

cyclohexane/ $\text{CCl}_4$  ratio indirectly reflects the cyclohexane/acid chloride ratio which appears to determine the relative amount of inhibitor producing reaction with the acid chloride, the nature of which is obscure.

### Experimental Section

**Chlorocarbonylations** were conducted in the previously described manner.<sup>2</sup> Volumetric solutions were prepared which contained the desired concentrations of cyclohexane and carbon tetrachloride as well as 1-chloro-3-fluorobenzene (50 mol % of  $\text{CCl}_4$ ) used as an inert internal standard for vapor phase chromatographic (vpc) analysis. In each run 20 ml of reaction mixture in a glass-lined bomb was pressurized with CO at 25° and then heated to 130°. The rocked bomb was then irradiated with a cobalt-60 source of approximately 6000 Ci.

Selectivities and conversions were determined by treating reaction mixtures with excess ethanol and analyzing for cyclohexane consumption and chloroform, chlorocyclohexane, and ethyl cyclohexanecarboxylate production, using an F & M 810 gas chromatograph equipped with a 2-ft D.C. 200 silicone oil column in series with a 7-ft Ucon LB550X, 20% on 60-80 mesh, acid-washed

Chromosorb W. The unit was programmed at 6°/min from 75 to 176° with a 10-min upper limit hold. Area ratios of the product peaks to the internal standard (1-chloro-3-fluorobenzene) were measured and multiplied by the appropriate correction factor determined by calibration with weighed mixtures of authentic samples.

Conversions were measured from both  $\text{CHCl}_3$  formation and ( $\text{C}_6\text{H}_{11}\text{Cl} + \text{C}_6\text{H}_{11}\text{COCl}$ ) formation, and when practical from cyclohexane consumption. The selectivity to acid chloride was determined from the relative ratio of  $\text{C}_6\text{H}_{11}\text{Cl}$  to  $\text{C}_6\text{H}_{11}\text{COCl}$ . Examples of data obtained at several pressures are presented in Table V.

**Chlorinations** of cyclohexane and acid chloride mixtures with  $\text{CCl}_4$  in the absence of carbon monoxide were conducted in glass tubes fitted with Fischer & Porter Teflon valves. The tubes were maintained at 130° by means of a thermostated cylindrical aluminum block drilled to accommodate the 1-in. o.d. glass tubes. The reaction tubes were arranged so that each received an equal dose of radiation. The chlorinations were analyzed in the same fashion as the chlorocarbonylations.

**Acknowledgment.** The author wishes to thank Mr. J. J. Werner for his valuable technical assistance.

## $\alpha$ -Silyl-*cis*-stilbenes from Silylcarbonium Ions and from the Platinum-Catalyzed Addition of Silanes to Diphenylacetylene

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**Abstract:** Treatment of triphenylsilylbenzylphenylcarbinols with  $\text{BF}_3$  gives rise to  $\alpha$ -triphenylsilyl-*cis*-stilbenes. These same compounds are produced by platinum-catalyzed addition of silanes to diphenylacetylene, and it is shown that the  $\alpha$ -silyl-*cis*-stilbenes are readily converted photochemically into 9-silylphenanthrenes. With the asymmetric silane  $\text{R}_3\text{Si}^*\text{H}$  the configuration of the asymmetric center is retained during the formation and photolysis of  $\alpha$ - $\text{R}_3\text{Si}^*$ -*cis*-stilbene.

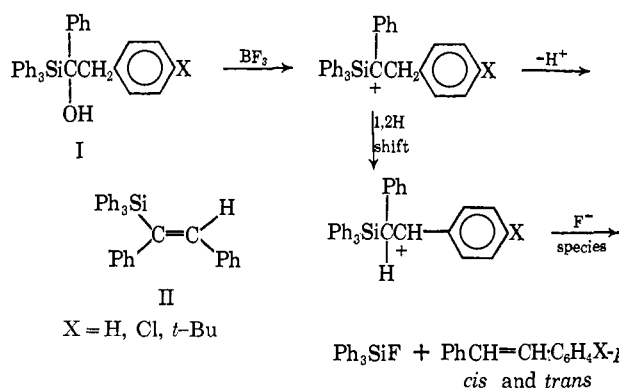
Considerable interest has developed in recent years in the stereochemistry of platinum-catalyzed additions of silanes to unsaturated carbon-carbon systems. Benkeser<sup>1</sup> has shown that chloroplatinic acid or platinum on carbon-catalyzed additions of trichlorosilane to 1-alkynes occur with *cis* stereochemistry. More recently, Sommer<sup>2</sup> has shown that when optically active 1-naphthylphenylmethylsilane adds to 1-octene using platinum catalysts, the addition occurs with complete retention of configuration at the asymmetric silicon atom, optically active adducts being obtained in good yield.

