomers (I, II and III) possible in methyldichlorosilylcyclopentadiene.

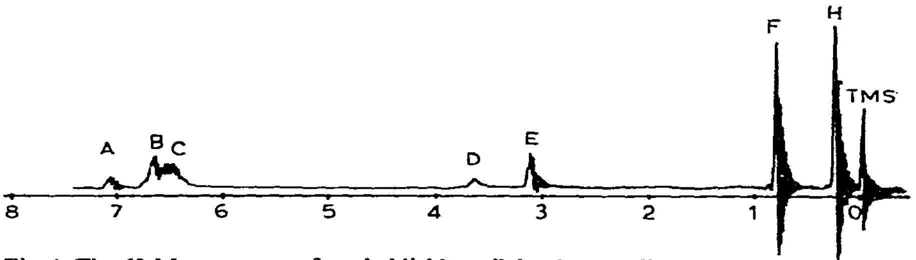
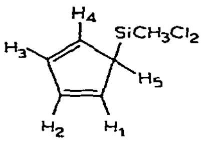
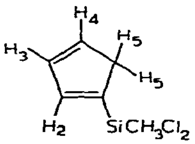


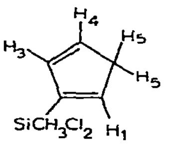
Fig. 1. The 60 Mc spectrum of methyldichlorosilylcyclopentadiene.



(I)



(II)



(III)

The farthest upfield signal (H) relates to the methyl group of isomer (I) (0.27 ppm); the signals (F) of the methyl groups of isomers (II) and (III) which coincide as to their chemical shifts are located downfield (0.82 ppm, *cf.* ref. 17). When $C_5H_5Si(CH_3)Cl_2$ is dissolved in benzene (concentration about 5%) the signals are resolved, the difference being about 0.05 ppm (the signal of isomer (III) is located downfield). Figure 2 gives the fragments of the $C_5H_5Si(CH_3)Cl_2$ spectrum recorded in detail. The $CH_2$ signal of isomer (III) (signal E′, 3.02 ppm) and the $CH_2$ signal of isomer (II) (signal E, 3.13 ppm) are located within 3.0 to 3.2 ppm. The signal of proton $H_5$ of isomer (I) (signal D, 3.65 ppm) is rather broadened thus indicating a metallotropic rearrangement of the isomer at room temperature. The downfield region (6.5–6.8 ppm) contains the signals of protons $H_1$, $H_4$ and $H_2$, $H_3$ (signals B and C) of isomer (I), the signals also being broadened through the exchange*.

The lines are seen against the background of this diffuse signal and relate to protons $H_3$ and $H_4$ of isomer (II). The farthest downfield multiplet (chemical shift 7.09 ppm) is that of proton $H_2$ of isomer (II). A weak signal at 6.94 ppm belongs to proton $H_1$ of isomer (III) (Fig. 2, signal A′). Signals of protons $H_3$ or $H_4$ of this isomer are hidden by stronger lines given by protons of isomers (II) and (III) within 6.5 to 6.8 ppm. The assignment is verified by the integral intensities, the multiple structure, the chemical shifts discussed in view of the results[6,17], and by the double resonance data discussed in detail below (Section IV).

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* Argument in favour of the assignment, and complete analysis of the spectrum of isomer (I) will be reported in Part III of the series.

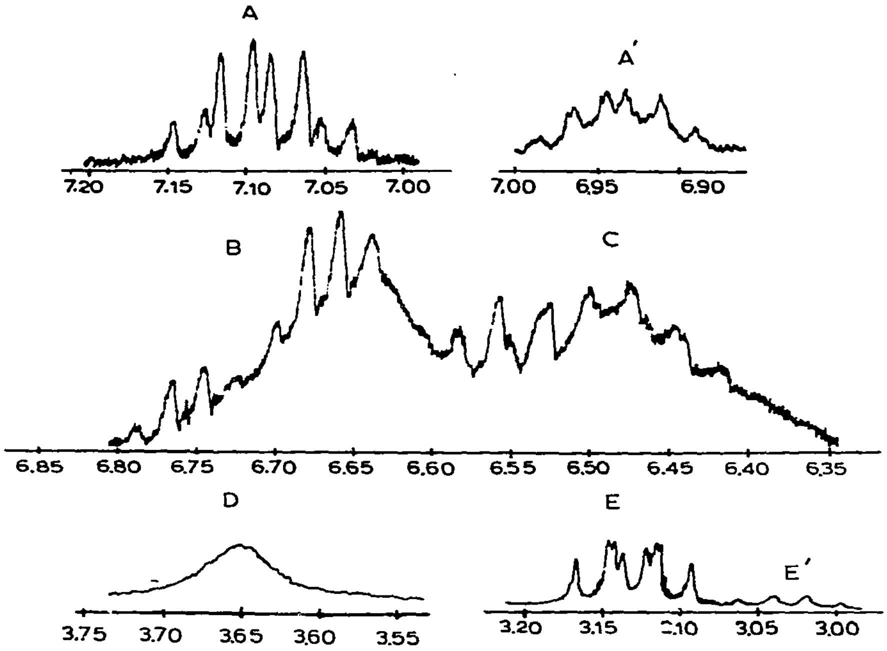

Fig. 2. Fragments of the overall spectrum recorded in detail.

