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NMR SPECTROSCOPY OF METAL CYCLOPENTADIENYLS VIII*. PROTOTROPISM AND DIMERISATIONS OF SILICON CYCLOPENTADIENYLS

G. I. AVRAMENKO, N. M. SERGEYEV AND YU. A. USTYNYUK
NMR Laboratory, Chemical Department, M. V. Lomonosov State University, Moscow (U.S.S.R.)

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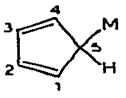
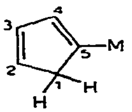
SUMMARY

Studies have been made of the slow dynamic processes which occur with the silicon cyclopentadienyls $C_5H_5Si(CH_3)Cl_2$, such as prototropic rearrangement and dimerisation. The product formed through spontaneous dimerisation has been found to consist almost entirely of the dimer of the main vinylic isomer of $C_5H_5Si(CH_3)Cl_2$. The dimeric structure has been proved by means of PMR spectra (100 MHz). From kinetic studies values of the rate constants at temperatures of 20, 44, 55, and 65° have been obtained and an approximate plot of log k *vs.* $(1/T) \times 10^3$, has enabled the thermodynamic characteristics of the prototropic rearrangement and of the dimerisation to be calculated. The ability of cyclopentadienyl systems to undergo hydrogen migration is discussed and the reactivity of fluxional systems is shown to be governed by the rate of metallotropic rearrangement.

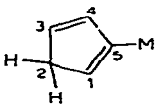
Silicon cyclopentadienyls undergo a number of dynamic processes. Thus, prototropic rearrangement results in the isomers (I), (II), and (III):



(I)



(II)



(III)

where M is $Si(CH_3)_3$, $Si(CH_3)_2Cl$, $Si(CH_3)Cl_2$ and $SiCl_3$. This was mentioned for the first time in ref. 1. Recently, the kinetics and thermodynamics of proton migration in the compound $C_5H_5Si(CH_3)_3$ have been studied[2] while equilibrium constants have been determined as a function of temperature[3] for the isomers (I), (II), and (III).

In addition, isomer (I) (and only this isomer) is subject to a degenerate intramolecular rearrangement which consists of a fast (six to seven orders faster than the prototropic rarrangement) migration of the silicon through a 1,2 shift[4]. The metallotropic rearrangement occurs in derivatives of all the Group IVB elements and in other σ-cyclopentadienyls[5,6].

Finally, silicon cyclopentadienyls dimerise according to a Diels–Alder

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* For Part VII see ref. 24.

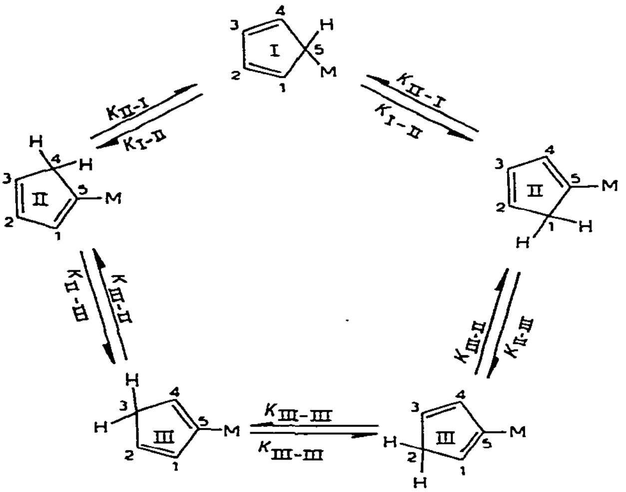
mechanism[7], the rate of dimerisation being comparable with that of the prototropic rearrangement.

Since the rate of metal migration is fast, it may be studied relatively easily by means of NMR techniques (exchange effects over the temperature range −40 to +50°) whereas the slower processes (prototropic rearrangement and dimerisation) are much more difficult to study since the prototropic rearrangement is non-degenerate while dimerisation proceeds via numerous routes*.

The results related to prototropic rearrangement and dimerisation in methyldichlorocyclopentadienylsilane $C_5H_5Si(CH_3)_3Cl_2$ are discussed below.

