Table VII. Root-Mean-Square Displacements Along the Principal Axes of the Thermal Ellipsoids and Direction Cosines of the Principal Axes Referred to *a*, *b*, and *c**

Atom	Axis	Displacement[a]	Direction Cosines		
Sn	1	0.255 (3)	0.104	0.991	−0.085
	2	0.284 (3)	−0.732	0.018	−0.681
	3	0.333 (3)	−0.673	0.133	0.728
Br(1)	1	0.331 (5)	0.756	−0.553	0.348
	2	0.373 (5)	−0.575	−0.816	0.049
	3	0.481 (5)	0.312	−0.164	0.936
Br(2)	1	0.271 (4)	−0.408	0.825	0.391
	2	0.307 (3)	−0.146	0.363	−0.920
	3	0.360 (5)	0.901	0.432	0.027

[a] Standard errors are given in parentheses.

thermal parameters for Sn and Br and isotropic for C. Four cycles of full-matrix least squares reduced R_1 to 0.107 and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$ to 0.131. The mean parameter shift in the final cycle was 0.009 σ with a maximum shift of 0.05 σ. A final electron-density difference map revealed no peaks greater than 1.4 e/Å^3 (and no peaks larger than 0.8 e/Å^3 apart from the regions occupied by the heavy atoms). In our judgment the structure was insufficiently overdetermined to justify further refinement with anisotropic thermal parameters for carbon.

The observed and calculated structure factors have been deposited[31] with the ASIS National Auxiliary Publication Service, New York, N. Y., as Document No. NAPS-00809. Table VI lists the final atomic parameters and their standard deviations. The root-mean-square displacements along the principal axes of the thermal ellipsoids, and the direction cosines of these axes, were computed from the anisotropic thermal parameters of the tin and bromine atoms; these are compiled in Table VII. Bond distances, with standard errors calculated[32] from the variance–covariance matrix obtained in the final least-squares cycle, are presented in Table II, while selected bond angles are given in Table III. The parameters of six important best planes in the molecular, together with distances of certain atoms from these planes, are given in Table IV.

If the 24 independent C–C bond distances of the phenyl rings are averaged, a standard deviation $\sigma = [\Sigma(\bar{d} - di)^2/(n - 1)]^{1/2}$ of 0.067 Å for an individual measurement is calculated. The maximum value of $(\bar{d} - di)$ is 0.17 Å. Similarly, the maximum deviation of an individual carbon atom from the best planes A–F is 0.09 Å, and several other atoms deviate by 0.05–0.07 Å.

These errors are sufficiently large that variations in bond lengths involving carbon from accepted standard values cannot be regarded as significant. The inaccuracy arises because of the presence of three heavy atoms, and because sufficient high-order intensity data could not be gathered. The latter difficulty is in turn related to the moderately high thermal parameters of the structure. In addition, some systematic errors have undoubtedly crept into the data set by way of decomposition of the crystals in the X-ray beam. We note, moreover, that the corrections for absorption, extinction, and anomalous scattering did little to improve the final parameters.

V. **Unit Cell Parameters.** Cell constants have been established for compounds V, VI, and VII. These compounds crystallize in needles elongated on *c*. Weissenberg photographs indicate the three species to be isomorphous, and the reflection conditions 0*kl*, $k + l = 2n$ and *h*0*l*, $h = 2n$ are consistent with space groups $Pna2_1$ and Pnam. Accurate cell constants have been determined by least-squares refinement of setting angles on the four-circle diffractometer (Mo Kα radiation). These values are: $Sn(CH_3)_2(C_5H_6)(C_{28}H_{20}Cl)$ (IV), a = 15.643 (7), b = 12.073 (4), c = 15.527 (7); $Sn(CH_3)_2$-$(C_5H_6)(C_{28}H_{20}Br)$ (V), a = 15.890 (3), b = 12.047 (1), c = 15.563 (3); $Sn(CH_3)_2(C_5H_6)(C_{28}H_{20}I)$ (VI), a = 16.295 (2), b = 12.156 (2), c = 15.633 (2) Å. The cell volume/density relationships indicate four molecules per unit cell. Space group Pnam would require molecular C_s symmetry, which is inconsistent with the severe steric crowding of the dienes. Therefore space group $Pna2_1$ is indicated. X-Ray intensity data have been gathered on compound VI.