Temperature variation within −30 to 100° seriously affects the shapes of the signals given by the ring protons of isomer (I) while those given by the protons of other isomers remain unaffected. The data above show that $C_5H_5Si(CH_3)Cl_2$ undergoes two dynamic processes: a fast metallotropic rearrangement in isomer (I), and a slow prototropic rearrangement occurring between isomers (I), (II), and (III).

Further, we have found* that the system is characterized by a rather complicated equilibrium between monomeric and dimeric modifications of $C_5H_5Si(CH_3)Cl_2$. The equilibrium is reached slowly at room temperature (lifetime $\tau \simeq 10^5$–$10^6$ sec), thus the NMR time scale enables the system to be considered as quasi-stationary. The relative contents of isomers (I), (II) and (III) depend significantly on the pretreatment of the sample. Slow distillation enriches the product in the most volatile isomer, (I). The content of isomer (III) never exceeds 10% of the content of isomer (II), which indicates the 1,2-mechanism of the prototropic rearrangement to be the most favourable as was believed to be the case with cyclopentadiene[15] or alkylated cyclopentadienes[16]. A similar isomer ratio containing vinyl- or allylsilicon groups was observed by us earlier with $C_5H_5Si(CH_3)_3$[17].

## IV. DOUBLE RESONANCE SPECTRA. SATURATION TRANSFER DURING EXCHANGE PROCESSES

The proton magnetic resonance spectrum of the compound under discussion is rather difficult to analyse because certain parts of the spectrum (*e.g.*, within 6.5 to 6.8 ppm, Fig. 2) contain superimposed signals from all three isomers differently participating in the dynamic processes. This problem becomes much simpler when we

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* To be published.

apply the double resonance technique, the simplification being partly due to the saturation transfer effect which is observed at fast enough exchanges[26].

Metallotropic rearrangement may be considered as a dynamic process wherein any ring proton of isomer (I) stands successively at the positions characterized by resonance frequencies $\nu_A$, $\nu_B$, and $\nu_X$ with lifetimes $\tau_M$. When observing resonance signal A its intensity is defined by magnetization $M_{Z_0}^A$. A qualitative theory[26] shows that when signal B or X is completely saturated by the second radio-frequency field, the magnetization created at position $\nu_A$ satisfies the condition:

$$M_Z^A = M_{Z_0}^A \cdot (\tau_M / T_{1_A}) \qquad (1)$$

Quantity $\tau_M$ may be estimated as $10^{-2}$ sec at room temperature, hence the condition $\tau_M \ll T_{1_A}$ is satisfied ($T_1$, the spin-lattice relaxation time, is about 1 sec). Consequently, when we irradiate any signal given by ring protons of isomer (I), the amplitude of the RF field, $H_2$, satisfying

$$\gamma H_2 / 2\pi > 1/\sqrt{T_1 T_2} \qquad (2)$$

then the signals given by other protons of the isomer will disappear entirely (saturation transfer effect).

Figure 3 shows the spectrum within 6.5 to 6.8 ppm obtained when irradiating the centre of signal D. The signals given by protons $H_1$–$H_4$ of isomer (I) are seen to disappear (part AA'BB') through the saturation transfer effect whereby a clear spectrum of protons $H_3$ and $H_4$ of isomer (I) is obtained (part MX of the spectrum of system $AMXY_2$).

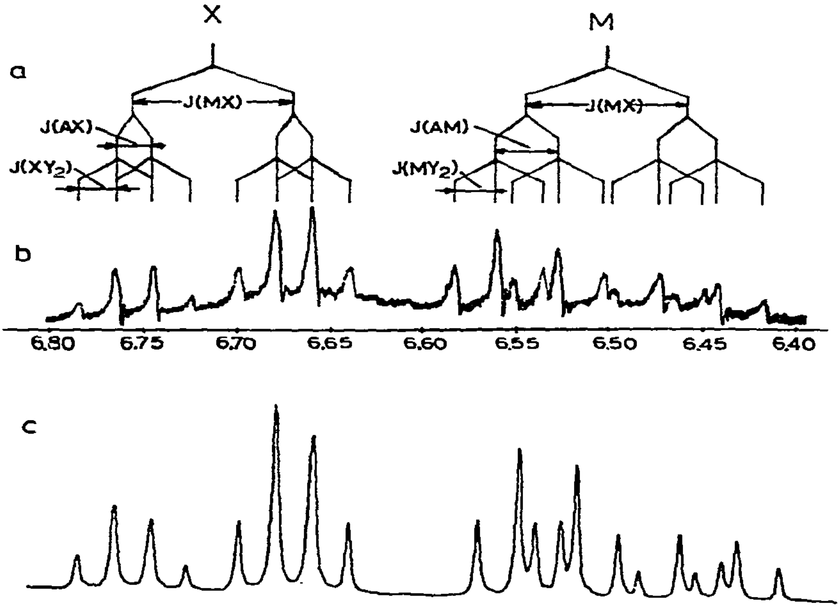

Fig. 3. Olefinic protons X and M of isomer (II), PMR spectrum. (a) Multiplet structure; (b) exptl. spectrum obtained by irradiating signal D of isomer (I) (no background present with signals of isomer (I)); (c) Theoretical spectrum calcd. with the parameters listed in Table 2 (the Lorentz shape of a line is presumed, the width is 0.2 cps at the semi-height).

A pronounced saturation transfer effect occurs not only when irradiating the centre of a line (*e.g.*, line D) but also takes place within the width of the line*. When irradiating the centre of signal D, the RF field has been selected so as to satisfy condition (2); consequently, a significant saturation is observed with signals B and C in part AA'BB' of isomer (I) (Fig. 4 a and b). As the irradiation frequency declines from the centre of the line, the intensities of signals B and C are re-increasing. The shape of signal D shows the dependence of the intensity on the unbalance, (Fig. 4 c and d).

