TABLE IV

PERFLUORO-2-HEXYL POLYSULFIDES

$[C_4F_9CF(CF_3)]_2S_n$ n value	B.p., °C.	B.p., Mm.	n^tD	t, °C.	Analyses, %[a] Carbon Calcd.	Carbon Found	Sulfur Calcd.	Sulfur Found
2	94	8	1.3300	23	20.5	20.4	9.1	9.6[b]
3	66	<0.1	1.3469	28.8	19.6	19.5	13.1	12.8
4	*ca.* 80	<0.1	1.3791	20	18.8	19.2	16.7	16.7
5	Residue (viscous oil)		1.3975	19.5	18.1	18.0	20.1	19.6

[a] Microanalyses by Schwarzkopf Microanalytical Laboratory. In all cases % H was zero. [b] *Anal.* Calcd. for $C_{12}F_{26}S_2$: F, 70.34. Found: F, 70.7.

Another experiment conducted in a sealed Pyrex tube at 180° for 75 hours gave similar results.

Thermal Reaction of Perfluoro-2-hexyl Polysulfide with Chlorine.—A 70-cc. heavy-wall Pyrex ampule containing 4.2 g. (0.059 mole) of chlorine and 8 g. (0.011 mole) of perfluoro-2-hexyl polysulfide, $[C_4F_9CF(CF_3)]_2S_n$, where $n = 2.5_{av}$, was sealed and heated at a temperature of 105° for 125 hours. The tube was cooled in Dry Ice and opened, and unreacted chlorine was removed by warming. The remaining liquid products were carefully fractionated in a small Vigreux still, and there was collected a total of 6.6 g. (0.017 mole) of perfluoro-2-hexylsulfenyl chloride, a pale yellow liquid, middle cut, b.p. 63–63.8° (97 mm.), n^{26}D 1.3237. *Anal.* Calcd. for $C_6ClF_{13}S$: C, 18.6; Cl, 9.2. Found: C, 18.8; Cl, 8.9.

The compound had ultraviolet absorption maxima (in isoöctane) at 213.5 mμ (strong) and at 340 mμ (weak).

Finally, there was recovered by further distillation 1.1 g. of perfluoro-2-hexyl disulfide. The conversion to the sulfenyl chloride was 77%, and the yield 89% of theoretical.

The Reaction of 1,2-Dichloro-2-iodo-1,1,2-trifluoroethane with Sulfur.—Into a 300-ml. nickel autoclave were charged 1,2-dichloro-2-iodo-1,1,2-trifluoroethane (279 g., 1 mole) and sublimed sulfur (64 g.). The sealed autoclave was heated in a shaker at 187° for 12.2 hours. Upon rectification of the 161 g. of crude liquid product, there were obtained 56 g. of recovered 1,2-dichloro-2-iodo-1,1,2-trifluoroethane, 15 g. of an intermediate cut, b.p. 68–85° (5 mm.), and *ca.* 90 g. of material boiling from 60° (1 mm.)->118° (0.5 mm.). From the latter fraction which was shown to be primarily $(CF_2ClCFCl)_2S_n$ where $n = 2–5$, the following three cuts were separated by rectification at 0.5 mm.: (1) b.p. 67–69° (0.5 mm.), n^{30}D 1.4638. *Anal.* Calcd. for $(CF_2ClCFCl)_2S_2$: C, 13.0; S, 17.4; Cl, 38.5. Calcd. for $(CF_2ClCFCl)_2S_3$: C, 12.0; S, 24.1; Cl, 35.5. Found: C, 12.3; S, 21.1; Cl, 36.5.

(2) B.p. 83–84°, n^{29}D 1.4888. *Anal.* Calcd. for $(CF_2ClCFCl)_2S_3$: C, 12.0; S, 24.1; Cl, 35.5. Found: C, 11.8; S, 25.2; Cl, 35.6.

(3) B.p. 112–118°, n^{29}D 1.5217. *Anal.* Calcd. for $(CF_2ClCFCl)_2S_4$: C, 11.1; S, 29.7; Cl, 32.8. Found: C, 10.8; S, 30.7; Cl, 32.8.

