istics for the polyol and its acetylated derivative. Solvents given preliminary attention were chloroform, carbon tetrachloride, ether, dioxane, ethyl acetate, acetic acid, benzene, and absolute ethanol. Of these carbon tetrachloride appeared to be most satisfactory.

Acetylation of D-glucose in carbon tetrachloride was found to be superior to acetylation in acetone in several respects. In the first place fewer steps are involved in the isolation of the final product. Secondly, a purer product is formed. Evidently the acetone solution is compatible with undesirable acidic side reactions as is indicated by the greater amount of sodium carbonate required in washing. The work of Rice and Greenburg[5] further substantiates this conclusion.

All available hydroxy groups in four typical glycols, glycerol, three Cellosolves, D-glucose, sorbitol, and mannitol were completely acetylated with ketene in the presence of a trace of sulfuric acid. Available ether linkages were not ruptured under similar treatment. Carbon tetrachloride was found to be a suitable solvent for the acetylation of solid polyols and definitely superior to acetone.

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The Addition of Trichlorosilane to Pentene-1 with Peroxide Initiators

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The addition of organosilicon hydrides and tribromosilane to olefinic double bonds in the presence of peroxide initiators has recently been described.[1] In continuing this work, using trichlorosilane, certain factors influencing the addition were observed.

The addition proceeds by a free radical mechanism, very likely as it is described by Sommer, *et al.*[2]

$$\mathrm{A\cdot + HSi{\equiv} \longrightarrow AH + \cdot Si{\equiv}}$$
$$\mathrm{RCH{=}CH_2 + \cdot Si{\equiv} \longrightarrow R\underset{\cdot}{C}HCH_2Si{\equiv}}$$
$$\mathrm{R\underset{\cdot}{C}HCH_2Si + HSi{\equiv} \longrightarrow RCH_2CH_2Si{\equiv} + \cdot Si{\equiv}}$$

In this mechanism A· is the free radical initiating the chain reaction. The manner in which the chain terminates is not known.

Burkhard and Krieble[3] have pointed out that mixtures containing methyldichlorosilane gave relatively poor yields of adduct per mole of initiator (peroxide efficiency). Trichlorosilane gave much better results and peroxide efficiencies as high as 17 were obtained with pentene-1 with diacetyl peroxide. We have found that this value may under favorable conditions rise considerably, for example, reaching 300 (Table III).

In order to find some of the factors influencing yields and peroxide efficiencies, a series of experiments were carried out in which pentene-1, trichlorosilane, and *tert*-butyl perbenzoate were mixed and sealed into small Claisen flasks. After a period of heating, the flasks were opened and the contents were distilled from them. Very good material balances and a fairly accurate estimate of yields were obtained in this way. To these flasks were also added miscellaneous components thought likely to have an effect on the yields. Such materials as silicone stopcock grease, traces of water, alcohol, nickel, lead, zinc, air, nitrogen, or carbon dioxide had little or no effect. Certain other materials had very obvious effects. Table I summarizes some results obtained in this way.

Metals and their salts may either hinder or aid the reaction. Iron and its salts were outstanding in preventing the formation of adduct. Tin was a promoter for the reaction, causing successful addition, at temperatures lower than those normally effective. Tin and its salts showed no catalytic activity alone, however, but presumably through some action on the peroxide acted as an effective promoter. Tin mixed with stannic chloride caused the addition to become violent even at room temperature.

Three samples of tin were tested and found to possess greatly differing effects as promoters. Granular tin (No. 1) used in Table II was 20 mesh, lot 15, from Baker and Adamson Co. A sample (No. 2) from J. T. Baker Co., 20 mesh, reagent grade, lot 3787, was less effective. A third sample (No. 3) filed from a bar of commercial tin of uncertain origin proved to be far the best. Addition of small amounts of it to the mixtures at room temperature caused violent reactions. Each sample of tin was analyzed spectroscopically and showed increasing activity with increasing amounts of impurities although the trace elements responsible could not be identified.

