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GAS PHASE ISOMERISATION OF (TRIMETHYLSILYL)CYCLOPENTADIENE

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SUMMARY

(Trimethylsilyl)cyclopentadiene is confirmed to exist as all three possible isomers, and by flow vacuum pyrolysis the proportion of the vinylic 1- and 2-isomers is considerably enhanced.

INTRODUCTION

During recent years much interest has been shown in the dynamic molecular phenomena exhibited by the σ-cyclopentadienyl compounds of the group IVB elements[1–10]. The now characteristic method of investigation of such systems is variable temperature NMR spectroscopy. Variable temperature ^{1}H NMR spectra of the following group IVB cyclopentadienyls have been studied: $Me_3SiC_5H_5$[1], $MeCl_2SiC_5H_5$[8], $Me_3SiC_5H_4Me$[7], $Me_3GeC_5H_5$[7], $Me_3GeC_5H_4Me$[7], $Me_3GeC_5Me_5$[7], $Me_3SnC_5H_5$[7], $Me_3SnC_5H_4Me$[7], $Me_3SnC_5Me_5$[7], and $Me_3PbC_5H_5$[3]. This is due to the ^{1}H NMR time scale being of the same order as the rates of the molecular processes involved (10^1–10^9 sec^{-1}).

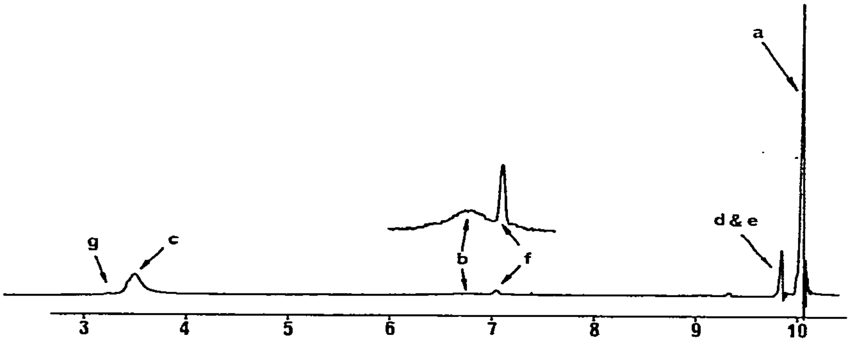
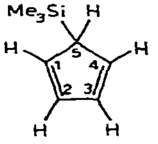
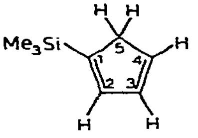


Fig. 1. ^{1}H NMR spectrum of (trimethylsilyl)cyclopentadiene at 30°.

Figure 1 illustrates the characteristic ^{1}H NMR spectrum of (trimethylsilyl)-cyclopentadiene at 30°. Those resonances characteristic of the 5-(trimethylsilyl)-cyclopentadiene (I), are (a) protons of the trimethylsilylgroup, (b) the unique proton



(I)



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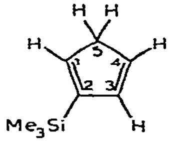
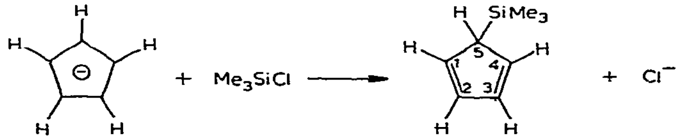


(III)

on the 5-carbon atom and, (c) the 1,2,3, and 4-olefinic protons. With increasing temperature, peaks (b) and (c) broaden further, collapse, and finally merge to form a sharp singlet at about 120° [1]. In this class of group IVB compound the effect has been explained as a temperature dependent 1,5-metallotropic shift[9], which causes ring proton equivalence at elevated temperature.

