

ticular mention must also be made of the fact that neither the originally expected **7** nor 9-acetylfuorene derivative due to **9** can be found in the photolysis of **6**.<sup>15</sup> In other words, extrusion of the bridgehead carbon atom from **6** is limited to the C<sub>1</sub> attached to the acetyl group. It is not clear at this time if the acetyl group favors the bridging of the di- $\pi$ -methane moiety in its vicinity or the phenyl-C<sub>1</sub> bonds  $\beta$  to the carbonyl group are weakened in the excited state. Although it is usually the case that the photochemical Wolff rearrangement dominates the carbene addition,<sup>16</sup> the work of Jones and Ando<sup>17</sup> has shown that the ketocarbene generated by the benzophenone sensitized decomposition of  $\alpha$ -diazo ketones can be trapped even by external olefins. Our results that only the Wolff rearrangement is operative in **4a** in spite of the favorable orientation of the  $\pi$  system of the fluorene ring together with the failure of the quenching experiment with 1,3-pentadiene in the case of **1** suggest that the excited state responsible for formation of the carbene intermediates is singlet. The concerted loss of two geminal aryl residues to give arylcarbenes **4** and **4a** should be a symmetry-allowed process in the excited state.<sup>18,19</sup>

**Acknowledgment.** The authors wish to express their appreciation to Professor M. Ōki for his stimulating discussion of this work.

(15) The uv and nmr spectra of the crude reaction mixtures from photolysis were carefully examined. In cyclohexane and ether the photolysis of **6** is very sluggish and the expected **7** can never be obtained.

(16) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, pp 339, 475.

(17) M. Jones, Jr., and W. Ando, *J. Amer. Chem. Soc.*, **90**, 2200 (1968).

(18) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie and Academic Press, New York, N. Y., 1970, p 144.

(19) Turning lastly to the reason why the di- $\pi$ -methane rearrangement which is operative in barrelene<sup>2</sup> and its benzo and dibenzo derivatives<sup>3</sup> cannot hold true in the tribenzo case, we note that the excited singlet of barrelenes leads to cyclooctatetraene derivatives rather than to semibullvalenes. A path from triptycenes to cyclooctatetraenes may be energetically unfavorable due to loss of aromaticity of two aryl rings in the course of their rearrangement through the quadricyclene type intermediate. Recently a diversion of the di- $\pi$ -methane reaction to the carbene mechanism has been reported for 2-methylenebenzonorbornene (F. Scully, J. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, **95**, 5100 (1973)). The high strain in the normal di- $\pi$ -methane product is considered as the driving force for the observed reaction.

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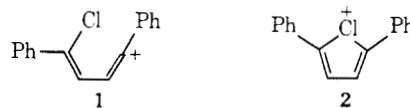
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Received November 9, 1973

## Silver Assisted Solvolysis of Halobutadienes. Evidence for a Chlorolium Ion Intermediate

Sir:

Neighboring halogen is known to interact with carbonium ion centers in aliphatic systems<sup>1</sup> and participation of  $\beta$ -sulfur<sup>2,3</sup> and iodine<sup>4</sup> has been reported in the solvolysis of vinyl derivatives. We here report the results of a study aimed at detecting the capture of a vinyl cation<sup>5</sup> (**1**) by neighboring chlorine. Present in

