

and potassium hydroxide to prevent hydrolysis of the borohydride. It was found that diglyme interfered with octalin on analysis by vapor phase chromatography, and the presence of the base was not needed. Under Brown's conditions, however, the same large yield of octalin was obtained.

**Registry No.**—*cis*-9-Chlorodecalin, 5597-83-1; *trans*-9-chlorodecalin, 5597-82-0; (N-Bu)<sub>3</sub>SnH, 688-73-3; (N-Bu)<sub>3</sub>SnD, 6180-99-0; (N-Bu)<sub>2</sub>SnH<sub>2</sub>, 1002-53-5; (Ph)<sub>3</sub>-SnH, 892-20-6.

## Silacyclopentadiene Chemistry. I.

### 1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene<sup>1</sup>

WILLIAM H. ATWELL AND DONALD R. WEYENBERG,

*Organometallic Research Laboratory, Dow Corning Corporation, Midland, Michigan*

AND HENRY GILMAN

*Chemistry Department, Iowa State University, Ames, Iowa*

Received October 6, 1966

The preparation of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (VII) together with a brief investigation of the chemistry of this compound is described. In addition, a comparison of the ultraviolet properties of VII with those of other silacyclopentadienes is presented.

Unlike cyclopentadienes, the study of silacyclopentadienes has received little attention. The first silacyclopentadiene, 1,1,2,3,4,5-hexaphenyl-1-silacyclopentadiene (hexaphenylsilole I<sup>2</sup>), was prepared in 1959 by Braye and Hübel<sup>2a</sup> *via* reaction of a diphenylacetylene-iron-carbonyl complex [Fe<sub>2</sub>(CO)<sub>6</sub>(PhC<sub>2</sub>Ph)<sub>2</sub>] with dichlorodiphenylsilane. Several years thereafter, these same workers<sup>2b</sup> synthesized I by treatment of 1,4-di-

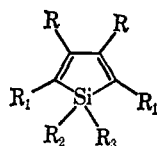
The reaction of 1,4-dithiotetraphenylbutadiene with dichlorodimethylsilane was employed for the synthesis of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (IV).<sup>4</sup> This latter compound underwent Diels-Alder reactions with acetylenic dienophiles to give 7-silanorbornadienes.<sup>4</sup> A similar study has been carried out with 1,1,2,3,4,5-hexaphenyl-1-silacyclopentadiene (I).<sup>5</sup>

In a recent report,<sup>6</sup> 1,4-dithiotetraphenylbutadiene was utilized in the synthesis of silacyclopentadienes functionality at the silicon, 1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (V) and 1,2,3,4,5-pentaphenyl-1-silacyclopentadiene (VI). In addition, numerous attempts<sup>7</sup> to prepare lesser substituted silacyclopentadienes by dehydrohalogenation of silacyclopentanes and silacyclopentenes have been reported by Benkeser, *et al.*

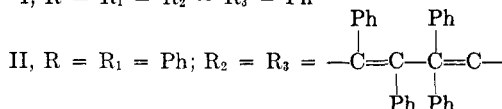
We now wish to report full details concerning the preparation and properties of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (VII), together with some reactions of the silacyclopentadiene ring system.<sup>1,8</sup>

### Results and Discussion

1,1-Dimethyl-2,5-diphenyl-1-silacyclopentane (IX) was prepared from styrene, dichlorodimethylsilane, and lithium according to a published procedure.<sup>9,10</sup> Treatment of IX with N-bromosuccinimide (NBS) gave *trans*-2,5-dibromo-1,1-dimethyl-2,5-diphenyl-1-silacyclopentane (X). Refluxing X in the presence of potassium acetate gave high yields of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (VII).



