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THE REACTION OF THE CYCLOOCTATETRAENYL DIANION AND CHLOROTRIMETHYLSILANE; SYNTHESIS AND DECOMPOSITION STUDIES OF 5,8-BIS(TRIMETHYLSILYL)CYCLOOCTATRIENE

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Summary

On the basis of PMR decoupling experiments and thermal decomposition studies, the reaction of the cyclooctatetraenyl dianion and chlorotrimethylsilane produces 5,8-bis(trimethylsilyl)-1,3,6-cyclooctatriene, in contrast to a previous report which suggested 7,8-bis(trimethylsilyl)-1,3,5-cyclooctatriene. The product is stable at room temperature in vacuo but undergoes decomposition (isomerization) reactions at higher temperatures or in contact with air.

Introduction

The cyclooctatetraenyl dianion (cyclooctatetraenyldilithium) [1] has been used in a number of dicarbanionic and electron-transfer reactions with esters, anhydrides, nitriles, nitroso compounds, aldehydes, ketones, selected acid chlorides, and alkyl halides [2].

Cyclooctatetraene derivatives with a silicon atom bound directly to the carbon atoms in the ring have been reported only in a few instances. Monosilyl derivatives of cyclooctane, cyclooctene, and cyclooctatriene were prepared by treating cyclooctene, cyclooctadiene, and cyclooctatetraene with Et_3SiH, Et_2SiH_2, and Cl_3SiH, but these reactions were carried out in an autoclave with a Pt/Al_2O_3 catalyst [3]. Bis-silyl derivatives were suspected but results were ambiguous in the reaction with Et_3SiH. The only previously reported reaction between the cyclooctatetraenyl dianion and a silyl halide [4] was postulated to give 7,8-bis(trimethylsilyl)-1,3,5-cyclooctatriene (I). This structure was assigned on the basis of comparison with the IR and UV spectra of the product with the spectra of the separate 1,3,5-cyclooctatriene and 1,3,6-cyclooctatriene isomers.

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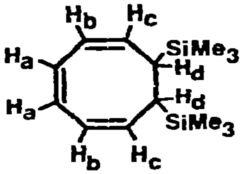
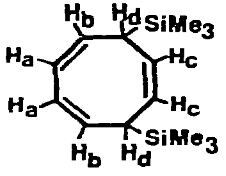
We wish to report evidence which would indicate that the product of this reaction is actually 5,8-bis(trimethylsilyl)-1,3,6-cyclooctatriene (II).



(I)



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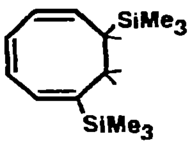


(III)

Experimental

Preparation of the cyclooctatetraenyl dianion

This reaction was carried out in a 500 ml three-neck flask equipped with a nitrogen gas inlet, a paddle stirrer, and a stopcock joint in the bottom of the flask to allow the cyclooctatetraenyl dianion solution to leave the flask without having to be poured in the air.

Lithium metal (0.8 g, about 115 mmoles) was pounded into a sheet and cut with scissors into tiny pieces which were dropped into a flask containing freshly distilled cyclooctatetraene (6.0 g, 58 mmoles) in 200 ml of dry ethyl ether. The flask was continually flushed with dry N_2 gas during the lithium addition. The flask was stoppered and stirred under N_2 for 12 to 36 hours, until no more lithium metal remained. The solution turned deep red-brown and contained tiny yellow crystals of the dianion which were flammable in contact with air. The cyclooctatetraenyl dianion could also be prepared by using potassium sand in monoglyme solvent, but the ease of handling indicated the use of lithium.

5,8-Bis(trimethylsilyl)-1,3,6-cyclooctatriene

A 2 liter three-neck round-bottom flask was fitted with a N_2 gas inlet and a paddle stirrer. Freshly distilled chlorotrimethylsilane (12.5 g, 115 mmole) was added to 150 ml of dry ethyl ether in the flask. The flask was then flushed with N_2 gas for several minutes before the stopcock joint of the dianion flask was fitted into the third neck of the large flask, thus sealing the contents of the large flask under N_2. The contents of the large flask were then cooled to ca. —50°C before slow addition of the dianion solution was begun. Addition of the dianion solution took 15 min during which time the reaction mixture was stirred. Following addition of the dianion solution, the reaction mixture was allowed to slowly reach room temperature and stir overnight. The LiCl precipitate was then filtered off the bright yellow solution. The ether solvent was removed from the filtrate by a rotary evaporator to leave an orange oil. This oil was dissolved in 40 ml of acetone and the solution was cooled to —78°C at which time white crystals formed. The crystals of bis(trimethylsilyl)cyclooctatriene (5.01 g, 35.2% yield) were collected and recrystallized from acetone three times; m.p. 54.5-55.5°C. (Found: C, 67.51; H, 10.65. $C_{14}H_{26}Si_2$ calcd.: C, 67.11; H, 10.76%).

Physical measurements

The mass spectrum of $C_8H_8[Si(CH_3)_3]_2$ was obtained on an Associated Electrical Industries MS-9 spectrometer using an ionizing voltage of 70 eV and an ionizing current of 50 microamps.