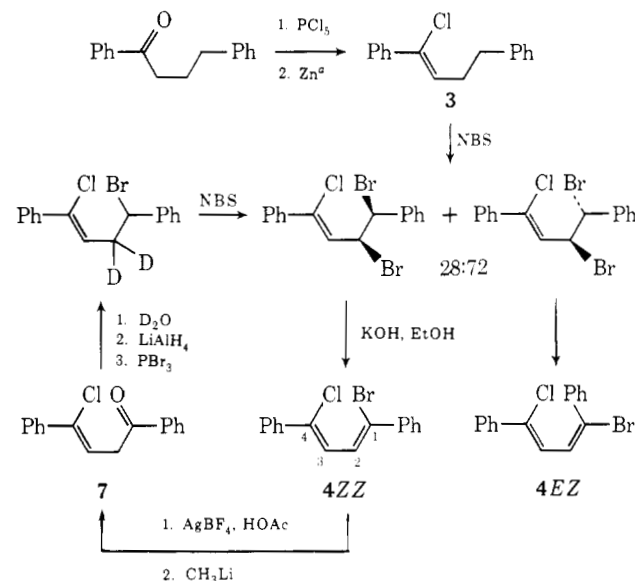


this system is an additional feature of interest since the intermediate formed is the potentially aromatic chlorolium ion (**2**).

Dibenzochlorolium, -bromolium, and -iodolium cations form stable salts,<sup>6</sup> and Beringer, *et al.*,<sup>7</sup> have recently reported the synthesis of the benziodolium and tetraphenyliodolium cations. No evidence for the existence of a species such as **2** has been reported, but Shechter<sup>8</sup> has proposed a bromolium ion as the intermediate in the bromination of 1,8-bisphenylethynyl-naphthalene.

The required precursor for **1** was synthesized as shown in Scheme I. The *N*-bromosuccinimide bro-

Scheme I



<sup>a</sup>The crude reaction mixture after PCl<sub>5</sub> treatment contains 16% 1,1,2-trichloro-1,4-diphenylbutane which can be converted to the desired vinyl chloride with Zn-AcOH.

mination of **3**<sup>9</sup> gave a 72:28 mixture of diastereomers, of which the major isomer could be crystallized to purity, mp 126–127°. Base promoted dehydrohalogenation of this isomer gave **4EZ**<sup>9</sup> (nmr<sup>10</sup>  $\delta_{\text{CCl}_4}$  7.32 (H<sub>2</sub>), 6.64 (H<sub>3</sub>), ABq, *J* = 11 Hz). Pure **4ZZ**<sup>9</sup> ( $\delta_{\text{CCl}_4}$  7.38 (H<sub>2</sub>), 7.24 (H<sub>3</sub>), ABq, *J* = 11 Hz) could be isolated by dehydrohalogenation of the crystallization mother liquor.

The vinyl chloride (**3**) was assigned the *Z* configuration about the double bond since it was the major isomer formed (*Z/E* = 4/1) with the vinyl proton coming at  $\delta$  6.01 ( $\delta$  5.86 for the *E* isomer). The chemical shift difference is consistent with a number of

(5) For a review of vinyl cation chemistry, see M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1970); G. Modena and U. Tonellato, *Advan. Phys. Org. Chem.*, **9**, 185 (1971).

(6) R. B. Sandin and A. S. Hay, *J. Amer. Chem. Soc.*, **74**, 274 (1952).

(7) F. M. Beringer, P. Ganis, G. Avitabile, and H. Jaffe, *J. Org. Chem.*, **37**, 879 (1972).

(8) B. Bossenbrock and H. Shechter, *J. Amer. Chem. Soc.*, **89**, 7111 (1967).

(9) Satisfactory elemental analysis by mass spectral peak match was obtained.

(10) The vinyl resonances were unambiguously assigned by comparison with the deuterated compounds, with and without deuterium decoupling.

(1) P. E. Peterson, *Accounts Chem. Res.*, **4**, 407 (1971).

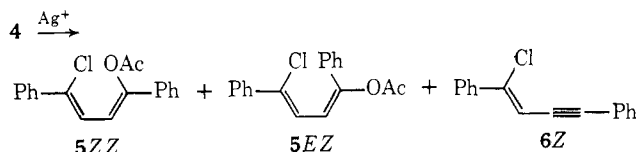
(2) A. Burighel, G. Modena, and U. Tonellato, *J. Chem. Soc., Perkin Trans. 2*, 2026 (1972).