Experiments using various initiators showed appreciable differences as might be expected. Benzoyl peroxide was very active and gave high peroxide efficiencies, but in certain mixtures tended to react so rapidly as to make control difficult. Table III summarizes some data concerning initiators and the effects of temperature. Higher temperatures than employed here would be likely to improve the yields from some of the initiators.

The pentyltrichlorosilane obtained as the product from all these experiments was examined closely to establish its identity beyond question. Sommer[2] has found that octene-1 and trichlorosilane formed *n*-

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[a] Now at Dow Corning Corporation, Midland, Michigan.

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(1) J. L. Speier, Ruth Zimmerman, and J. A. Webster, *J. Am. Chem. Soc.*, **78**, 2278 (1956).

(2) L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Am. Chem. Soc.*, **69**, 188 (1947).

(3) C. A. Burkhard and R. H. Krieble, *J. Am. Chem. Soc.*, **69**, 2687 (1947).

TABLE I

EFFECTS OF VARIOUS MATERIALS ON ADDITION OF Cl_3SiH TO PENTENE-1 WITH *tert*-BUTYL PERBENZOATE AS INITIATOR

moles Cl_3SiH/moles pentene-1	Added Material	moles pentene-1/moles initiator	T., °C.	Hours	Yield,[a] %
3	Steel wool	70	80–85	15	0
3	Fine copper wire	50	80–85	18	52
3	None	70	80–85	16	88
2	Chromium chips	50	80–90	16	34
3	Nickel chips	50	80–90	16	100
2	None	50	80–90	16	100
2	Lead filings	50	80–90	16	90
2	Lead filings	50	25–30	24	0
2	Zinc dust	50	80–90	16	100
2	Tin granules	50	25–30	1.5	67
2	Tin granules	(b)	25–30	24	0
2	$SnCl_4$	50	25–30	24	11
2	SnO	50	25–30	24	18
2	$SnCl_2$	50	25–30	22	9
2	None	50	25–30	24	0
2	Tin granules + $AlCl_3$	50	25–30	24	0
2	Tin granules + $SnCl_4$	50		flask blew up	
2	Bu_2SnCl_2	50	25–30	24	0

[a] Based upon the pentene-1 charged. [b] No *tert*-butyl perbenzoate.

TABLE II

SPECTROSCOPIC ANALYSES OF TIN SAMPLES

Element	No. 1 Tin	No. 2 Tin	No. 3 Tin
Fe	0.003-0.03	0.003 -0.03	0.01 -0.1
Co	None	None	.003 - .03
Cu	.01 - .1	.0001- .001	.003 - .03
Pb	.003- .03	None	.03 - .3
Bi	None	None	.003 - .03
Si	.01 - .1	.003 - .03	.01 - .1
Cr	.001- .01	.001 - .01	.0003- .003
Ni	.001- .01	None	.001 - .01
In	None	0.01	.01 - .1

octyltrichlorosilane. By analogy Burkhard and Krieble[3] assigned the *n*-pentyl configuration to the product they obtained from pentene-1. Bygden[4] reported the properties of 2-pentyltrichlorosilane as prepared by Melzer[5] but inspection of Melzer's paper showed he had prepared only isopentyltrichlorosilane. No reference giving the properties of 2-pentyltrichlorosilane could be found. Pentene-2 and trichlorosilane were used to form a pentyltrichlorosilane easily distinguished from that obtained with pentene-1. These products proved to be essentially pure *n*-pentyltrichlorosilane from pen-