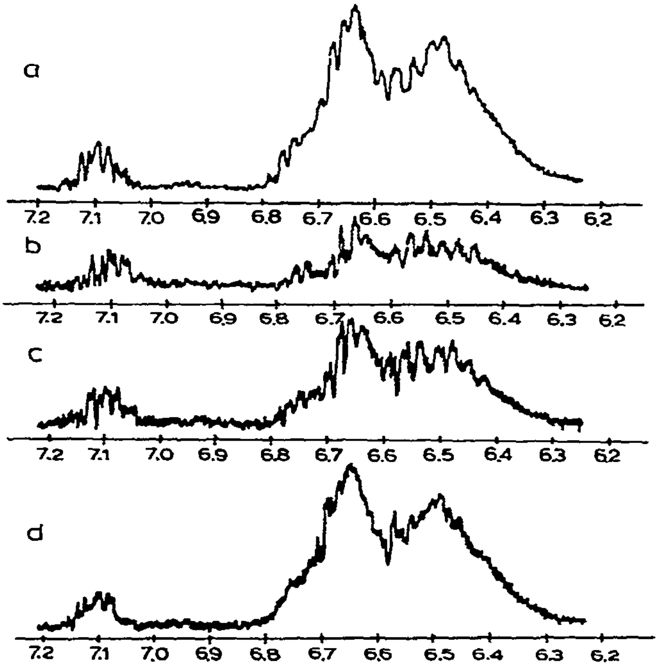

Fig. 4. Saturation transfer in signals of isomer (I). The spectrum of olefinic protons: (a) Single resonance; (b) irradiation frequency, $\nu_2$, coincides with the centre of signal D($\Delta\nu=0$); (c) $\Delta\nu=10$ cps; (d) $\Delta\nu=30$ cps, frequency $\nu_2$ is adjusted to the centre of signal E. RF power always satisfies $\gamma H_2/2\pi > 1/\sqrt{T_1 T_2}$.

Under the same conditions, signal D is suppressed when the other radiofrequency field irradiates resonance signals $\nu_A$ and $\nu_B$ (protons $H_1$, $H_4$ and $H_2$, $H_3$ of isomer (I); Fig. 5c).

The spin decoupling experiments are sometimes accompanied by saturation transfer phenomena, *e.g.*, if we increase the RF amplitude, $H_2$, so that it satisfies the collapse condition[26]

$$\gamma H_2/2\pi > \bar{J} \qquad (3)$$

($\bar{J}$ is a mean measure of multiplicity for a nucleus), and irradiate resonance signal E ($CH_2$ group of isomer (II)), then the spectrum of protons $H_2$, $H_3$, and $H_4$ of isomer (II) transforms to system AMX (Fig. 6a and b) while "the background" of the spectrum given by part AA'BB' of isomer (I) disappears. This does not suggest, however, a

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* The exchange broadening is homogeneous.

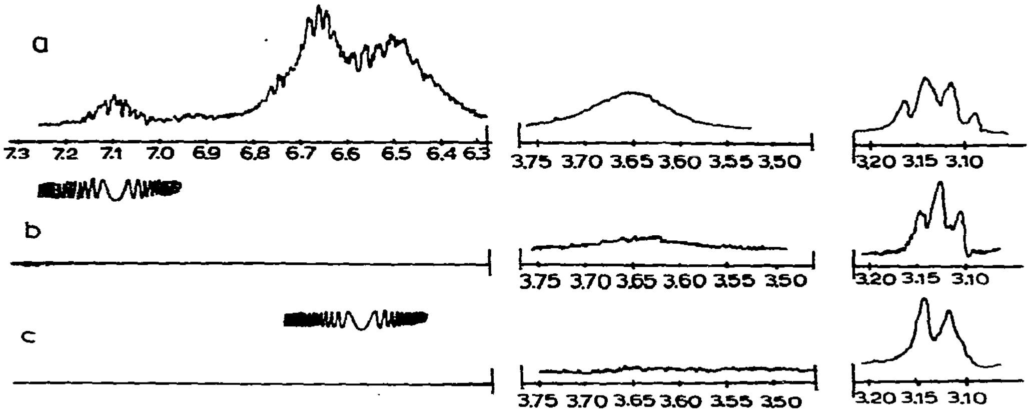

Fig. 5. The spectra of signals D and E obtained by irradiating the olefinic region ($\gamma H_2/2\pi \sim 10$ cps). (a) Single resonance; (b) signal A irradiated; (c) multiplet, B, C irradiated.

