Pyrolysis of Allylic Acetates. II

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2-Acetoxy-*trans*-3-hexene and 4-acetoxy-*trans*-2-hexene have been pyrolyzed under conditions that gave partial pyrolysis. Both esters gave rise to a mixture of 1,3- and 2,4-hexadiene, the 2-acetoxy compound giving somewhat more of the 1,3-diene and the 4-acetoxy compound giving more of the 2,4-diene. The 1,3-diene was predominantly the *trans* isomer, and about half of the 2,4-diene was the *trans, trans* isomer. The unpyrolyzed ester recovered in each case was the same mixture of 2-acetoxy and 4-acetoxy compounds. Clearly, the esters underwent isomerization during the pyrolysis, and in this isomerization the *trans*-alkene configuration was essentially retained.

It was the report of van Pelt and Wibaut[1] that 4-acetoxy-2-hexene could be pyrolyzed to a 66% yield of 2,4-hexadiene which led us to adapt this procedure for the preparation of 2,4-heptadiene. The results[2] of the pyrolysis of 2-acetoxy-*trans*-3-heptene and 4-acetoxy-*trans*-2-heptene were that both esters gave rise to 1,3- and 2,4-diene, the former ester producing slightly more of the 1,3-diene and the latter producing somewhat more of the 2,4-diene. The recovered, unpyrolyzed ester in each case was found to be the same mixture of the 2-acetoxy and 4-acetoxy compounds, and the data indicated that when the one ester isomerized to the other the *trans* configuration of the alkene linkage was essentially retained. These results would make one expect that the acetates of the corresponding six-carbon alcohols would behave in a similar fashion, and that one should not anticipate a good yield of 2,4-hexadiene from the pyrolysis of 4-acetoxy-2-hexene.

The literature relative to the pyrolysis of allylic esters has been cited previously.[2] Additional interesting examples are those reported by Alder and von Brachel[3] where acetates of 3-hexene-2,5-diols were pyrolyzed to yield 1,3-cyclohexadienes. These would appear to be instances of the elimination of two molecules of acetic acid followed by a Cope rearrangement[4] to give, finally, the cyclic 1,3-dienes.

The allylic esters, 2-acetoxy-*trans*-3-hexene and 4-acetoxy-*trans*-2-hexene, have now been prepared and pyrolyzed. *trans*-2-Pentenal was prepared by the method of Hoaglin and Hirsch.[5] The *trans* configuration of this aldehyde was confirmed by silver oxide oxidation of the aldehyde to *trans*-2-pentenoic acid, and comparison of this acid with a sample of *trans*-2-pentenoic acid which was prepared by the Doebner reaction. The infrared absorption curves of the two samples of *trans*-2-pentenoic acid were identical. It is rather well established[6] that the Doebner reaction gives rise to a *trans* alkene linkage. The aldehyde was converted to the allylic alcohol by reaction with the methyl Grignard reagent, and the alcohol esterified with acetic anhydride–pyridine to give the 2-acetoxy-*trans*-3-hexene. The infrared absorption curves of the aldehyde, the alcohol, and the acetate had very strong absorption at or near 965 cm.$^{-1}$ characteristic of a *trans* alkene linkage, and no absorption which could be attributed to a *cis* alkene linkage.[7] Gas chromatography of this ester showed it to contain 93% of the *trans* ester, 2% of the *cis* ester, and 5% of unidentified material. The 4-acetoxy-*trans*-2-hexene was obtained from the corresponding alcohol which was prepared from crotonaldehyde and the ethyl Grignard reagent. Crotonaldehyde has a *trans* alkene linkage.[8] The infrared absorption curves of this acetate and the corresponding alcohol had very strong absorption at 965 cm.$^{-1}$, and no absorption which could be attributed to a *cis* double bond. By gas chromatography this ester was found to contain 97% of the *trans* ester and 3% of the *cis* ester.

