Journal of Organometallic Chemistry, 82 (1974) 29—40

REACTION OF CYCLOOCTATETRAENE DIANION WITH HALOSILANES: PREPARATION OF 3,4-(TETRAMETHYLDISILOXY)-1,3,5-CYCLOOCTATRIENE AND 5,8-BIS(TRIMETHYLSILYL)-1,3,6-CYCLOOCTATRIENE*

M.N. ANDREWS** and P.E. RAKITA***

William Rand Kenan, Jr., Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514 (U.S.A.)

(Received May 21st, 1974)

Summary

The dipotassium salt of cyclooctatetraene dianion, COT^{2-}, reacts at −35° with dimethyldichlorosilane, followed by aqueous workup, to give $C_8H_8[Si(CH_3)_2]_2O$ (I) in 4.4% yield. On the basis of spectroscopic (IR, mass, ^1H and ^{13}C NMR spectra) and chemical data, compound I is formulated as 3,4-(tetramethyldisiloxy)-1,3,5-cyclooctatriene. Reaction of COT^{2-} with trimethylchlorosilane yields the compound $C_8H_8[Si(CH_3)_3]_2$ in 50% yield, which is shown to be 5,8-bis(trimethylsilyl)-1,3,6-cyclooctatriene.

Introduction

The utility of cyclooctatetraene dianion, (COT^{2-}) prepared from the reaction of one mole of cyclooctatetraene [1] in ether with two moles of alkali metal, in organic synthesis has been extensively explored [2]. Recently, a number of di-π-cyclooctatetraene complexes of lanthanide [3] and actinide [4] metals have been prepared from the reaction of COT^{2-} with the appropriate metal halide. Relatively little work has appeared, however, on the COT derivatives of main-group metals. Katz [5] reported that COT^{2-} reacts with phenylphosphorous dichloride to give initially 9-phenyl-9-phosphabicyclo[6.1.0]nonatriene which undergoes an internal rearrangement at 70° to give 9-phenyl-9-phosphabicyclo-[4.2.1]nonatriene, presumably via a 1,5-rearrangement, and Azatyan [6]

---

* Presented at the 167th National Meeting, American Chemical Society, Los Angeles, 5 April 1974.

** Recipient of University Research Assistantship, 1973-74.

*** To whom correspondence should be addressed.

synthesized a compound of composition $C_8H_8[Si(CH_3)_3]_2$ from the reaction of COT^{2-} with trimethylchlorosilane, to which he assigned the structure 7,8-bis-(trimethylsilyl)-1,3,5-cyclooctatriene on the basis of IR and UV data.

Our interest in the Group IVA derivatives of cyclooctatetraene is two-fold: (1) as novel potential ligands for transition metals and (2) to extend our previous studies of rearrangements in Group IVA metal unsaturated carbocyclic systems. We report here the syntheseis and characterization of 3,4-(tetramethyldisiloxy)-1,3,5-cyclooctatriene (I) and 5,8-bis(trimethylsilyl)-1,3,6-cyclooctatriene (II).

Experimental

General data

Infrared spectra were recorded on liquid films using a Perkin—Elmer 257 spectrophotometer. NMR spectra were obtained with a Jeolco C60-HL, a Varian HA-100, or a Varian XL-100 spectrometer equipped with FT mode and a Varian 620/L computer with disk accessory.

The ^1H chemical shifts were calibrated using an internal reference chloroform peak, assumed to be 7.24 ppm downfield from TMS. The proton-decoupled ^{13}C NMR spectra were obtained using a ^2H internal lock and the chemical shifts were calibrated using the center of the internal reference chloroform-*d* peak, assumed to be 77.2 ppm downfield from TMS. Mass spectra were obtained at 70 eV with a Hitachi—Perkin—Elmer RMU-6E spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee and Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Gas chromatographic separations and purifications were carried out using a Varian Aerograph Model 90-P3 chromatograph equipped with a thermal conductivity detector. Columns (1/4" × 120") packed with either 15% SE-30 on Chromosorb W or 3% UC-W98 on Chromosorb W were employed using helium elution.

Preparation of 3,4-(tetramethyldisiloxy)-1,3,5-cyclooctatriene (I)

Compound I was prepared by the addition of the potassium salt of cyclooctatetraene dianion (prepared from the reaction of potassium metal (4.2 g, 0.108 mol) and cyclooctatetraene (5.01 g, 0.048 mol) in 90 ml THF) under nitrogen at —35°C to a solution of dimethyldichlorosilane (14.89 g, 0.115 mol) with stirring. The mixture was warmed to room temperature and stirred for two hours. Water was added and the organic phase was extracted with pentane and dried. The pentane was removed by distillation, and the fraction boiling at 65-75°/0.05 mmHg was collected. The crude product, a pale yellow liquid (0.493 g, 2.09 mmol, 4.4% yield based on cyclooctatetraene), was purified by GLPC (SE-30 column) at 115°, retention time 12.5 min. (Anal. Found: C, 60.78; H, 8.41; mol. wt. (osmometry, CCl_4) 227. $C_{12}H_{20}Si_2O$ calcd.: C, 60.95; H, 8.53%; mol. wt. 236.)