In addition to the peaks (a), (b) and (c) of the 1-isomer, Fig. 1 shows additional resonances (d), (e), (f), and (g). Although previously considered due to impurities, these resonances are now known to be an inherent feature of (trimethylsilyl)cyclopentadiene spectra[6,10]. The ^{1}H chemical shifts of (d) and (e) are characteristic of trimethylsilyl groups attached to sp^2 carbon atoms[6], and are now recognised to be due to the presence of small amounts of the vinylic isomers 1-(trimethylsilyl)cyclopentadiene (II) and 2-(trimethylsilyl)cyclopentadiene (III)[10]. The ring protons of these two isomers are represented in Fig. 1 by (f) (methylene groups) and (g) [olefinic protons, though these are also partly under (c)].

The synthesis of (trimethylsilyl)cyclopentadiene from the cyclopentadienide anion and trimethylchlorosilane should produce exclusively the 5-isomer.



The metallotropic shift does not provide a subsequent route to the 1- and 2-isomers which must therefore be formed by prototropic shifts[10].

RESULTS

We and others have noted that freshly prepared and distilled samples of (trimethylsilyl)cyclopentadiene are almost exclusively the 5-isomer. On standing, however, the proportion of 1- and 2-isomers increases to a maximum of about 15%.

We find that on flow vacuum pyrolysis (~800°), of (trimethylsilyl)cyclopentadiene we convert the compound to a mixture of 5-, 1- and 2-isomers, in which the vinylic 1- and 2-isomers predominate. It is interesting that in kinetic studies of this reaction at 200°, the 5-isomer still predominates[11].

Fig. 2 (*i*) illustrates the spectrum of the mixture of 5-, 1- and 2-isomers immediately after flow vacuum pyrolysis. The peak labels are equivalent to those of Fig. 1, and the considerable increase in intensity of peaks (d), (e), (f) and (g) are indicative of the now dominating vinylic isomers present. Provided the sample is stored at −80° the proportion of isomers remains unchanged. On standing at room temperature, however, this predominantly 1- and 2-mixture of isomers reverts to mainly the 5-

isomer. This reversion is temperature dependent and is much more rapid at 40° than at 20°.

The NMR spectrum of the mixture is illustrated in Fig. 2 (*ii*), which is seen to be essentially identical to the spectrum of the pre-pyrolysis mixture in Fig. 1.