In connection with our work on the behavior of silylcarbonium ions,<sup>3</sup> we found that treatment of a variety of silylbenzylphenylcarbinols (I) with boron trifluoride gave rise, in 30-40% yield, to compounds which appeared to be  $\alpha$ -silyl-*cis*-stilbenes (II), as well as to other fragments such as triphenylfluorosilane, and *cis*- and *trans*-stilbenes derived from decomposition of the original silylcarbonium ion.

(1) R. A. Benkeser and R. A. Hickner, *J. Amer. Chem. Soc.*, **80**, 5298 (1958).

(2) L. H. Sommer, K. W. Michael, and H. Fugimoto, *ibid.*, **89**, 1519 (1967).

(3) A preliminary report of some of this work has appeared. See A. G. Brook, K. H. Pannell, G. E. LeGrow, and J. J. Sheeto, *J. Organometal. Chem.* (Amsterdam), **2**, 491 (1964).

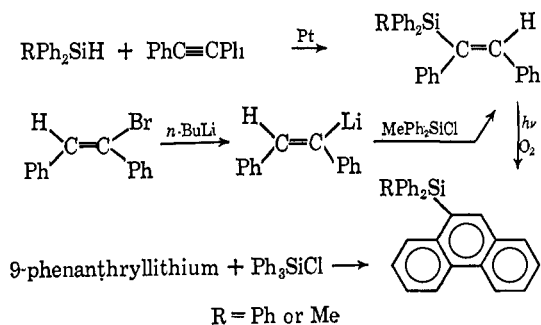


A possible alternative synthesis which would establish the identity of these compounds was the platinum-catalyzed addition of triphenylsilane to diphenylacetylene. Although little study has been made of additions to disubstituted alkynes, Speier has stated that trichlorosilane-*d* adds in a *cis* manner to diphenylacetylene,<sup>4</sup> and Polyakova, *et al.*,<sup>5</sup> have examined the polymers formed in silane additions to diphenylacetylene using chloroplatinic acid as catalyst.

(4) J. W. Ryan and J. Speier, *J. Amer. Chem. Soc.*, **86**, 895 (1964).

(5) A. M. Polyakova, V. V. Korshak, M. D. Suchkova, V. M. Vdovin, and N. A. Chumaevskii, *Vysokomolekul. Soedin.*, **2**, 1360 (1960); *Chem. Abstr.*, **55**, 21643 (1961).

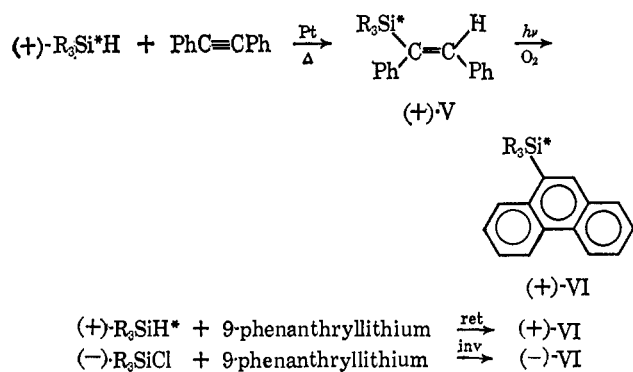
When triphenylsilane or diphenylmethylsilane was treated for a short time either neat at about 110° or in cyclohexane at 80° with diphenylacetylene in the presence of either platinum on carbon or chloroplatinic acid, high yields of the adducts II were obtained. The triphenylsilane adduct was identical with the product derived from the silylbenzylphenylcarbinol. The diphenylmethylsilyl adduct (II, R = Me) was shown unambiguously to have the *cis*-stilbene geometry since it was independently synthesized from the known *cis*-stilbenyllithium (III)<sup>6</sup> by coupling with diphenylmethylchlorosilane. Thus *cis* addition of silanes to diphenylacetylene is clearly established.