I, R = R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = Ph



III, R = R<sub>1</sub> = H; R<sub>2</sub> = R<sub>3</sub> = Me

IV, R = R<sub>1</sub> = Ph; R<sub>2</sub> = R<sub>3</sub> = Me

V, R = R<sub>1</sub> = Ph; R<sub>2</sub> = Me; R<sub>3</sub> = H

VI, R = R<sub>1</sub> = R<sub>2</sub> = Ph; R<sub>3</sub> = H

VII, R = H; R<sub>1</sub> = Ph; R<sub>2</sub> = R<sub>3</sub> = Me

VIII, R = R<sub>1</sub> = R<sub>2</sub> = Ph; R<sub>3</sub> = Me

lithiotetraphenylbutadiene with dichlorodiphenylsilane. The strong fluorescence and ultraviolet spectrum of I were reported at this time. A spirooctaphenyl-1-silacyclopentadiene derivative (II) was also prepared<sup>2b,c</sup> in low yield (*ca.* 1%).

1,1-Dimethyl-1-silacyclopentadiene (III) has been prepared by the catalytic dehydrogenation of 1,1-dimethyl-1-silacyclopentane<sup>3</sup> at high temperature. Compound III decolorized bromine solutions and reduced silver nitrate; however, the reaction products were not identified.<sup>3a</sup>

(1) Presented in part at the Division of Organic Chemistry, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstracts, p 100K.

(2) Since the silacyclopentadienes can be regarded as members of a general class of compounds designated as metaloles, the term "silole" has been used previously in naming these derivatives: (a) E. H. Braye and H. Hübel, *Chem. Ind. (London)*, 1250 (1959); (b) E. H. Braye, W. Hübel, and I. Caplier, *J. Am. Chem. Soc.*, **83**, 4406 (1961); (c) U. S. Patent 3,151,140 (1964); *Chem. Abstr.*, **61**, 16097 (1964).

(3) (a) J. Groubeau, T. Kolmar, and H. Hofman, *Ann.*, **659**, 39 (1962). (b) O. M. Nefedov and M. N. Manakov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 769 (1963); *Chem. Abstr.*, **59**, 8781 (1963).

(4) H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Am. Chem. Soc.*, **86**, 1956 (1964).

(5) H. Gilman, S. G. Cottis, and W. H. Atwell, *ibid.*, **86**, 5584 (1964).

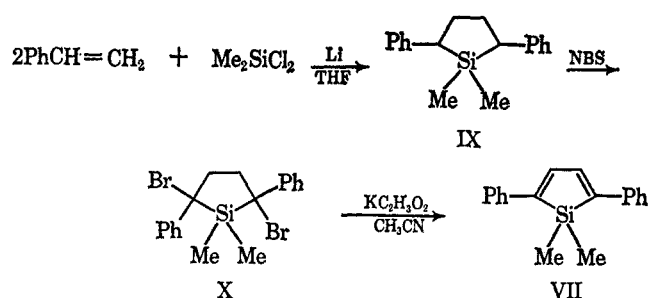
(6) K. Ruhmann, *Z. Chem.*, **5**, 354 (1965).

(7) (a) R. A. Benkeser and G. M. Stanton, *J. Am. Chem. Soc.*, **85**, 834 (1963); (b) R. A. Benkeser, L. Noe, and Y. Nagai, *J. Org. Chem.*, **30**, 378 (1965); (c) R. A. Benkeser, Y. Nagai, J. L. Noe, R. F. Cunico, and Peter H. Gund, *J. Am. Chem. Soc.*, **86**, 2446 (1964).

(8) For a preliminary report of compound VII, see H. Gilman and W. H. Atwell, *J. Organometal. Chem.*, **2**, 291 (1964).

(9) D. R. Weyenberg, L. H. Toporcer, and A. E. Bey, *J. Org. Chem.*, **30**, 4096 (1965).

(10) O. M. Nefedov, M. N. Manakov, and A. D. Petrov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1228 (1962). These workers did not determine the position of the phenyl substituents in IX. For a reported dehydrogenation of this 1,1-dimethyl-*z,z'*-diphenyl-1-silacyclopentane, see ref 3b.