The observed mass spectrum contained a large parent ion at *m/e* 250, and major fragments at *m/e* 177, 162, 147, 135, 73, 59, 45, and 28. The 100% abundant peak was *m/e* 73, corresponding to the $(CH_3)_3Si^+$ ion. The exact mass for the peak at *m/e* 250 (calcd. 250.158; error = + 3.4 ppm) confirmed the molecular formula $C_{14}H_{26}Si_2$.

The PMR spectra were obtained on a Varian HA-100 equipped with a Muirhead-Wigan D-840-A Decade Oscillator for decoupling experiments. All samples were run as solutions in CS_2 solvent using $CHCl_3$ as internal standard. Positive values on the δ scale refer to ppm downfield from TMS.

The PMR spectrum of $C_8H_8[Si(CH_3)_3]_2$ as shown in Fig. 1 consists of a multiplet equivalent to 2 protons at δ 5.82 [H_a], a multiplet equivalent to 4 protons at δ 5.50 [H_b and H_c], a multiplet equivalent to 2 protons at δ 2.77 [H_d], and a sharp singlet equivalent to 18 protons at δ 0.05 [$Si(CH_3)_3$].

The IR spectra were run on a Perkin—Elmer Model 257 Spectrometer in CCl_4 solution between NaCl plates. Bands (in cm^{-1}) were observed at 3000(s), 2950(s), 2925(w), 2893(m), 2850(m), 1622(m), 1412(m), 1247(vs), 1092(m), 930(m), 905(m), 840(vs), 725(m), 709(m), 682(m), 658(m), 641(s), and 614(w). The very strong bands at 1247 and 840 cm^{-1} are attributed to the Si—CH_3 deformation and the Si—CH_3 stretch, respectively [5].

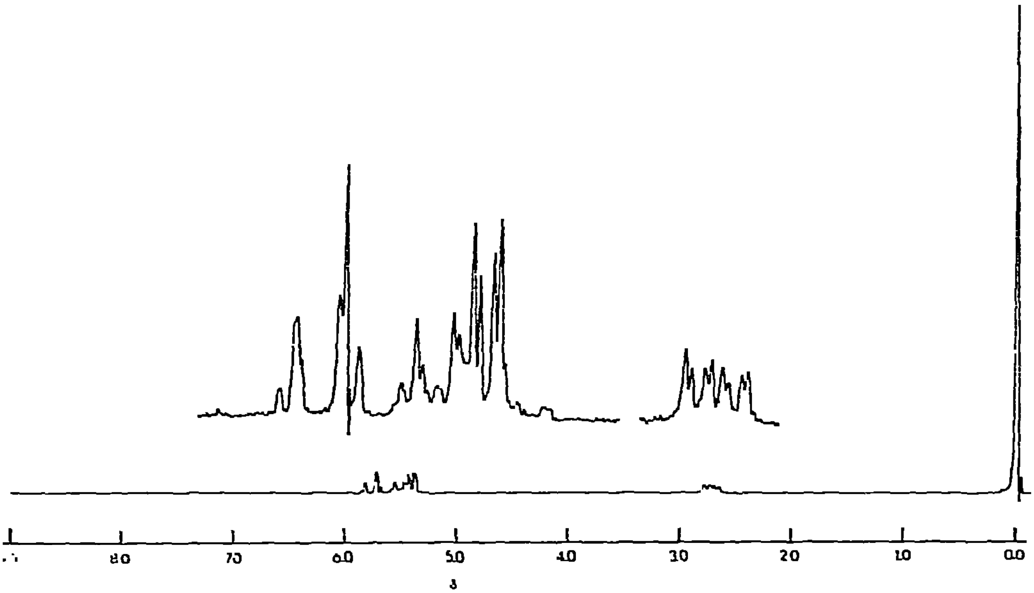


Fig. 1. PMR spectrum (100 MHz) of 5,8-bis(trimethylsilyl)-1,3,6-cyclooctatriene in CS_2 solution.

Results and discussion

PMR decoupling experiment

The reaction of cyclooctatetraenyldilithium with chlorotrimethylsilane should produce only two possible isomers, I and II, of bis(trimethylsilyl)cyclooctatriene. A 6,8-bis(trimethylsilyl)-1,3,5-cyclooctatriene (numbering as in I and II) isomer III is less likely from this reaction as only the 5, 7, and 8 positions on the dianion bear significant negative charges [2]. To help determine which isomer, I or II, was produced, the multiplet at δ 2.77 was irradiated. This multiplet has been assigned to the saturated protons on the ring carbons bound to silicon and labelled H_a in structures I and II. The effect of this decoupling on II should be a decreased splitting of the signals due to strong coupling between protons H_d and both H_c and H_b. Decoupling protons H_d in I however, should have its main effect on the signal produced by the two H_c protons. When, in fact, the signal at δ 2.77 is irradiated, the multiplet at δ 5.50 (equivalent to 4 protons) collapses to a broad singlet while the multiplet at δ 5.82 (equivalent to 2 protons) remains unchanged. In addition, although there is apparent long range allylic coupling between protons H_d and H_a (as labelled in structure II), the lack of measurable coupling between protons H_d and H_a is strongly suggestive of structure II.