Furthermore, although not necessarily indicative of the geometry of the parent compound, when  $\alpha$ -triphenylsilyl-*cis*-stilbene (II, R = Ph) was photolyzed in cyclohexane in the presence of air, a high yield of 9-triphenylsilylphenanthrene (IV) was obtained, a photochemical conversion well-studied with a variety of stilbenes.<sup>7</sup> The 9-silylphenanthrene IV was prepared alternatively from 9-phenanthryllithium and triphenylchlorosilane.

Photolysis of the  $\alpha$ -silyl-*cis*-stilbene in the absence of air gave a 52:48 mixture of  $\alpha$ -silyl-*cis*-stilbene with a compound assigned the  $\alpha$ -silyl-*trans*-stilbene structure on the basis of its nmr and infrared spectra: no 9-silylphenanthrene was observed.

With these findings, it was of interest to examine the behavior of 1-naphthylphenylmethylsilane (designated R<sub>3</sub>Si\*H hereafter) in these reactions. When R<sub>3</sub>Si\*H was heated in cyclohexane for 3 hr with an equivalent of diphenylacetylene and a trace of platinum on carbon, a 93% yield of optically active (+)- $\alpha$ -(1-naphthylphenylmethylsilyl)-*cis*-stilbene (V) was isolated. This material was converted into the corresponding (+)-9-silylphenanthrene (VI) photochemically, and the con-



(6) D. Y. Curtin and E. E. Harris, *J. Amer. Chem. Soc.*, **73**, 4519 (1951).

(7) C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964), and references cited therein.

figuration at silicon was unambiguously established by alternative syntheses.

Thus coupling 9-phenanthryllithium with (+)-R<sub>3</sub>Si\*H, a type of reaction shown previously to occur with retention of configuration at silicon,<sup>8,9</sup> also gave (+)-9-silylphenanthrene which had the same sign and magnitude of specific rotation as was observed for the product of photolysis of the (+)-silane-diphenylacetylene adduct. Hence it is clear that R<sub>3</sub>Si\*H adds stereospecifically with complete retention of configuration to the triple bond of diphenylacetylene.

While couplings of silanes (SiH) with organometallics have been observed occasionally to have variable stereochemistry,<sup>8,9</sup> couplings of chlorosilanes (R<sub>3</sub>Si\*Cl) with all types of organometallic reagents have in all cases been observed to occur with inversion of configuration. Hence the fact that the other enantiomer, (-)-9-silylphenanthrene, (-)-VI, was obtained by coupling of (-)-R<sub>3</sub>Si\*Cl<sup>10</sup> with 9-phenanthryllithium involving inversion of configuration completely confirms the assigned stereochemistries of the reactions and products.

Attempts were also made to add triphenylgermane or (+)-R<sub>3</sub>Ge\*H to diphenylacetylene. More vigorous conditions were required, and the yields of germyl-*cis*-stilbenes were lower than the yields of *cis*-stilbenes from silanes. While  $\alpha$ -triphenylgermyl-*cis*-stilbene was obtained pure, reactions using (+)-R<sub>3</sub>Ge\*H gave noncrystallizable oils which on the basis of spectral evidence appeared to be mixtures of optically active (+)- $\alpha$ -(1-naphthylphenylmethylgermyl)-*cis*- and -*trans*-stilbenes, but pure crystalline material could not be obtained.

These studies show that the boron trifluoride catalyzed dehydrations of triphenylsilylbenzylphenylcarbinols yield  $\alpha$ -triphenylsilyl-*cis*-stilbenes. The exclusive formation of this isomer would logically appear to be the result of steric effects, steric interaction being less when the bulky triphenylsilyl group is *trans* to the neighboring phenyl group. It is evident also that asymmetric silanes add to disubstituted acetylenes in a *cis* manner with high stereospecificity involving the retention of configuration at silicon in platinum-catalyzed reactions.