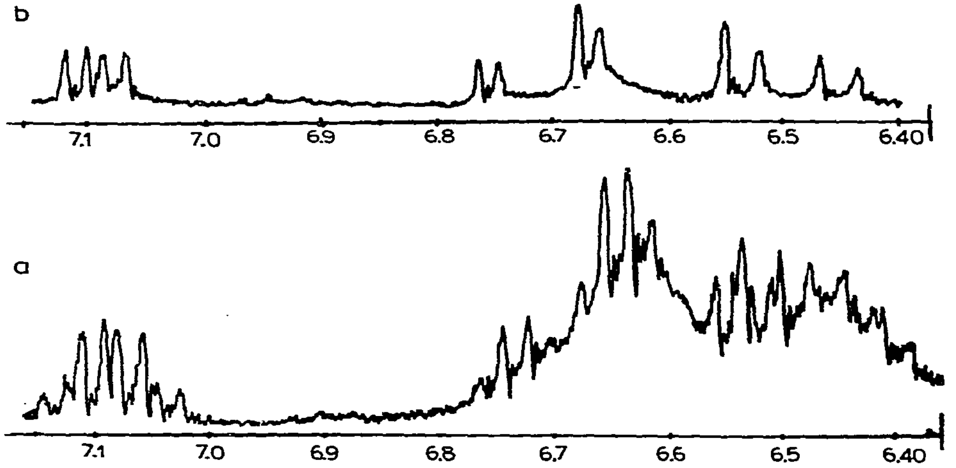

Fig. 6. The spectra of olefinic protons of isomer (II). (a) Single resonance; (b) signal E irradiated.

dynamic process (prototropic rearrangement) which transforms isomer (II) to isomer (I), the characteristic time $\tau_n$ being comparable to time $T_1$. Actually, condition (3) requires so great an RF power that line D positioned 30 cps away from signal E is affected and the saturation transfer effect occurs.

Similarly, when irradiating signal A (proton $H_2$ of isomer (II)) during the spin decoupling experiments, the spectrum becomes simpler (*cf.* the triplet at 3.13 ppm, Fig. 5b) while signal D (proton $H_5$ of isomer (I)) becomes somewhat less intense because the olefinic signals of isomer (I) are affected. Note that no frequency achieves selective decoupling of nuclei $H_3$, $H_4$ (signals M, X) because the difference between the shifts of the nuclei is comparable to the RF power ($\Delta\nu \simeq 10$ cps). When irradiating the centre of multiplet B, C, simultaneous decoupling of the two protons is observed (see Fig. 5c, the doublet given by the $CH_2$ group interacting with proton $H_2$) while signal D disappears entirely (see above) through the saturation transfer effect.

## V. DOUBLE RESONANCE SPECTRA. COMPLETE ANALYSIS OF THE SPECTRUM OF ISOMER (II), SIGNS OF THE CONSTANTS IN SYSTEM $AMXY_2$

The spin decoupling experiments described above interrelated the signals of the protons of isomer (II) and resolved the multiplet structure in detail (Fig. 3a). If resolution is not worse than 0.2 cps, proton $H_3$ (M) or protons of group $CH_2$ ($Y_2$) will give maximal possible numbers of lines, eight or twelve, respectively. Each of the nuclei, $H_2$ or $H_4$ (A or X[*], respectively), gives eight instead of twelve lines because the $J$(HH) constants are close. The analysis of the spectrum of isomer (II) gives the results shown in Table 2. Figure 3 shows the spectrum of part MX calculated with the program YaMR-1 (NMR-1) at an M-20 computer[27].

TABLE 2

METHYLDICHLOROSILYLCYCLOPENTADIENE $C_5H_5Si(CH_3)Cl_2$, ISOMER II. ANALYSIS OF THE PMR SPECTRUM

CHEMICAL SHIFTS[a]

| $\delta$(A) | $\delta$(X) | $\delta$(M) | $\delta(CH_2)$ | $\delta(CH_3)$ |
|---|---|---|---|---|
| 7.09 | 6.72 | 6.52 | 3.13 | 0.82 |

SPIN–SPIN COUPLING CONSTANTS[b]

| $J$(AX) | $J$(AM) | $J$(MX) | $J(AY_2)$ | $J(XY_2)$ | $J(MY_2)$ |
|---|---|---|---|---|---|
| 1.20 | 1.85 | 5.10 | 1.80 | 1.25 | 1.45 |

[a] The shifts are in ppm, $\delta$-scale; accuracy, ±0.01 ppm. [b] The constants are in cps, accuracy, ±0.05 cps.

Let us try to prove that the main vinylic isomer of $C_5H_5Si(CH_3)Cl_2$ which gives the signals whose chemical shifts are listed in Table 2, has structure (II). The constants (Table 2) may be sufficient evidence that protons X and M are located at a double bond because the constant, $J$(MX), is equal to 5.1 cps. Similar constants were reported with indene (5.58 cps[28]), vinyl fulvenes (about 5.2 cps[29]), and with the five-membered heterocycles containing S, N and O atoms[30]. Other constants are not characteristic and are thus useless in assigning the signals. The constants reported do not make it possible to select an unambiguous structure (II or III) for the main vinylic isomer.

To resolve the structure, we can only use relative signs of spin–spin coupling constants. Elleman and Manatt[28] who analysed the spectrum of indene and attempted to do so with cyclopentadiene[**] showed that the constant, $^3J$(HH), characterizing the interaction of $CH_2$ protons with the nearest olefinic proton was positive, whereas that with the farther one, $^4J$(HH), was negative. At the same time, absolute values of the constants are close, about 1.5 cps. The results of Elleman and Manatt were confirmed by many other data reported with the constants of the allyl fragments[32].

First, we have proved that all the constants ($J$(AM), $J$(AX), $J$(MX)) characterizing the coupling of the olefinic protons have the same sign (probably, all are positive).

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[*] The notation A,M,X corresponds to the condition $|J(MX)| > |J(AM)| > |J(AX)|$.

[**] The full analysis of $C_5H_6$ will follow[31].

This is achieved by the triple resonance. Figure 7a shows the double resonance spectrum obtained with system $AMXY_2$ when irradiating $CH_2$ protons. When the signal of proton $H_2$ is irradiated by the third, powerful, RF field, we obtain the spectrum of system MX used to calculate the shifts of nuclei M or X.