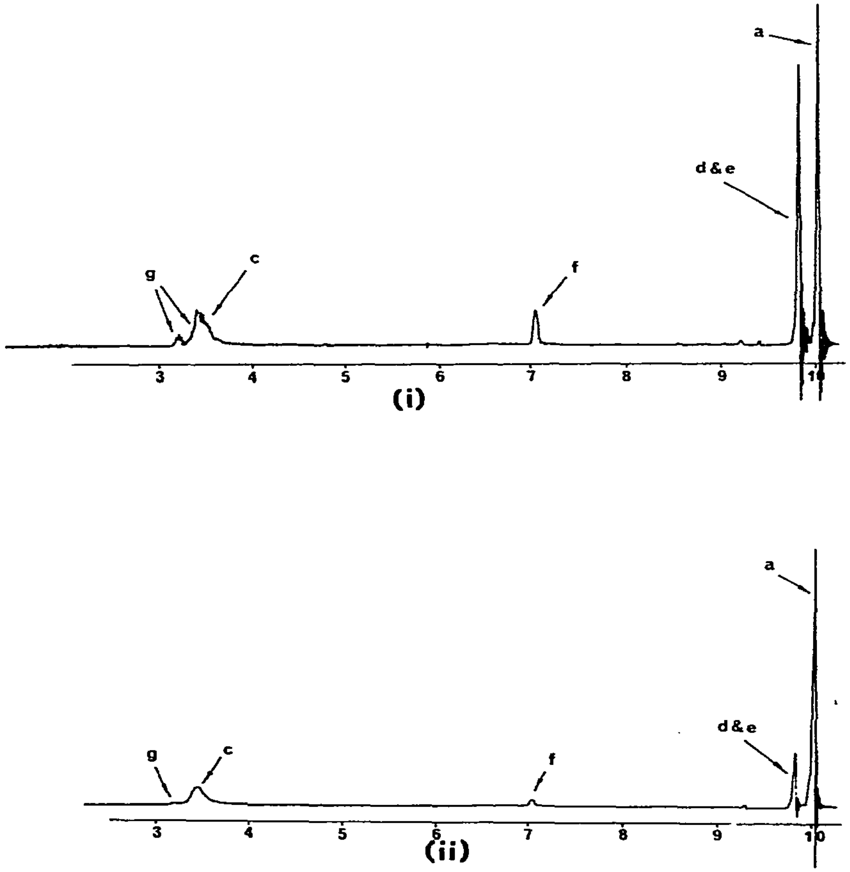


Fig. 2. (*i*): ^{1}H NMR spectrum of the mixture of 5-, 1- and 2-isomers of (trimethylsilyl)cyclopendadiene immediately after flow vacuum pyrolysis. (*ii*): Spectrum after reversion at room temperature to the 5-isomer.

In addition to these changes in the NMR spectra, the relative isomeric concentrations of 5-, 1-, and 2-(trimethylsilyl)cyclopentadiene have a marked effect upon the ultraviolet spectrum of the compound. The absorbances of the initial, largely 5-isomer, is illustrated in Fig. 3 (A). The UV spectrum of the predominantly 1- and 2-substituted isomeric mixture is illustrated in Fig. 3 (B), with λ_{max} shifted by ~5 nm to ~245 nm together with increase of the extinction co-efficient from ~2650 to ~3060. Fig. 4 illustrates the reversion of the predominantly vinylic mixture of isomers to the mainly 5-isomer.

The Diels–Alder reaction of dimethyl acetylenedicarboxylate and (trimethylsilyl)cyclopentadiene has been reported[10,12] and we are substantially in agreement with these results. Freshly prepared 5-(trimethylsilyl)cyclopentadiene adds to form

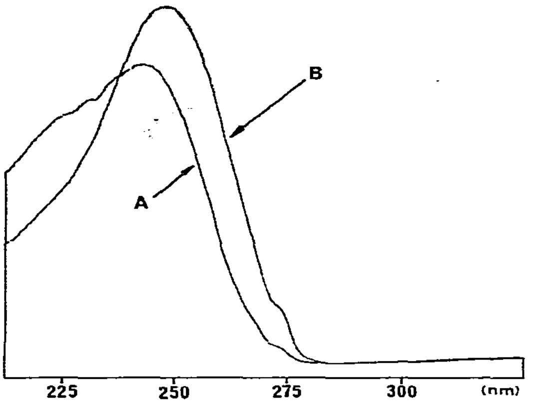


Fig. 3. (A): UV spectrum of predominantly 5-(trimethylsilyl)cyclopentadiene. (B) UV spectrum of predominantly 1- and 2-(trimethylsilyl)cyclopentadiene.

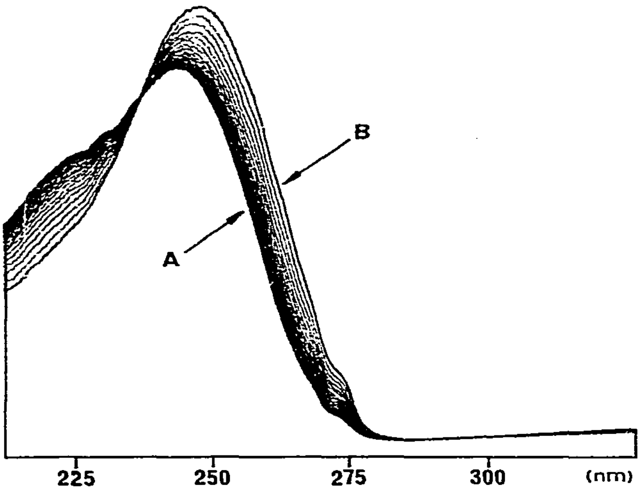
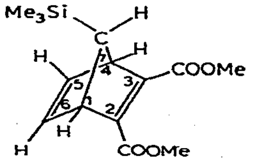
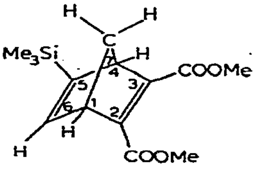