Acknowledgment. We are grateful to Francois van Remoortere for communicating preliminary structural data on compound VI. We are also pleased to acknowledge the contributions of Vernon R. Sandel and John J. Flynn to the earlier part of this work and some helpful discussions with S. W. Tobey, H. G. Langer, and J. W. Rakshys, Jr.

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[31] Material supplementary to this article has been deposited as Document No. NAPS-00809 with the ASIS National Auxiliary Publication Service, c/o CCM Information Sciences, Inc., 909 Third Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

[32] J. Gvildy's version (ANL Program Library B-115) of Busing, Martin, and Levy's FORTRAN function and error program, OR-FFE, was used.

Hydrogen and Trimethylsilyl Migrations in 5-Trimethylsilylcyclopentadiene

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Abstract: 5-Trimethylsilyl, 1-trimethylsilyl-, and 2-trimethylsilylcyclopentadiene were identified by nmr spectroscopy and formation of adducts with dimethyl acetylenedicarboxylate. The rate of hydrogen migration of 5-trimethylsilylcyclopentadiene is 2.0 × 10^{13} exp(−26.2 kcal mole^{-1}/RT). This is 10^6 slower than trimethylsilyl migration.

5-Trimethylsilylcyclopentadiene exhibits a temperature dependent nmr spectrum.[1] At −10° the expected spectrum of a four-proton vinylic multiplet and one allylic proton signal is observed and at high temperature these signals coalesce into a single intermediate frequency. It has been estimated that the ring protons are being interconverted at a rate of 10^3 sec^{-1} at 80°.[1] According to one postulate, a series of 1,5-

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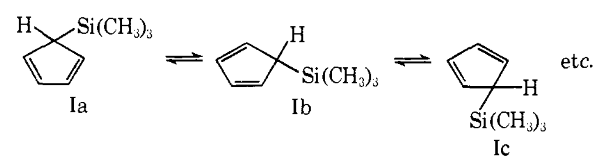
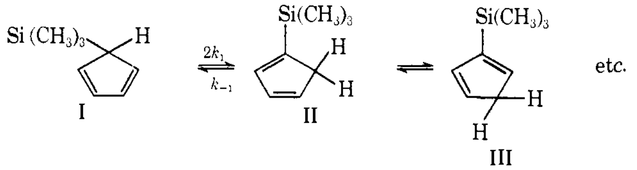
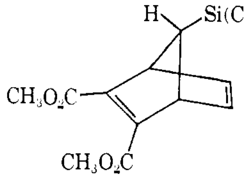
(1) H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.*, 4, 313 (1965).

trimethylsilyl shifts (IA ⇄ Ib ⇄ Ic ⇄ etc.) would interconvert the ring protons.[1] On the other hand, Kraihanzel and Losee pointed out that a series of 1,5- (or 1,3-) hydrogen shifts (I ⇄ II ⇄ III ⇄ etc.) would also explain the temperature-dependent spectrum[2] and these workers obtained some evidence in favor of hydrogen shifts. Dimethyl acetylenedicarboxylate reacted with 5-trimethylsilylcyclopentadiene to give predominately 7-trimethylsilyl-2,3-dicarbomethoxybicyclo[2.2.1]heptadiene (IV) at 0°. But as the temperature was raised increasing quantities of 5-trimethylsilyl-2,3-dicarbomethoxybicyclo[2.2.1]heptadiene (V) were isolated. V is the expected adduct of III with the dienophile. Presumably III was in equilibrium with I at high temperatures. No 1-trimethylsilyl-2,3-dicarbomethoxybicyclo[2.2.1]heptadiene (VI), the expected adduct from II, was reported.

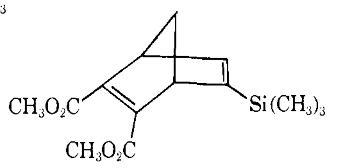
Although hydrogen migrations were clearly occurring the question remains: are the hydrogen shifts responsible for the temperature dependent nmr spectrum of I?