I. SLOW DYNAMIC PROCESSES IN METHYLDICHLOROCYCLOPENTADIENYLSILANE

PMR spectra of the compound have demonstrated[10] that at room temperature this consists of a mixture of all three isomers (I), (II), and (III) although their relative ratio is somewhat dependent on the conditions of isolation (temperature of distillation). The isomers are equilibrated through a prototropic rearrangement.



Reaction paths corresponding to 1,3 hydrogen shifts have been omitted from this scheme (*e.g.*, k_{I-III}, ref. 10) because intramolecular migration of the proton has been proved experimentally (cyclopentadiene[11]) and demonstrated theoretically[12] to occur via a 1,2 shift. In a similar manner, the 1,2 mechanism was also assumed to apply to methylcyclopentadiene[8,9], methyldichlorocyclopentadienylsilane[10], and trimethylcyclopentadienylsilane[5].

The most appropriate method of measuring the ratio of the isomers (I), (II), and (III), appears to be PMR integration in the methyl region (Fig. 1a). At zero time, methyl singlets [isomer (I), 0.27 ppm; isomers (II) and (III), 0.82 ppm] are observed, and although the methyl signals of (II) or (III) appear to coincide in the initial mixture, they are discernible in dilute solutions of the samples in benzene.

Spectra recorded successively with time for a sample kept at constant temperature in the cavity of the spectrometer (Figs. 1a–d) reveal that two more singlets of

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* Similar difficulties are encountered in the study of alkylated cyclopentadienes[8,9].

equal intensity are built up at about 0.7 ppm. Their intensities increase, while those of the isomers (I), (II), (III) decrease, with time. Simultaneously, the ring proton signals become less intense and new signals appear at 1.4 to 3.9 and 5.8 to 6.5 ppm, as a direct consequence of dimerisation. The signals of equal intensities belong to the dimer D_1 whose $(CH_3)Cl_2Si$ groups are in non-equivalent structural positions; at more extensive conversions methyl signals are also observed for the other dimer (D_2) also of equal intensities but shifted upfield from the signals of D_1 (Fig. 1c). In all cases the relationship $[D_1] \gg [D_2]$ was observed for the overall process, the concentrations differing by a factor of about ten.

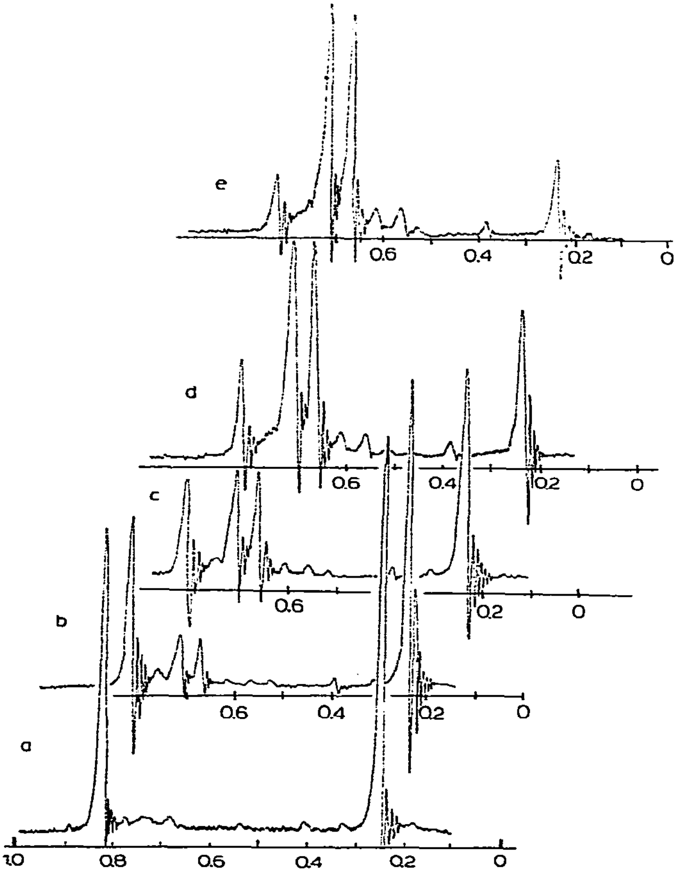
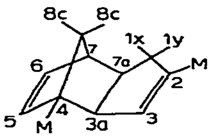
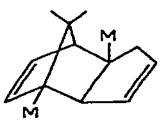


Fig. 1. Methyl region of the PMR spectra of $C_5H_5Si(CH_3)Cl_2$ at 44°, as a function of time: (a), 0; (b), 31; (c), 196; (d), 451; (e), 770 min.