The mass spectrum showed the molecular ion ($C_{12}H_{20}{}^{28}Si_2O$) at *m/e* 236. Other prominent peaks appeared at *m/e* 221 ($M—CH_3$), 193 ($M—SiCH_3$), 134 ($(CH_3)_2HSiOSi(CH_3)_2H$), 132 ($(CH_3)_2SiOSi(CH_3)_2$), 73 ($Si(CH_3)_3$), 59 (CH_3SiO). The infrared spectrum displayed bands at: 2996 m, 2946 s, 2891 m, 2876 m, 2831 m, 1670-1570 vw, 1463-1403 w, 1252 s, 1128-1038 w, 987 s, 877 m, 842 m, 792 s, 727 m, 702 m, 662 m, 637 m cm^{-1}.

The proton NMR spectrum ($CDCl_3$) had the following resonances: δ (ppm) 0.21 (singlet), 2.31 (multiplet), 5.72-5.98 (broad multiplets), 6.01 (singlet), 6.12 (singlet) in the area ratio 12.0/3.9/4.3.

The proton decoupled ^{13}C NMR spectrum ($CDCl_3$) had the following resonances: δ (ppm) 0.04, 33.6, 128.1, 128.8, 133.1 (all singlets).

Catalytic reduction of I

A sample of compound I (0.335 g, 1.419 mmol) in ethanol (20 ml) was reduced at 1 atm. hydrogen pressure using 10% Pd on carbon catalyst (82.8 mg). The volume of hydrogen uptake was 63.2 ml (2.829 mmol at s.t.p.), 99.7% of theoretical based on 2 moles of H_2 per mole of I. The reaction mixture was filtered to remove the catalyst, and the crude product obtained by rotary evaporation. The mass spectrum of the product showed a molecular ion at *m/e* 240. Other prominent peaks appeared at *m/e* 225 ($M-CH_3$), 197 ($M-SiCH_3$), 134 ($(CH_3)_2HSiOSi(CH_3)_2H$), 132 ($(CH_3)_2SiOSi(CH_3)_2$), 106 (C_8H_{12}), 73 ($Si(CH_3)_3$), 59 (CH_3SiO). The proton NMR spectrum ($CDCl_3$) of the crude product revealed resonances in the methylene and methylsilyl regions in the area ratio 12/12, with no evidence for vinyl protons. Because of the small quantity of compound isolated, we did not obtain a pure sample of the reduced material for analysis.

Preparation of 5,8-bis(trimethylsilyl)-1,3,6-cyclooctatriene (VII)

Compound VII was prepared by a modification of the published procedure [6]. To a solution of the potassium salt of cyclooctatetraene dianion, prepared from potassium metal (6.408 g, 0.164 mol) and cyclooctatetraene (7.526 g, 0.0724 mol) in THF (75 ml) and maintained at 0°, was added a solution of trimethylchlorosilane (18.7 g, 0.172 mol) in THF (30 ml) with stirring. The mixture was allowed to warm to room temperature and was stirred for an additional 12 h. Water was added and the mixture was extracted with ether. The organic layer was separated, dried (Mg_2SO_4), and the ether was removed at reduced pressure. The product was recrystallized from pentane/methanol to give 9.065 g (0.0363 mol) of white crystals, m.p. 55-56°, which yellowed and softened on standing at room temperature in air. The yield was 50% (based on cyclooctatetraene). (Anal. Found: C, 67.39; H, 10.53. $C_{14}H_{26}Si_2$ calcd.: C, 67.12; H, 10.46%.)

The mass spectrum showed the molecular ion ($C_{14}H_{26}{}^{28}Si_2$) at *m/e* 250. Other prominent peaks appeared at *m/e* 235 ($M-CH_3$), 207 ($M-SiCH_3$), 177 ($M-Si(CH_3)_3$), 163 ($C_8H_8Si(CH_3)_2H$), 147 ($C_8H_8SiCH_3$), 135 ($C_8H_{11}Si$), 104 (C_8H_8), 73 ($Si(CH_3)_3$), 59 (SiC_2H_7), 43 ($SiCH_3$).

The infrared spectrum displayed bands at: 3000 m, 2955 s, 2900 m, 2850 w, 1765 w, 1685 w, 1620 w, 1590 w, 1410 w, 1255 s, 1145 w, 1055 w, 1025 w, 920 m, 840 s, 780 m, 750 m, 725 m, 692 m cm^{-1}.

The proton NMR spectrum ($CDCl_3$) had the following resonances: δ (ppm) −0.02 (singlet); 2.7-2.9 (multiplet); 5.2-5.9 (multiplet), in the ratio 15.7/2.0/6.1.