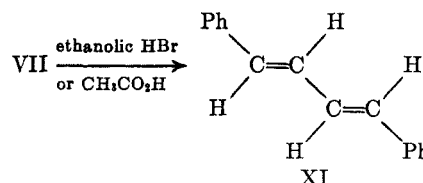
Compound VII is a bright yellow-green solid, mp 132–133°. The nmr spectrum shows, in addition to the aromatic multiplet, a sharp singlet at  $\tau$  9.52. The aromatic (olefinic protons included under this multiplet) to aliphatic proton ratio was 2.01 (calcd 2.00). In agreement with other silacyclopentadiene derivatives<sup>2,4,6</sup> this compound exhibits a brilliant fluorescence in ultraviolet light in the solid state. The ultraviolet properties of several silacyclopentadienes are given in Table I. Silacyclopentadiene VII exhibits a significant bathochromic shift (13 m $\mu$ ) for the longest wavelength maximum when compared with values reported<sup>11</sup> for the nearly analogous carbon compound 1,4-diphenylcyclopentadiene:  $\lambda_{\text{max}}^{\text{dioxane}}$  239 m $\mu$  ( $\epsilon$  12,600), 357 m $\mu$  ( $\epsilon$  21,000). While the nature of this effect is not known, a similar shift is observed upon comparison of the spectra of the tetraphenylsilacyclopentadienes with those reported<sup>12</sup> for 2,3,4,5-tetraphenylcyclopentadiene:  $\lambda_{\text{max}}^{\text{cyclohexane}}$  245 m $\mu$  ( $\epsilon$  27,100), 269 (20,400), 346 (14,000).

TABLE I  
ULTRAVIOLET PROPERTIES OF  
SOME SILACYCLOPENTADIENE DERIVATIVES

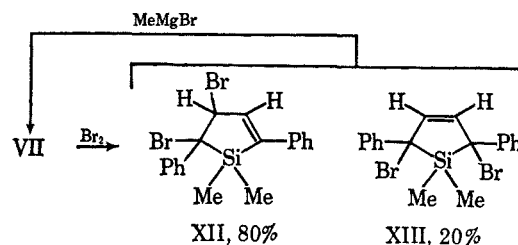
Compd	$\lambda_{\text{max}}$ , m $\mu$ (cyclohexane)	Molar absorbivity, $\epsilon$	Ref
I	249	27,200	2a
	365	8,200	
IV	247	24,900	4
	357	10,000	
V	246		a
	362		
VII	230	13,000	b
	370	20,000	
VIII	248	24,600	c
	362	9,000	

<sup>a</sup> Prepared from 1,4-dilithiotetraphenylbutadiene and methyl-dichlorosilane, mp 223–225°: W. H. Atwell and D. R. Weyenberg, unpublished studies (see also ref 6). <sup>b</sup> This work. <sup>c</sup> Prepared from 1,4-dilithiotetraphenylbutadiene and methylphenyl-dichlorosilane, mp 173–175°: H. Gilman and W. H. Atwell, unpublished studies.

With the lesser ring substituted silacyclopentadiene (VII) readily available, a brief investigation of its chemistry was undertaken. Treatment of VII with hydrogen bromide in refluxing ethanol resulted in a rapid loss of the characteristic yellow-green color to produce 1,4-diphenyl-*trans,trans*-butadiene (XI). The butadiene XI was also obtained by prolonged refluxing of VII in glacial acetic acid.