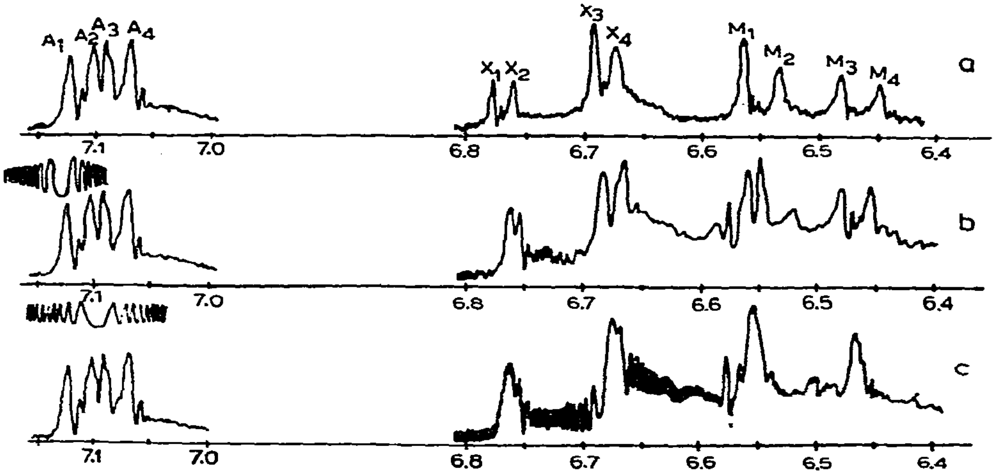
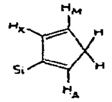
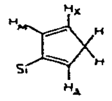
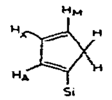
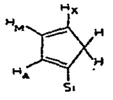


Fig. 7. Triple resonance spectra of olefinic protons M and X. (a) Double resonance, signal E irradiated; (b) the triple resonance tickling, line $A_1$ irradiated simultaneously with spin decoupling of nuclei $CH_2$ (signal E); (c) the triple resonance collapse (spin-decoupling of nuclei $Y_2$ and A).

TABLE 3

SIGNS COMBINATIONS OF THE CONSTANTS POSSIBLE WITH OLEFINIC PROTONS A, M, OR X INTERACTING WITH $CH_2$ PROTONS[a]

| Combination No. | Constants J(HH) | | | Comment |
|---|---|---|---|---|
| | $AY_2$ | $MY_2$ | $XY_2$ | |
| 1 | + | + | + | less probable, because $J(MY_2)$ should be signed oppositely to $J(XY_2)$ |
| 2 | + | + | − | structure (isomer (III)) and assignment shown alongside  |
| 3 | + | − | + | structure (isomer (III)) and assignment shown alongside  |
| 4 | − | + | + | as with array 1 |
| 5 | + | − | − | as with array 1 |
| 6 | − | + | − | structure (isomer (II)) and assignment shown alongside  |
| 7 | − | − | + | structure (isomer (II)) and assignment shown alongside  |
| 8 | − | − | − | as with array 1 |

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[a] Constants $J(AX)$, $J(AM)$, and $J(MX)$ are assumed positive.

To select a sign combination from the four combinations possible in system AMX *a priori*, one has to use the tickling experiment to irradiate one of the four transitions of multiplet A and observe the resonance at nuclei M and X[33]. Thus, the irradiation of line $A_1$ should lead to splitting of lines $X_1$ and $M_1$ (type $\Lambda=0$) and lines $X_2$ and $M_2$ (type $\Lambda=2$) if the sign combination $(+ + +)$ is correct. The experiment (Fig. 7b) verifies this combination. Hence, constants $J$(AM), $J$(AX), and $J$(MX) have actually the same sign. The result is confirmed by the relative signs of the constants found with the five-membered heterocycles containing S, N and O atoms[30].

If we consider all possible combinations of signs of the constants given by olefinic protons interacting with $CH_2$ protons, we have to select from one of the eight combinations ($2^3$). The combinations are listed in Table 3.

Structure (II) requires (Table 3) proof that combination 6 or 7 is correct. The assignment of protons M and X also depends on the selection of one of the two combinations.

Note that parameter $J/\delta$ is 0.4 for protons M and X of the system, which is thus not a weakly bonded spin system. It could be hoped, therefore, that the signs of the constants would have some meaning regarding the positions and intensities of the lines when calculating the various spectra possible with $AMXY_2$. Our calculations have shown, however, that the spectra obtained with various combinations of the signs do not differ much, and the difference cannot be a reliable criterion for the assignment. To overcome this, double resonance (tickling) has been used.

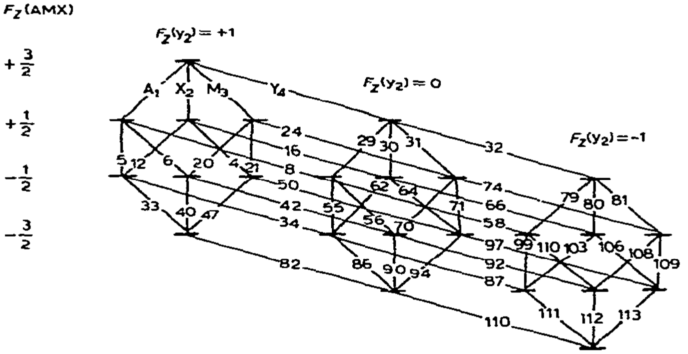

Fig. 8. Diagram of energy levels and transitions for system $AMXY_2$ (sub-system AMX not shown). $F_Z$ is projection of total spin momentum.