On pyrolysis these esters gave the same type of data as was obtained previously[2] with the acetates of the seven-carbon allylic alcohols. A temperature of 440–450° was required for pyrolysis of the acetates, and under the conditions employed the ester had a contact time of 3.5 sec. About an 80% yield of diene was obtained from each ester. The diene obtained from 2-acetoxy-*trans*-3-hexene was 54% 1,3-hexadiene and 46% 2,4-hexadiene, whereas that obtained from the 4-acetoxy-*trans*-2-hexene was 54% 2,4-diene and 46% 1,3-diene. The infrared absorption curves of the 2-acetoxy and 4-acetoxy compounds were not sufficiently different to make possible an accurate analysis of a mixture of the two esters. However, it was possible to obtain an approximate analysis of an unknown mixture of the esters by comparing its infrared absorption with that of known mixtures of the esters. The infrared absorption curve of the unpyrolyzed ester recovered from the pyrolysate of each ester was superimposable on the infrared curve for a 50–50 mixture of 2-acetoxy-*trans*-3-hexene and 4-acetoxy-*trans*-2-hexene. The ester recovered from the py-

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[1] A. J. van Pelt and J. P. Wibaut, *Rec. trav. chim.*, **60**, 55 (1941).

[2] F. L. Greenwood, *J. Org. Chem.*, **24**, 1735 (1959).

[3] K. Alder and H. von Brachel, *Ann.*, **608**, 195 (1957).

[4] A. C. Cope, L. Field, D. MacDowell, and M. Wright, *J. Am. Chem. Soc.*, **78**, 2547 (1956).

[5] R. I. Hoaglin and D. H. Hirsch, *ibid.*, **71**, 3468 (1949).

[6] L. Crombie, *Quart. Rev.*, **6**, 101 (1952).

[7] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, 1958, pp. 45–48.

[8] W. G. Young, *J. Am. Chem. Soc.*, **54**, 2498 (1932).

rolysate of the 2-acetoxy compound was found by gas chromatography to be composed of 84% of *trans* esters and 15% of *cis* esters, and that from the 4-acetoxy pyrolysate contained 82% of *trans* esters and 18% of *cis* esters. The preparation of maleic anhydride adducts of the various diene samples indicated[9] that the 1,3-hexadiene obtained from both esters was predominantly the *trans* isomer, and that about half of the 2,4-diene obtained from each ester was the *trans, trans* isomer. The results clearly show that during pyrolysis these esters underwent isomerization, and that when this isomerization occurred the *trans* configuration of the alkene linkage was primarily retained. The fact that the 2-acetoxy compound gave rise to more of the 1,3-diene than of the 2,4-diene and that the 4-acetoxy compound gave the opposite result indicates that the rate of elimination is slightly greater than the rate of isomerization of the esters.

All of the work that has been reported[10] on the isomerization of allylic esters indicates that this isomerization is intramolecular and that some kind of a cyclic transition state is involved. In this transition state the carbonyl-oxygen atom must be coming into bond forming distance of the γ-carbon atom of the allylic system. With an allylic ester with a *trans* alkene linkage there are two principal conformations in which the proper transition state may be approached. In one of these conformations the hydrogen atoms on the α- and β-carbon atoms (the carbon atoms between which the double bond will appear in the isomerized ester) of the allylic system are essentially *trans* (*trans*-conformation). In the other conformation the hydrogen atoms on the α- and β-carbon atoms are essentially *cis*. Examination of Leybold models of an allylic ester with a *trans* alkene linkage will show that the *trans* conformation is the more favorable one, and the essential retention of the *trans* alkene configuration when such an ester isomerizes may be explained on this basis.

Experimental

All operations in which compounds sensitive to oxygen were used were carried out in a nitrogen atmosphere.

1,1,3-Triethoxypentane was prepared from diethylpropional (b.p. 120–122°/758 mm.), ethyl vinyl ether (b.p. 37°/770 mm.), and boron trifluoride etherate by a method described by Hoaglin and Hirsch.[5] The product was distilled from a Claisen flask having a distilling arm (16 mm. o.d. × 310 mm.) filled with $^1/_8$-inch helices. The material was obtained in 65% yield, and had b.p. 73–77°/4 mm., n^{25}_{D} 1.4096–1.4102.