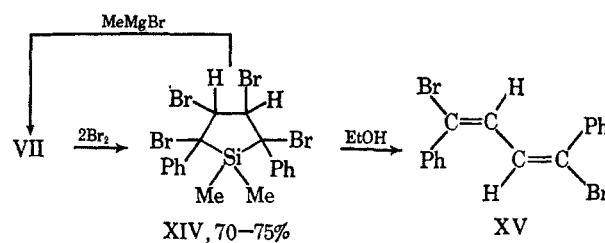
Compound VII rapidly absorbed 1 equiv of bromine to give a mixture of *trans*(?)–2,3-dibromo-1,1-dimethyl-2,3-dibromo-1-silacyclopent-4-ene (XII) and *trans*-2,5-dibromo-1,1-dimethyl-2,5-diphenyl-1-silacyclopent-3-ene (XIII). The nmr spectrum of XII



showed a pair of doublets centered at  $\tau$  2.93 (CH,  $J$  = 3.7 cps) and 4.06 (C=CH,  $J$  = 3.7 cps) and two singlets at 9.13 and 9.38 for the methyl groups. A *trans* position for the bromines is assumed on the basis of the known mode of addition of bromine to olefins. The nmr spectrum of XIII consisted of two singlets at  $\tau$  4.72 and 9.82 characteristic of the olefinic and the methyl protons, respectively. The *trans* assignment follows from the equivalence of the methyl groups.

Treatment of a mixture of XII and XIII with methylmagnesium bromide regenerated the silacyclopentadiene VII. While dehydrohalogenation of a cyclic organosilicon compound *via* a Grignard reagent has been reported,<sup>13</sup> this appears to be the first example of the use of this reagent for debromination.

Compound VII reacted slowly with a second equivalent of bromine to give 2,3,4,5-tetrabromo-1,1-dimethyl-2,5-diphenyl-1-silacyclopentane (XIV). The nmr spectrum of XIV showed singlets at 4.54 and 9.79 characteristic of the CH and SiMe protons, respectively. The assignments made with compounds XII and XIII together with their nmr spectra (particularly the single absorption for the methyl groups) suggests that the stereochemistry of XIV is such that all vicinal bromines are *trans* to each other. Reaction of XIV with methylmagnesium bromide regenerated silacyclopentadiene VII.



Compound XIV reacted rapidly with refluxing ethanol to give an almost quantitative yield of 1,4-dibromo-*trans,trans*-1,4-diphenylbutadiene (XV). Since the cleavage of  $\beta$ -halogenated alkyl groups from silicon

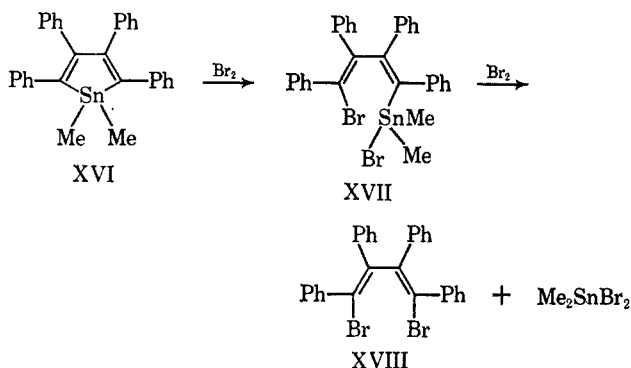
(11) S. G. Cohen, R. Zand, and C. Steel, *J. Am. Chem. Soc.*, **83**, 2895 (1961).

(12) (a) N. O. V. Sonntag, S. Linder, E. I. Becker, and P. E. Spoerri, *ibid.*, **75**, 2283 (1953); (b) H. Kainer, *Ann.*, **578**, 232 (1952).

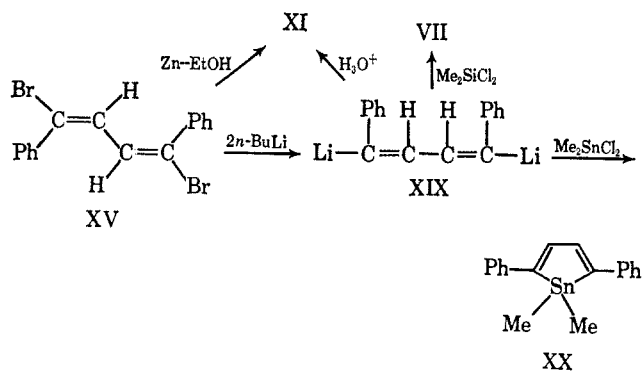
(13) See H. Gilman and W. H. Atwell, *J. Am. Chem. Soc.*, **87**, 2678 (1965), and pertinent references cited therein.