The proton decoupled ^{13}C NMR spectrum had the following resonances: δ (ppm) −1.7, 34.7, 125.6, 126.3, 129.7 (all singlets).

Heating a sample of VII in a sealed tube under N_2 at 150° for 43 h resulted in changes in the proton NMR spectrum: the appearance of several new methyl-silyl resonances in the region 0.0-0.5 ppm, indicative of vinylsilyl methyl groups with a concommitant decrease in the intensity of the signal at —0.02, changes in the signals and a decrease in the vinyl resonances. Comparable spectra were observed for samples which were distilled at 72°/0.05 mm Hg upon workup. These samples remained liquid on standing at room temperature.

Catalytic reduction of VII

A sample of compound VII (0.4060 g, 1.624 mmol) in ethanol (15 ml) was reduced at atmospheric pressure with hydrogen using 10% Pd on carbon catalyst (80.0 mg). The volume of hydrogen uptake was 82.8 ml (3.696 mmol at s.t.p.), 114% of theoretical based on 2 moles of H_2 per mole of VII. The reduced material was filtered to remove the catalyst, and two fractions were separated by GLPC (SE-30 column, 150°, retention times 26.4 and 43.5 minutes Both of the fractions remained unchanged when they were separately rechromatographed under the original conditions. The mass spectra of both fractions showed the molecular ion at *m/e* 254 with identical fragmentation patterns at *m/e* 239 ($M-CH_3$), 180 ($M-Si(CH_3)_3H$), 165 ($C_8H_{12}SiC_2H_5$), 151 ($C_8H_{12}SiCH_3$), 106 (C_8H_{10}), 73 ($Si(CH_3)_3$), 59 ($Si(CH_3)_2H$), 43 ($SiCH_3$). The proton NMR spectra ($CDCl_3$) of both fractions showed multiple peaks in the trimethylsilyl region, broad structureless bands for methine protons at 1.3-2.7 and in the vinyl region at 5.7-6.5 with relative areas 18.5/10.3/1.1. (Anal. Found: C, 65.87, 65.99; H, 11.94, 11.84. $C_{14}H_{30}Si_2$ calcd.: C, 66.14; H, 11.81%.)

Parr hydrogenation of VII

A sample of compound VII dissolved in glacial acetic acid was reduced using a platinum oxide catalyst at 47 psi hydrogen pressure and room temperature. The mixture was filtered, washed with water, extracted (pentane) and concentrated to obtain the crude product. The product was isolated by GLPC (SE-30 column, 155°, retention time 31 minutes). The mass spectrum showed the molecular ion at *m/e* 256. Prominent fragments appeared at *m/e* 182 ($M-Si(CH_3)_3H$), 153 ($C_8H_{14}SiCH_3$), 108 (C_8H_{12}), 106 (C_8H_{10}), 73 ($Si(CH_3)_3$), 59 ($Si(CH_3)_2H$), 45 ($SiCH_5$). The proton NMR spectrum ($CDCl_3$) displayed three bands in the methyl silyl region and a broad signal in the methine region in the area ratio 18/13.9. No resonances were observed in the vinyl region.

Results

Proton NMR spectra

The proton NMR spectrum of I exhibits a sharp singlet at δ 0.21, a three line pattern at 2.31 and a complex multiplet in the vinyl region at 5.7-6.1 in the area ratio 12/3.9/4.3. The pattern at 2.31 appears the same at 60 and 100 MHz. (Fig. 1A), but the vinyl resonances appear as four signals at 100 MHz, the two bands at lowest field being sharp single lines and the two upfield bands being broad, complex, featureless signals. In a double-resonance experiment (Fig. 1B), irradiation of the signal at 2.31 causes the two broad upfield bands of the vinyl pattern to collapse to single lines, giving what appears to be an AB pattern (J_{AB} 11.5 Hz) in the vinyl region. Irradiation of the upfield portion of the vinyl signals (Fig. 1C) causes the three line resonance pattern at 2.31 to collapse to a

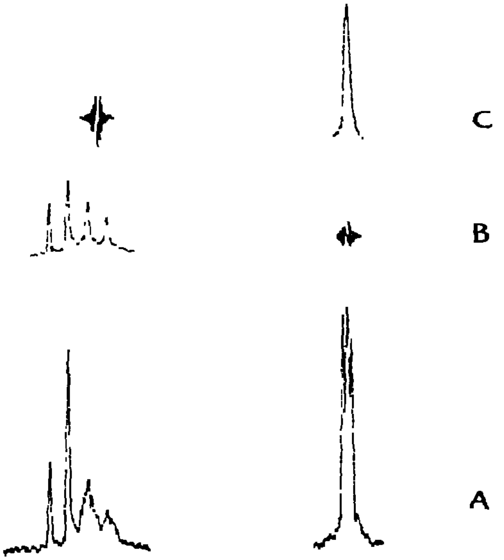


Fig. 1. (A) Details of the resonances for I in the region 5.7-6.2 and 2.3 ppm at 100 MHz. (B) Results of double irradiation at 2.3 ppm. (C) Results of double irradiation at 5.8 ppm.