Anal. Calcd. for $C_{11}H_{24}O_3$: C, 64.7; H, 11.8. Found: C, 64.8; H, 11.6.

***trans*-2-Pentenal** was obtained from 1,1,3-triethoxypentane by the method of Hoaglin and Hirsch.[5] The aldehyde was distilled through a helix-packed column (16 mm. o.d. × 310 mm.) and had b.p. 73–75°/132 mm., n^{25}_{D} 1.4393–1.4403; 45% yield. The infrared curve[11] had a very strong band at 970 cm.$^{-1}$ characteristic of a *trans* alkene linkage and no absorption attributable to a *cis* alkene linkage.[7]

***trans*-2-Pentenoic acid** was prepared by two methods. The above-mentioned *trans*-2-pentenal was oxidized with silver oxide in aqueous alcohol at 2° to give a 50% yield of acid, b.p. 73–76°/6 mm., n^{25}_{D} 1.4490–1.4497. The acid was also prepared[12] by a Doebner reaction of propionaldehyde (b.p. 47°/762 mm.) and malonic acid in a mixture of pyridine and piperidine. The *trans*-2-pentenoic acid, b.p. 64–66°/3 mm., n^{25}_{D} 1.4492–1.4496, was obtained in 75% yield. Titration with standard alkali showed this acid to have an acid value of 100.0. Calcd. acid value, 100.1. The infrared curves of the two samples of *trans*-2-pentenoic acid were identical, thus establishing the 2-pentenal as the *trans* isomer.

***trans*-2-Hexen-4-ol** was prepared from crotonaldehyde (*trans* isomer,[8] b.p. 100.5–101.0°/775 mm.) and ethyl Grignard reagent. The addition complex was decomposed with saturated, aqueous ammonium chloride, and the alcohol distilled from a Claisen flask having a distilling arm (18 mm. i.d. × 240 mm.) filled with $^1/_8$-inch helices. The alcohol was obtained in 78% yield and had b.p. 60.0–60.3°/27 mm., n^{25}_{D} 1.4317–1.4322. (literature,[13] b.p. 62°/30 mm.; n^{22}_{D} 1.4312). The infrared curve of the alcohol had a very strong band at 960 cm.$^{-1}$ characteristic of a *trans* alkene linkage and no absorption attributable to a *cis* alkene linkage.

4-Acetoxy-*trans*-2-hexene was obtained by acetylation of the corresponding alcohol by the method of Heilbron, *et al.*[14] The ester was distilled through a column (25 mm. o.d. × 245 mm.) which was packed with $^1/_8$-inch helices, and had b.p. 54.0–55.7°/14 mm., n^{25}_{D} 1.4187–1.4189, 93% yield (literature[15]: b.p. 153°/750 mm., n^{20}_{D} 1.4222). The infrared curve of this ester had a very strong absorption at 965 cm.$^{-1}$ and no absorption assignable to a *cis* alkene linkage. Gas chromatography (1,2,3-tris(2-cyanoethoxy)propane column) showed this ester to be 97% of one component and 3% of a second component. This second component had a relative retention time of 0.84 (relative to the main component) and from the gas chromatographic behavior of the various ester samples it was believed to be the *cis* ester.

***trans*-3-Hexen-2-ol** was prepared from *trans*-2-pentenal and methyl Grignard reagent. After decomposition of the addition complex with saturated, aqueous ammonium chloride the alcohol was obtained in 81% yield, b.p. 62–66°/27 mm., n^{25}_{D} 1.4317–1.4335. The infrared curve of the alcohol had a very strong band at 965 cm.$^{-1}$ and no absorption assignable to a *cis* alkene linkage.

