phite used in the reaction. The chlorine-containing compound was identified as diethyl phosphorochloridate as follows. Thirteen grams of fraction A, containing 0.86 g. of chlorine, was treated with 4.5 g. of aniline (2 moles) and the mixture heated to 80° for 10 minutes. After adding 18 ml. of water, the solution was cooled to 5° and seeded with diethyl N-phenylphosphoroamidate. The resulting solid after recrystallization from ethanol–water had m.p. 95.5–96° which was not depressed by mixing with an authentic sample of diethyl N-phenylphosphoroamidate (lit.[7] m.p. 95–96°).

When this preparation was repeated without solvent at −40°, the reaction was very vigorous and smoke and flame were occasionally observed when a drop of phosphite entered the chloropicrin. The yield of oxime ester was 32% and about 11% of the phosphite was converted to phosphorochloridate.

Preparation of Ethyl Isopropylideneamino Phenylphosphonate.—Sixty-five grams (0.31 mole) of diethyl phenylphosphonite was added dropwise with stirring and cooling at 15–28° to 26 g. (0.155 mole) of 2-bromo-2-nitropropane. When addition was complete, stirring was continued at 30° for 1 hour. Distillation gave 14.5 g. (86%) of ethyl bromide and fractionation of the remainder gave 28.5 g. (82%) of diethyl phenylphosphonate, b.p. 100° (0.5 mm.), and $n^{35}\mathrm{D}$ 1.4897 (lit.[8] b.p. 104–105° (0.5 mm.), $n^{25}\mathrm{D}$ 1.4935), and 10 g. (27%) of oxime ester, b.p. 140° (0.5 mm.), and $n^{35}\mathrm{D}$ 1.5082. There was a large tarry residue.

Anal. Calcd. for $C_{11}H_{16}NO_3P$: N, 5.8; P, 12.8. Found: N, 5.6; P, 12.5.

Preparation of Diethyl Benzylideneamino Phosphate.—To a mixture of 19.6 g. of benzaldehyde oxime (0.16 mole) and 12.6 g. of pyridine (0.16 mole) was gradually added at 0° 27.6 g. of diethyl phosphorochloridate (0.16 mole). The mixture was allowed to warm to room temperature where it was stirred for 1 hr. and then heated at 50–60° for 1 hr. After cooling, ether was added to the mixture and pyridine hydrochloride removed by filtration. Removal of volatile matter by heating *in vacuo* gave 36.5 g. (88%) of crude oxime ester which decomposed when distillation was attempted at 1 mm. pressure.

Anal. Calcd. for $C_{11}H_{16}NO_4P$: P, 12.1. Found: P, 11.9.

Pyrolysis of Diethyl Isopropylideneamino Phosphate.—Twenty grams of oxime ester was placed in a 50-ml. flask equipped with a thermometer dipping into the liquid and a water condenser. When heated to 175°, a vigorous exothermic reaction began which was controlled with difficulty by immersing the flask in a Dry Ice-bath. After the reaction subsided, heating was continued at 180–185° for 2 hr. Distillation at 0.6 mm. gave only 3 g., b.p. 53–55°, $n^{35}\mathrm{D}$ 1.4060, the remainder being a viscous tar. Not only is the boiling point of the distillate considerably lower than would be expected for the Beckmann rearrangement product, but the phosphorus and nitrogen contents were low (12.4 and 4.45%, respectively).

Hydrolysis of Diethyl Isopropylideneamino Phosphate.—Ten grams of the oxime ester and 50 ml. of 5% hydrochloric acid were placed in a flask equipped with a distillation condenser. When heated to gentle boiling, a few drops of blue liquid distilled followed by 3.5 ml. of colorless distillate. This was identified as acetone by conversion to the 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 126° (lit.[9] m.p. 126°).

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[7] F. R. Atherton, H. T. Howard and A. R. Todd, *J. Chem. Soc.*, 1106 (1948).

[8] G. M. Kosolapoff, "Organic Phosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 162.

[9] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 262.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM STANFORD RESEARCH INSTITUTE]

The Addition of Chloro- and Ethoxysilanes to Vinyl and Allyl Monomers[1,2]

BY LEON GOODMAN, ROBERT M. SILVERSTEIN AND ALLEN BENITEZ

RECEIVED NOVEMBER 6, 1956

The platinum-catalyzed addition of some chloro- and ethoxysilanes to a variety of vinyl and allyl monomers has been accomplished in good yield under mild conditions. Nuclear magnetic resonance spectra make it clear that the addition of methyldichlorosilane to vinyl acetate gives the linear compound $CH_3SiCl_2CH_2CH_2OCOCH_3$, while addition to methyl acrylate gives the branched compound $CH_3SiCl_2CH(CH_3)COOCH_3$. The latter compound represents the first reported example of a reversed addition orientation in additions of the elements of the Si–H bond to carbon–carbon double bonds.