## Experimental Section

**Reaction of Triphenylsilylbenzylphenylcarbinol in Toluene at 110°.** Boron trifluoride gas was bubbled into a refluxing solution of 0.9 g (0.002 mol) of triphenylsilylbenzylphenylcarbinol in 50 ml of toluene for about 15 sec until fumes were evolved from the top of the reflux condenser. The reaction mixture was drowned in water, and the ether extracts were dried over magnesium sulfate. The oil obtained on removal of the ether was crystallized from methanol to yield 0.25 g (29%) of  $\alpha$ -triphenylsilyl-*cis*-stilbene, mp 121–123°. The mother liquors, after removal of the solvent, were chromatographed on a 1 × 3 in. silica gel column. Elution with 500 ml of hexane yielded 0.095 g (26%) of *cis*-stilbene, identified by its spectral properties. Further elution with 150 ml of hexane gave 0.005 g (3%) of *trans*-stilbene, mp 122–124°, identified by mixture melting point, and from the next 300 ml of hexane was isolated 0.023 g (4%) of triphenylfluorosilane, mp 62–64°, identified by mixture melting point. Elution with 150 ml of carbon tetrachloride gave an additional 0.05 g (5%) of  $\alpha$ -triphenylsilyl-*cis*-stilbene, and elution then with 150 ml of benzene gave 0.077 g (14%) of triphenylsilanol, mp 152–154°, identified by mixture melting point.

(8) A. G. Brook, C. M. Warner, and W. W. Limburg, *Can. J. Chem.*, **45**, 1231 (1967).

(9) L. H. Sommer and W. D. Korte, *J. Amer. Chem. Soc.*, **89**, 5802 (1967).

(10) (+)-R<sub>3</sub>SiH and (-)-R<sub>3</sub>SiCl are known to have the same configuration. L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *ibid.*, **86**, 3271 (1964).

**Reaction of Triphenylsilyl-*p*-chlorobenzylphenylcarbinol with BF<sub>3</sub>.** In a manner similar to that described above, 0.33 g (0.00067 mol) of the *p*-chlorobenzylcarbinol, prepared by treatment of benzoyltriphenylsilane with *p*-chlorobenzylmagnesium chloride, was treated with BF<sub>3</sub> in refluxing toluene. When worked up as described above, there was obtained 0.09 g (28%) of  $\alpha$ -triphenylsilyl-*p*-chloro-*cis*-stilbene, mp 151–152.5°, from methanol;  $\nu_{\max}$  (C<sub>6</sub>H<sub>12</sub>): 269 m $\mu$  ( $\epsilon$  18,800).

*Anal.* Calcd for C<sub>32</sub>H<sub>28</sub>ClSi: C, 81.30; H, 5.33. Found: C, 81.40; H, 5.38.

In addition, 0.006 g (4%) of *p*-chloro-*trans*-stilbene, mp 131–132.5° (lit.<sup>11</sup> mp 132°), 0.06 g (40%) of *p*-chloro-*cis*-stilbene, 0.008 g (4%) of triphenylfluorosilane, mp 62–64°, and 0.053 g (29%) of triphenylsilanol, mp 153–154°, were isolated, the last two identified by mixture melting point.

**Reaction of Triphenylsilyl-*p*-*t*-butylbenzylphenylcarbinol with BF<sub>3</sub>.** In the manner described above, 1.0 g (0.00195 mol) of the *p*-*t*-butylcarbinol in refluxing toluene, prepared by treatment of benzoyltriphenylsilane with *p*-*t*-butylbenzylmagnesium chloride, was treated with BF<sub>3</sub>. Work-up gave 0.35 g (36%) of  $\alpha$ -triphenylsilyl-*p*-*t*-butyl-*cis*-stilbene, mp 209–211°, after recrystallization from methanol;  $\nu_{\max}$  (C<sub>6</sub>H<sub>12</sub>): 269 m $\mu$  ( $\epsilon$  19,400); nmr (CCl<sub>4</sub>)  $\delta$  1.21 (s, 9) and 6.8–7.4 ppm (m, 25).

*Anal.* Calcd for C<sub>38</sub>H<sub>34</sub>Si: C, 87.40; H, 6.92. Found: C, 87.75; H, 6.85.