The ultraviolet spectra of these fractions showed λ_{max} in 95% ethanol at 242–245 mμ, which is characteristic of S–S bonds in compounds of this type.[24]

The residue, b.p. >118° (0.5 mm.), had an n^{29}D of 1.5595 and probably contained some of the pentasulfide.

Infrared and Ultraviolet Spectra.—The infrared spectra were determined by use of a Perkin–Elmer model 21 instrument with sodium chloride optics. The ultraviolet spectra were determined with a Beckman ratio recording spectrophotometer, model DK-2.

Acknowledgment.—We wish to thank Mr. Fred Curtis and Mr. John J. Mullaney for technical assistance, Miss Ruth Kossatz for infrared spectra determinations and Mr. John Y. Steel for viscosity measurements.

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[24] G. R. A. Brandt, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 2549 (1952).

PHILADELPHIA 18, PENNA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

Meerwein Reactions on Isolated Olefinic Bonds. Free Radical Addition Reactions on Vinylsilanes

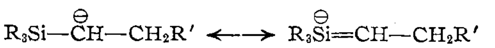
BY ROBERT A. BENKESER, EVERETT W. BENNETT AND RICHARD A. HICKNER

RECEIVED MAY 20, 1957

Aromatic diazonium salts add to vinyl groups attached to a silicon atom under conditions typical for the Meerwein reaction. Since the latter is usually successful only with conjugated olefins, the reaction is diagnostic of the "conjugative nature" of a vinyl group joined to silicon. Vinylsilanes also add chloroform, carbon tetrachloride and ethyl bromoacetate with great ease under free radical conditions.

Evidence has been presented in recent years which indicates that the valence joining a silicon atom to an aromatic ring may possess some double bond character, particularly when the silicon atom is conjugated with strong electron-supplying groups[1–3] such as $-NH_2$, $-OH$, or $-N(CH_3)_2$. In a similar fashion the enhancement of acidity of various silylbenzoic acids has been attributed to d-pπ bonding between the π-orbital system of the aromatic ring and the vacant 3-d orbitals of the silicon atom.[4]

It would seem reasonable that this conjugative ability of silicon might well be reflected in the chemistry of an attached vinyl group, since one can envision (at least in a transition state) contributions from electronic forms such as



$$R_3Si-\overset{\ominus}{C}H-CH_2R' \longleftrightarrow R_3\overset{\ominus}{Si}=CH-CH_2R'$$

I

If such forms have any validity one might expect the chemistry of such a vinyl group to resemble that of a conjugated olefin. Thus such a group might be expected to undergo Michael-type addition reactions. In keeping with this prediction, vinylsilanes reportedly do undergo nucleophilic additions, in a manner such that the anion portion of the attacking group becomes attached to the β-

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[1] H. Soffer and T. DeVries, THIS JOURNAL, **73**, 5817 (1951).

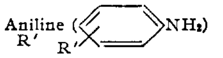
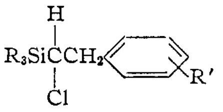
[2] R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 2421 (1953).

[3] R. A. Benkeser, C. E. DeBoer, R. E. Robinson and D. M. Sauve, *ibid.*, **78**, 682 (1956).

[4] J. Chatt and A. A. Williams, *J. Chem. Soc.*, 4403 (1954); 688 (1956).

TABLE I

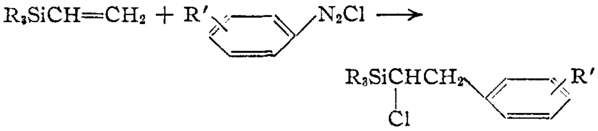
MEERWEIN REACTIONS[a]