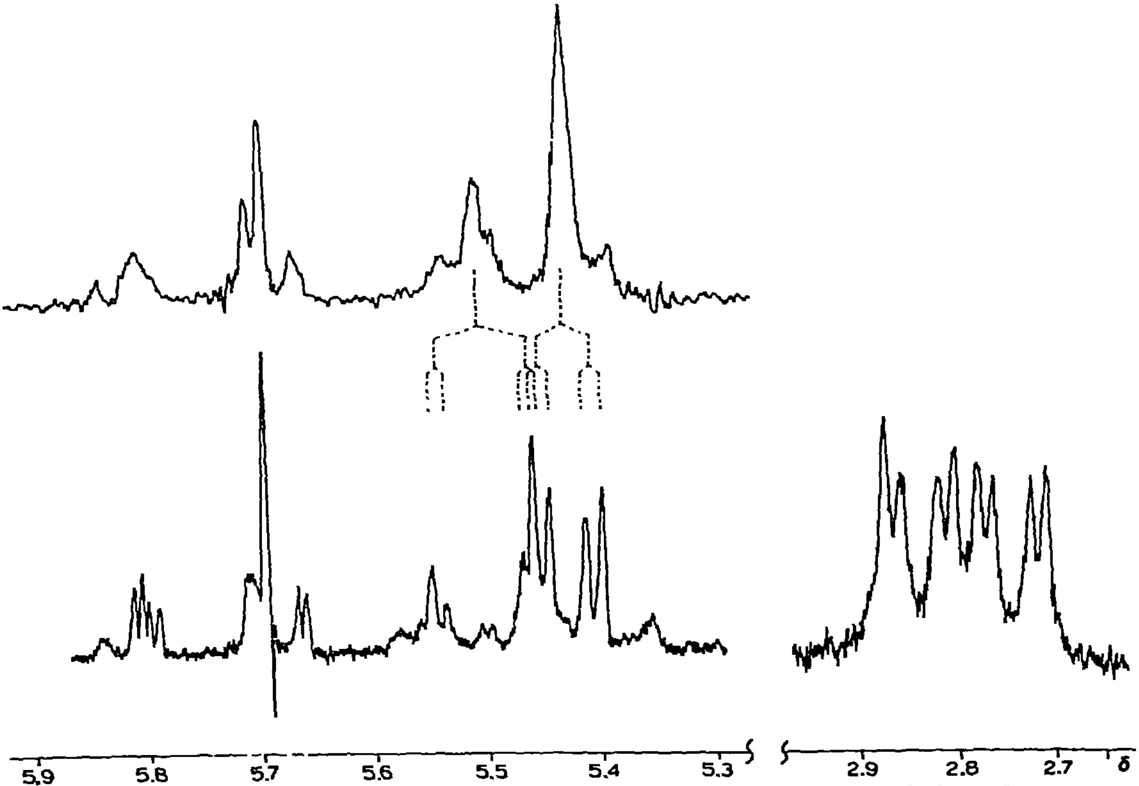


Fig. 2. Lower trace: Detail of the vinyl and methine resonances of compound VII at 100 MHz. Upper trace: Results of double irradiation at 2.8 ppm.

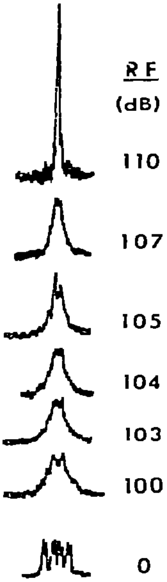


Fig. 3. Spectral changes of the methine resonance at 2.8 ppm for compound VII upon double irradiation at ~ 5.42 ppm.

broadened singlet. Variable temperature spectra were recorded on this compound in the range of —50 to + 130° with no significant change in the spectrum being observed.

The proton NMR spectrum VII shows a sharp singlet at —0.02, a symmetrical eight line multiplet at 2.7-2.9, and a complex vinyl resonance pattern at 5.3-5.9 in the area ratio 15.7/2.0/6.1. The details of the methylene and vinyl regions at 100 MHz are given in Fig. 2. The methine resonance, centered at 2.8, consists of two 4-line patterns split by a coupling of *J* 7.9 Hz. The 4-line signal characteristic of an AA'XX' pattern is repeated in the vinyl region at 5.42. When the signals at 2.8 are irradiated in a double resonance experiment (upper portion of Fig. 2), the 4-line pattern at 5.42 collapses to a broadened singlet, the patterns at 5.47 and 5.55 coalesce to a multiplet at 5.51, and some of the fine structure on the low field half of the vinyl resonances is removed, leaving what appears to be a symmetrical (AA'BB') pattern centered at 5.6 with a broadened singlet superimposed at 5.42. Irradiation of the vinyl resonances at ~5.42 (Fig. 3) results in collapse of the eight line pattern at 2.8 initially to a doublet and, with increasing radio frequency power, to a sharp singlet.