Fig. 4. UV spectrum following the process of reversion from the 1- and 2-(trimethylsilyl)cyclopentadiene (B) to 5-(trimethylsilyl)cyclopentadiene (A) (15 min intervals at 40°).

predominantly the 7-*exo*-(trimethylsilyl)norbornadiene (IV), along with a small amount of the 5-(trimethylsilyl)norbornadiene (V).



(IV)



(V)

The cycloaddition of dimethyl acetylenedicarboxylate and the mixture consisting largely of vinylic isomers, however produces a high yield of the 5-(trimethylsilyl)-

norbornadiene. This must arise by cycloaddition to the 3-(trimethylsilyl)cyclopentadiene. Neither ourselves nor Kraihanzel[12] detected observable quantities of the 4-(trimethylsilyl)norbornadiene. This may be due to the steric hindrance[13] of the trimethylsilyl group in the 2-(trimethylsilyl)cyclopentadiene precursor as the rate of conversion at room temperature of the 2-isomer to the 5-isomer is much faster than the reaction with dimethyl acetylenedicarboxylate. We note, however, that Ashe has observed the 4-(trimethylsilyl)norbornadiene as a minority product[10]

DISCUSSION

Fig. 5 (*i*) illustrates the trimethylsilyl resonances of the room temperature equilibrium mixture of 5-, 1- and 2-(trimethylsilyl)cyclopentadiene. We believe the 5-, 1- and 2-(trimethylsilyl) resonances are respectively (a) (d) and (e). Fig. 5 (*ii*) shows the same resonances in the mixture after cryoquench of the flow vacuum pyrolysate. Notably the high temperature equilibrium mixture has a considerably enhanced

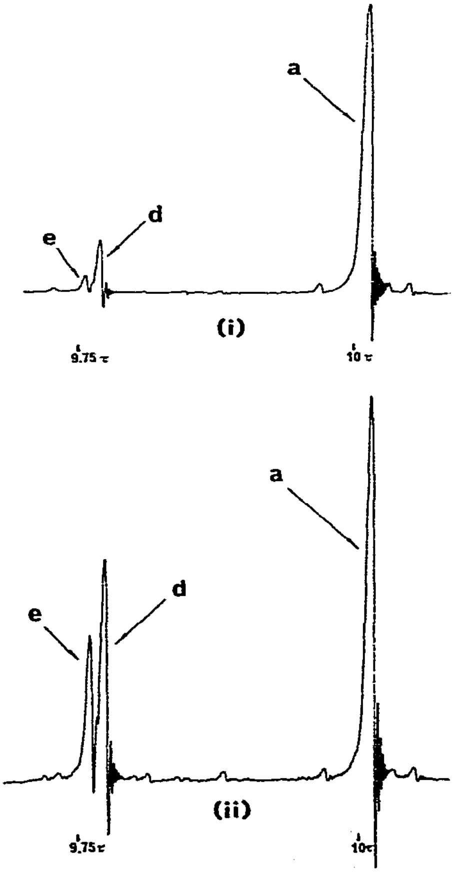


Fig. 5. (*i*): ^{1}H NMR spectrum of predominantly 5-(trimethylsilyl)cyclopentadiene, showing the traces of 1- and 2-isomers at room temperature. (*ii*): Enhancement of the 1- and 2-isomers in the product of flow vacuum pyrolysis.

content of the 1- and 2-vinylic isomers. These may be formed by either 1,2- and/or 1,3-prototropic shifts[11,14,15]. Reversion to the room temperature equilibrium is presumably by a reversal of these prototropic shifts.