In addition 0.17 g (37%) of *p*-*t*-butyl-*trans*-stilbene, mp 96–97°, identified by mixture melting point with an authentic sample, 0.07 g (15%) of *p*-*t*-butyl-*cis*-stilbene, identified by spectral comparison with an authentic sample, 0.06 g (12%) triphenylfluorosilane, mp 62–64°, and 0.09 g (17%) of triphenylsilanol, mp 152–154°, were obtained. The latter compounds were identified by mixture melting point.

**Addition of Triphenylsilane to Diphenylacetylene.** A mixture of 2.6 g (0.01 mol) of triphenylsilane, 1.78 g (0.01 mol) of diphenylacetylene, and approximately 0.1 g of 10% platinum on carbon were heated at 110° for 8 hr at which time an infrared spectrum of the viscous liquid showed only a weak Si–H band at 4.7  $\mu$ . The material was dissolved in boiling hexane, and the solution was filtered. The filtrate, on cooling, deposited 2.7 g (61%) of  $\alpha$ -triphenylsilyl-*cis*-stilbene, which on recrystallization from ethanol containing a trace of benzene melted at 122–123°; a mixture melting point with the material described above was not depressed;  $\nu_{\max}$ : 224 (36,800), 263 (18,300), 278 (s) (13,600), 287 (s) (10,750), and 296 m $\mu$  (s) ( $\epsilon$  6570).

*Anal.* Calcd for C<sub>32</sub>H<sub>26</sub>Si: C, 87.61; H, 5.98. Found: C, 87.65; H, 5.90.

**Preparation of  $\alpha$ -Diphenylmethylsilyl-*cis*-stilbene from Diphenylacetylene and Diphenylmethylsilane.** A mixture of 3.0 g (0.0151 mol) of diphenylmethylsilane and 2.94 g (0.0163 mol) of diphenylacetylene in 25 ml of dry cyclohexane with 0.05 g of 10% platinum on carbon was refluxed for 4 hr, when the infrared spectrum of a sample showed the absence of Si–H absorption at 4.7  $\mu$ . Filtration followed by evaporation gave an oil which on recrystallization from *n*-hexane gave 5 g (88%) of  $\alpha$ -diphenylmethylsilyl-*cis*-stilbene, mp 78–82°. Subsequent recrystallizations raised the melting point to 88.5–89° which was not depressed when a mixture melting point with an authentic sample was taken.

**Preparation of  $\alpha$ -Bromo-*cis*-stilbene.** *meso*-Dibromostilbene, prepared by the method of Fieser,<sup>12</sup> was converted in 79% yield by the method of Wislicenus and Seeler<sup>13</sup> to  $\alpha$ -bromo-*cis*-stilbene, mp 19–19.5°.

**Preparation of  $\alpha$ -Diphenylmethylsilyl-*cis*-stilbene.** *n*-Butyllithium (0.014 mol) in 9 ml of *n*-hexane was added over 6 min to a solution of 3.3 g (0.0128 mol) of  $\alpha$ -bromo-*cis*-stilbene in 70 ml of dry diethyl ether–benzene (60:40) at –35° to produce  $\alpha$ -*cis*-stilbenyllithium.<sup>6</sup> After 5 min 3.0 g (0.0128 mol) of diphenylmethylchlorosilane in 25 ml of dry diethyl ether was added rapidly. This mixture was stirred for 1.5 hr while warming from –40° to room temperature, and for 4 hr at room temperature. Hydrolysis with dilute aqueous acid and work-up gave after removal of the ether solvent 4 g (83%) of an oily product which after several recrystallizations from *n*-hexane gave 2.4 g (50%) of  $\alpha$ -diphenylmethylsilyl-*cis*-stilbene, mp 88.5–89°; nmr (CCl<sub>4</sub>)  $\delta$  0.53 (s, 3) and 6.78–7.79 ppm (m, 21);  $\nu_{\max}$  (C<sub>6</sub>H<sub>12</sub>): 215 (34,200), 254 (16,400), 259 (16,600), 276 (12,700), 284 (9960), and 292 m $\mu$  ( $\epsilon$  6870).

(11) P. Schmid, U. S. Atomic Energy Commission UCRL-8883, 1959, p 114; *Chem. Abstr.*, **54**, 7647 (1960).

(12) L. F. Fieser, *J. Chem. Educ.*, **31**, 291 (1954).

(13) J. Wislicenus and F. Seeler, *Chem. Ber.*, **28**, 2693 (1895).