TABLE III

ADDITION OF TRICHLOROSILANE TO PENTENE-1 USING VARIOUS INITIATORS

$HSiCl_3$[a]/Pentene-1	Initiator[b]	Pentene-1[a]/Initiator	Temp., °C.	Time, hours	Conversion,[c] Percent	Peroxide[d] Efficiency
3	Bz_2O_2	33	55	2.5	Explosion	—
2.5	Bz_2O_2	100	80	0.25	Explosion	—
2	Bz_2O_2	1000	80	16	30	300
3	AZO-I	33	55	18	68	22
2.5	AZO-I	100	80	18	98	98
3	TBPA	33	55	18	0	0
2.5	TBPA	100	80	18	82	82
3	DTBP	33	55	18	0	0
2.5	DTBP	100	80	18	5.6	5.6
3	MAKP	33	55	18	0	0
1	MAKP	50	80	18	72	36
2.5	TBPB	100	80	18	82	82
2	TBPB	100	95	1.4	10	10
2	TBPB	100	95	5	79	79
3	TBPB	65	35	16	0	0
2	TBPA	100	95	1.4	8	8
2	TBPA	100	95	5	71	71

[a] In moles. [b] Bz_2O_2, benzoyl peroxide; AZO-I, N,N'-azo-bis-isobutyronitrile; TBPA, *tert*-butyl peracetate; DTBP, di-*tert*-butyl peroxide; MAKP, methyl amyl ketone peroxide; TBPB, *tert*-butyl perbenzoate. [c] Based on pentene-1. [d] Moles of product/mole of initiator.

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(4) A. Bygden, *Inaug. Diss. Upsala, Sweden* (1916).

(5) W. Melzer, *Ber.*, **41**, 3370 (1908).

tene-1 and a mixture of two isomers in the ratio of 70/30 from pentene-2. The isomers are likely to be the 2-pentyl- and 3-pentyl-silanes.

EXPERIMENTAL

Addition of trichlorosilane to pentene-1. Burkhard and Krieble[3] added trichlorosilane to pentene-1 and reported the formation of *n*-pentyltrichlorosilane. *n*-Pentyltrichlorosilane has also been made from the *n*-pentylmagnesium bromide and tetrachlorosilane.[6] The reported properties were not sufficient to indicate with certainty that the pentyltrichlorosilane we obtained was *n*-pentyltrichlorosilane free of isomers. Therefore, the product obtained as described in the discussion was carefully distilled through a column 3 ft. long and 1 inch in diameter packed with $^1/_{16}$ inch "Helipak" packing. The product was *n*-pentyltrichlorosilane essentially free of isomers: b.p. 171.0° at 742 mm., n_D^{25} 1.4379, d_4^{25} 1.128; R_D 0.2327, Calc'd 0.2320.

Methylation with excess methylmagnesium bromide in ether gave an 80% yield of *n*-pentyltrimethylsilane: b.p. 139.3° at 743 mm., n_D^{25} 1.4069, d_4^{25} 0.7271; R_D 0.3385, Calc'd 0.3382.[7]

n-Pentyltrimethylsilane was prepared by adding a mixture of *n*-amyl chloride and trimethylchlorosilane to molten sodium in refluxing toluene, b.p. 138.9–139.1° at 740 mm., n_D^{25} 1.4069, d_4^{25} 0.7267; R_D 0.3387, Calc'd 0.3382.

The infrared absorption curves of the two samples were identical.

Addition of trichlorosilane to pentene-2. Under the same conditions pentene-2 yielded a pentyltrichlorosilane with properties quite easily distinguishable from those of *n*-pentyltrichlorosilane. From pentene-2 one might expect 2-pentyl- or 3-pentyl-trichlorosilane or a mixture of the two.

A gas-phase chromatographic analysis was performed on a 15 microliter sample on a six-foot Celite column impregnated with didecyl phthalate as the liquid substrate at 80°. Nitrogen was used as the carrier gas with an inlet pressure of 2 p.s.i. at a flow rate of 10 ml. per minute. Two peaks were obtained. The first had a retention time of 21.2 min. and amounted to 70% of the sample. The second at 23.1 min. contained about 30% of the sample. Because standard samples were not available it is impossible to ascertain the structures of the two components[8] at this time. The product had the properties: b.p. 165–167°, n_D^{25} 1.4455, d_4^{25} 1.145; R_D 0.2327, Calc'd 0.2320. An adduct prepared in this way has been reported[3] to boil at 164–168°.