Run no.	Aniline 	Yield of adduct, %	M.p., °C.	Analyses, % Calcd.	Found
					
1	p-Br (0.0174 m.)	15	141.5–143	C, 65.34	65.54
				H, 4.64	4.92
2	p-Cl (0.084 m.)	37	142–143	C, 72.2	72.14
				H, 5.1	4.98
				Cl, 17.1	17.1
3	p-NO_2 (0.035 m.)[b]	28	143–144	C, 70.5	70.75
				H, 4.98	4.85
				N, 3.16	3.00
				Cl, 8.00	8.00
4	p-CO_2H (0.0174 m.)	23	196–197	C, 73.21	72.88
				H, 5.23	5.50
5	m-NO_2 (0.0174 m.)	16	129–130	C, 70.33	70.24
				H, 5.00	5.29
6	p-Phenyl (0.0174 m.)	11	174–175	C, 80.9	81.20
				H, 5.7	6.00
7	p-CO_2H (0.04 m.)[a]	13	131.5–132	C, 60.3	60.02
				H, 7.76	7.52
8	p-OCH_3 (0.0174 m.)	0	.....		
9	p-CH_3 (0.0174 m.)	0	.....		
10	Aniline (0.0174 m.)	0	.....		

[a] The silicon compound employed in each instance was triphenylvinylsilane (0.0174 m.) except in run 7 where triethylvinylsilane (0.04 m.) was used. [b] The solid diazonium salt was employed in this case (caution).

carbon of the vinyl group, as form I would predict.[5,6]

As supplementary evidence of this conjugation we now wish to report that vinylsilanes undergo the Meerwein reaction[7-9] with relative ease

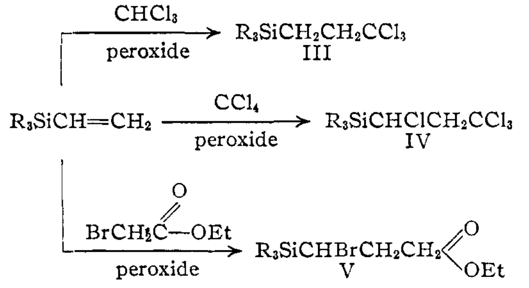


II

In general this reaction is successful only with conjugated olefins. Only a few examples are known in which the reaction has proved successful with olefins containing isolated double bonds, and these require quite vigorous conditions.[8] On the other hand, we have found that vinylsilanes undergo the Meerwein reaction under normal conditions and in fair yield. It will be noted from Table I that only those aromatic amines which contained electron-withdrawing groups would react. This is in keeping with the usual pattern for the Meerwein reaction.

The structures of the Meerwein adducts (II) could be deduced easily from the inert character of the chlorine atom they contained. Treatment with silver nitrate did not result in the precipitation of silver halide and only vigorous basic treatment would effect dehydrohalogenation. Compounds in which a halogen is located on a carbon beta to silicon are known to be very susceptible to hydrolytic cleavage.[10] In addition, infrared spectra of the dehydrohalogenation products showed no peaks in the 11 μ region which are typical of terminal olefins.

In connection with our study of radical addition reactions it was observed that chloroform, carbon tetrachloride and ethyl bromoacetate also would add in good yield to triethyl- and triphenylvinylsilanes.[11]



The chloroform adduct did not contain any β-halogen as evidenced by its resistance to hydrolysis. Structure III shown above was thus clearly indicated. The structure of adduct IV was deduced by analogy to reaction III and also from the work of Kharasch[12] in which it was demonstrated that

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(5) L. F. Cason and H. G. Brooks, THIS JOURNAL, **74**, 4582 (1952).

(6) M. Prober, Abstracts of the 130th A.C.S. Meeting, Atlantic City, N. J., p. 53-O; see also L. H. Sommer and co-workers, THIS JOURNAL, **76**, 1613 (1954).

(7) H. Meerwein, E. Buchner and K. Van Emster, *J. prakt. Chem.*, **152**, 237 (1939).

(8) E. Müller, *Angew. Chem.*, **61**, 179 (1949).

(9) J. K. Kochi, THIS JOURNAL, **77**, 5090 (1955).

(10) F. C. Whitmore and co-workers, *ibid.*, **68**, 488 (1946).

(11) See A. F. Gordon, U. S. Patent 2,715,113 where similar additions are described.