The addition of the elements of the Si–H bond to a carbon–carbon double bond was first reported in 1947[3] and has been the object of much study since that time. Peroxides and ultraviolet light were used as catalysts in the original study,[3] and since that report the reaction has been carried out by employing high temperatures and pressures without catalyst[4] and by using platinum and palladium as catalysts.[5]

We have utilized this platinum-catalyzed reaction for the synthesis of silicon monomers which contain functional groups. The additions of trichlorosilane, methyldichlorosilane and methyldiethoxysilane to a variety of vinyl and allyl monomers were accomplished using mild conditions. These reactions are listed in Table I.

A 5% platinum-on-carbon catalyst was used in all these additions. It was demonstrated to be necessary in the trichlorosilane additions to vinyl acetate and to methyl acrylate, and we presume it to be necessary in all the reactions listed in Table I. The catalyst was used in the amount of about 0.25–0.50% by weight of the silane employed and, in most cases, that same weight of Ionol (2,6-di-*t*-butyl-4-methylphenol) was used as a polymerization inhibitor for the olefin.[6]

Two techniques were used in carrying out these reactions—use of a stainless steel sealed bomb

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[1] This work was supported by the Wright Air Development Command under Contract AF 33(616)-2998.

[2] (a) A preliminary communication appeared in THIS JOURNAL, **78**, 4493 (1956). (b) Presented in part at the 130th meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1956.

[3] L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, THIS JOURNAL, **69**, 188 (1947).

[4] A. J. Barry, L. DePree, J. W. Gilkey and D. E. Hook, *ibid.*, **69**, 2916 (1947).

[5] G. H. Wagner and C. O. Strother (to Union Carbide and Carbon), U. S. 2,632,013 (March 17, 1953).

[6] The effectiveness of polymerization inhibition is shown by an experiment in which methyl acrylate, Ionol and a large excess of trichlorosilane were heated in a steel bomb at 150° for 20 hr. No polymerization of the acrylate was detectable, and there was no evidence of a silane–acrylate addition product.

TABLE I

SUMMARY OF SILANE ADDITIONS

$RSiX_2H + CH_2{=}CH(CH_2)_nY \longrightarrow$ Products[a]

	RSiX₂H		$CH_2{=}CH(CH_2)_nY$				Products		Hydrolyzable chlorine (%)[g]		Silicon	
R	X	n	Y	Method[b]	Conditions for method I °C. (hr.)	Conversion,[c] %	B.p.[d] °C.	Mm.	Calcd.	Found	Calcd.	Found
Cl	Cl	0	$OCOCH_3$	II		76	44–46	1	48.0	47.7		
Cl	Cl	1	$OCOCH_3$	II		72	87.0	10	45.2	46.2	11.9	12.0
Cl	Cl	1	OC_2H_5	II		64	75.8	17	48.0	48.0		
Cl	Cl	0	CN	I	100(20)	42.5	70.0	8	56.4	59.0[e]	14.9	15.8
Cl	Cl	0	$COOCH_3$	I	100(20)	65[f]	88.5	20	48.0	47.9		
Cl	Cl	0	$COO(CH_2)_2OCH_3$	I	100(20)	70[f]	89–90	3	40.0	39.8		
CH_3	Cl	0	$OCOCH_3$	II		76	80.0	9.6	35.3	35.2		
CH_3	Cl	1	$OCOCH_3$	II		72	84.2	6.5	33.0	32.8		
CH_3	Cl	1	OC_2H_5	II		56	73.5	15	35.3	35.4		
CH_3	Cl	0	CN	I	75(26)	26	60–62.5	4	42.2	41.5[e]		
CH_3	Cl	0	$COOCH_3$	II		65[f]	71.0	12.8	35.3	35.0		
CH_3	Cl	0	$COO(CH_2)_2OCH_3$	II		59[f]	87–88	0.5	28.9	28.6		
CH_3	OC_2H_5	0	OC_2H_5	II		81	69–72	8			13.6	13.9
CH_3	OC_2H_5	0	OC_4H_9-n	II		75	88–90	5			11.9	12.3
CH_3	OC_2H_5	0	$CH(OCOCH_3)_2$	II		51	113.0	2			9.6	9.6