2-Acetoxy-*trans*-3-hexene was prepared from the alcohol by the method of Heilbron, *et al.*[14] The ester was obtained in 80% yield and had b.p. 55.5–59.0°/15 mm., n^{25}_{D} 1.4187–1.4197. The infrared curve of the ester had a very strong absorption at 960 cm.$^{-1}$ and no absorption assignable to a *cis* alkene linkage. On gas chromatographic analysis this ester was found to contain 93% of one component, 2% of a component of relative retention time 0.76 (relative to the main component), and 5% of two components of relative retention times 1.19 and 1.43. From the gas chromatographic behavior of the various ester samples this component of relative retention time 0.76 was believed to be the *cis* ester. The other components were unidentified.

Pyrolysis of 4-Acetoxy-*trans*-2-hexene.—The apparatus was the same as that described previously.[2] The pyrolysis tube was maintained at 440°, and oxygen-free nitrogen was

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(9) K. Alder and W. Vogt, *Ann.*, **571**, 137 (1951).

(10) R. A. Sneen, *J. Am. Chem. Soc.*, **82**, 4261 (1960) and references cited in ref. 2.

(11) All infrared spectra were taken with a Perkin-Elmer Model 221 spectrophotometer.

(12) J. Koo, M. S. Fish, G. N. Walker, and J. Blake, "Organic Syntheses," Vol. 31, John Wiley and Sons, New York, p. 35.

(13) E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 3144 (1953).

(14) I. M. Heilbron, E. R. H. Jones, J. T. McCombie, and B. C. L. Weedon, *ibid.*, 88 (1945).

(15) J. Cologne and M. Reymermier, *Bull. soc. chim. France*, 1531 (1955).

passed through the tube at a rate of 18.1 l./hr. The ester (105.7 g., 0.743 mole) was added at the rate of 0.30 g./min. over a period of 5.93 hr. The conditions gave a contact time[16] of 3.5 sec. for the ester in the pyrolysis tube. At the conclusion of the pyrolysis the helices were only slightly carbonized. The pyrolysate was diluted with pentane, and the pentane solution extracted with five 100 ml. and two 75-ml. portions of water. The aqueous extracts were combined, and titration of an aliquot showed 0.398 mole of acetic acid to have been formed. This indicated 53.6% of the ester underwent pyrolysis. After drying over sodium sulfate the pentane was removed through an 18-plate column from the pentane solution until a pot temperature of 55° was reached. The residue was then distilled through a spinning-band column (7 mm. i.d. × 600 mm.). By carefully raising the flask temperature and decreasing the pressure the unpyrolyzed ester and diene could be rather quickly separated.

Careful distillation of the ester portion through the spinning-band column gave 18 fractions of b.p. 53.0–56.9°/15 mm., n^{25}_{D} 1.4180–1.4192. The weight of the fractions (44.79 g.) was 91.2% of the theoretically recoverable ester. Gas chromatographic analysis of various fractions showed that the *cis* esters were concentrated in the early fractions, and that the later fractions were pure *trans* esters. The ester fractions were combined into a composite sample, and this subjected to infrared and gas chromatographic analysis. The infrared curves of the 2-acetoxy-*trans*-3-hexene and the 4-acetoxy-*trans*-2-hexene were different, but not sufficiently so to make possible an accurate analysis of a mixture of the esters. However, it was possible to obtain an approximate analysis by comparing the infrared absorption of an unknown mixture of the esters with that of a known mixture of the esters. The infrared curve of the composite ester sample was superimposable on that of a 50–50 mixture of the two esters. By gas chromatographic analysis the composite ester sample was found to contain 82% of *trans* esters and 18% of *cis* esters.