The shift in the UV spectrum to longer wavelength of the mixture of vinylic isomers is possibly due to *d*-orbital participation with the double bond of the olefin, but other effects cannot be excluded[16].

CONCLUSION

We would therefore confirm that (trimethylsilyl)cyclopentadiene exists at room temperature as a mixture of 1-, 2- and 5-isomers, and that the rate of interconversion by prototropic shifts, and the composition of the isomeric mixture are both temperature dependent. These prototropic changes in this molecule are taking place in addition to the metallotropic shifts.

In contrast to the simple alkyl substituted cyclopentadienes, where the vinylic isomers are the more stable at ordinary temperatures; the non-vinylic isomer of (trimethylsilyl)cyclopentadiene is the major component at room temperature[17].

EXPERIMENTAL

5-(*Trimethylsilyl*)*cyclopentadiene*

Freshly distilled cyclopentadiene (66 g, 1 mole) cooled at −80° was added dropwise to finely divided sodium sand (24 g, 1 mole) in dry tetrahydrofuran (350 ml). The resulting mixture was stirred for 1 h, then trimethylchlorosilane (109 g, 1 mole) was added over 1 h. After further stirring (1 h), the mixture was hydrolysed with distilled water (250 ml), and the organic layer separated off. The resulting aqueous layer was shaken with two portions (50 ml) of ether, and the combined organic fractions were dried over magnesium sulphate. After filtration, solvent was removed 25°/15 mm, and the residue was distilled to yield 5-(trimethylsilyl)cyclopentadiene (80 g, 60%) b.p. 40°/10 mm, n_D^{20} 1.4612. This material was stored at −80° until required for use. Even at room temperature, however, dimerization of pure $Me_3SiC_5H_5$ is very slow, and only minute traces of dimer are apparent after standing for four weeks.

Flow vacuum pyrolysis was carried out in a quartz tube at 800°/0.01 mm. The furnace was controlled by an Ether 15-98B controller with a NiCr/NiAl thermocouple. The emergent vapour from the pyrolysis impinged upon a liquid nitrogen cooled probe, where it instantly crystallized.

The pyrolysate was removed as a liquid on warming the cold probe, and physical measurements were carried out instantly on these samples.

Diels–Alder reactions

5-(Trimethylsilyl)cyclopentadiene with dimethyl acetylenedicarboxylate. To (trimethylsilyl)cyclopentadiene (3.45 g, 25 mmol) in carbon tetrachloride (10 ml) was added dimethyl acetylenedicarboxylate (3.55 g, 25 mmol) and the mixture stirred at room temperature for 10 h. Distillation produced a product (4 g, 50%) b.p. 104–105°/0.05 mm, which consisted[10] of 2,3-bis(methoxycarbonyl)-7-(trimethylsilyl)bicyclo[2.2.1]heptadiene (IV) and 2,3-bis(methoxycarbonyl)-5-(trimethylsilyl)bicyclo[2.2.1]heptadiene (V) in the ratio of 85/15 respectively.

This reaction was previously reported to proceed in 20 min at room temperature to yield the 7- and 5-substituted isomer in 2/1 ratio[12]. As noted above, in our hands this ratio was different and the reaction much slower.

Repeating the above reaction with the pyrolysed predominantly 1- and 2-(trimethylsilyl)cyclopentadiene yielded the 5- and 7-substituted norbornadiene in approximately equal quantities.

The ^1H NMR spectra of (trimethylsilyl)cyclopentadiene were recorded on a Varian T60 spectrometer, and a Varian HA 100 spectrometer (Fig. 5). UV spectra were recorded in iso-octane on a Unicam S.P. 800 A spectrometer.

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