( $\beta$ -silicon effect) is well documented,<sup>14,15</sup> compound XV most likely arises *via* a double  $\beta$  elimination of this type. The unusually high reactivity of XIV may reflect the relief of ring strain in the first elimination and the loss of an allylic bromine in the second elimination.

It is interesting to contrast the bromination of the silacyclopentadiene VII with that previously reported for a related heterocycle, 1,1-dimethyl-2,3,4,5-tetraphenylstannole (XVI).<sup>16</sup> Freedman has demonstrated<sup>16</sup> that bromination of XVI proceeds *via* scission of the SnC bond to give the ring-opened specie (XVII). Further bromination gives dimethyltin dibromide and 1,4-dibromotetraphenylbutadiene (XVIII). Thus, while both heterocycles VII and XVI are capable of yielding 1,4-dibromobutadienes, the reaction paths are quite different.



The formation of the butadiene XV was of considerable synthetic interest and an effort was made to characterize this material in some detail. The ultraviolet spectra properties [ $\lambda_{\max}^{\text{cyclohexane}}$  327  $m\mu$  ( $\epsilon$  33,200), 233  $m\mu$  ( $\epsilon$  12,400)] show a hypsochromic shift of the absorption maxima and a lowering of the molar absorptivity when compared with values reported<sup>17,18</sup> for 1,1,4,4-tetraphenylbutadiene [ $\lambda_{\max}^{\text{EtOH}}$  343  $m\mu$  ( $\epsilon$  37,250), 249  $m\mu$  ( $\epsilon$  22,800)]. This observation is consistent with substitution in a molecule of 1,4-diphenylbutadiene which leads to steric interference about the conjugated system. Reaction of XV with zinc in refluxing ethanol gave 1,4-diphenyl-*trans,trans*-butadiene (XI). Treatment of XV with 2 equiv of *n*-butyllithium gave the novel 1,4-dilithio-1,4-diphenyl-



(14) C. Eaborn, "Organosilicon Compounds," Butterworth and Co. (Publishers) Ltd., London, 1960.

(15) P. D. George, M. Prober, and J. R. Elliott, *Chem. Rev.*, **56**, 1065 (1956).

(16) H. H. Freedman, *J. Org. Chem.*, **27**, 2298 (1962).

(17) K. B. Alberman, R. N. Haszeldine, and F. B. Kipping, *J. Chem. Soc.*, 3285 (1952).

(18) Y. Hirshberg, E. Bergmann, and F. Bergmann, *J. Am. Chem. Soc.*, **72**, 5120 (1950).

butadiene (XIX). Subsequent hydrolysis of the dilithio reagent gave butadiene XI (85%), while derivitization with dichlorodimethylsilane regenerated silacyclopentadiene (VII). The synthetic utility of the dilithio reagent XIX was further demonstrated by derivitization with dimethyltin dichloride to give 1,1-dimethyl-2,5-diphenylstannole (XX).

Compound XX is a yellow-green solid, mp 121–122°. The nmr spectrum of XX shows, in addition to the aromatic multiplet, a sharp tin-methyl singlet at  $\tau$  9.38 ( $J_{\text{Sn}^1\text{H}} = 55.1$  cps;  $J_{\text{Sn}^1\text{H}} = 58.5$  cps). The aromatic (olefinic protons included under this multiplet) to aliphatic proton ratio was 2.01 (calcd 2.00). The ultraviolet spectrum of XX was similar to that of the silicon analog, exhibiting maxima at 366  $m\mu$  ( $\epsilon$  22,600) and 230  $m\mu$  ( $\epsilon$  10,200). This investigation has provided synthetic procedures and additional knowledge of the chemical reactivity of silacyclopentadienes which will be of value in further exploration of this field. Further studies on lesser substituted and silicon-functional systems are in progress.