*Anal.* Calcd for C<sub>27</sub>H<sub>24</sub>Si: C, 86.28; H, 6.42. Found: C, 86.51; H, 6.41.

**Photolysis of  $\alpha$ -Triphenylsilyl-*cis*-stilbene.** A 0.32-g sample of  $\alpha$ -triphenylsilyl-*cis*-stilbene dissolved in 180 ml of cyclohexane was photolyzed over 18 hr using a 450-W Hanovia high-pressure mercury lamp with Corex filter, during which time air was slowly bubbled through the system. After filtration of a small amount of insoluble material, removal of the solvent gave a gum which on recrystallization from ethanol gave 0.09 g (28%) of 9-triphenylsilylphenanthrene, mp 214–216°, identified by spectral comparison and mixture melting point with an authentic sample prepared as described below.

**Preparation of 9-Triphenylsilylphenanthrene.** To a suspension of 2.57 g (0.01 mol) of 9-bromophenanthrene in 15 ml of dry hexane in a nitrogen atmosphere was added 6.25 ml of 1.6 *M* *n*-butyllithium in hexane (0.01 mol). The suspension became somewhat yellow, and over 2.5 hr more yellow precipitate formed. The solid was allowed to settle, and the supernatant liquid was drawn off by syringe through a serum cap. Additional hexane was added to the precipitate, which was briefly stirred and allowed to settle, prior to removal of the supernatant again. To the residue was added 2.0 g (0.0068 mol) of triphenylchlorosilane in 20 ml of ether. After 18 hr of stirring, hydrolysis and work-up yielded 2.65 g (90%) of 9-triphenylsilylphenanthrene, mp 215–216°, from ethanol–benzene;  $\nu_{\max}$  (C<sub>6</sub>H<sub>12</sub>): 225 (55,000), 249 (57,000), 257 (71,800), 272 (s) (20,400), 279 (15,700), 291 (14,800), 302 (16,500), 326 (306), 333 (347), 341 (297), and 348 m $\mu$  ( $\epsilon$  230).

*Anal.* Calcd for C<sub>32</sub>H<sub>24</sub>Si: C, 88.02; H, 5.54. Found: C, 87.92; H, 5.63.

**Addition of R<sub>3</sub>Si\*H to Diphenylacetylene.** When a mixture of 1.18 g (0.0066 mol) of diphenylacetylene, 1.65 g (0.0064 mol) of (+)-1-naphthylphenylmethylsilane,  $[\alpha]^{25}_D$  33.85° (c 9.9, C<sub>6</sub>H<sub>12</sub>), and about 0.1 g of 10% platinum on charcoal were either heated neat at 115° for 0.75 hr or better were refluxed in 15 ml of cyclohexane for 3 hr, addition of 25 ml of ethanol, filtration, and cooling gave 2.65 g (93%) of (+)- $\alpha$ -(1-naphthylphenylmethylsilyl)-*cis*-stilbene, mp 94–97°, which on recrystallization from ethanol gave 1.77 g (63%) of pure product, mp 95–96.5°;  $[\alpha]^{25}_D$  40.2° (c 4.2, C<sub>6</sub>H<sub>12</sub>);  $\nu_{\max}$  (C<sub>6</sub>H<sub>12</sub>): 224.5 (85,800), 266 (20,300), 275 (20,900), 281 (s), (21,000), 296.5 (14,500), 314 (s) (2370), and 319 m $\mu$  (s) ( $\epsilon$  1415); nmr (CDCl<sub>3</sub>):  $\delta$  0.67 (s, 3) and 6.7–8 ppm (m, 23).

*Anal.* Calcd for C<sub>31</sub>H<sub>26</sub>Si: C, 87.25; H, 6.15. Found: C, 87.16; H, 6.06.

Similar results were obtained when 1–2 ml of a 1% solution of chloroplatinic acid in isopropyl alcohol was used instead of platinum on carbon.