(12) M. S. Kharasch, E. V. Jensen and W. H. Urry, THIS JOURNAL, **69**, 1100 (1947).

TABLE II

PEROXIDE CATALYZED REACTIONS[h]

	$R_3SiCH{=}CH_2$ R	Reactant	Time, hr.	Temp., °C.	Product	Yield, %	M.p. or b.p. °C.	Mm.	d^{20}_4	n^{20}_D
1	C_6H_5	$CHCl_3$								
	(0.035 m.)	(0.753 m.)	20	67	$(C_6H_5)_3Si(CH_2)_2CCl_3$[a]	69	141–142	..	...	....
2	C_6H_5	CCl_4								
	(0.017 m.)	(0.67 m.)	20	78	$(C_6H_5)_3SiCHClCH_2CCl_3$[b]	75	93–94	..	...	....
3	Et-	$CHCl_3$	24	67	$Et_3Si(CH_2)_2CCl_3$[c]	37	74–75	0.3	1.078	1.4767
	(0.295 m.)	(1.33 m.)			$C_{17}H_{37}Cl_3Si_2$[d,i]	19	120–150	.08	1.026	1.4938
4	Et-	$BrCH_2CO_2Et$								
	(0.25 m.)	(0.74 m.)	5	90	$Et_3SiCHBr(CH_2)_2CO_2Et$[e,j]	45	82–87	.04	1.150	1.4830
5	Dimethyldivinylsilane	$CHCl_3$	25	67	$CH_2{=}CHSi(CH_3)_2(CH_2)_2CCl_3$[f]	12	35–37	.5	1.109	1.4743
	(0.214 m.)	(1.67 m.)			High boiling residue[g,i]		115–117	.05	1.136	1.5061

[a] *Anal.* Calcd. for $C_{21}H_{19}SiCl_3$: C, 62.14; H, 4.71; Cl, 26.21. Found: C, 61.97; H, 4.68; Cl, 26.22. [b] *Anal.* Calcd. for $C_{21}H_{18}SiCl_4$: C, 57.28; H, 4.12; Cl, 32.21. Found: C, 57.52; H, 4.23; Cl, 32.01. [c] *Anal.* Calcd. for $C_9H_{19}SiCl_3$: C, 41.34; H, 7.31; Cl, 40.64; *MR*, 67.96. Found: C, 41.10; H, 7.14; Cl, 40.44; *MR*, 68.42. [d] *Anal.* Calcd. for $C_{17}H_{37}Cl_3Si_2$: C, 50.53; H, 9.23; Cl, 26.32; *MR*, 114.62. Found: C, 50.66; H, 9.04; Cl, 26.50; *MR*, 114.39. [e] *Anal.* Calcd. for $C_{12}H_{25}O_2BrSi$: C, 46.59; H, 8.14; Br, 25.83; *MR*, 76.77. Found: C, 49.85; H, 7.57; Br, 24.56; *MR*, 76.75. [f] *Anal.*, Calcd. for $C_7H_{13}Cl_3Si$: C, 36.29; H, 5.56; Cl, 45.92; *MR*, 58.22. Found: C, 36.12; H, 5.67; Cl, 46.12; *MR*, 58.65. [g] Analysis of this material: C, 42.43; H, 6.96. [h] Each reaction was catalyzed with 2–2.5 g. of benzoyl peroxide except no. 4 in which 3 g. of acetyl peroxide (25% solution in dimethyl *o*-phthalate) was employed. [i] Structure not established. [j] Infrared spectra showed this material to be contaminated with dimethyl *o*-phthalate.

the $-CCl_3$ group assumes a position at the end of the chain in a terminal olefin. The compounds corresponding to structures III and IV also gave negative tests with silver nitrate solution.

In the reaction of chloroform with triethylvinylsilane another product (VI) was obtained along with the expected adduct (see Table II, run 3).