### Experimental Section

The nmr spectra were measured with either a Varian HR-60 or A-60 spectrometer using tetramethylsilane as internal standard. Unless stated otherwise, all spectra were run using carbon tetrachloride as solvent. Ultraviolet spectra were determined on a Beckman DK-2A spectrophotometer using cyclohexane as solvent. All melting points are uncorrected. The methylmagnesium bromide (3 *M* in ether) was purchased from Arapahoe Chemicals, Inc. The *n*-butyllithium (15% in hexane) was purchased from Foote Mineral.

***trans*-2,5-Dibromo-1,1-dimethyl-2,5-diphenyl-1-silacyclopentane (X).**—A solution of 40 g (0.15 mole) of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane (IX)<sup>9</sup> and 50 ml of carbon tetrachloride was added dropwise to a refluxing mixture of 52 g (0.29 mole) of NBS and 250 ml of carbon tetrachloride containing a small amount of benzoyl peroxide. An exothermic reaction occurred and the remaining solution of IX (*cis/trans* ratio, 1.2) was added as rapidly as possible while maintaining a controlled reaction.

The reaction mixture was cooled in an ice bath and filtered to remove succinimide. Solvent was removed as completely as possible from the filtrate using a rotary evaporator and a 50° temperature bath. The residue was recrystallized from acetonitrile to give 57.2 g of the title compound (X), mp 96–98° dec (90%).

*Anal.* Calcd for  $\text{C}_{18}\text{H}_{20}\text{Br}_2\text{Si}$ : C, 51.0; H, 4.71; Si, 6.62. Found: C, 51.9, 51.9; H, 5.21, 5.03; Si, 6.46.

The nmr spectrum showed a sharp SiMe singlet at  $\tau$  9.80 together with an  $\text{A}_2\text{B}_2$  pattern in the  $\text{CH}_2$  region. Compound X tended to decompose upon standing and was generally used immediately following its preparation.

**2,5-Diphenyl-1,1-dimethyl-1-silacyclopentadiene (VII).**—To a suspension of crude X (prepared as above from 0.15 mole of IX) in 150 ml of acetonitrile was added 30 g of potassium acetate and 1 ml of acetic acid. The rapidly stirred mixture was refluxed for 1–2 hr, cooled, and poured into a 50:50 ethanol–water mixture. Filtration gave 27.2 g (68%) of VII, mp 130–133°. Recrystallization from a methylene chloride–ethanol mixture gave 26 g (65%) of pure VII, mp 132–133°.

*Anal.* Calcd for  $\text{C}_{18}\text{H}_{18}\text{Si}$ : C, 82.4; H, 6.90; Si, 10.7; mol wt, 262. Found: C, 82.8, 82.8; H, 6.83, 6.82; Si, 10.7, 10.8; mol wt, 262 (by mass spectroscopy).

Compound VII was considerably more reactive to air oxidation than previously reported silacyclopentadienes<sup>2,4,5</sup> and, after 2 to 3 weeks of routine laboratory exposure, samples of VII no longer melted sharply.

**Reaction of VII with Ethanolic Hydrogen Bromide.**—A mixture of 1.0 g (3.82 mmoles) of VII, 3 ml of hydrogen bromide (48% aqueous solution), and 15 ml of ethanol was refluxed for 30 min. The colorless solution was cooled and filtered to give 0.70 g (90%) of 1,4-diphenyl-*trans,trans*-butadiene (XI), mp and mmp 153–154°.

**Reaction of VII with Glacial Acetic Acid.**—A mixture of 0.5 g (1.91 mmoles) of VII and 20 ml of glacial acetic acid was heated at reflux temperature for 48 hr. The light yellow solution was cooled and filtered to give 0.25 g of the butadiene XI, mp 152–154° (64%).