(3) A. S. Denes, I. G. Csizmadia, and G. Modena, *J. Chem. Soc., Chem. Commun.*, **8** (1972).

(4) P. Bassi and U. Tonellato, *Gazz. Chim. Ital.*, **102**, 387 (1972).

related cis and trans isomers that have been observed.<sup>11</sup> The stereochemistry of **4EZ** and **4ZZ** was obtained by treating each compound with 1 equiv of *n*-butyllithium followed by quenching with water, a reaction sequence that proceeds with retention of configuration.<sup>12</sup> From **4EZ**, (*Z*)(*Z*)-1-chloro-1,4-diphenyl-1,3-butadiene ( $J_{3,4} = 8$  Hz) is obtained whereas **4ZZ** gives the (*Z*)(*E*)-isomer ( $J_{3,4} = 16$  Hz).

In acetic acid or acetic anhydride in the presence of silver fluoroborate, both **4EZ** and **4ZZ** solvolyze to give three products. These could be separated by prepara-



tive tlc and were pure by glc analysis. In addition to the aromatic multiplet, the solvolysis products showed the following nmr resonances:<sup>10</sup> **5EZ**<sup>9</sup>  $\delta_{\text{CCl}_4}$  6.58 ( $H_2$ ), 6.84 ( $H_3$ ), ABq,  $J = 11$  Hz, 2.17 ( $\text{CH}_3$ ), s; **5ZZ**<sup>9</sup> 6.91 ( $H_2$ ), 6.81 ( $H_3$ ), ABq,  $J = 11$  Hz, 2.26 ( $\text{CH}_3$ ), s; **6Z**<sup>9</sup> 6.41, s. The stereochemistry of **5EZ** and **5ZZ** was assigned with the aid of  $\text{Eu}(\text{DPM})_3$  shift reagent.<sup>13</sup> The acetylene **6Z** underwent facile dehydrohalogenation with ethanolic sodium hydroxide to give 1,4-diphenylbutadiyne. The stereochemistry was assigned on the basis of a 70-fold larger rate of elimination compared to **6E**<sup>9</sup> (prepared by photochemical isomerization of **6Z**).

In order to test for a symmetrical intermediate, labeled compounds were required. (*E*)(*Z*)- and (*Z*)(*Z*)-1-bromo-4-chloro-1,4-diphenyl-1,3-butadiene-2-*d* (**4-2-d**,  $97 \pm 1\%$   $d_1$ )<sup>14a</sup> were prepared from the enol acetates **5EZ** and **5ZZ** via the ketone **7**. The isomers of **4-3-d** ( $98 \pm 1\%$   $d_1$ )<sup>14a</sup> were prepared starting with 1,4-diphenyl-1-butanone-2,2- $d_2$  as shown in Scheme I.

Table I gives the yields of the solvolysis products of the halobutadienes. Some variation in yield is caused by decomposition during the reaction. The errors are larger for **4ZZ** both because of longer reaction time (**4ZZ** is one-fifth as reactive as **4EZ** in acetic acid) and difficulty in the glc analysis. The intervention of a symmetrical intermediate, the chlorolium ion **2**, is evidenced by the observation of substantial deuterium isomerization in the acetylene **6Z**. Since the deuterium content of **6Z** is dependent on the position of deuterium in the starting material, some of the acetylene is arising from a nonsymmetrical species, probably the vinyl cation **1**. The acetates **5EZ** and **5ZZ**, on the other hand, must be derived almost entirely from the ion **1** since only small amounts (2–6%)<sup>14b</sup> of deuterium isomerization were found. Unfortunately, the small amount of scrambling, together with our inability to accurately assess the deuterium distribution in **4-2-d**,<sup>14</sup>