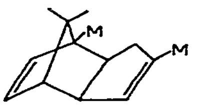
Considering the possible ways in which the $C_5H_5Si(CH_3)Cl_2$ dimerisation may occur, since the cyclopentadienyl derivative is both a diene and a dienophile in its Diels–Alder reaction, nine possible dimers exist, namely (I,I), (II,II), (III,III), (I,II), (II,I), (I,III), (III,I), (II,III), (III,II) where the first symbol in parentheses denotes the diene and the second the dienophile. In addition four space isomers may exist for each of the dimers, for example, for (II,II):



(a)



(b)



(c)

(d)

Thus, if we neglect the *exo* isomers, thirty-six different dimerisation products may be assumed to result from the reaction*.

II. STRUCTURE OF THE MAJOR DIMER, D_1

The equilibrated system contains the isomers (I), (II), (III) together with the dimers D_1 and D_2, D_1 being present as 85% of the total. The resulting spectrum (Fig. 2) is not surprisingly very complicated and difficult to analyse. For this reason the PMR spectra of the cyclopentadiene dimer and of its derivatives were studied individually[14]. The pertinent results essential for the analysis of the D_1 spectrum are presented below.

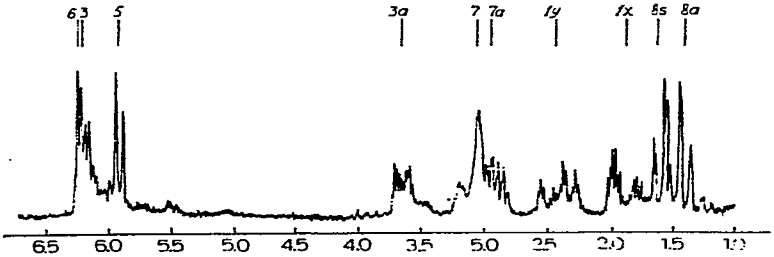


Fig. 2. PMR spectrum (100 MHz) of the product of spontaneous dimerisation of $C_5H_5Si(CH_3)Cl_2$. The structure of the major dimer is shown in the text as structure (a). The proton assignment is listed at the top of the figure.

The spectrum of D_1 (100 MHz) readily displays two pairs of geminal protons: 8s, 8a and 1x, 1y, the shifts being 1.52, 1.40 and 1.89, 2.40 ppm respectively. Thus, all dimers which would contain isomer (I), that is (I,II), (I,I), (II,I), (I,II), (I,III), and (III,I) may be ruled out. The spectrum also contains the signals of the 3a proton (3.64 ppm; the lowest-field signal of all belonging to the protons at the tertiary carbons) and of the 7a proton (2.92 ppm; assigned through its multiplicity). Consequently, the dienophile in the dimer contains the substituent at position 2 (or 3), which corresponds to the isomer (II) (or (III)). On integration three olefinic protons are observed, one of which having been already assigned to the dienophile. Hence, both the protons of the diene are adjacent to the double bond (the protons at the carbons C_5 and C_6), so that the diene is (II). For this reason dimers of type (III,II) and (III,III) can also be ruled out.

When the lowest-field signal (at 6.2 ppm) is irradiated by the second RF field whose power is sufficient to cause spin-decoupling (Fig. 3) a partial collapse of the signals 1x, 1y occurs together with a similar collapse of the signal at 3.10 ppm which

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* Extensive literature data[13] suggest that only the *endo* isomers are formed under the experimental conditions employed. *Exo* isomers are ruled out from the analysis of the NMR spectra, see below.