[a] Trichlorosilane and dimethyl itaconate gave a 40% conversion to 1:1 adduct, b.p. 106–107° (4 mm.), hydrolyzable chlorine, calcd. 36.2, found 35.5. [b] See Experimental. [c] Conversion based on total olefin used, some of which was recovered. Conversions based on wider boiling ranges than in next column. [d] Boiling ranges of analytical samples. [e] Unstable compounds which darkened rapidly and were difficult to handle. [f] Lower boiling materials were present in additions to acrylates. These appear to be isomeric with desired adducts and require further investigation. [g] Chlorine determined by Volhard method after hydrolysis in a water–isopropyl alcohol mixture.

which enabled higher temperatures to be attained, and simple refluxing of the silane while the olefin was slowly added. The sealed bomb technique was necessary in the additions of the low boiling (32°) trichlorosilane to acrylonitrile and to the α,β-unsaturated esters. In these additions a large excess of the silane was necessary in order to obtain good conversions to the 1:1 adduct. The technique of slowly adding the olefin to the refluxing mixture of silane and catalyst allowed good conversion to the 1:1 adduct to be realized when equimolar amounts of the silane and olefin were employed and was used in the additions of methyldichlorosilane[7] (b.p. 42°) and methyldiethoxysilane (b.p. 98°). In the chlorosilane additions to acrylonitrile and the acrylate esters, large residues remained after the distillation of the 1:1 adducts. These contained silicon–chlorine bonds, and it is felt that they are best explained as telomerization products wherein the ratio of olefin to silane is greater than 1. These residues were especially large in the acrylonitrile reactions and were much more prominent in the additions of methyldiethoxysilane than in those of the chlorosilanes.

Methyldiethoxysilane added in excellent yield to the two vinyl ethers, systems where telomerization is not a competing reaction. These olefins gave poor, or no, yields in the reactions with the chlorosilanes where traces of hydrogen chloride, which were present under our conditions, polymerized the ethers. It is interesting to note that Prober has obtained the same products by a base-catalyzed addition of alcohols to vinylmethyldiethoxysilane.[8] Addition of methyldiethoxysilane to acrolein diacetate gave a good conversion to 1:1 adduct. Under the same conditions, the attempted addition of methyldiethoxysilane or methyldichlorosilane to acrolein gave an intractable mixture as did the reaction between methyldichlorosilane and acrolein diacetate.

The additions of the elements of the Si–H bond to olefins, which were catalyzed by peroxides and ultraviolet light, have been regarded as typical free-radical reactions[3] and certainly obey the criteria of such a mechanism. There has been no speculation regarding the mechanism involved in the platinum-catalyzed addition. That addition has been shown to involve the addition of the silicon-containing moiety to the terminal carbon of the vinyl compound in several cases,[9,10] and no example of a reversed addition orientation has been noted. It is clear that the addition of a silane $RSiX_2H$ to an olefin $CH_2 = CHZ$ can lead to two possible products: $RSiX_2CH_2CH_2Z$ (A) or $RSiX_2$-$CH(CH_3)Z$ (B).

Hydrolysis studies of the methyldichlorosilane and methyldiethoxysilane adducts indicated that two classes of compounds had been formed by these reactions. The adducts from vinyl acetate, the vinyl ethers and all of the allyl monomers yielded oils on hydrolysis that did not change after being heated at 200° *in vacuo*. The adducts from acrylonitrile and the acrylate esters gave oils on hydrolysis that became resinous solids after heating *in vacuo* at temperatures up to 200°. Methyl propionate and methoxyethyl propionate were isolated as decomposition products from the hydrolyzate of the methyldichlorosilane adducts with methyl acrylate and methoxyethyl acrylate, respectively. It is known that the ester $(CH_3)_3SiCH_2COOR$ yields CH_3COOR readily on neutral hydrolysis as a result of Si–C bond cleavage[11] while $(CH_3)_3SiCH_2CH_2$-

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[7] The addition of methyldichlorosilane to acrylonitrile required the use of the bomb in order to achieve even low conversions to the 1:1 adduct.

[8] M. Prober, 130th Amer. Chem. Soc. Meeting, Sept., 1956, Abstracts of Papers, p. 53-O.

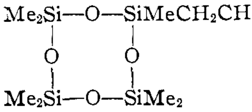
[9] G. H. Wagner, D. L. Bailey, A. N. Pines, M. L. Dunham and D. B. McIntire, *Ind. Eng. Chem.*, **45**, 367 (1953).

[10] J. W. Curry, THIS JOURNAL, **78**, 1686 (1956).

[11] C. R. Hauce and C. R. Hauser, *ibid.*, **75**, 994 (1953).