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(6) F. C. Whitmore, *et al.*, *J. Am. Chem. Soc.*, **68**, 475 (1946).

(7) F. C. Whitmore, *et al.*[6] report b.p. 139° at 760 mm., n_D^{20} 1.4096, d_4^{20} 0.7313.

(8) This analysis was carried out in the Department of Research in Physical Chemistry at Mellon Institute.

Preparation of 6-Quinolyl- and 6-Quinolylmethyl-phosphonic Acids

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Although several phosphonic acids, in which the phosphono group is attached to a heterocyclic ring, have been prepared in recent years by various procedures, there is still a decided paucity of data about the phosphonic acids with the simple, more common nitrogen-bearing heterocyclic rings. In view of the fact that the classical Skraup reaction does not appear to have been applied to the readily available aminoarylphosphonic acids, it was felt that this application of the Skraup reaction should be examined. In order to avoid the separation of isomeric phosphonic acids the present synthesis was confined to amino derivatives which can give only one compound by the Skraup reaction.

EXPERIMENTAL

6-Quinolylphosphonic acid. *p*-Nitrophenylphosphonic acid was prepared according to Doak and Freedman[1] and was hydrogenated to *p*-aminophenylphosphonic acid over a palladium-charcoal catalyst in aqueous solution at room temperature and atmospheric pressure. The amino acid (3.0 g.), 13 ml. of 70% sulfuric acid, 4.0 g. of dry glycerol, and 3.5 g. of nitrobenzene were mechanically stirred and refluxed gently for 1.5 hours. The dark mixture was diluted with 20 ml. of water, steam-distilled, cooled, and filtered from tarry material. The filtrate was adjusted to the Congo Red end-point with 20% sodium hydroxide and the crude product which precipitated was collected. The precipitate was dissolved in 15% hydrochloric acid and re-precipitated by the addition of sodium hydroxide solution. It was finally dissolved in 10% sodium hydroxide solution and precipitated by the addition of 15% hydrochloric acid. At each step of the purification the solution was treated with charcoal. There was obtained 2.0 g. (56%) of 6-quinolylphosphonic acid, in the form of colorless, stubby flat needles which melted to a bright red liquid at 303–304°. Titration of the material with 0.1 *N* sodium hydroxide yielded a curve with inflections near *p*H 5 and 10.5, the latter inflection being the more clearly defined of the two.

Anal. Calc'd for $C_9H_8NO_3P$: P, 14.85; Equiv. wt. 209. Found: P, 14.7, 14.8; Equiv. wt. 210.

6-Quinolylmethylphosphonic acid. The procedure described above was followed, with 6.0 g. of *p*-aminobenzylphosphonic acid,[2] 26 ml. of 70% sulfuric acid, 8.0 g. of glycerol, and 7.0 g. of nitrobenzene. There was obtained, after three acid-base re-precipitations, 3.9 g. (54%) of 6-quinolylmethylphosphonic acid, in the form of light-tan colored, fine plates which decomposed to a red liquid at 328–329°.

Anal. Calc'd for $C_{10}H_{10}NO_3P$: P, 13.9; Equiv. wt., 223. Found: P, 13.8, 13.75; Equiv. wt., 219, 220 (inflection points on the titration curve occurred at approximately *p*H 5.8 and 11).

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(1) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951).

(2) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **69**, 2112 (1947).

The Geminal Alkyl Effect on the Rates of Ring Closure of Bromobutylamines

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In view of the temporary interruption of an investigation[1] of the profound effect which geminal

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(1) R. F. Brown and N. van Gulick, *J. Am. Chem. Soc* **77**, 1079, 1083, 1089 (1955).