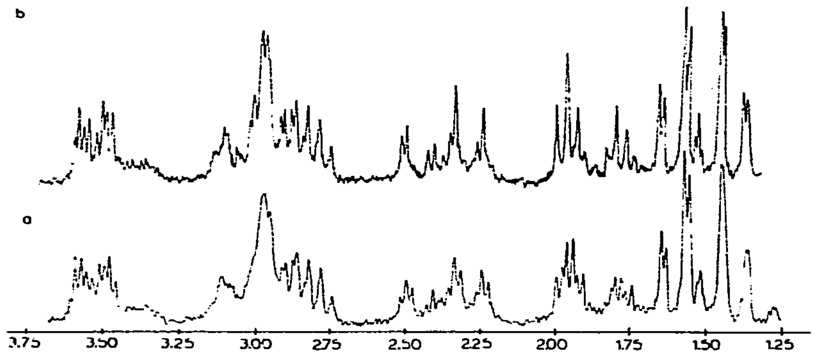
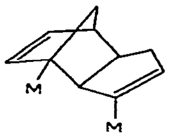


Fig. 3. Dimer of $C_5H_5Si(CH_3)Cl_2$, PMR spectra at 2.50 to 4.00 ppm. (a) using monoresonance methods; (b) with double resonance techniques, the signals at 6.2 ppm being irradiated.

belongs to the proton 4 or 7, and of the 3a signal. Under these circumstances it is now possible to analyze the multiplet structure of the 3a signal. The signal displays no splitting of the order of 3–4 Hz characteristic of the J(3a–4) constant[14]. Consequently, there is no proton 4 in the compound while a substituent is attached to the C_4 carbon. From these results it is possible to state that the structure of the dimer D_1 can be visualized either as (a), type (II,II), or as (e), type (II,III).



(e)

To achieve an unambiguous choice of the correct structure, it is necessary to obtain a complete analysis of the spectrum, including the signs of the constants[14]. In this particular case it is necessary to find the sign of the spin–spin coupling constant characterising the interaction of the proton 3a with the protons adjacent to the double bond (proton 2 or 3, at 6.26 ppm). Due to experimental difficulties, however, this has not yet been achieved. Nevertheless, the following evidence in favour of structure (a) is relevant. At zero time, $[II] \gg [III]$, ref. 7, and hence structure (a) is more probable from the kinetic point of view. Structure (e) would predominate only if the dienophiles (II) and (III) differed in the rates of their reaction with the diene (II) by at least two orders of magnitude ($k^D_{II,III}/k^D_{II,II} \approx 100$). This rate difference appears to be unlikely. What is more likely is that formation of an isomer of type (III,II) would be expected since isomer (III) is known to be a much more reactive diene than (II) in its reaction with maleic anhydride[2] or acetylenedicarboxylic ester[15]. Structure (a) is, in addition, more favourable from the thermodynamic point of view because of its lower strain. For these reasons, therefore, structure (a) appears to be preferable.

The D_2 dimer whose content relative to that of D_1 is ca. 15% has not been analysed structurally. It is possible to suggest, however, that the dimer belongs to the type (III,II) since, as shown in Fig. 2, triplets are observed in the spectral region corresponding to the bridge protons, which may be thus assumed to be situated at positions 4 and 7.

III. SELECTION OF KINETIC SCHEME

The PMR analysis discussed above suggests that the kinetic scheme must include three species *viz.*, the isomers (I) and (II), and the dimer D_1

$$(\mathrm{I}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\mathrm{II}) \xrightarrow{k} \mathrm{D}_1 \qquad (2)$$

A more detailed scheme would include (III), D_2, and the reversible isomerisation.