COOR gives $(CH_3)_3SiCH_2CH_2CCOH$ under severe conditions of acidic or basic hydrolysis.[12] The isolation of the above-noted decomposition products was the first hint that some of our adducts had the reversed addition orientation of structure B.

The cohydrolysis of dimethyldichlorosilane and the methyldichlorosilane–vinyl acetate adduct, using a 3:1 mole ratio of the silanes, respectively, gave a reasonable yield (*ca.* 30%) of the functionally substituted cyclic siloxane, β-acetoxyethylheptamethylcyclotetrasiloxane (III).



$$\begin{array}{lll} \mathrm{Me_2Si} & \text{—O—} & \mathrm{SiMeCH_2CH_2OAc} \\ \;\;| & & | \\ \;\;\mathrm{O} & & \mathrm{O} \\ \;\;| & & | \\ \mathrm{Me_2Si} & \text{—O—} & \mathrm{SiMe_2} \end{array}$$

III

The isolation of III in a reasonable yield shows that this cohydrolysis method offers a convenient route to such unsymmetrical cyclic siloxanes.

Attempts were made to add trimethylsilane to ethyl acrylate using platinum catalysis in an effort to prepare a compound which could be compared with a known compound, $(CH_3)_3SiCH_2CH_2CO\text{-}OC_2H_5$, in physical constants and chemical behavior. Such a structure proof is based on the assumption that trimethylsilane and methyldichlorosilane would give the same addition orientation. The only product isolated from the reaction was a low yield of a high-boiling liquid which seems to contain about three acrylate ester units for each trimethylsilane unit. Attempts to add trimethylsilane to vinyl acetate gave no evidence of addition. It should be noted that the platinum-catalyzed addition of methyldichlorosilane to vinyl acetate gives high yields of 1:1 adduct under very mild conditions.

An unequivocal answer to the structure problem was available from a study of the proton nuclear magnetic resonance spectra of the silane adducts. The methyldichlorosilane adducts of vinyl acetate and methyl acrylate (these are isomeric compounds) were chosen as representative examples of compounds which give stable hydrolyzates and unstable hydrolyzates, respectively. Simply on the basis of the proton spin–spin interactions, it is clear that the structures of the two adducts are as shown in Fig. 1. The two triplet peaks (a) and (c) (of equal area) of the vinyl acetate adduct are assignable to the $-CH_2CH_2-$ structure and the doublet, quartet groupings (g) and (f) (with the areas in the ratio 3:1) of the methyl acrylate adduct clearly shows the presence of the $\overset{\overset{\mathrm{CH_3}}{|}}{-\mathrm{CH}-}$ structure. The fact that (h) lies at a higher field than (a) and that (b) lies at a higher field than (f) conforms to the general pattern of NMR spectra wherein the more highly protonated of two otherwise similar groups shows resonance at a higher field. The NMR spectrum of the methyldichlorosilane–allyl acetate adduct shows that it has the linear structure with three $-CH_2-$ groups. The NMR spectrum of the methyldiethoxysilane–allylidene diacetate adduct shows that it too has the linear structure. This indicates that a route is available to the stable isomers in the additions of Si–H-containing compounds to acrolein *via* acrolein diacetate or acrolein acetals. The methyldichlorosilane–methyl acrylate adduct (and presumably the acrylonitrile adduct and other adducts to α,β-unsaturated carbonyl compounds) then represents the first example of a reversed addition orientation in Si–H additions.