The diene portion was distilled through the spinning-band column and the fractions were combined to give the following materials: 1,3-hexadiene, 9.40 g., 29% yield, b.p. 73.6–74.6°/766 mm., n^{25}_{D} 1.4372–1.4382 (literature[17]: b.p. 72°/760 mm., n^{20}_{D} 1.4403); intermediate fraction, 3.70 g., b.p. 74.6–82.7°/766 mm., n^{25}_{D} 1.4384–1.4482; 2,4-hexadiene, 10.95 g., 34% yield, b.p. 82.7–83.0°/766 mm., n^{25}_{D} 1.4490–1.4497 (literature[17]: b.p. 83°/760 mm., n^{20}_{D} 1.4566). By gas chromatography (benzyl cyanide–silver nitrate column) the 1,3-hexadiene was found to be 96% 1,3-diene and 4% 2,4-diene, the intermediate fraction contained 43% 1,3-diene and 57% 2,4-diene, and the 2,4-diene was 100% 2,4-diene. Calculating from the gas chromatographic data, the total yield of 2,4-diene was 54% and that of the 1,3-diene was 46%. The infrared curve of the 1,3-diene had a very strong band at 950 cm.$^{-1}$ characteristic of a *trans* double bond, and strong bands at 1000 and 895 cm.$^{-1}$ characteristic[7] of a terminal methylene group. The 1,3-diene was further identified by nuclear magnetic resonance spectroscopy.[18] The spectrum (carbon tetrachloride solution, tetramethylsilane as internal reference, 60 megacycles) had a triplet signal centered about 60 c.p.s. and a quintet of lines centered about 75 c.p.s. which are assignable to the ethyl group, and signals at 288, 298, and 305 c.p.s. which are characteristic of a terminal methylene group. The 2,4-hexadiene had very strong infrared absorption at 980 cm.$^{-1}$ characteristic of a *trans* alkene linkage, and no absorption assignable to a terminal methylene group. The NMR spectrum[18] of the 2,4-diene had a doublet peak at 98 and 103 c.p.s. which are assignable to the two methyl groups and signals between 300 and 400 c.p.s. which are from the olefinic protons.

An approximate analysis of the 1,3- and 2,4-dienes for various geometric isomers was obtained[9] by the preparation of maleic anhydride adducts. One-gram samples of the dienes in benzene solution were refluxed with maleic anhydride under a nitrogen atmosphere for 1 hr. The 1,3-diene gave a 96% yield of crude adduct, m.p. 46–50°, which on recrystallization from ligroin (b.p. 66–99°) gave a 75% yield of adduct (plates), m.p. 49.6–50.8° (literature,[9] m.p. 52°). The 2,4-diene gave a 65% yield of crude adduct, m.p. 93.8–96.6°, which on recrystallization gave a 55% yield of adduct (needles), m.p. 96.1–96.8° (literature,[19] m.p. 95–96°). These data indicated that the 1,3-diene was predominantly the *trans* isomer, and that the 2,4-diene was about 50% *trans, trans* isomer.

Pyrolysis of 2-Acetoxy-*trans*-3-hexene.—The pyrolysis of the ester (109.7 g., 0.771 mole) and work-up of the pyrolysate were the same as described for the 4-acetoxy compound, except that the pyrolysis tube was maintained at 450°. Titration of the aqueous extract showed 0.539 mole of acetic acid to have been eliminated; this indicated 70% of the ester underwent pyrolysis.

Distillation of the ester portion gave fourteen fractions of b.p. 53.7–57.2°/15 mm., n^{25}_{D} 1.4186–1.4194. The ester (27.95 g.) was 85% of the theoretically recoverable ester. High-boiling residue (4.58 g.) which was mostly ester remained after distillation of the diene (*vide infra*); hence, nearly all of the unpyrolyzed ester was accounted for. The ester fractions were combined to give a composite ester sample. By gas chromatography this composite sample was found to contain 84% of *trans* esters and 15% of *cis* esters. The infrared curve of this composite sample was superimposable on that of a 50–50 mixture of the 2-acetoxy-*trans*-3-hexene and 4-acetoxy-*trans*-2-hexene. The data indicated that the unpyrolyzed ester in this case was nearly identical with that recovered from the pyrolysis of the 4-acetoxy compound.