$$\begin{array}{lll}
(\mathrm{I}) \rightleftharpoons (\mathrm{II}) \rightleftharpoons (\mathrm{III}) & (\mathrm{I}) \rightleftharpoons (\mathrm{II}) \rightleftharpoons (\mathrm{III}) & (\mathrm{I}) \rightleftharpoons (\mathrm{II}) \rightleftharpoons (\mathrm{III}) \\
(\mathrm{II}) + (\mathrm{II}) \rightleftharpoons \mathrm{D}_1 & (\mathrm{II}) + (\mathrm{II}) \rightleftharpoons \mathrm{D}_1 & (\mathrm{II}) + (\mathrm{II}) \rightleftharpoons \mathrm{D}_1 \\
(\mathrm{III}) + (\mathrm{III}) \rightleftharpoons \mathrm{D}_2 & (\mathrm{II}) + (\mathrm{III}) \rightleftharpoons \mathrm{D}_2 & (\mathrm{II}) + (\mathrm{II}) \rightleftharpoons \mathrm{D}_2 \\
(3) & (4) & (5)
\end{array}$$

To unambiguously select the correct scheme, it is necessary that the D_2 spectrum should be analysed in sufficient detail. However, only the methyl groups of the dimer have been assigned unequivocally (Figs. 1 and 2) so that such a selection cannot, as yet, be made. Reversibility of the reaction may be neglected at temperatures below 65° although it is important at higher temperatures. It is also important to remember that since the component concentrations are measured in terms of the magnitude of the methyl signals (Fig. 1), only the total concentrations of (II) and (III) can be measured since the methyl signals for these isomers coincide[7]. This leads to the following scheme

$$(\mathrm{I}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\mathrm{II'}) \xrightarrow{k_2} \mathrm{D} \qquad (6)$$

where $(\mathrm{II'}) = (\mathrm{II}) + (\mathrm{III})$; $\mathrm{D} = \mathrm{D}_1 + \mathrm{D}_2$. It should be emphasized that if the rates of dimerisation are assumed equal for (II) and (III) in scheme (3) or (4) or if the same is assumed for the formation of (II,III) or (III,II), then the actual reaction will be more accurately described by scheme (6) rather than scheme (2). Parallel polymerisations may also confuse the scheme. However, any major errors in the thermodynamic description of the reaction are more likely to arise from the fact that the component concentrations determined by integration are rather approximate (±5%) (see below), since these deviations are noticeably greater than those attributable to an imperfect kinetic scheme.

IV. EXPERIMENTAL

Dimerisation products of $C_5H_5Si(CH_3)Cl_2$ were studied by NMR-spectroscopic methods using Varian HA-100D and JEOL C60HL instruments with 10% solutions in CCl_4. Kinetic studies were undertaken for the neat liquids whose methyl intensities were measured accurately to ±5%. The temperature was controlled with a VT-3 controller accurately to ±1°.

The measurements were carried out at 20, 44, 55, and 65°. Kinetic curves were also obtained for samples with a variable initial content of the isomers (I), (II), and