Figure 8 shows a diagram of the energy levels and transitions in system $AMXY_2$. Group $Y_2$ is considered as a composite particle having spin $I=1$ (subspectrum AMX is not shown). Figure 9 arranges the lines of spectrum $AMXY_2$ for protons A and $Y_2$ for five combinations (1, 2, 3, 6, 7). Table 3 has already indicated that combinations 1, 4, 5, 8 are less probable because constant $J(MY_2)$ should be of opposite sign to $J(XY_2)$. For the sake of generality, these combinations are also covered by our discussion; one of them, combination 1, is shown in Fig. 9b.

Tickling in a multi-spin system is somewhat complicated, therefore we have limited ourselves to the case when the lines belonging to nuclei A and M are irradiated while the lines positioned in part $Y_2$ of the spectrum are observed. Here, the farthest positioned components of spectrum $Y_2$ are the most reliable, other lines are resolved poorly and their variation is difficult to follow.

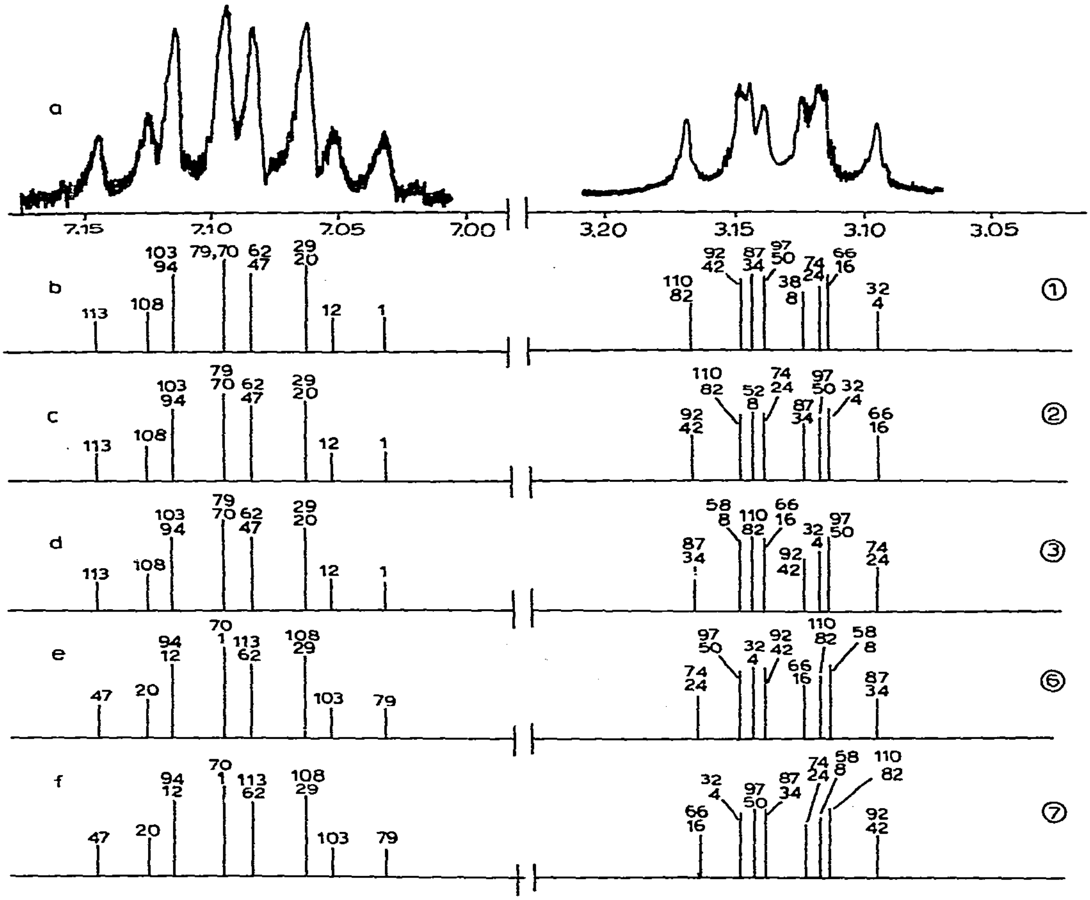

Fig. 9. Signals A and $Y_2$ in spectrum $AMXY_2$. The lines are arranged with five sign combinations of the constants (Table 3).

The tickling experiments are reflected by Fig. 10. When irradiating the first line in the spectrum of nucleus A the far lines are not affected (Fig. 10) therefore combination 1 (this may be shown to be true with combinations 4, 5, 8 also) is ruled out, as expected. Complicated variations shown by the central lines of spectrum $Y_2$ are explained by unsymmetric splitting and by the nuclear Overhauser effect (unsymmetry of the intensities) which always accompanies double resonance. The inverse picture is obtained when irradiating another line ($A_8$) (Fig. 10c). When irradiating the second line $A_2$ (Fig. 10d) tickling of the extreme right line is observed. The splitting must be complicated in nature because tickling affects only one component of the two components of the line. This experiment rules out two other sign combinations, 2 and 6, because these combinations should lead to splitting of the extreme left line in spectrum $Y_2$ (see the diagram, and the line arrangement of these combinations). Finally, to resolve combinations 3 and 7, M-transitions have been irradiated. The pattern requires that the irradiation of line $M_5$ (line 64 in both arrays) lead to splitting of lines 16, 66, 50, and 97. The experiment (Fig. 11e) shows the splitting of the central line and that of the extreme left line in part $Y_2$. This enables combination 3 to be ruled out because this array should not affect the farthest positioned lines. Combination 7 is confirmed also by the irradiation of line $M_2$ (86 in both combinations) as this is not accompanied by splitting of the far lines (Fig. 11d). Combination 7 fixes the constant signs as follows: $J(AX) = +1.20$, $J(AM) = +1.85$, $J(MX) = +5.10$, $J(AY_2) = -1.85$, $J(MY_2) = -1.45$, $J(XY_2) = +1.25$ cps. Constant $^4J(HH)$ is always positive, therefore the vinylic isomer is believed to have structure (II). Also, combination 7 gives the assignment:

$$\delta(Y_2) = \delta(CH_2) = 3.13,\ \delta(H_M) = \delta(H_3) = 6.52,\ \delta(H_X) = \delta(H_4) = 6.75,$$
$$\delta(H_A) = \delta(H_2) = 7.09 \text{ ppm}.$$

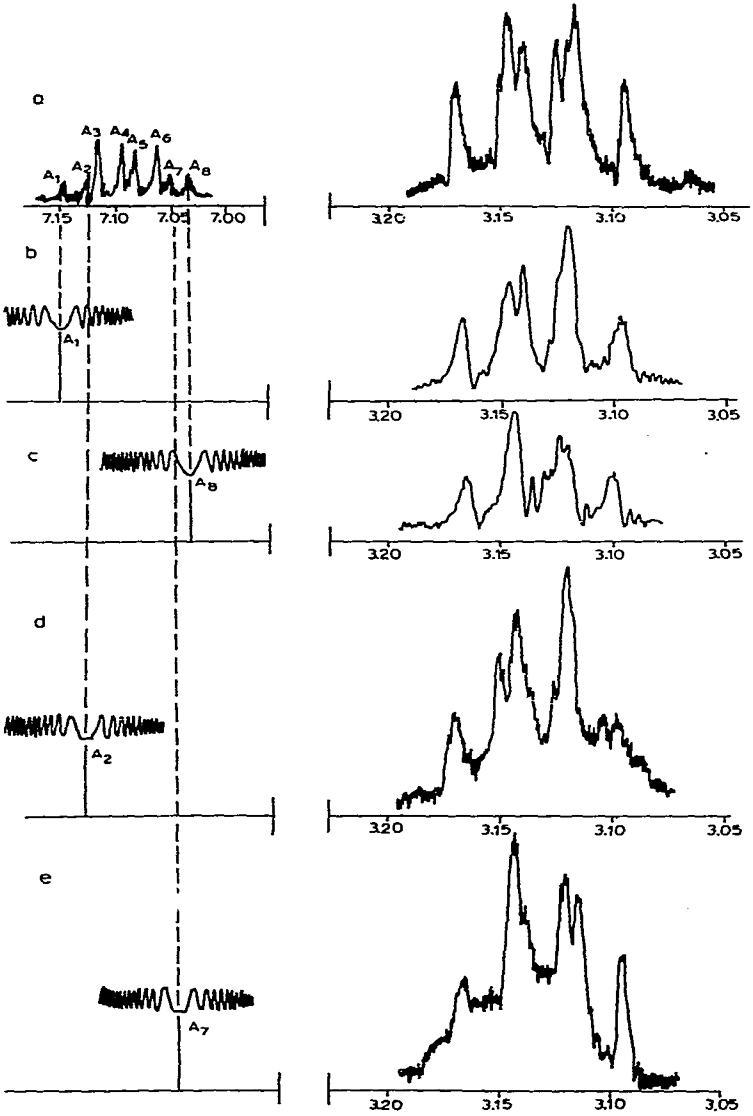

Fig. 10. Tickling experiments in system $AMXY_2$. (a) Single resonance; (b) line $A_1$ irradiated; (c) line $A_8$ irradiated; (d) line $A_2$ irradiated; (e) line $A_7$ irradiated.