Carbon-13 NMR spectra

The proton decoupled carbon-13 spectrum of I showed three signals characteristic of vinyl carbons (133.1, 128.8, 128.1), a single resonance in the region of sp^3 carbons (33.6), and a single resonance characteristic of methyl-silyl carbons (0.04). Since only a very dilute sample was available, requiring 125000 transients for the ^1H decoupled spectrum, it was not possible to obtain the undecoupled spectrum. The carbon-13 spectrum of VII (Fig. 4) shows three vinyl carbon resonances (125.6, 126.3, 129.7), one sp^3 carbon (34.7) and one

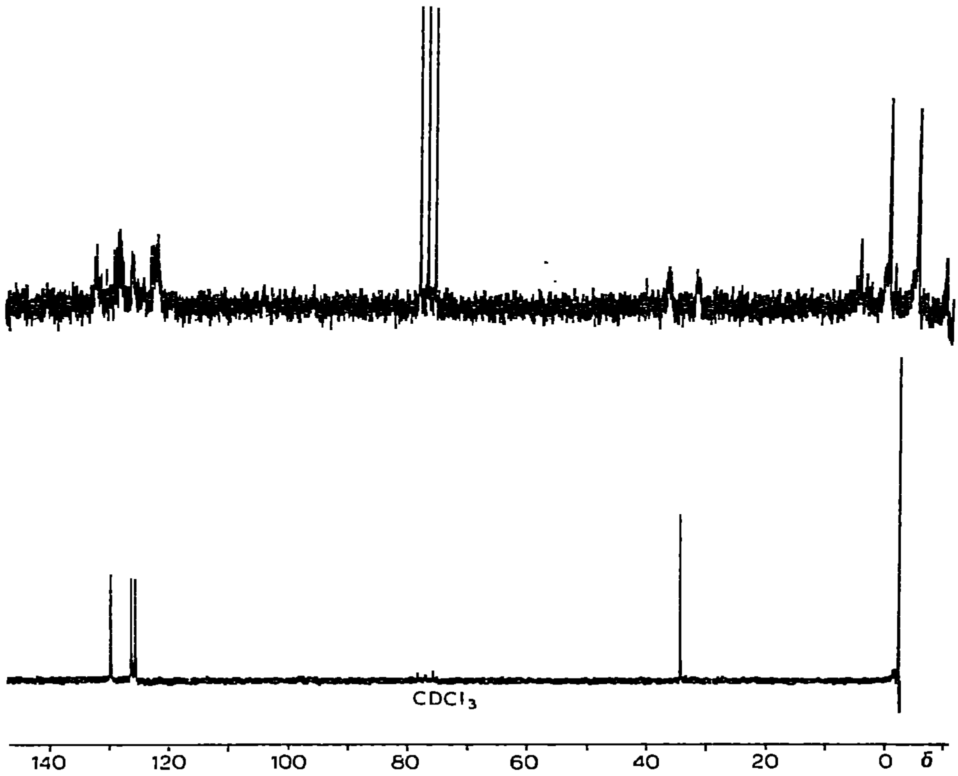


Fig. 4. Lower trace: Proton decoupled ^{13}C NMR spectrum of compound VII at 25.2 MHz (CDCl$_3$). Upper trace. Undecoupled ^{13}C NMR spectrum of compound VII.

methyl-silyl carbon signal (—1.7). The undecoupled carbon-13 spectrum clearly indicates that each of the vinyl and sp^3 carbons is split into a doublet characteristic of a single, direct C—H coupling, and the methyl-silyl carbons give the expected quartet for an Si—CH$_3$ group. The values of $J(^{13}C—^{1}H)$ are found to be ~153, 125, and 125 Hz for the vinyl, sp^3, and methyl-silyl signals respectively.

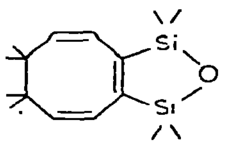
Mass spectra

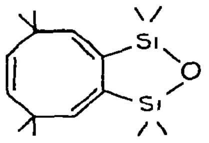
The mass spectra of both compound I and its hydrogenation product displayed prominent molecular ions and fragments at *m/e* 134 and 132 characteristic of a tetramethyldisiloxane unit.

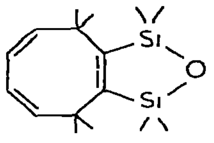
Molecular ions were present for compound VII and the partially and totally reduced derivatives at *m/e* 250, 254 and 256 respectively. Analogous fragments of composition $C_8H_xSiCH_3$ (x = 8, 12, 14 at *m/e* 147, 151, 153 for VII, the partially and totally reduced derivatives) were also observed.