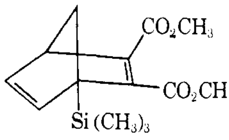




IV



V



VI

Results and Discussion

The reaction of sodium cyclopentadienide with trimethylsilyl chloride gave trimethylsilylcyclopentadiene, which could be recrystallized to a constant melting point of −19°. Reaction with dimethyl acetylenedicarboxylate at 0° gave greater than 90% adduct IV. The identity of the nmr spectrum of this material with the reported low temperture nmr spectrum left little doubt it was pure I.[1] Warming a benzene solution of I showed the reported hydrogen averaging in the nmr. However, warming also led to irreversible changes in nmr spectra as well. Two new trimethylsilyl peaks at τ 9.81 and 9.86 appeared near the original at 10.11.[3] A new allylic signal at 7.2 also appeared.[4] The ratio of the new trimethylsilyl peaks to the new allylic peak was 9:2 suggesting that these peaks were due to isomers II and III. At 30° the equilibrium ratio of the three trimethylsilyl peaks was 3:7:90. An examination of the mother liquors from the original recrystallization showed a great enrichment in the components with low frequency trimethylsilyl groups (ratio 2:4:4). However, upon standing at 30° for 3 days, this ratio decayed to the same equilibrium position as the sample from pure I.

Repeated attempts to separate the isomers I, II, and III by glpc failed. The isomers could be identified by formation of Diels–Alder adducts. Reaction of excess dimethyl acetylenedicarboxylate with the isomers of trimethylsilylcyclopentadiene (2:4:4) at 0° gave a mixture of adducts which could be separated into three components by glpc. They were present in the ratio of 20:37:43 in the order of retention time on a Carbowax 20M column. The 20% component corresponded to the previously reported V, while the high retention time component was IV. Elemental analysis and spectra of the second component were unambiguously in accord with structure VI. Thus assuming the rate of reaction of the isomers I, II, and III with dienophile at 0° is faster than their rates of interconversion, the trimethylsilyl peaks at τ 9.81, 9.86, and 10.11 correspond to III, II, and I, respectively.

The relative reactivities of I, II, and III with dienophiles could be determined. When a small amount of dimethyl acetylenedicarboxylate was allowed to react with an excess of a mixture of trimethylsilylcyclopentadiene isomers, III reacted 22 times faster than I while II was only 20% less reactive than I. At 140° equimolar quantities of I and dimethyl acetylenedicarboxylate gave V, VI, and IV in the ratio of 58:6:36, respectively. In a dilute solution at this temperature isomers I, II, and III are interconverting more rapidly than they are trapped by the bimolecular reaction with dienophile. Thus, the higher reactivity of III is responsible for the previously noted preferential formation of adduct V at high temperature.

At room temperature pure I is slowly partially converted to II. Only when a considerable concentration of II builds up does the trimethylsilyl peak due to III become observable. Thus, the conversion of isomers is by 1,5-hydrogen migration (I ⇄ II ⇄ III). The appearance of the trimethylsilyl peak due to II from pure I could be measured quite precisely by comparing its nmr peak height to that of a small quantity of added cyclohexane. Appearance of II followed a good first-order plot slightly longer than one half-life. At 30.0° k_{obsd} was $6.9 \pm 0.1 \times 10^{-5}$ sec^{-1} and at 50.0° k_{obsd} was $8.65 \pm 0.15 \times 10^{-4}$ sec^{-1}. At times longer than a half-life the conversion of II to III caused a drop-off in the rate of appearance of II. A measure of the equilibrium ratio II/I allowed the rate constants for the forward and reverse reactions to be separated from the observed rate constants: at 30.0° K was 0.126 and k_1 was 3.98×10^{-6} sec^{-1}, while at 50.0° was 0.150 and k_1 was 57×10^{-6} sec^{-1}. Thus the rate was equal to 2.0×10^{13} exp(-26.2 kcal/mole$^{-1}/RT$).[5] The rate constant is very similar to the well-investigated 1,5-hydrogen trans-

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(2) C. S. Kraihanzel and M. L. Losee, *J. Amer. Chem. Soc.*, **90**, 4701 (1968).

(3) The spectra were taken in benzene since the peaks at τ 9.81 and 9.86 were not separated in carbon tetrachloride.

(4) At 120° new vinylic multiplets at τ 3.63 and 3.41 (neat) are also present. None of these peaks are present in the spectra of trimethylsilylcyclopentadiene illustrated in ref 1. However, in our hands it has been found impossible to obtain nmr spectra at greater than 80° without these peaks.