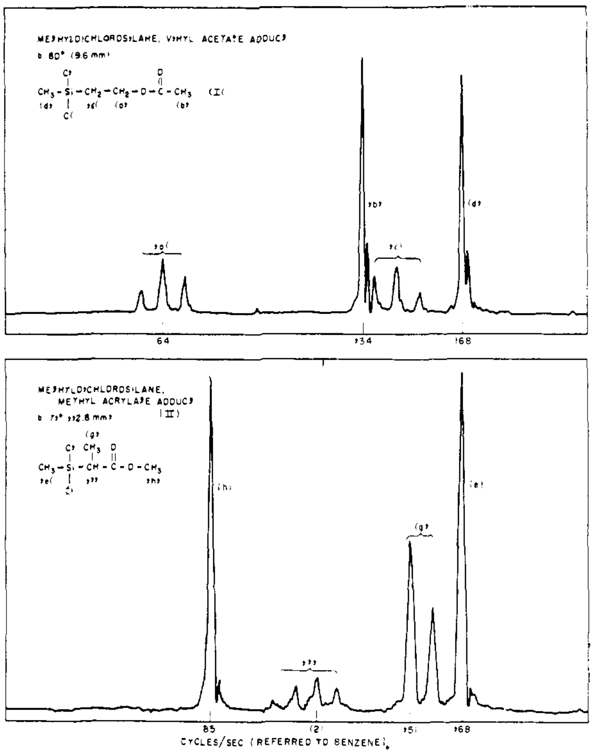
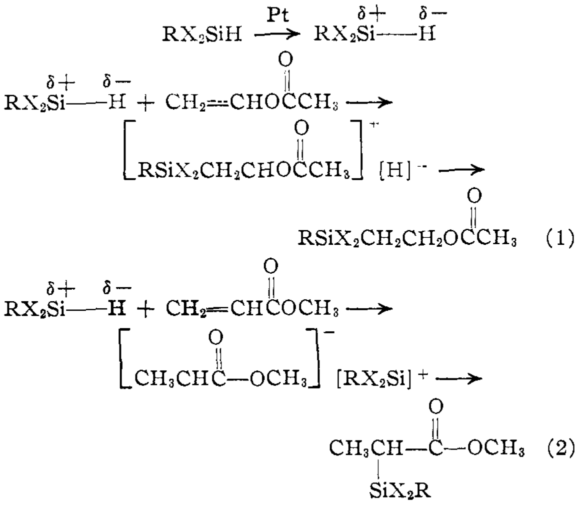


Fig. 1.—Proton nuclear magnetic resonance spectra of methyldichlorosilane adducts. Samples in 5 mm. tubes and Varian Associates High Resolution Spectrometer (V-4300B) at 30 mc. and 7050 gauss.

The fact that these platinum-catalyzed silane additions proceed well in the presence of a polymerization inhibitor is an indication, at least, that the reaction is not a typical free-radical reaction. We think that the difference of addition orientation in the two classes of olefins can be accommodated by the ionic mechanism



$$\mathrm{RX_2SiH} \xrightarrow{\mathrm{Pt}} \overset{\delta+}{\mathrm{RX_2Si}}\text{——}\overset{\delta-}{\mathrm{H}}$$

$$\overset{\delta+}{\mathrm{RX_2Si}}\text{——}\overset{\delta-}{\mathrm{H}} + \mathrm{CH_2{=}CHO\overset{\overset{O}{\|}}{C}CH_3} \longrightarrow$$

$$\left[\mathrm{RSiX_2CH_2CHO\overset{\overset{O}{\|}}{C}CH_3}\right]^{+} [\mathrm{H}]^{-} \longrightarrow \mathrm{RSiX_2CH_2CH_2O\overset{\overset{O}{\|}}{C}CH_3} \qquad (1)$$

$$\overset{\delta+}{\mathrm{RX_2Si}}\text{——}\overset{\delta-}{\mathrm{H}} + \mathrm{CH_2{=}CH\overset{\overset{O}{\|}}{C}OCH_3} \longrightarrow$$

$$\left[\mathrm{CH_3CH\overset{\overset{O}{\|}}{C}{—}OCH_3}\right]^{-} [\mathrm{RX_2Si}]^{+} \longrightarrow \mathrm{CH_3\underset{\underset{SiX_2R}{|}}{CH}{—}\overset{\overset{O}{\|}}{C}{—}OCH_3} \qquad (2)$$

(12) L. H. Sommer and N. S. Marans, This Journal, **72**, 1935 (1950).

The platinum serves to polarize the silane as shown, silicon being electro-positive with respect to hydrogen.[13,14] Addition to ordinary olefins occurs by typical electrophilic initiation and leads to linear adducts (equation 1). Addition to double bonds conjugated with strongly electronegative groups (*e.g.*, the acrylate esters) is initiated by nucleophilic addition of hydride ion and leads to branched adducts (equation 2). The telomerization noted with the α,β-unsaturated compounds is accommodated in the mechanism by addition of the intermediate negative ion to another molecule of olefin before terminating with the silane molecule.

There is ample precedent in the literature[15] for a difference in mode of ionic addition of a given reagent to unconjugated double bonds and to double bonds conjugated with strongly electronegative groups.[16]