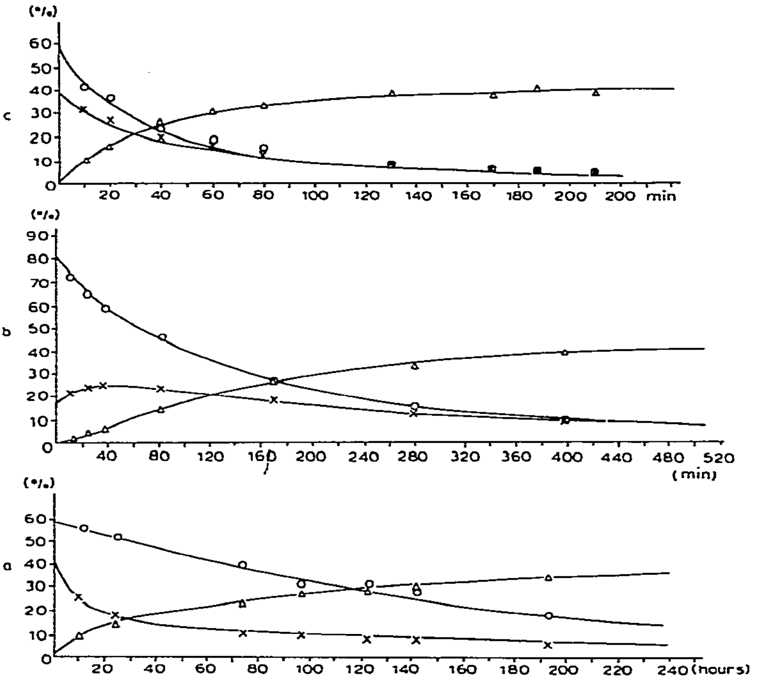


Fig. 4. Kinetic functions (concentration *vs.* time) for the dimer and isomers of $C_5H_5Si(CH_3)Cl_2$, experimental values and theoretical curves at temperature: (a), 20°; (b), 55°; (c), 65°. The notation: ○, concentration of isomer (I); ×, total concentration of vinylic isomers; △, total concentration of dimers.

(III) at 20° and 55°. The experimental curves obtained at 20, 55, and 65° are shown in Fig. 4. The reaction may be described by the series of equations:

$$-\frac{d[I]}{dt} = k_1\cdot[I] - k_{-1}\cdot[II']$$

$$-\frac{d[II']}{dt} = -k_1\cdot[I] + k_{-1}\cdot[II'] + 2k_2\cdot[II']^2$$

$$-\frac{d[D]}{dt} = -k_2\cdot[II']^2$$

An MN-7 analog computer has been used to solve these differential equations, the system being transformed to make it appropriate for the construction of a block-diagram incorporating the diagrams of the functional units and of the problem as a whole. The parameters in the differential equations were varied in order to achieve agreement between the theoretical curves and the transformed experimental data, the final solution being recorded on a two-coordinate recording potentiometer. Unit time scale was used for the integration.

V. RESULTS AND DISCUSSION

The theoretical curves obtained by the above method are shown in Fig. 4

together with the experimental data. The optimal rate constants k_1, k_{-1}, and k_2 are listed in Table 1.

The relation log k_{eff} *vs.* $1/T \times 10^3$*, was used to determine the thermodynamic characteristics of the prototropic rearrangement [(I)→(II) and (II)→(I)] and of the dimerisation [(II)→D] (see Table 2).

TABLE 1

RATE CONSTANTS FOR THE PROTOTROPIC REARRANGEMENT (k_1,k_{-1}) AND DIMERISATION (k_2) OF $C_5H_5Si(CH_3)Cl_2$ AT VARIOUS TEMPERATURES

T(°K)	Rate constants		
	k_1 (sec^{-1})	k_{-1} (sec^{-1})	k_2 (sec^{-1}·mole^{-1})
338	1.36×10^{-3}	1.23×10^{-3}	2.12×10^{-3}
328	1.85×10^{-4}	1.34×10^{-4}	6.04×10^{-4}
317	1.11×10^{-4}	1.24×10^{-4}	3.34×10^{-4}
298	5.89×10^{-6}	1.79×10^{-6}	4.96×10^{-5}

Considering first the effect of substituents in the cyclopentadienyl on the rate of rearrangement, although the data are scarce they enable the detection of a regular effect in the series C_5H_5R where R is CH_3, $Si(CH_3)_3$, $Ge(CH_3)_3$, $Sn(CH_3)_3$. An alkyl (methyl) attached to the ring lowers the activation energy of the rearrangement of (I) to (II) to 22.5 kcal/mole[17] in comparison with a value of 25.2 kcal/mole for C_5H_6**. The final equilibrated mixture of methylcyclopentadienes consists virtually entirely of the latter two isomers in a 1/1 ratio [the content of (I) being at or below 1%]. The value of the equilibrium constant suggests that the inverse process, (II)→(I), possesses an activation energy of about 25 kcal/mole of the same magnitude as that for unsubstituted cyclopentadiene. In the case of $C_5H_5Si(CH_3)Cl_2$, all three isomers are present in the reaction mixture and from Table 2 it may be seen that both the (I)→(II) rearrangement and the inverse process have activation energies of about 25 kcal/mole, as for the cases of C_5H_6 and $C_5H_5CH_3$ noted above. The proportion of the vinylic isomer in the equilibrated mixture gradually increases as it decreases from $n=3$ to 0 in the series $(C_5H_5)Si(CH_3)_nCl_{3-n}$; in other words, the stability of (I) falls with an increase in the total electronegativity of the substituents attached to the silicon. At the same time, the ratio of the vinylic isomers, (II)/(III), is nearly constant and close to 10 in all cases. In contrast, for the corresponding germanium and tin cyclopentadienyls, $C_5H_5Ge(CH_3)_3$ and $C_5H_5Sn(CH_3)_3$, the same equilibrium is shifted completely towards (I). Thus an increase in atomic number in the series C, Si, Ge, Sn leads to an increase in the thermodynamic stability of the (I) isomers which may be linked with an increase in the overlap integrals charácterising the interaction of the π-orbitals