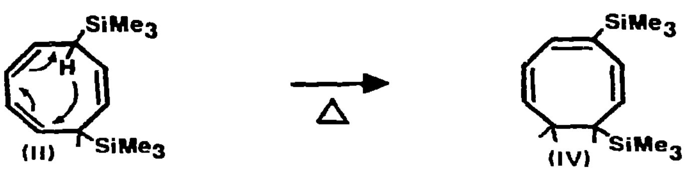
Additional evidence in support of structure II is gained from the use of the bis(trimethylsilyl)cyclooctatriene as a ligand with metal carbonyls. When II is treated with iron carbonyls, the products have PMR spectra which are consistent with the indicated structure [6], and the X-ray structure of a ruthenium compound with this ligand indicates that the $(CH_3)_3Si$ groups are 1,4 to each other [7].

In the original report of the synthesis of bis(trimethylsilyl)cyclooctatriene [4], the product was a yellow oil obtained by vacuum distillation (118-121°/8 mm and 127-129°/8 mm) of the yellow reaction mixture (following removal of LiCl). When the conditions of the original synthesis were repeated, excluding the vacuum distillation step, the only product found was a white crystalline product identified as II.

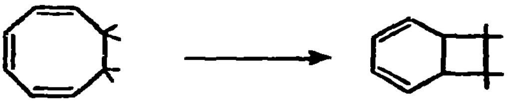
Decomposition study of II

Pure II is a white crystalline solid at room temperature. However, after several hours in the air at room temperature, II decomposes to a yellow oil. Since it has been reported that dialkylcyclooctatrienes react with oxygen in the atmosphere [8], a simple experiment was designed to determine whether the decomposition of II was simply a thermal one, or if it was a reaction with oxygen, or both. A sample of pure II was placed in a tube and left exposed to the air. Two other samples were sealed in tubes in vacuo. One tube was placed in an oven at 84°C for 48 h, while the other tube was kept at room temperature for two months.

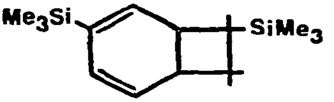
It should be mentioned here that there are several possibilities for thermal decomposition products. Roth [9] has studied the thermal transformation of 1,3,6-cyclooctatriene to the 1,3,5-isomer involving a 1,5-hydrogen shift. If this occurred with II, isomer IV, 3,8-bis(trimethylsilyl)-1,3,5-cyclooctatriene would be the result. This type of isomerization was observed with 5,8-dimethyl-


(II) (IV)

1,3,6-cyclooctatriene which was never isolated pure from its 1,3,5-isomer [10]. Furthermore, 1,3,5-cyclooctatrienes are known to thermally bicyclize [10-12].



Therefore, two of the possibilities for the thermal decomposition products of II are IV and V.


(V)

The sample which was exposed to air decomposed to an orange-yellow oil within a few hours. A PMR spectrum of this oil dissolved in CS_2 did not appear to be that of a single compound. There was a multiplet centered at δ 7.35 and what appeared to be two sets of doublets at δ 0.30 and 0.20. Only very small traces remained of the aliphatic proton signal at δ 2.77 and the olefinic proton signals at δ 5.82 and 5.50. The two sets of doublets in the TMS region are probably two sets of identical singlets, thus indicating the presence of two compounds, each of which has two nonchemically-equivalent $(CH_3)_3Si$ groups. The shift of the olefinic protons to lower field in the decomposition product suggests that II indeed may have reacted with oxygen in the air to form some type of oxygenated species. This suggestion gains support from the fact that elemental analyses run on samples of II which had been exposed to the air for several hours gave carbon and hydrogen values lower than those calculated. It should be noted that Azatyan observed the same phenomenon in his original report of the reaction of $C_8H_8^{2-}$ with the Me_3SiCl; he had established previously that absorption of atmospheric oxygen occurs with dialkylcyclooctatrienes [8].

The sample which was sealed under vacuum and kept at 84°C for 48 h turned to a pale yellow liquid. The PMR spectrum of this sample dissolved in CS_2 also did not appear to be that of a single compound. The olefinic signals had decreased in intensity while the aliphatic multiplet at δ 2.77 had gained in intensity and complexity. Three sharp singlets of different intensity appeared in the TMS region. It was not possible from the PMR spectrum to determine how much, if any, of II, IV, and V were present. It is obvious, however, that heat does cause decomposition of II even in vacuo. This means that under the conditions of the previously reported [4] vacuum distillation (118-129°C/8 mm), compound II could have isomerized to several products. Any of the thermal decomposition isomers would give the same elemental analysis as II. Therefore, there may be some question as to whether a pure bis(trimethylsilyl)cyclooctatriene was actually isolated, or if the previously reported compound [4] was simply a mixture of II and its thermal decomposition products.

The third sample of pure II which remained at room temperature showed little or no decomposition after two months. So it may be concluded that pure II is thermally stable at room temperature in vacuo, thermally decomposes (isomerizes?) in vacuo, and that another type of decomposition, probably involving reaction with oxygen, occurs even more rapidly in air.

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