(5) The rate constants are corrected for the statistical factor of 2.

fer of cyclopentadiene itself. At 50° the rate of hydrogen migration of **I** is 1.1 times that of pentadeuteriocyclopentadiene.[6]

The estimated rate for averaging the ring protons of I was 10^3 sec^{-1} at 80°.[1] The extrapolated rate of hydrogen migration for 5-trimethylcyclopentadiene is 1.4×10^{-3} sec^{-1}. Since hydrogen migration is 10^6 too slow, the observed temperature dependence must be explained by the migration of the trimethylsilyl group.

A number of 5-substituted cyclopentadiene derivatives[7] such as $(\sigma\text{-}C_5H_5)CuP(C_2H_5)_3$,[8] $(\sigma\text{-}C_5H_5)Fe(CO)_2(\pi\text{-}C_5H_5)$,[9] etc., show temperature-dependent nmr spectra similar to I. If these groups are transferred by 1,5-sigmatropic rearrangements[10,11] their migratory aptitude must be greater than hydrogen's. The trimethylsilyl group is somewhat unique in this series, since it alone is nonpolar, easy to introduce into a variety of organic molecules, and thermally very stable when bound to carbon. Thus, the trimethylsilyl group may be an extremely useful group for the investigation of sigmatropic rearrangements.

Nmr Spectra of Dimethyl Acetylenedicarboxylate Adducts. V and IV. These nmr spectra were identical with those reported.[2] However, the spectra are mislabeled in both tables and figures in this paper. The spectrum labeled **4a** in Figure 1 is that of IV, while that labeled **4c** is that of V.

VI. The nmr spectrum is unambiguously in accord with the proposed structure. The two vinylic protons form an AB pattern centered at τ 3.30 (J_{AB} = 5.0 Hz) split by a single bridgehead proton: J_{AX} = 3.0 Hz and J_{BX} = 0 Hz. This bridgehead proton occurs as a complex multiplet at τ 6.20. The two nonequivalent carbomethoxy groups are two three-proton singlets at τ 6.40 and 6.43. A second AB pattern (J_{AB} = 6.5 Hz) centered at 8.19 is due to the methylene bridge. This is split by the single bridgehead proton: $J_{AX} = J_{BX}$ = 1.5 Hz. The nine-proton singlet due to the trimethylsilyl group occurs at τ 9.89.

Experimental Section

General. Infrared spectra were recorded in dilute solutions of carbon tetrachloride with balanced 0.1-mm sodium chloride cells using a Perkin-Elmer 237 spectrometer. Proton magnetic resonance spectra were recorded using either benzene or carbon tetrachloride solutions in either a Varian A-60 or HR 100 spectrometer. Percentage of components was measured by integration.

A Varian Aerograph 90P chromatograph was employed for both analytical and preparative work. In the analytical work percentage of components was assumed to be proportional to the area of peaks. No corrections were made for different thermal conductivity of isomers. The column used in separations was packed with 20% Carbowax 20M on Chromosorb W. It was packed in an aluminum column (12 ft × 0.25 in. in diameter). Helium elution was used. Elemental analysis was performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

Trimethylcyclopentadiene Isomers. 5-Trimethylsilylcyclopentadiene was prepared as has been previously described.[1,2] If the temperature is kept below 20° in all operations the product is essentially pure 5-trimethylsilylcyclopentadiene. But if the material is heated during work-up a mixture of isomers is obtained. These can be partially separated by fractional recrystallization. The mixture is allowed to crystallize partially at −20 to −30°, then poured onto a cold Büchner funnel surrounded by Dry Ice. After covering the funnel with a rubber dam, gentle suction removes the mother liquor from the crystals of 5-trimethylsilylcyclopentadiene. Repetition of this operation on these crystals several times results in pure-5-trimethylcyclopentadiene, mp −19°.

The mother liquors are cooled in Dry Ice–acetone until about half of the material solidifies. The crystals are then removed by filtration. This operation is repeated until no more crystals come out of solution. The material is then approximately 40% I, 40% II, and 20% III, by nmr integration of the trimethylsilyl peaks, at τ 10.11, 9.86, and 9.81, respectively.