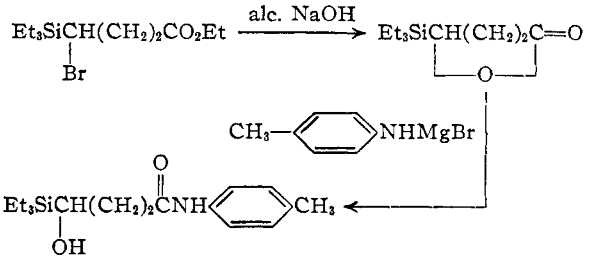
$$Et_3SiCH{=}CH_2 \xrightarrow[\text{peroxide}]{CHCl_3}$$

$$Et_3Si(CH_2)_2CCl_3\ (37\%) + \underset{\text{VI}}{C_{17}H_{37}Cl_3Si_2}\ (19\%)$$

Compound VI also was obtained by heating a solution of 1,1,1-trichloro-3-triethylsilylpropane in triethylvinylsilane with benzoyl peroxide. The identity of these two materials was demonstrated by the complete superimposability of their infrared spectra and by their boiling points and indices of refraction. Since no chloroform was present in the latter instance, compound VI would appear to be some combination of two molecules of the vinylsilane with one of chloroform. Its elemental analysis and molar refraction would tend to bear out this supposition.

There was evidence that a similar type of reaction was occurring in the addition of chloroform to dimethyldivinylsilane (Table II, run 5). In addition to the expected monoadduct a very high boiling material was obtained. Its analysis and molar refraction suggest that it is some type of bis adduct. No structure proof of either compound V or the latter material was attempted.

Infrared spectra of the adduct obtained from triethylvinylsilane and ethyl bromoacetate showed contamination by dimethyl *o*-phthalate. The latter was introduced by way of the acetyl peroxide catalyst which was employed as a 25% solution in dimethyl *o*-phthalate. To substantiate the structure of the ethyl bromoacetate adduct it was saponified with ethanolic base, presumably to the lactone. This product was then converted to the *p*-toluidide by treatment with the magnesium salt of *p*-toluidine.



Experimental

Since the general procedure employed in most of the addition reactions was similar, only a few experiments, deemed as representative of all, are outlined in detail.

Meerwein Reactions. Triphenyl-1-chloro-2-(*p*-chlorophenyl)-ethylsilane.—*p*-Chloroaniline (10.8 g., 0.084 mole) was diazotized in 18 ml. of concd. hydrochloric acid at 0° with 6.0 g. of sodium nitrite in 10 ml. of water. Solid urea was added until a negative starch–potassium iodide test was obtained and the solution was then decolorized with Norit. It was then added to 150 ml. of purified acetone containing 5.0 g. (0.017 mole) of triphenylvinylsilane. The flask was purged with nitrogen for 8 minutes. The solution was cooled to 0° and a catalyst solution composed of 0.5 g. of tech. cuprous chloride and 0.5 g. of lithium chloride in 20 ml. of acetone was added over the course of 1.5 hr. Gas was evolved. The mixture turned red and separated into two layers.

A liter of water was then added, and the mixture was extracted in small portions with 1 liter of ether. The ethereal extracts were combined and dried over calcium sulfate. When the ether was removed by a rotary evaporator a red sludge remained. This sludge yielded a white solid when taken up in an ethanol–water mixture. This solid, after crystallization from 1:1 ethanol–acetone, yielded 2.8 g. (37% yield) of white needles melting at 142–143°.

Chloroform and Carbon Tetrachloride Reactions. 1,1,1-Trichloro-3-triphenylsilylpropane.—A solution of 10 g. (0.035 mole) of triphenylvinylsilane in 60 ml. (89 g., 0.75 mole) of chloroform was held at vigorous reflux under nitrogen for 20 hr. Dibenzoyl peroxide (2.0 g., 0.008 mole) was added in equal portions at 0, 5, 10 and 15 hr. The excess chloroform was removed at room temperature in a rotary evaporator, and the solid residue was dissolved in 100 ml. of acetone. Sodium iodide was added until no more sodium benzoate formed. The precipitate was filtered off and washed with 50 ml. of acetone. The combined filtrate and washings were treated with sodium thiosulfate solution to destroy the iodine. The acetone was taken off in the rotary evaporator, and the slurry remaining was extracted with 150 ml. of ether. The ether extracts were washed with 5% sodium carbonate and then dried over Drierite. Evaporation of the ether and two crystallizations from acetone yielded 9.8 g. of product and 2.2 g. of a straw-yellow gum.