Table I. Products of Silver Assisted Solvolyses<sup>a</sup>

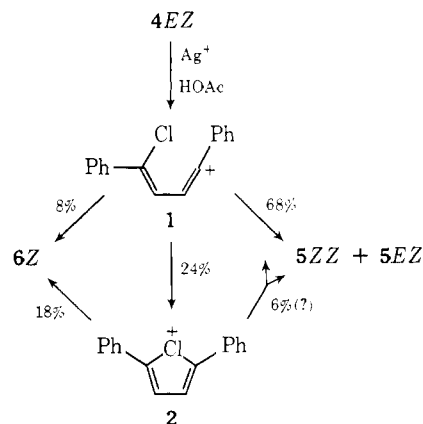
Compd	% yield	(% reaction)	% <b>5EZ</b> <sup>b</sup>	% <b>5ZZ</b> <sup>b</sup>	% <b>6Z</b>	% D in <b>6Z</b> <sup>c</sup>
In Acetic Acid at 118°						
<b>4EZ</b>	97	(62)	21	52	27	
<b>4EZ-2-d</b>	96	(63)	25	52	23	56
<b>4EZ-3-d</b>	91	(72)	23	52	25	79
<b>4ZZ</b>	78	(58)	24	52	24	
<b>4ZZ-2-d</b>	73	(64)	27	53	20	50
<b>4ZZ-3-d</b>	75	(57)	22	51	27	83
In Acetic Anhydride at 80°						
<b>4EZ</b>	93	(89)	19	53	28	
<b>4EZ-2-d</b>	87	(61)	22	52	26	61
<b>4EZ-3-d</b>	83	(67)	20	52	28	72

<sup>a</sup>Yields were determined by glc with correction for detector response;  $[\text{AgBF}_4] = 0.09\text{--}0.18$  M;  $[\textbf{4}] = 0.04\text{--}0.05$  M. About 1 equiv of  $\text{AgOAc}$  (insoluble) was added to neutralize the acid formed. Estimated errors for the determination of product yields are  $\pm 1\%$  for **4EZ** and  $\pm 2\%$  for **4ZZ**. <sup>b</sup>The acetates do not interconvert under solvolysis conditions. <sup>c</sup>Determined mass spectrometrically, error  $\pm 1\%$ . Compound **6Z** undergoes neither geometric isomerization to **6E** nor hydrogen deuterium exchange under the solvolysis conditions.

makes conclusions drawn from this result somewhat tentative. Since vinyl halides are extremely reluctant to undergo  $\text{S}_\text{N}2$  displacements, nucleophilic opening of **2** should be a poor pathway, and reversal to open ion seems a more likely mechanism.

These considerations lead to the mechanism depicted in Scheme II. Yields refer to 100% of isolated prod-

Scheme II



ucts. Assuming that the isotope effect for the direct elimination (**1**  $\rightarrow$  **6Z**) is 2.0,<sup>15</sup> we find that in acetic acid 24% of the solvolysis proceeds through the chlorolium ion, with  $k_\text{H}/k_\text{D}$  for **2**  $\rightarrow$  **6Z** of  $2.4 \pm 0.2$ . In acetic anhydride, 30% of chlorolium ion is formed, and  $k_\text{H}/k_\text{D}$  is 2.2. If the isotope effect for **1**  $\rightarrow$  **6Z** is 1.0, then the amount of chlorolium ion in acetic acid only changes from 24 to 27%, and the isotope effect for **2**  $\rightarrow$  **6Z** becomes 2.8. The observation of lower acetylene yields from **4-2-d** in all cases is consistent with an isotope effect of about 2 for the deprotonation of **1**.<sup>15</sup>

The solvolysis of **4ZZ** in acetic acid gives essentially the same product distribution as does **4EZ**. In the case of **4ZZ**, however, slightly less of the acetylene is formed

(15) (a) We have determined that the product isotope effect ( $k_\text{H}/k_\text{D}$ ) is  $2.0 \pm 0.2$  for silver assisted acetolysis of (*E*)-1-bromo-1-phenylpropene-2-*d* as a model for the conversion **1** to **6Z**. (b) The kinetic analysis of the two routes to **6Z** cannot simultaneously give values for both isotope effects unless the decrease in yield of **6Z** between **4** (or **4-3-d**) and **4-2-d** is used. Unfortunately, the yields are not sufficiently accurate or reproducible to do this.