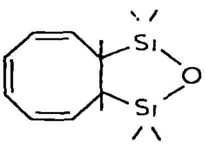
Discussion

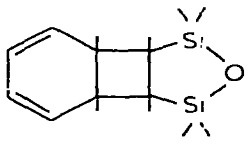
Reaction of the potassium salt of COT^{2-} with dimethyldichlorosilane followed by an aqueous workup gives, in low yield, a monomeric compound of composition $C_8H_8[Si(CH_3)_2]_2O$ (I). The infrared spectrum showed the presence of a $(CH_3)_2Si-O-Si(CH_3)_2$ unit, and the simplicity of the methyl-silyl and methine regions of the proton NMR spectrum indicated a relatively symmetrical structure. From these data several possible structures I-VI can be considered.

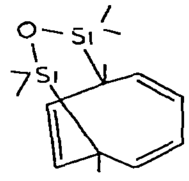

(I)


(II)

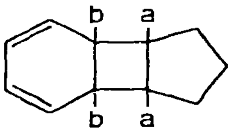

(III)


(IV)


(V)


(VI)

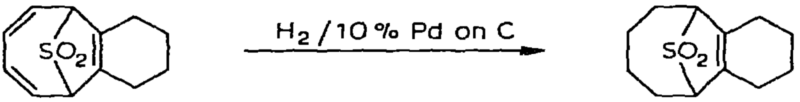
From the observed relative intensities of the vinyl and methine ring protons (4/4) and the equivalence of the four methylsilyl groups, structures IV and VI can be eliminated. Structure V, which would exist in a folded conformation, would also be expected to exhibit two resonances for the methylsilyl groups and can be eliminated. Moreover, the two sets of aliphatic protons on the four-membered ring would be expected to give distinct resonances as in the hydrocarbon analog [7] where $\delta_a = 2.7$, $\delta_b = 2.35$, and $\delta_{vinyl} \simeq 5.5$ ppm.



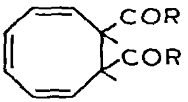
The choice between structures I, II and III is based on two points: (1) the chemical shift of the methine resonance and (2) the double resonance results. Structures II and III have doubly allylic methine protons which typically occur in the range δ 2.6-2.9 ppm [8] (cf. compound VII $\delta_{methine} = 2.79$). For compound I the methine signal occurs at 2.31, comparable to that observed in 1,3,5-cyclooctatriene ($\delta_{methine} = 2.43$) [9] and in the region for singly allylic protons [8]. The double resonance results confirm the assignment of structure I to compound I. Removal of the methine coupling would leave the following patterns in the vinyl region: structure I, AB $J_{AB} \sim$ 6-13 Hz; structure II, AX $J_{AX} \sim 0$; structure III, AA'BB' complex multiplet. The observed AB pattern ($J_{AB} = 11.5$ Hz) in the vinyl region upon double irradiation together with the fact that the methine protons are measurably coupled to only half of the vinyl protons is consistent only with structure I.

If compound I adopts a "tub" configuration, the observed equivalence of the four methyl groups, even at −50°, requires a relatively low activation barrier for the inversion process. Estimates from the low temperature spectra place an upper limit of < 8 kcal/mole for the inversion barrier. This compares favorably with the value of 6.2 found [9] for 1,3,5-cyclooctatriene.

The observed partial reduction of compound I under moderate hydrogenation conditions has precedence in the literature for substituted cyclooctatriene compounds [10] with hindered double bonds:

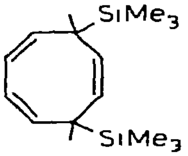


whereas the unhindered triene [11]:

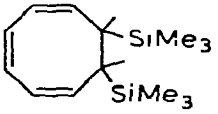


can be reduced to a saturated hydrocarbon under similar conditions.

Bis(trimethylsilyl)cyclooctatriene was prepared by a procedure analogous to that reported previously by Azatyan [6]. Isolation of the product by recrystallization rather than distillation [6] was preferable, since the compound was found to undergo facile thermal isomerization. There are two possible structures consistent with the single resonance in the methyl-silyl region of the proton NMR, the integration results 6/2/18 (vinyl/methine/methyl-silyl), and the undecoupled ^{13}C spectrum which confirmed one proton attached to each of the C_8 ring carbons, viz:



(VII)



(VIII)

Azatyan assigned structure VIII to the compound on the basis of similarities in the IR and UV spectra with 1,3,5-cyclooctatriene. From the NMR data and the results of double resonance experiments, we conclude that the crystalline solid isolated from the reaction has structure VII (5,8-bis(trimethylsilyl)-1,3,6-cyclooctatriene). Chemical shift and proton coupling constant data for compound VII and several 5,8-disubstituted 1,3,6-cyclooctatrienes are summarized in Table 1. The methine proton resonance, which occurs in the region typical for doubly allylic protons, simplifies to a singlet upon irradiation at 5.43 ppm in the center of four line pattern in the upfield portion of the vinyl resonances. The eight line methine multiplet appears to be the XX' portion of an AA'XX' pattern for H(5,6,7,8) with $J_{AX} + J_{AX'} = 4.6$ Hz, further split by the coupling between protons H(1,4) and H(5,8) ($J_{1-8} = J_{4-5} = 7.9$ Hz).