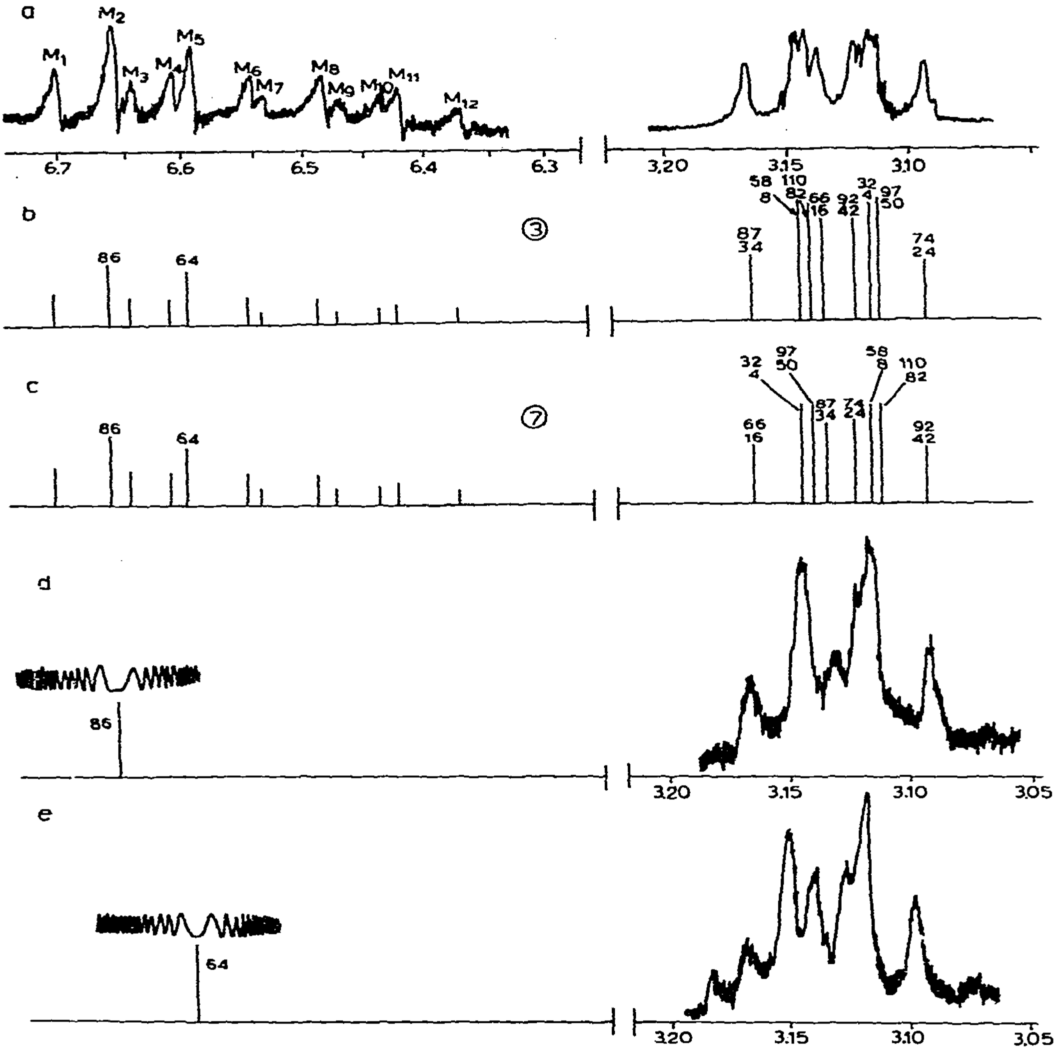

Fig. 11. Tickling experiments with isomer (II). (a) Exptl. spectrum obtained with nucleus M and $CH_2$ protons. (b) Arrangements of certain lines, combination 3; (c) arrangement of certain lines, combination 7; (d) line $M_2$ irradiated; (e) line $M_5$ irradiated.

## VI. ANALYSIS OF THE PMR SPECTRUM OF ISOMER (III)

As the concentration of isomer (III) is not greater than five molar per cent, it could not be analysed in sufficient detail. A reliable assignment is made with the methyl group (0.82 ppm), $CH_2$ group (3.02 ppm), and proton $H_4$ (6.94 ppm). The spin decoupling experiments confirm an interaction of proton $H_4$ with the $CH_2$ group. When irradiating the signal given by protons of the $CH_2$ group (Fig. 12b) the quadruplet is observed with proton $H_1$, which allows the constants characterizing its coupling with two other olefinic protons, $H_3$ and $H_4$, to be determined and the multi-

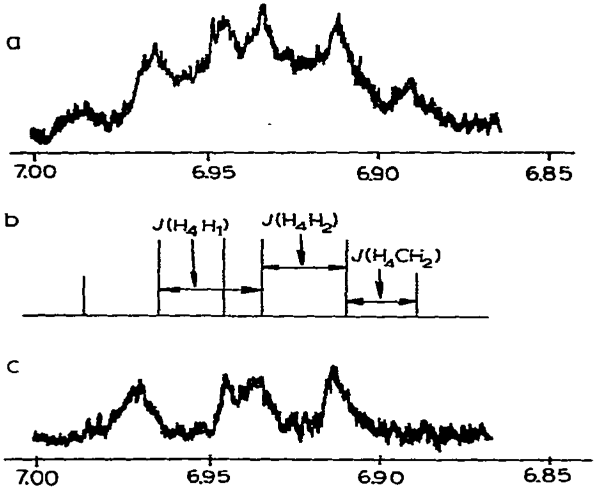

Fig. 12. Double resonance spectra obtained with proton $H_1$ of isomer (III). (a) Single monoresonance; (b) multiplet structure; (c) double resonance spectrum, $CH_2$ signal (E′) irradiated.

plet analysis to be carried out (Fig. 12c). The signals given by protons $H_3$ and $H_4$ of the isomer lie within 6.5 to 6.8 ppm, thus they are obscured by the more intense signals produced by other isomers. The double resonance applied to find the obscured signals of protons $H_3$ and $H_4$, showed only that they are at about 6.5 ppm. The multiplet structure yields the following spin–spin coupling constants for isomer (III): $J(H_1H_4) = 1.9$, $J(H_4H_5) = 1.5$, $J(H_3H_5) = 1.5$, $J(H_1H_5) = 1$, $J(H_1H_3) = 1.2 \pm 0.2$ cps.

The main isomers, (I) and (II), have been analysed reliably with regard to their structures; the remaining isomer, (III), which thus does not need such an analysis has not therefore been studied from the point of view of the relative signs of the constants.

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*Note added in proof*: Recently we have studied vinylic isomers of the series $C_5H_5Si(CH_3)_nCl_{3-n}$ ($n=0$–3), which give similar results (to be published).