(11) (a) R. C. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, **87**, 5172 (1965); (b) G. F. P. Kernaghan and H. M. R. Hoffmann, *ibid.*, **92**, 6988 (1970).

(12) The organolithium prepared from **4EZ** gave back 93% isomerically pure **4EZ** on treatment with 1,2-dibromoethane: G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Amer. Chem. Soc.*, **93**, 1379 (1971).

(13) D. R. Kelsey, *J. Amer. Chem. Soc.*, **94**, 1764 (1972).

(14) (a) Deuterium was determined mass spectrometrically. For **4EZ-3-d** it was shown by nmr that all of the deuterium was at the desired position; for **4EZ-2-d** and both deuterated **4ZZ** isomers the region of interest was obscured by aromatic peaks. (b) Determined by pmr with deuterium decoupling (Varian XL-100 system).

via the symmetrical intermediate. In order to obtain the same isotope effect<sup>15b</sup> for deprotonation of **2** during the solvolysis of **4ZZ** as was obtained from **4EZ**, it is necessary for the remainder of the elimination reaction to proceed with an isotope effect of 2.6 instead of the 2.0 as used for **4EZ**. Since E<sub>2</sub> elimination is a commonly observed pathway for vinyl halide solvolysis when hydrogen is trans to the leaving group, we assume that a small contribution from this process is present. It is this contribution which results in the higher isotope effect for the nonchlorolium portion of the elimination. Analyzing the yields and deuterium distribution for **4ZZ** according to Scheme II, we find that 20% of the reaction proceeds via the chlorolium ion **2**, of which 14% appears as acetylene, and, tentatively, 6% as acetate.

An important feature of the solvolysis mechanism may be that the vinyl cation is present in cisoid and transoid conformations, which do not readily interconvert. Thus, the amount of chlorolium ion formed is a function of the fraction of cisoid ion generated and not one of thermodynamic stability or vinyl cation lifetime. Such a hypothesis explains the lack of solvent sensitivity to the amount of chlorolium ion formed. It is also consistent with the smaller than usual amount of elimination product (**6Z**) formed from the open ion since in the transoid ion attack of base on the proton at C<sub>2</sub> is hindered.

The product distribution observed rules out cyclization of **1** to give cyclobutenyl cations, since this would result in the formation of a tertiary benzylic chloride which would rapidly solvolyze further. No halogen-containing products would be expected. Halogen-substituted cyclobutenyl cations apparently do not open to chlorolium or bromolium ions under conditions where cation lifetime is short.<sup>16</sup>

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(16) (a) T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, **86**, 1600 (1964); (b) H. H. Freedman and A. M. Frantz, Jr., *ibid.*, **84**, 4165 (1962).

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### Stereochemical Course in the Photochemistry of the 1,2,3-Trisilacycloheptane System

Sir:

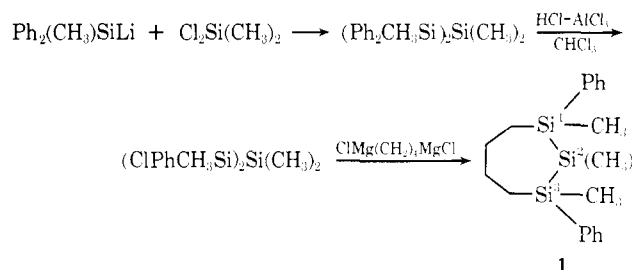
In a recent communication<sup>1</sup> we have reported that 1,2,3-trisilacycloheptane derivatives release a central silicon atom as a silylene on irradiation and that this system can be used generally as a precursor for a tailor-made organosilylene. The unique photochemical reaction in cyclic organopolysilicon compounds may be a cheletropic reaction in the system composed of only a "σ" electron framework.<sup>2</sup> This possibility prompted

(1) H. Sakurai, Y. Kobayashi, and Y. Nakadaira, *J. Amer. Chem. Soc.*, **93**, 5292 (1971).