TABLE 1

PROTON CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR 5,8-DISUBSTITUTED-1,3,6-CYCLOOCTATRIENES $C_8H_8R_2$

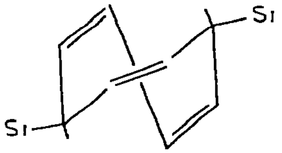
R	H(5,8)	H(1,4)	H(2,3)	H(6,7)	J_{1-8}	J_{5-6}	J_{1-2}	Ref.
$Si(CH_3)_3$	2.79	~5.5(m)[a]	~5.7(m)	5.43(m)	7.9	4.6[b]	11.6[c]	this work
CH_3	2.94	5.03(d)	6.01(d)	5.25(s)	6.5	0	9.0	15
$C(CH_3)_2CN$	2.89	5.29(d)	6.38(d)	5.75(s)	7.1	<0.3	9.3	16
NO_2	5.84(d)	~5.6(m)	6.35(d)	6.26(s)	unresolved	0	7.4	17
H				5.68				18

[a] s, singlet; d, doublet; m, multiplet. [b] $|J_{5-6} + J_{5-7}|$. [c] $|J_{1-2} + J_{1-3}|$.

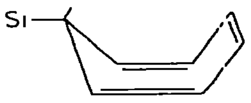
Irradiation of the methine signal results in the upfield portion of the vinyl resonances simplifying to a single line (assigned to H(6,7)) and changes in the remaining vinyl signals in what appears to be a BB'CC' pattern for H(1,2,3,4) overlapped by the broadened singlet of H(6,7). The loss of fine structure in the downfield portion of the vinyl region, assigned to H(2,3), upon irradiation of H(5,8) can be ascribed to a small long range allylic coupling J_{2-8}. The significant feature in the analysis of the decoupled vinyl region is the negligible coupling between two of the vinyl protons, H(6,7) and the other four, H(1,2,3,4), a result consistent with structure VII and not with structure VIII.

The results of the hydrogenation studies confirm the presence of three double bonds in VII, but, as with compound I, only two of the double bonds are reduced under mild conditions, presumably because of steric crowding around the C(6)—C(7) bond.

In contrast to the trimethylsilyl derivatives of cyclopentadiene [12] and indene [13], VII does not appear to undergo a facile trimethylsilyl migration. In this respect it resembles 7-trimethylsilylcycloheptatriene (IX) which at higher temperature isomerizes exclusively by hydrogen migration [14]. It is appealing to speculate that both VII and IX adopt conformations in which the trimethylsilyl group is in a quasi-equatorial position for which a facile 1,5-hydrogen shift, but not a $(CH_3)_3Si$-shift, is possible.



(VII)

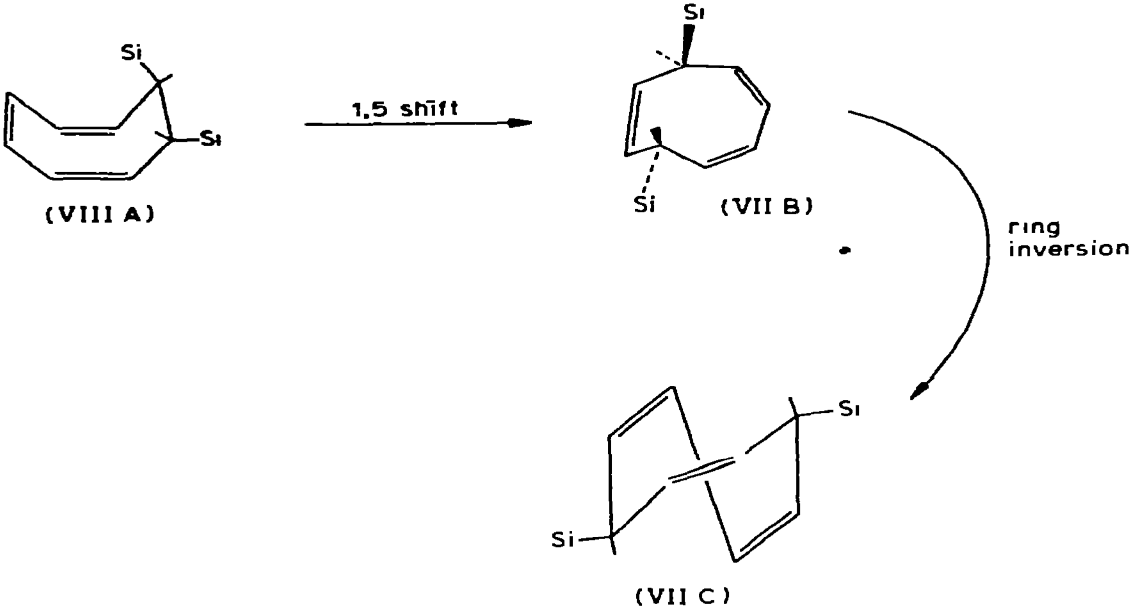


(IX)