The marked inferiority of trimethylsilane as compared to trichlorosilane in additions to vinyl acetate seems readily rationalized. Both the positive inductive effect and hyperconjugative resonance of the methyl groups tend to increase the electron density at the silicon atom in the $(CH_3)_3Si^+$ ion and thus reduce its effectiveness as an electrophilic entity. The negative inductive effect of the chlorines in trichlorosilane should lead to a strong electron deficiency on the silicon atom in the Cl_3Si^+ ion making it the potent electrophilic group it seems to be. The NMR measurements show that the silane hydrogen peak in trimethylsilane occurs at 110 ± 5 cycles/sec. higher than in trichlorosilane while the peak in methyldichlorosilane occurs at about 26 cycles/sec. higher than in trichlorosilane. These measurements emphasize the inductive effect of chlorine and indicate that, at least in the ground state, the silane hydrogen in trimethylsilane has a higher electron density than that in trichlorosilane and would be expected to donate a hydride hydrogen better than trichlorosilane. In view of these data it is difficult to understand why trimethylsilane seems to be inferior to trichlorosilane in additions to the acrylate esters. We recognize that our postulated (and admittedly speculative) mechanism may be a gross oversimplification of the picture which neglects the adsorption, desorption interactions of the catalyst and reactants. However we do not expect to do further work on this problem, and we wish to report our work to date.

Acknowledgments.—We gratefully acknowledge the aid of Dr. James N. Shoolery and Mr. Robert C. Jones of Varian Associates in running and interpreting the NMR spectra that are reported. We also express our thanks to Mr. Oliver D. Smith and the members of the analytical staff of the Stanford Research Institute for the analytical data. The Divisional Research Committee of Stanford Research Institute furnished funds to complete certain phases of this work.

Experimental[17]

Silane–Olefin Adducts. Method I.—A mixture of the olefin (*ca.* 0.10 mole), the chlorosilane (*ca.* 0.30 mole), Ionol (0.25 g.) and 5% Pt-on-carbon (Baker and Co., Newark, N. J.) (0.25 g.) was sealed in a 100-ml. stainless steel bomb and heated, with rocking, at the proper temperature for the desired time. The bomb was cooled and opened, and the contents were filtered. The excess silane was removed by distillation at atmospheric pressure, and the residue was distilled at reduced pressure using a simple Claisen flask. Analytical samples were obtained by redistillation using a 50 × 1 cm. column packed with glass helices.

When trimethylsilane was used, it was condensed into the bomb using a Dry Ice–acetone bath. Excess trimethylsilane was distilled from the bomb and collected at the end of the reaction. When vinyl acetate was used as the olefin with trimethylsilane, there was no distillation residue after heating at 60° and 35 mm., indicating that no addition had occurred. About 25% of the vinyl acetate was isolated from the distillation trap, and more was present in the trimethylsilane which was distilled from the bomb. When ethyl acrylate was used as the olefin, a brown liquid (4.2 g.) was the residue from 10 g. of ethyl acrylate and 23 g. of trimethylsilane heated at 75° for 30 hr. This residue could not be distilled at 130° and 1 mm.

Anal. Calcd. for $Me_3Si(CH_2CHCOOEt)_3H$: Si, 7.5. Found: Si, 7.1.

About 3.5 g. of ethyl acrylate was recovered from the distillation trap.

Method II.—A mixture of chloro- or ethoxysilane (0.10 mole) and 5% Pt-on-carbon (0.25 g.) was stirred magnetically under reflux, while a solution of Ionol (0.25 g.) in the olefin (0.10 mole) was added dropwise (3–6 hr. was required for the additions). After a further 18 hr. of heating (the temperature gradually rose from the reflux temperature of the silane to that of the adduct), the mixture was filtered, and the filtrate was distilled as in method I.

Hydrolysis Studies.—The adducts from methyldichlorosilane were added slowly to an aqueous solution of sodium sulfate according to the directions of Wright.[18] The siloxanes formed were extracted with ether and, after drying the extract over magnesium sulfate, the ether was evaporated and the residue heated under vacuum to remove volatile materials. The adducts from methyldiethoxysilane were hydrolyzed using 10% hydrochloric acid, and the hydrolyzates were recovered as above with the additional step of a sodium bicarbonate wash of the ether extract to remove acid.

The silane adducts with vinyl acetate, allyl acetate, allyl ethyl ether and the vinyl ethers yielded hydrolyzates that could be heated at 200° and 1 mm. for several hours without change.

The hydrolyzate of the methyldichlorosilane–acrylonitrile adduct was an oil which changed to a resinous solid when it was warmed on the steam-bath. No effort was made to collect volatile decomposition products. The hydrolyzate of the methyldichlorosilane–methyl acrylate adduct was an oil which slowly changed to a resinous solid when it was heated to 200° at 1 mm. The liquid condensed in the trap was redistilled using a Claisen flask and a fraction, presumed to be methyl propionate, b.p. 80–81° (lit.[19] 79.9°), was collected.

Anal. Calcd. for $C_4H_8O_2$: C, 54.46; H, 9.15. Found: C, 54.1; H, 9.01.