1,1,1,3-Tetrachloro-3-triphenylsilylpropane.—A solution of 5 g. (0.017 mole) of triphenylvinylsilane in 60 ml. (95.7 g., 0.67 mole) of carbon tetrachloride was held at vigorous reflux for 20 hr. One gram (0.004 mole) of dibenzoyl peroxide was added in half-gram portions at 0 and 2 hours. The reaction was worked up as described above except that a 1:1 solution of ethanol and acetone was used to crystallize the product.

Reaction of 1,1,1-Trichloro-3-triethylsilylpropane with Triethylvinylsilane.—Fifteen grams (0.057 mole) of 1,1,1-trichloro-3-triethylsilylpropane was dissolved in a solution of 0.5 g. of benzoyl peroxide in 15 g. (0.105 mole) of triethylvinylsilane and held at 70° under a nitrogen atmosphere for 12 hours. Another 0.5 g. of peroxide (total of 1.0 g. or 0.0041 mole) was added and the solution held at 75° for an additional 12 hours. The reaction was worked up in the usual manner. Fractional distillation yielded 6.4 g. of triethylvinylsilane (b.p. 63-64° (44 mm.), n^{20}D 1.4341), 13.1 g. of 1,1,1-trichloro-3-triethylsilylpropane (b.p. 56-57° (0.08 mm.), n^{20}D 1.4760), and 2.5 g. of material boiling at 120-150° (0.015 mm.), n^{20}D 1.4930. An infrared spectrum of the latter was superimposable on that of the material isolated from the reaction of triethylvinylsilane with chloroform.

Silver Nitrate Tests.—To establish whether halogen substituents were located alpha or beta to the silicon atom the stability of the compounds to silver nitrate was determined under conditions known to result in immediate and quantitative removal of halogen from trimethyl-β-bromoethylsilane.

Volhard titration of trimethyl-β-bromoethylsilane dissolved in methanol or acetone was conducted as follows: The sample (0.2591 g.) was added to 50 to 100 ml. of methanol containing 25.00 ml. of 0.0894 *N* silver nitrate solution, and 5 ml. of dilute nitric acid and allowed to stand for ten minutes. In all cases a precipitate formed immediately upon mixing; 1 ml. of 40% ferric alum indicator was added and the excess nitrate titrated with standard KCNS; theoretical Br content 44.11, found 43.11.

To test the compounds described in this paper, 5 ml. of 0.1022 *N* silver nitrate solution was mixed with 5 ml. of acetone and then 0.2 g. of the compound in question added as an acetone solution. Occasionally some turbidity occurred but this was caused by the insolubility of the compound since it disappeared when a little more acetone was added. As a check, after 15 minutes, a drop of *t*-butyl chloride was added to each solution and caused an immediate precipitate that was unchanged by further dilution with acetone.

Attempted Basic Hydrolysis of 1,1,1-Trichloro-3-triphenylsilylpropane.—Two grams (0.0049 mole) of the silane and 1.1 g. (0.0197 mole) of potassium hydroxide were dissolved in 50 ml. of 80% ethanol mixed with 25 ml. of tetrahydrofuran and refluxed for two hours. Application of the usual isolation procedure resulted only in the recovery of 1.7 g. of pure starting material.

Dehydrohalogenation of the *p*-Nitrophenyl Meerwein Adduct.—A solution of 500 mg. of the *p*-nitro adduct was refluxed in γ-picoline for 8 hours. The solution was then poured into water, extracted with ether, and the ether extract washed with aqueous acid. Evaporation of the ether deposited 0.37 g. (82%) of light yellow needles melting at 171.5–172.5° after crystallization from a 1:1 ethanol–acetone solution. A duplicate run utilizing 1.7 g. of nitro adduct resulted in an 81% yield. An infrared spectra showed a strong olefin band at 10.12 μ.