On the basis of the reaction of the cyclooctatetraene dianion with phenylphosphorus dichloride [5], one might except initial 1,2 addition of the substituents. For the trimethylsilyl groups, molecular models show steric preference for addition of the second trimethylsilyl group *trans* to the first. This configuration (VIIIA) places both a Me_3Si and a proton in position over the 3,4-double bond, in an optimum position for a 1,5-shift. An intramolecular 1,5-silicon shift would result in isomer VIIB with *endo*- and *exo*-silyl groups, and with severe steric crowding between the *endo*-silyl (C(5)) and the *endo*-proton (H(8)), which could easily be relieved by ring inversion to conformer VIIC, with two *exo*-silyl groups. This conformer has a C_2 symmetry axis which makes the silyl groups equivalent, and protons H(1), H(2), H(7), H(8) equivalent to H(4), H(3), H(6), and H(5), respectively.

By contrast, an initial 1,4-addition of the trimethylsilyl groups would be expected to give a significant amount of axial, equatorial-bis(trimethylsilyl) groups. Assuming a reasonable barrier to ring inversion, this isomer would be expected to have more than one peak in the methylsilyl region. (The NMR spectrum of compound VII, recorded at 0°, showed no broadening of the trimethylsilyl peak.)

A similar mechanism can be postulated for the formation of I from the reaction of COT^{2-} with dimethyldichlorosilane. Initial 1,2-addition of dimethylchlorosilyl groups, followed by hydrolysis upon workup, would give structure IV, followed by two 1,5-hydrogen shifts to give compound I. Structure I must



be a thermodynamically more stable isomer since the compound remains unchanged on heating to 130°.

Acknowledgements

We thank the Graduate School for the award of a University Research Assistantship (1973-74) to Mary N. Andrews, and Dr. David L. Harris for recording the ^{13}C NMR spectra.

References

1 W. Reppe, O. Schlichting, K. Klager and T. Topepel, Ann., 560 (1948) 1.
2 For example: T.S. Cantrell, J. Amer. Chem. Soc., 92 (1970) 5480.
3 K.O. Hodgson, F. Mares, D.F. Starks and A. Streitwieser, J. Amer. Chem. Soc., 95 (1973) 8650 and refs. therein.
4 A. Streitwieser, U. Muller-Westerhoff, G. Sonnichsen, F. Mares, D.G. Morrell, K.O. Hodgson and C.A. Harmon, J. Amer. Chem. Soc., 95 (1973) 8644.
5 T.J. Katz, C.R. Nicholson and C.A. Reilly, J. Amer. Chem. Soc., 88 (1966) 3832.
6 V.D. Azatyan, Izv. Akad. Nauk. Arm. SSR, Khim. Nauk., 17 (1964) 706; Chem. Abstr., 63 (1965) 4323 j.
7 F.A. Cotton and G. Deganello, J. Amer. Chem. Soc., 95 (1973) 396.
8 R.M. Silverstein and G.C. Bassler, Spectroscopic Identification of Organic Compounds, Wiley, New York, 1967.
9 M. St.-Jacques and R. Prud'homme, Tetrahedron Lett., (1970) 4833.
10 L.A. Paquette, J. Amer. Chem. Soc., 95 (1973) 2230.
11 V.D. Azatyan and R.S. Gyuli-Keukhyan, Izv. Akad. Nauk. SSR, Khim. Nauk., 14 (1961) 451; Chem. Abstr., 58 (1963) 3327a.
12 A. Davison and P.E. Rakita, Inorg. Chem., 9 (1970) 289.
13 P.E. Rakita and A. Davison, Inorg. Chem., 8 (1969) 1164.
14 A.J. Ashe, J. Org. Chem., 37 (1972) 2053.
15 D.A. Bak and K. Conrow, J. Org. Chem., 31 (1966) 3958.
16 J.L. Kice and T.S. Cantrell, J. Amer. Chem. Soc., 85 (1963) 2298.
17 H. Schechter, J.T. Gardikes, T.S. Cantrell, and G.V. Treus, J. Amer. Chem. Soc., 89 (1967) 3005.
18 W.R. Roth, Ann., 671 (1964) 25.