The hydrolyzate of the methyldichlorosilane–methoxyethyl acrylate adduct similarly yielded a resinous solid when it was heated *in vacuo* at 200°. The liquid condensed in the trap was redistilled using a 50 × 1 cm. packed column and a fraction, b.p. 92–93° (82.5 mm.), was collected. The in-

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[13] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 64.

[14] E. G. Rochow, "An Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 22.

[15] L. S. Luskin, G. E. Gantert and W. E. Craig, This Journal, **78**, 4965 (1956), have recently pointed out such a difference in the additions of isothiocyanic acid.

[16] A recent report by G. J. M. van der Kerk, J. G. A. Luijten and J. G. Noltes, *Chem. and Ind.*, 352 (1956), is of interest here. These authors added $(C_6H_5)_3SnH$ and $(n\text{-}C_4H_9)_3SnH$ to acrylonitrile and methyl acrylate in an uncatalyzed reaction run at low temperatures (80°). Their adducts had the linear structures $R_3SnCH_2CH_2X$ and the authors were of the opinion that an ionic mechanism was involved. The systems studied seem to be quite analogous to ours, and it would be interesting to observe what effect, if any, platinum catalysis would have on addition orientation in the tin hydride additions.

[17] Boiling points are uncorrected.

[18] J. G. E. Wright, U. S. Patent 2,426,912 (September 2, 1947).

[19] "Handbook of Chemistry and Physics," 13th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1948, p. 1006.

frared spectrum of this material showed the strong carbonyl band at 1750 cm.$^{-1}$, weak carboxyl carbonyl at 1725 cm.$^{-1}$, the C–O–C absorptions at 1205, 1136, 1090 and 1045 cm.$^{-1}$ and the absence of typical Si–O–Si bands. It appeared to be an impure sample of methoxyethyl propionate contaminated with propionic acid.

Anal. Calcd. for $C_6H_{12}O_3$: C, 54.5; H, 9.16. Found: C, 51.6; H, 8.75; Si < 0.5.

Cohydrolysis of Dimethyldichlorosilane and the Methyldichlorosilane–Vinyl Acetate Adduct.—A mixture of 53.7 g. of methyldichlorosilane (Dow–Corning, pure grade) and 28 g. of the methyldichlorosilane–vinyl acetate adduct (mole ratio 3:1) was added, over a 5-hr. period, to a well-stirred mixture of 250 ml. of water and 250 ml. of ether, maintained at 0–10°. The ether layer was separated and the aqueous phase was extracted with four 50-ml. portions of ether. The total ether solution was dried over magnesium sulfate and the ether was evaporated to leave a residue (49.5 g.). The residue was first distilled from a Claisen flask to give the following fractions: (1) 6.8 g., b.p. 48–57° (7 mm.), n^{20}_D 1.3952–1.3970; (2) 2.1 g., b.p. 56–79° (2.5 mm.), n^{20}_D 1.4112; (3) 11.3 g., b.p. 79–86° (2.5 mm.), n^{20}_D 1.4137–1.4152; (4) 3.6 g., b.p. 86–91° (2.5 mm.), n^{20}_D 1.4155–1.4157; (5) 8.2 g., b.p. 91–132° (2.0 mm.), n^{20}_D 1.4198–1.4268. A residue of 14.4 g., n^{20}_D 1.4291, remained. Fraction (1) was a mixture of hexamethylcyclotrisiloxane and tetramethylcyclotetrasiloxane. Fractions (3) and (4) were redistilled using a 50 × 1 cm. column packed with glass helices and gave the following fractions: (1) b.p. 75–80° (2 mm.), n^{20}_D 1.4122; (2) b.p. 80–81.5° (2 mm.), n^{20}_D 1.4141; (3) b.p. 81.5–82°, n^{20}_D 1.4150; (4), (5) and (6) b.p. 82.0° (2.0 mm.), n^{20}_D 1.4153. Fraction V, considered to be β-acetoxyethylheptamethylcyclotetrasiloxane (III), was analyzed.

Anal. Calcd. for $C_{11}H_{28}O_6Si_4$: C, 35.83; H, 7.65; Si, 30.48; mol. wt., 368.69. Found: C, 35.5, 36.1; H, 7.55, 7.86; Si, 30.85; mol. wt. (cryoscopic in benzene), 361, 353.

Nuclear Magnetic Resonance Spectra.—The samples were sealed in 5 mm. tubes and the spectra were measured by the audio side band method using the Varian Associates Model V-4300B High Resolution Spectrometer at 30 mc. and 7050 gauss.