**Reaction of VII with Bromine. A. 1:1 Ratio.**—A solution of 3.1 g (0.019 mole) of bromine in 30 ml of carbon tetrachloride was added dropwise to 5 g (0.019 mole) of VII in 50 ml of the same solvent. Following the addition the solvent was removed using a rotary evaporator. Nmr analysis of the crude reaction product gave a XII/XIII ratio of 4:1. Several recrystallizations of this residue from hexane gave XII, mp 94–96°.

*Anal.* Calcd for  $C_{18}H_{18}Br_2Si$ : C, 51.2; H, 4.28; Br, 38. Found: C, 48.0, 48.0; H, 4.14, 4.15; Br, 43.4, 43.3.

When isolated from solution XII tended to decompose rapidly and analysis was difficult. Repeated attempts to isolate XIII free of significant amounts of XII were unsuccessful.

**B. 1:2 Ratio.**—A solution 12.4 g (0.076 mole) of bromine in 25 ml of carbon tetrachloride was added dropwise to 10 g (0.038 mole) of VII in 30 ml of the same solvent. Initially the bromine color was discharged rapidly; however, heating was utilized during the addition of the second equivalent of bromine. Subsequent to heating overnight (some precipitate present at this time) the solvent was removed with a rotary evaporator. Recrystallization of the residue from a benzene–hexane mixture gave 16 g (72%) of tetrabromo adduct XIV, mp 173–174° dec.

*Anal.* Calcd for  $C_{18}H_{18}Br_4Si$ : C, 37.1; H, 3.10; Br, 55.0; Si, 4.80. Found: C, 37.8, 37.7; H, 3.50, 3.47; Br, 55.2, 55.8; Si, 4.82.

**Debromination of a Mixture of XII and XIII.**—An excess of methylmagnesium bromide was added rapidly to a suspension of 2.0 g (0.047 mole) of a mixture of XII and XIII (ratio ca. 4:1). A yellow-green color developed as the exothermic reaction proceeded. After stirring for 1 hr the reaction mixture was poured into a 50:50 ethanol–water mixture. The ether was removed on a rotary evaporator and the solid VII was isolated by filtration, mp 130–133° (65%).

**Debromination of XIV.**—Using the procedure described above, debromination of 1.0 g (1.72 mmoles) of XIV gave 0.27 g of VII, mp 129–132° (58%).

**Preparation of 1,4-Dibromo-*trans,trans*-1,4-diphenylbutadiene (XV).**—A mixture of 16 g (0.0275 mole) of the tetrabromo-silacyclopentane XIV and 150 ml of ethanol was refluxed for 30 min. Cooling and filtration gave 9.0 g (90%) of XV, mp 121–123°.

*Anal.* Calcd for  $C_{18}H_{18}Br_2$ : C, 52.80; H, 3.30; mol wt, 362. Found: C, 52.86, 52.70; H, 3.31, 3.20; mol wt, 362 (by mass spectroscopy).

**Reaction of XV with Zinc.**—A mixture of 0.5 g (1.36 mmoles) of XV, 0.5 g of zinc dust, and 30 ml of ethanol was refluxed for 18 hr. Filtration, cooling, and concentration gave 0.19 g (68%) of 1,4-diphenyl-*trans,trans*-butadiene (XI), mp 151–154°.

**Preparation of 1,4-Dilithio-1,4-diphenylbutadiene (XIX).**—To a suspension of 0.5 g (1.36 mmoles) of XV and 20 ml of ether (cooled to ice-bath temperature) was added 2.72 mmoles of *n*-butyllithium. The mixture was allowed to come to room temperature during a 30-min period and then hydrolyzed with 5% hydrochloric acid. Following the usual work-up the residue was recrystallized from cold ethanol to give 0.18 g of XI, mp 151–154° (64.5%).

**Reaction of XIX with Dichlorodimethylsilane.**—To a solution of XIX, prepared as described above, was added 0.3 g (1.36 mmoles) of dichlorodimethylsilane in 10 ml of THF. After stirring for 1 hr the mixture was hydrolyzed with 5% hydrochloric acid, extracted with ether, and dried, and the solvents were removed. The residue was recrystallized from ethanol to give 0.21 g (58%) of VII, mp 130–133°.