Reaction of Trimethylsilyl Isomers with Dimethyl Acetylenedicarboxylate. (1) Pure 5-trimethylsilylcyclopentadiene (43.4 mg, 0.31 mmole) was added to 148 mg (1.07 mmoles) of dimethyl acetylenedicarboxylate in 300 mg of benzene at 0°. The mixture was allowed to stand at 0° for 3 days. The products were analyzed by glpc. At 230° (50 lb of He pressure), the product was 94% a single component (retention time 9.0 min). There were two minor components: 3% (retention time 5.9 min) and 3% (retention time 7.0 min). The major component was collected and shown to have spectra identical with those reported for 7-trimethylsilyl-2,3-dicarbomethoxybicyclo[2.2.1]heptadiene (IV).[2]

(2) A sample of 229 mg (1.65 mmoles) of mixed isomeric trimethylsilylcyclopentadienes (III:II:I 18:41:41 by nmr) was added to 359 mg (2.6 mmoles) of dimethyl acetylenedicarboxylate at 0°. After standing for 3 days at 0° the products were analyzed by glpc. There were three components: 19% (retention time 5.9 min), 38% (retention time 7.0 min), and 42% (retention time 9.0 min). These were collected. The 19% component had an nmr spectrum identical with that reported for 5-trimethylsilyl-2,3-dicarbomethoxybicyclo[2.2.1]heptadiene (V) while the 9.0-min retention component was IV.

The 7.0-min retention time component was an isomer. *Anal.* Calcd for $C_{14}H_{20}O_4Si$: C, 60.00; H, 7.14. Found: C, 60.07; H, 7.17. Ir and nmr spectra were consistent with the structure 1-trimethylsilyl-2,3-dicarbomethoxybicyclo[2.2.1]heptadiene (VI).

(3) To a refluxing solution of 15 ml of xylene and 3.5 g (50 mmoles) of dimethyl acetylenedicarboxylate 3.5 g (50 mmoles) of pure I was added dropwise. The mixture was allowed to reflux for 30 min. Analysis by glpc showed the ratio V:VI:IV to be 58:6:36.

(4) To a 200-mg (1.45 mmoles) sample of mixed isomers of trimethylsilylcyclopentadiene (I:II:III 40:45:15) at 0° 5 mg (0.036 mmole) of dimethyl acetylenedicarboxylate was added. After 18 hr at 0° analysis by glpc showed V:VI:IV to be 82.2:8.1:9.5. Relative reactivity is therefore 1.2:1.0:26 for I:II:III.

Kinetic Experiments. A solution was prepared at 0° from 2.00 ml of benzene, 250 μl of pure 5-trimethylcyclopentadiene, and 15 μl of cyclohexane. A 300-μl aliquot of this solution was placed into each of a series of nmr tubes. The nmr tubes were placed in a constant-temperature bath and allowed to warm to bath temperature for 5 min. They were removed at intervals and quenched in Dry Ice–acetone, and the time was recorded. The last tube was removed at ten half-lives.

The appearance of II was followed by measuring the peak height of the trimethylsilyl peak at τ 9.86 relative to the cyclohexane peak height with a Varian A-60 spectrometer at constant instrument settings throughout a run. At least four scans were taken per tube and the average value was used. In each case the observed rate constant was determined by a plot of ln $(H_\infty - H)$ against time. Good first-order plots were obtained for the first half-life only. The drop-off in the rate constants at longer times corresponded approximately to the appearance of the peak at τ 9.81 due to the trimethylsilyl group of III. At least two determinations were made at each temperature and the rate constants agreed to within 5%. Runs were also made at different concentrations of I. There was no observable difference in these rate constants.

The equilibrium ratio of II/I was measured by integrating the infinity tube at 50-Hz sweep width. Several determinations were made at each temperature. The small concentration of III was ignored throughout.

Acknowledgment. We are pleased to acknowledge support of this work by the Petroleum Research Fund (Grant 829-G1) of the American Chemical Society.

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[6] W. R. Roth, *Tetrahedron Lett.*, 1009 (1964).

[7] See, for example, F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

[8] G. M. Whitesides and J. S. Fleming, *J. Amer. Chem. Soc.*, **89**, 2855 1967).

[9] M. J. Bennett, Jr., F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *ibid.*, **88**, 4371 (1966).

[10] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965).

[11] D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Lett.*, 999 (1966).