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Hydroxybenzeneboronic Acids and Anhydrides

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RECEIVED JANUARY 23, 1957

ortho-, *meta-* and *para*-hydroxybenzeneboronic acids and/or anhydrides were prepared by the reaction of tri-*n*-butyl borate with the corresponding organolithium compounds. The properties of the three "isomers" (boronic acid or anhydride), including anhydride formation ability, were found to vary considerably. The preparation of 2-(*m*-bromophenoxy)-tetrahydropyran and the optimum conditions for the halogen–metal interconversion of *m*-bromophenol also are reported.

In the approach to the synthesis of boron-containing azo dyestuffs,[1,2] which have been found to be of interest in the irradiation therapy of brain tumors,[3] it was thought that compounds such as *o*-hydroxybenzeneboronic acid and *m*-hydroxybenzeneboronic acid or their anhydrides would be active enough to couple with various diazonium salts. This coupling could occur either *ortho* or *para* to the hydroxy group, but primarily *para*. Perhaps the *p*-hydroxybenzeneboronic acid or its anhydride would also couple successfully with various diazonium salts. However, the possibility of losing the boronic acid group exists here more so than in the other two cases unless, of course, the coupling tends to go *ortho* to the hydroxy group. The *para* isomer was thus prepared primarily for comparison with the other members of this series.

In addition to the purposes already discussed, these compounds, as such, should also be of interest for testing in brain tumor therapy, since the work of several[3–12] has shown that any boron compound containing some of the boron isotope 10[13] might be useful in irradiation research of this type. In addition, other pharmacological studies indicate that the hydroxyl group should increase the efficacy of such compounds.

The *m*-hydroxybenzeneboronic acid has been prepared previously[1,14,15] and was used for the preparation of azo boronic acids.[1] In these instances, the compound was prepared from *m*-aminobenzeneboronic acid by diazotization followed by hydrolysis.

The preparation of *p*-hydroxybenzeneboronic acid has been attempted in the past[14] but it never has been isolated.

The *o*-hydroxybenzeneboronic acid anhydride has not been reported as yet.

Only one other arylhydroxyboronic acid is mentioned in the literature. This is 3-hydroxy-4-methylbenzeneboronic acid[14] which was prepared from the 3-nitro-4-methylbenzeneboronic acid using catalytic reduction followed by diazotization and hydrolysis.

In the work reported here, two different approaches were tried for the preparation of each of the three isomers and a third approach was attempted for the *ortho* and *para* isomers.

The best of the three approaches involved the halogen–metal interconversion of a bromophenol isomer with *n*-butyllithium using 2 moles of the lithium reagent to 1 mole of the halogen com-

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(1) H. R. Snyder and Clay Weaver, THIS JOURNAL, **70**, 232 (1948).

(2) H. R. Snyder and S. L. Meisel, *ibid.*, **70**, 774 (1948).

(3) P. G. Kruger, *Radiation Research*, **3**, 1 (1955).

(4) P. G. Kruger, *Proc. Nat. Acad. Sci.*, **26**, 181 (1940).

(5) P. A. Zahl, F. S. Cooper and J. R. Dunning, *ibid.*, **26**, 589 (1940).

(6) P. A. Zahl and F. S. Cooper, *Science*, **93**, 64 (1941).

(7) P. A. Zahl and L. L. Waters, *Proc. Soc. Exper. Biol. Med.*, **48**, 304 (1941).

(8) P. A. Zahl and F. S. Cooper, *Radiology*, **37**, 673 (1941).

(9) W. H. Sweet and M. Javid, *J. Neurosurg.*, **9**, 200 (1952).

(10) M. Javid, G. L. Brownell and W. H. Sweet, *J. Clin. Invest.*, **31**, 604 (1952).

(11) L. E. Farr, W. H. Sweet, J. S. Robertson, C. G. Foster, H. B. Locksley, D. L. Sutherland, M. L. Mendelsohn and E. E. Stickley, *Am. J. Roentgenol. Radium Therapy Nuclear Med.*, **71**, 279 (1954).

(12) L. E. Farr, J. S. Robertson and E. E. Stickley, *Proc. Nat. Acad. Sci.*, **40**, 1087 (1954). See, E. E. Stickley, *Am. J. Roentgenol. Radium Therapy Nuclear Med.*, **75**, 609 (1956).

(13) Naturally occurring boron compounds contain 18.83% of the boron isotope 10. See NBS Circular No. 499, p. 7.

(14) F. R. Bean and J. R. Johnson, THIS JOURNAL, **54**, 4415 (1932).

(15) M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956). This is a review article on organoboron chemistry and contains most of the organoboronic acids that have been prepared up to the writing of this paper.