(2) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

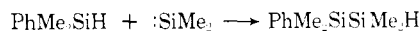
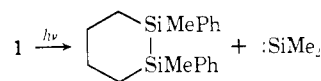
us to prepare *cis*- and *trans*-1,2,3-tetramethyl-1,3-diphenyl-1,2,3-trisilacycloheptane (**1a** and **1b**), in an attempt to study stereochemistry of photochemical generation of dimethylsilylene from the 1,2,3-trisilacycloheptane system.

The synthesis of **1** was accomplished by procedures depicted in the following reactions.



A mixture of *cis*- and *trans*-1,2,3-tetramethyl-1,3-diphenyl-1,2,3-trisilacycloheptane (**1**) was obtained as an oil in 48.1% yield: bp 159–161° (0.38 mm); mass spectral, M<sup>+</sup>, *m/e* 354.<sup>3</sup> Since the *cis*-*trans* mixture showed a single peak on vpc under various conditions and also gave one spot on silica gel tlc, the separation of these two isomers was rather tedious and proceeded as follows. The single spot on a preparative silica gel tlc plate developed with *n*-hexane was divided into lower and upper parts. Each portion was crystallized several times from ethanol at –78°. The *cis* isomer **1a** was obtained from the lower portion as a crystal: mp 45°; uv (*n*-hexane) 251 nm (20,400); nmr (CCl<sub>4</sub>, δ) three singlets at –0.41 (6 H, Si<sup>1</sup>-CH<sub>3</sub> and Si<sup>3</sup>-CH<sub>3</sub>), –0.09 (3 H, Si<sup>2</sup>-CH<sub>3</sub>), and 0.23 (3 H, Si<sup>2</sup>-CH<sub>3</sub>) and three multiplets at 1.12 (4 H, Si-CH<sub>2</sub>–), 1.82 (4 H, C-CH<sub>2</sub>–), and 7.37 (10 H, C<sub>6</sub>H<sub>5</sub>). Similarly the *trans* isomer **1b** was afforded from the upper portion of the spot: mp 33.5–34.5°; uv (*n*-hexane) 247.5 nm (23,400); nmr (CCl<sub>4</sub>, δ) two singlets at 0.16 (6 H, Si<sup>1</sup>-CH<sub>3</sub>) and 0.45 (6 H, Si<sup>1</sup>-CH<sub>3</sub> and Si<sup>3</sup>-CH<sub>3</sub>) and three multiplets at 1.18 (4 H, Si-CH<sub>2</sub>–), 1.90 (4 H, C-CH<sub>2</sub>–), and 7.37 (10 H, C<sub>6</sub>H<sub>5</sub>). Stereochemical assignments of these isomers, **1a** and **1b**, were established unequivocally by inspection of their nmr spectra, especially of the signals due to the Si<sup>2</sup>-CH<sub>3</sub> groups. Thus, in the case of *cis* isomer **1a**, two Si<sup>2</sup>-CH<sub>3</sub> groups are magnetically nonequivalent and appear as two separate singlets. On the other hand, in *trans* isomer **1b**, these groups are magnetically equivalent so that they give a single absorption at δ 0.16.

On irradiation externally through a Vycor filter with a 160-W low-pressure mercury arc lamp for 3 hr, **1** (*cis*/*trans* = 1/1.4) in *n*-hexane yielded 1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane (**2**) in 99.8% yield at 11.5% conversion with accompanying evolution of dimethylsilylene. The latter was trapped by dimethylphenylsilane.



Stereochemistry of the 1,2-disilacyclohexane (**2**) formed from pure **1a** and **1b** was determined by comparing spectral and vpc properties with those of

(3) Satisfactory elemental analyses were obtained.