**Reaction of XIX with Dimethyltin Dichloride.**—A solution of XIX, prepared as described above from 1 g (2.72 mmoles) of XV and 5.74 mmoles of *n*-butyllithium, was added to 0.6 g (2.72 mmoles) of dimethyltin dichloride in 10 ml of ether. After stirring for 1 hr the ether was removed using a rotary evaporator. The residue was extracted with methylene chloride and filtered. Ethanol was added to the filtrate and concentration gave 0.37 g (38.5%) of 1,1-dimethyl-2,5-diphenylstannole (XIX), mp 119–121°. Recrystallization from ethanol gave an analytical sample, mp 120–121°.

*Anal.* Calcd for  $C_{18}H_{18}Sn$ : Sn, 33.6. Found:<sup>19</sup> Sn, 33.7, 33.8.

**Registry No.**—VII, 7688-03-1; I, 752-28-3; IV, 7641-40-9; V, 4071-99-2; VIII, 7641-42-1; X, 7641-43-2; XI, 538-81-8; XII, 7641-44-3; XIV, 7688-04-2; XV, 7641-45-4; XIX, 7641-46-5; XX, 7641-47-6.

**Acknowledgment.**—The authors are indebted to Dr. G. Kallos for his mass spectral determinations and to Mrs. Barbara Taub for technical assistance. A portion of this research was supported by the U. S. Air Force under Contract AF 33(616)-6463 monitored by the Materials Development Center, Wright-Patterson Air Force Base, Ohio

<sup>(19)</sup> The authors wish to thank Dr. W. J. Considine for part of this analysis.

## The Kinetics of the Addition of Bromine to *cis*- and *trans*-Stilbene

ROBERT E. BUCKLES, JAMES L. MILLER, AND ROLAND J. THURMAIER

*Department of Chemistry, University of Iowa, Iowa City, Iowa 52240*

*Received July 27, 1966*

The addition of bromine to *cis*- and *trans*-stilbene in 1,2-dichloroethane, chlorobenzene, and carbon tetrachloride was found to be first order in stilbene and second order in bromine. The results in valeronitrile were too erratic for the order to be established. With tetrabutylammonium tribromide as the sole source of bromine, the reaction in 1,2-dichloroethane, chlorobenzene, and valeronitrile was first order in each reagent. With both bromine and the tribromide present in 1,2-dichloroethane and chlorobenzene the third-order kinetics characteristic of the reaction with bromine were observed. The rate constants increased with increasing concentration of tribromide, but not in a linear fashion. The catalytic effect was found to be decreased at relatively high concentrations of tribromide. In all cases the reaction of *cis*-stilbene was faster than the corresponding reaction of the *trans* isomer. The rates of bromine addition tended to be higher in the more polar solvents. These kinetic results are consistent with polar mechanisms involving an electrophilic attack by bromine. The complex resulting from this interaction can apparently give dibromide product in a variety of ways.

Data on the mechanism of addition of bromine and other halogens to carbon–carbon double bonds have been reported<sup>1–3</sup> for a number of systems. In most

cases<sup>2,4</sup> the reactions have involved an electrophilic attack, but, in some cases<sup>2,3,5,6</sup> involving double bonds substituted with electron-withdrawing groups, a nucleophilic attack is also of importance.

(1) S. V. Anantakrishnan and R. Venkataraman, *Chem. Rev.*, **33**, 27 (1943).

(2) P. B. D. de la Mare, *Quart. Rev.* (London), **3**, 126 (1949).

(3) P. W. Robertson, *Rev. Pure Appl. Chem.*, **7**, 155 (1957).

(4) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 214.

(5) R. E. Buckles and J. P. Yuk, *J. Am. Chem. Soc.*, **75**, 5048 (1953).

(6) R. E. Buckles and L. Harris, *ibid.*, **79**, 886 (1957).