**Photolysis of (+)- $\alpha$ -(1-Naphthylphenylmethylsilyl)-*cis*-stilbene.** A solution of 1.9 g of the title compound in 190 ml of cyclohexane was photolyzed over 18 hr using a 450-W Hanovia high-pressure lamp with Corex filter, during which time air was slowly bubbled through the solution. After filtration of about 0.1 g of white insoluble material and then removal of the solvent, the resulting yellow gum, on crystallization from methanol containing a little benzene or from ethyl acetate, gave 0.76 g (40%) of white (+)-9-(1-naphthylphenylmethylsilyl)phenanthrene which after recrystallization to constant melting point and rotation had mp 206–207.5°,  $[\alpha]^{25}_D$  36.4° (c 1.32, C<sub>6</sub>H<sub>12</sub>). A mixture melting point with a sample prepared as described below was not depressed; nmr (CDCl<sub>3</sub>):  $\delta$  1.2 (s, 2.9, Si–Me) and 7–8 ppm (m, 21, aromatic);  $\nu_{\max}$  (C<sub>6</sub>H<sub>12</sub>): 227.5 (113,000), 250 (s) (47,000), 257 (56,800), 272 (s) (21,300), 279 (18,900), 289 (18,000), 301 (16,500), 315 (827), 319 (581), 325 (309), 333 (294), 341 (268), and 348 m $\mu$  ( $\epsilon$  196).

*Anal.* Calcd for C<sub>31</sub>H<sub>24</sub>Si: C, 87.68; H, 5.70. Found: C, 87.29; H, 5.72.

**Preparation of 9-(1-Naphthylphenylmethylsilyl)phenanthrene. A.** To the 9-phenanthryllithium prepared from 2.57 g (0.01 mol) of 9-bromophenanthrene as described above was added 1.5 g (0.006 mol) of (+)-1-naphthylphenylmethylsilane dissolved in 20 ml of ether, and the mixture was stirred for 18 hr at which time a negative color test<sup>14</sup> was obtained. After hydrolysis with dilute acid and work-up, the ether layer on evaporation yielded 1.70 g (67%) of (+)-9-(1-naphthylphenylmethylsilyl)phenanthrene, mp 206–208°, after recrystallization from methanol–benzene,  $[\alpha]^{25}_D$  35.3° (c 1.1, C<sub>6</sub>H<sub>6</sub>).

**B.** In a similar manner to the above 0.75 g (0.0026 mol) of (–)-1-naphthylphenylmethylchlorosilane,  $[\alpha]_D$  –6.3°, was added to the 9-phenanthryllithium prepared from 1.3 g (0.005 mol) of 9-bromophenanthrene. After stirring overnight, work-up gave

(14) H. Gilman and F. Schulze, *J. Amer. Chem. Soc.*, **47**, 2002 (1925).

0.72 g (65%) of (-)-9-(1-naphthylphenylmethylsilyl)phenanthrene, mp 205–206.5°, from ethyl acetate,  $[\alpha]^{25}_D -35.4^\circ$  ( $c$  1.5,  $C_6H_6$ ).

*Anal.* Calcd for  $C_{21}H_{24}Si$ : C, 87.68; H, 5.70. Found: C, 87.40; H, 5.74.

**Photoisomerization of  $\alpha$ -(1-Naphthylphenylmethylsilyl)-*cis*-stilbene.** When 1.0 g of the title compound (nmr at  $\delta$  0.67 ppm) was photolyzed in cyclohexane as described above, except in an atmosphere of dry, oxygen-free nitrogen, examination of the product at the end of 7 and 20 hr revealed the presence of two singlets at 0.43 and 0.67 ppm with the intensity ratio 48:52. These peaks were ascribed to  $\alpha$ -(1-naphthylphenylmethylsilyl)-*trans*- and *cis*-stilbenes, respectively. No peak at 1.2 ppm, associated with the silylphenanthrene was observed.

**Reaction of Triphenylgermane with Diphenylacetylene.** A mixture of 0.4 g (0.00013 mol) of triphenylgermane and 0.24 g (0.00013 mol) of diphenylacetylene was heated to 130° for 24 hr in the presence of a trace of a 10% platinum on charcoal catalyst. The resultant oily wax was dissolved in carbon tetrachloride and the solution filtered. After removing the solvent under reduced pressure, the thick oil was dissolved in the minimum of boiling methanol. On cooling to room temperature a total of 0.31 g (48%) of  $\alpha$ -triphenylgermyl-*cis*-stilbene precipitated which after recrystallization from methanol melted at 113–114°;  $u_{V_{max}}$  ( $CCl_4$ ): 264  $m\mu$  ( $\epsilon$  15,600).