The diene portion was distilled to give fractions which were combined to give the following materials: 1,3-hexadiene, 16.76 g., 38% yield, b.p. 72.9–74.4°/761 mm., n^{25}_{D} 1.4371–1.4379; intermediate fraction, 4.12 g., b.p. 74.4–82.3°/761 mm., n^{25}_{D} 1.4391–1.4480; 2,4-hexadiene, 14.01 g., 32% yield, b.p. 82.4–83.0°/761 mm., n^{25}_{D} 1.4494–1.4502. By gas chromatography the 1,3-hexadiene was found to be 90% 1,3-diene and 10% 2,4-diene, the intermediate fraction contained 49% 1,3-diene and 50% 2,4-diene, and the 2,4-hexadiene was found to be 100% 2,4-diene. Calculation from the gas chromatographic data indicated the total yield of 1,3-diene to be 54% and that of the 2,4-diene to be 46%. The infrared curve of the 1,3-hexadiene had very strong bands at 950 cm.$^{-1}$ and at 1000 and 895 cm.$^{-1}$, characteristic of a *trans* alkene linkage and a terminal methylene group, respectively. In the ultraviolet this diene had $\epsilon_{224}^{C_2H_5OH}$ 25,500. The infrared curve of the 2,4-hexadiene had a very strong band at 980 cm.$^{-1}$ attributable to a *trans* alkene linkage, and in the ultraviolet the diene had $\epsilon_{226}^{C_2H_5OH}$ 23,500.

Maleic anhydride adducts were prepared as described above. The 1,3-diene gave a 97% yield of crude adduct, m.p. 47.4–51.0°, which on recrystallization gave a 79% yield of adduct, m.p. 49.8–50.8°. The 2,4-diene gave a 60% yield of crude adduct, m.p. 93.8–96.6°, which on recrystallization gave a 49% yield of adduct, m.p. 96.1–96.8°. These data indicated that in this case, also, the 1,3-diene is predominantly the *trans* isomer, and that the 2,4-diene is about 50% *trans, trans* isomer.

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[17] W. G. Braun, D. F. Spooner, and M. R. Fenske, *Anal. Chem.*, **22**, 1074 (1950).

[18] The spectrum and its interpretation were obtained by L. F. Johnson of Varian Associates, Palo Alto, California.

[19] P. Nayler and M. C. Whiting, *J. Chem. Soc.*, 3037 (1955).

search, and to it we express our gratitude. We are indebted to the Texas Research Laboratories, Beacon, New York, for the gas chromatographic and ultraviolet analyses. Roy S. Anderson did the experiments responsible for the assignment of the *trans* configuration to the 2-pentenal.

The Rearrangement of α-Silyl Ketones with Alkoxides

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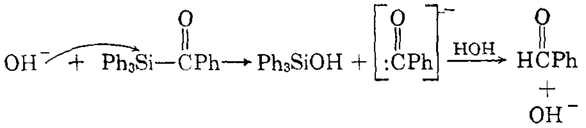
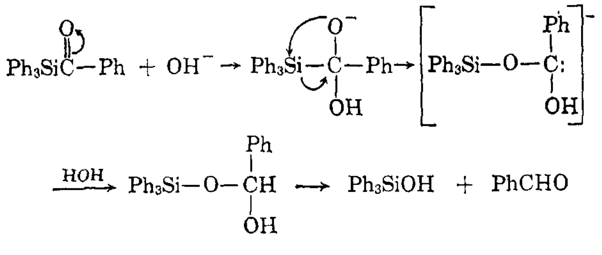
Treatment of a variety of benzoylsilanes and acetyltriphenylsilane with simple sodium alkoxides leads to two competing reactions—rearrangement of the ketone to a dialkoxysilane involving the migration of a phenyl or methyl group from silicon to carbon, and displacement of the acyl group from silicon to give an alkoxysilane and aldehyde. The polarity of the solvent appears to play an important role in determining the ratio in which these two competing reactions occur.