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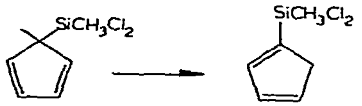
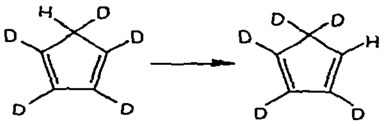
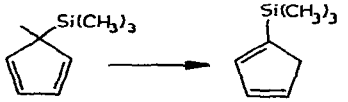
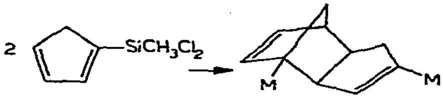
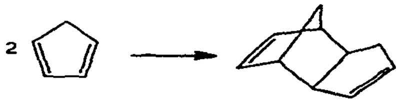
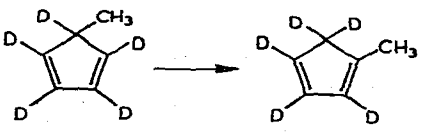
* Statistical corrections were introduced during the calculation of the thermodynamic characteristics, *i.e.*, $k_{1(\text{eff})} = (\frac{1}{2})k_1$ and $k_{-1(\text{eff})} = 2k_{-1}$.

** The data reported were for the migration of deuterium in C_5D_5H[11] rather than of the proton in C_5H_6. The data on the primary kinetic isotopic effect in $CH_3C_5H_5$ demonstrate that the difference $\Delta G_{300}(D) - \Delta G_{300}(H)$ is ca. 1 kcal/mole, hence the activation energy for proton migration in C_5H_6 may be estimated as 24.2 kcal/mole.

TABLE 2

THERMODYNAMIC CHARACTERISTICS FOR THE PROTOTROPIC REARRANGEMENT AND DIMERISATION OF CYCLOPENTADIENYL COMPOUNDS

No.	Process	Parameters				
		E_a (kcal/mole)	$\Delta S^{\neq}$ (e.u.)	log A	ΔG_{300}	References
1		23.7±1	−6.2±4	11.9	25.1	[a]
2		26.8±1	+6.0±4	14.5	25.6	[b]
3		24.3	−5	12.1	25.2	
4		19.9	−10.8	10.9	22.5	[c]
5		26.2	+0.5	13.3	25.5	[d]
6		16.6	−25.3	7.7	24.2	
7		17.3	−31	6.5	26.0	[e]
8		22.35	−6.2	11.9	23.5	

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[a] This paper. [b] Ref. 11. [c] Ref. 17. [d] Ref. 2. [e] Ref. 16, cited from ref. 19.

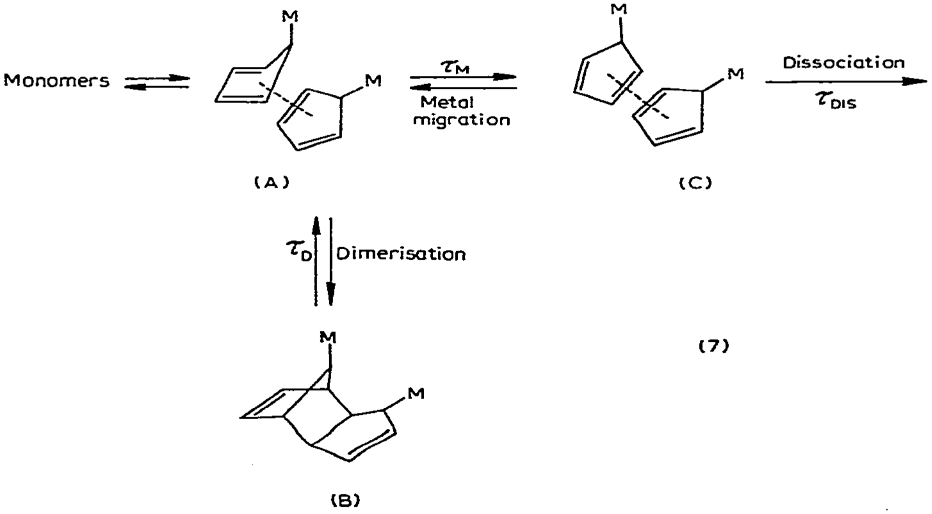
of the carbon ring with the vacant *d* orbitals of the element[18,*]. Consequently, the prototropic equilibration may be assumed to be governed by the free energy of the (I) isomers.