*Anal.* Calcd for  $C_{32}H_{26}Ge$ : C, 79.54; H, 5.43. Found: C, 79.16; H, 5.36.

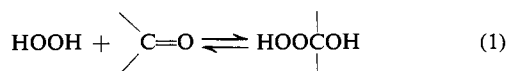
## General Acid and Base Catalysis of the Reversible Addition of Hydrogen Peroxide to Aldehydes<sup>1</sup>

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**Abstract:** The rates of general acid and base catalyzed breakdown of the hemiacetals formed by the addition of hydrogen peroxide to *p*-chlorobenzaldehyde and *p*-methoxybenzaldehyde have been measured spectrophotometrically, and the rates of the addition reactions have been calculated from the equilibrium constants. The general base catalyzed breakdown of the *p*-chlorobenzaldehyde adduct exhibits a  $\beta$  value of 0.66. It is suggested that this reaction actually involves general acid catalysis of the breakdown of the conjugate base of the adduct, possibly through a "one-encounter" mechanism. A positive deviation of the hydroxide ion catalyzed reaction suggests that this represents specific base catalysis, *i.e.*, uncatalyzed expulsion and attack of the hydroperoxide anion. The general acid catalyzed reaction exhibits an  $\alpha$  value equal or close to 1.0 and is detectable because of a negative deviation of the proton-catalyzed reaction. It is suggested that this reaction involves proton transfer by the general acid to and from the carbonyl oxygen atom, possibly through a cyclic mechanism in catalysis by carboxylic acids. The higher affinity of hydrogen peroxide than of water for the carbonyl group appears as a slower rate of decomposition of the hydrogen peroxide adduct. The high nucleophilic reactivity of free hydrogen peroxide is apparent in the similarity of its rate of nucleophilic attack to that of water, in spite of its much smaller basicity.

The reversible addition of water to the carbonyl group has been examined in detail,<sup>3</sup> but much less information is available regarding the analogous addition and loss of the more acidic and less basic hydrogen peroxide molecule (eq 1). It is known that the affinity of hydro-



gen peroxide for the carbonyl group is much greater than that of water, and the addition of hydrogen peroxide to formaldehyde and acetaldehyde occurs through pH-independent and hydrogen ion catalyzed pathways.<sup>4–6</sup> The experiments reported here were carried out in order to obtain a more complete understanding of the mechanism of catalysis of this reaction.

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### Experimental Section

**Materials.** Reagent grade inorganic salts were used without further purification. Glass-distilled water was used in all experiments. Organic acids and bases were either recrystallized or redistilled before use. 1,1-Cyclobutanedicarboxylic acid was a gift from Dr. Gustav Lienhard. *p*-Chlorobenzaldehyde was twice recrystallized from ethanol–water. *p*-Methoxybenzaldehyde was redistilled under reduced pressure and stored at 4°. Solutions containing the *p*-chlorobenzaldehyde–hydrogen peroxide hemiacetal were freshly prepared just prior to use by adding sufficient *p*-chlorobenzaldehyde and hydrogen peroxide to make the final concentrations in the stock solution approximately  $2 \times 10^{-2}$  *M* and 5.1 *M*, respectively, in 20% ethanol. Sufficient ethylenediaminetetraacetic acid was added to this stock solution to give a concentration in the final reaction mixtures of  $1 \times 10^{-4}$  *M*. The same rate constants were obtained with solutions which had stood for 24 hr at room temperature as with fresh solutions. A similar procedure was followed to prepare *p*-methoxybenzaldehyde–hydrogen peroxide hemiacetal except that 0.1 ml of 0.11 *M* *p*-methoxybenzaldehyde in ethanol was added to 0.9 ml of 30% hydrogen peroxide to give final concentrations of  $1 \times 10^{-2}$  *M* *p*-methoxybenzaldehyde and 8.0 *M* hydrogen peroxide; these solutions were prepared just prior to each kinetic run. Dimethyl phosphate was purified as the barium salt<sup>7</sup> and twice recrystallized from 85% ethanol–water. Just prior to use the barium salt was dissolved in a solution containing an equivalent amount of standardized sulfuric acid, and barium sulfate was removed by centrifugation and filtration.

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