It has been reported that benzoyltriphenylsilane (I), a typical α-silyl ketone, is cleaved at room temperature by dilute aqueous alcoholic alkali into triphenylsilanol and benzaldehyde.[1] This reaction is readily explained, based on the great susceptibility of silicon to nucleophilic attack, as attack by hydroxide ion on silicon followed by elimination of benzoyl anion, which yields benzaldehyde on reaction with the solvent.



$$OH^- + Ph_3Si{-}\overset{O}{\overset{\|}{C}}Ph \rightarrow Ph_3SiOH + \left[:\overset{O}{\overset{\|}{C}}Ph\right]^- \xrightarrow{HOH} H\overset{O}{\overset{\|}{C}}Ph + OH^-$$

However an alternative scheme can also explain the formation of the products. Spectral data[2] have established that the carbonyl group in α-silyl ketones is highly polarized (absorption at 6.18 μ in the infrared, comparable to an enolized β-diketone) and hence the possibility of nucleophilic attack by hydroxide ion on the carbon of the carbonyl group cannot be neglected.



$$Ph_3Si\overset{O}{\overset{\|}{C}}{-}Ph + OH^- \rightarrow Ph_3Si{-}\underset{OH}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}{-}Ph \rightarrow \left[Ph_3Si{-}O{-}\underset{OH}{\underset{|}{\overset{Ph}{\overset{|}{C}}}}:\right]^- \xrightarrow{HOH} Ph_3Si{-}O{-}\underset{OH}{\underset{|}{\overset{Ph}{\overset{|}{C}H}}} \rightarrow Ph_3SiOH + PhCHO$$

The product of such an attack would be an α-alkoxide. Since alkoxides from α-silylcarbinols have been shown to rearrange readily to the isomeric silyl ethers by intramolecular attack on silicon with displacement of carbon,[3–5] a similar rearrangement in this case would lead, after reaction of the carbanion with solvent, to the triphenylsilylhemiacetal of benzaldehyde, which would hydrolyze to the observed products during work-up. While the mode of attack on the ketone might be established by using ketone labelled with O^{18}, it seemed likely that the two mechanisms could be distinguished by using ethoxide ion in place of hydroxide, since in the first case triphenylethoxysilane, a known compound, would be the product, whereas in the second case the product would be expected to be the ethyltriphenylsilylacetal of benzaldehyde, which might be isolable.

When the reaction between sodium ethoxide and benzoyltriphenylsilane in benzene–ethanol was carried out, the yellow color of the ketone disappeared and the main product isolated was benzhydryloxyethoxydiphenylsilane (VI) together with smaller amounts of triphenylethoxysilane (III), benzaldehyde, diphenyldiethoxysilane (VII), benzhydrol, triphenylsilanol, and diphenylsilanediol.[6] The structure of the major product clearly indicated: (a) that initial attack by ethoxide ion occurred at silicon; (b) that displacement of a phenyl group from silicon to neighboring carbon occurred; (c) that additional rearrangement occurred in which a silicon-oxygen bond was formed and a silicon-carbon bond was broken. These facts together with the other products isolated are satisfactorily explained by the reaction scheme on the following page.

Thus attack by ethoxide ion must occur on the silicon atom of benzoyltriphenylsilane (I), presumably giving rise to the pentacovalent (sp^3d) intermediate II. This intermediate either eliminates benzoyl anion yielding ethoxytriphenyl- (III) and benzaldehyde (or some triphenylsilanol by hydrolysis of III during work-up) or else undergoes rearrangement. Which path predominates seems to depend in part at least on the polarity of the solvent as will be discussed later. If rearrange-

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[1] A. G. Brook, *J. Am. Chem. Soc.*, **79**, 4373 (1957).

[2] A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *ibid.*, **82**, 5102 (1960).

[3] A. G. Brook, *ibid.*, **80**, 1886 (1958).

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[5] A. G. Brook and Bruno Iachia, *ibid.*, **83**, 827 (1961).

[6] A. G. Brook, *J. Org. Chem.*, **25**, 1072 (1960).