The effect of the substituents at the metal on the hydrogen migration has not been studied in detail. However, data concerning the equilibrium concentrations[4] indicate that the equilibrium is shifted towards (II) and (III) on increasing the number of electronegative substituents. The vinylic isomers (II) and (III) may be expected to be formed with $C_5H_5GeCl_3$.

The kinetic characteristics of the dimerisation of isomer (II) of $C_5H_5Si(CH_3)Cl_2$ are of the same order of magnitude as those for cyclopentadiene[16,19]. The values of the activation energies listed in Table 2 demonstrate that methyldichlorosilylcyclopentadiene dimerises somewhat faster than cyclopentadiene. The dimerisation rate increases with the number of chlorine atoms attached to the silicon. It is noteworthy that isomer (I) apparently does not undergo dimerisation, yet its structure resembles that of norbornene in that the cycle is probably not planar [*cf.* the data for the 1-isomer of $C_5H_5Si(CH_3)_3$[20]], thus favouring dimerisation. Nevertheless, both $C_5H_5Ge(CH_3)_3$ and $C_5H_5Sn(CH_3)_3$ do not dimerise even above 100°.

The decrease in the dimerisation rate of (I) may be explained by assuming that the reaction proceeds via a charge-transfer complex. Such a mechanism was first proposed by Woodward[21]. When considered from this viewpoint it must be assumed that the reaction starts with the formation of the complex (A) [see scheme (7)] in which the molecular geometries are virtually the same as in the free species. The dimer (B) is then formed from this complex. Metallotropic rearrangement is also possible in both molecules which give rise to the complex (A), and for this reason it is also possible to obtain products which result from the dissociation of the complex (C).

On comparing the activation energies of the metallotropic rearrangement, the prototropic rearrangement, and of dimerisation in silicon cyclopentadienyls (see



(7)

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[*] It is interesting that the activation energy for metallotropic rearrangement decreases over the same series C, Si, Ge, Sn[5].

Table 2 and ref. 4), the usual relationship obtained is that

$$\tau_M \ll \tau_H \approx \tau_D$$

where τ_M, τ_H and τ_D are the half lives for metal migration (M), hydrogen migration (H), and dimerisation (D), respectively. The faster the metallotropic rearrangement in complex (A), the more readily does the complex dissociate since $\tau_M \ll \tau_D$. For this reason the fluxional isomers of Si, Ge, Sn cyclopentadienyls, (I), should undergo Diels–Alder reactions less readily than the "rigid" isomers (II) and (III).

Consequently, the assumption that the reactions of the cyclopentadienyl compounds with maleic anhydride are characteristic of all σ-complexes should be accepted only with caution (*cf.* the discussion in refs. 22, 23). The reaction is characteristic only if the reaction half life τ_r satisfies the condition $\tau_r \ll \tau_M$. However, if $\tau_r \gg \tau_M$, no reaction will occur since in this case the cyclopentadienyl derivative has virtually C_{5v} symmetry[24], in other words, it is to all intents and purposes a π complex. By measuring the ratio of the products formed from the reactions possessing different values of τ_r (*i.e.*, reactions with different dienophiles), it should be possible not only to verify the fact that a metallotropic rearrangement does occur but also to estimate the rate.

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