Anal. Calcd. for $C_{26}H_{21}O_2NSi$: C, 76.6; H, 5.19; N, 3.43. Found: C, 76.6; H, 5.19; N, 3.58.

Toluidide of Ethyl Bromoacetate Adduct.—A mixture of 10 g. (0.033 mole) of ethyl 4-bromo-4-triethylsilylbutanoate, 30 ml. of water, 30 ml. of ethanol and 10 ml. of 50% sodium hydroxide was refluxed on a steam-cone for 4 hours. The solution was concentrated and then acidified with dilute hydrochloric acid. This was extracted with ether and dried over calcium sulfate.

This ether solution of the lactone was refluxed for 20 minutes with a suspension of the magnesium salt of *p*-toluidine in ether. The latter was prepared by adding ethylmagnesium bromide (from 0.05 mole of ethyl bromide and 0.05 g. atom of magnesium in 50 ml. of dry ether) to 5.36 g. (0.05 mole) of *p*-toluidine in 30 ml. of dry ether.

After working up in the usual fashion a brown oil was obtained which eventually solidified. Crystallization of this material from 1:1 petroleum ether (60-70°) and ethyl ether yielded white needles melting at 67.5–69°. A qualitative test for nitrogen was positive and a halogen test negative.

Anal. Calcd. for $C_{17}H_{29}O_2NSi$: C, 66.39; H, 9.55; N, 4.55. Found: C, 66.46; H, 9.44; N, 4.70.

Acknowledgment.—This investigation was supported by the National Science Foundation whose financial assistance is gratefully acknowledged.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

An O-18 Tracer Study of the "Wet" and "Dry" Prevost Reactions

BY KENNETH B. WIBERG AND KLAUS A. SAEGEBARTH[1]

RECEIVED JULY 23, 1957

The reaction of *erythro*-1-benzoxy-2-bromo-1,2-diphenylethane-carbonyl-O^{18} with silver benzoate under the conditions of the "dry" Prevost reaction followed by hydrolysis resulted in the formation of *meso*-hydrobenzoin having one-half the O-18 of the bromobenzoate. The bromobenzoate when treated with silver benzoate under the conditions of the "wet" Prevost reaction resulted in the formation of *threo*-2-benzoxy-1,2-diphenylethanol. The hydroxybenzoate on hydrolysis gave the D,L-hydrobenzoin which was found to have the same O-18 content as the bromobenzoate. These results are discussed in terms of the mechanisms of the reactions.

Introduction

Our interest in hydroxylation reactions has led us to investigate some aspects of the Prevost reaction.[2] This is particularly interesting since it has been shown recently that the reaction of an olefin with silver acetate and bromine in the presence of some water will give a product corresponding to *cis*-hydroxylation,[3] whereas the same reaction carried out in a dry solvent gives *trans*-hydroxylation. The wet reaction has been postulated to involve a cyclic acetoxonium ion intermediate which may add water and then be cleaved to the hydroxyacetate

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(1) Taken from part of a thesis submitted by K. A. Saegebarth to the University of Washington in partial fulfillment of the requirements for the Doctor of Philosophy degree, May, 1957.

(2) C. Prevost, *Compt. rend.*, **196**, 1129 (1933); **197**, 1661 (1933); C. Prevost and M. Losson, *ibid.*, **198**, 659 (1934); C. Prevost and R. Lutz, *ibid.*, **198**, 2264 (1934); C. Prevost and J. Weinman, *ibid.*, **204**, 700 (1937); C. Prevost, *Atti Xth cong. intern. chim.*, **3**, 318 (1939) (*C. A.*, **33**, 8187 (1939)).

(3) D. Ginsburg, THIS JOURNAL, **75**, 5746 (1953); L. B. Barkley, W. M. Farrar, W. S. Knowles, H. Raffelson and Q. E. Thompson, *ibid.*, **76**, 5014 (1954).