was determined by (1) glpc analysis which showed two peaks with retention times of 14 (1-bromo-2-propanol) and 18 min (2-bromo-1-propanol) using a 2 m × 0.25 in. diethylene glycol succinate column at 100° with 160 ml/min helium flow and (2) nmr spectral analysis which showed two separate doublets for the methyl groups. Good correspondence was achieved in comparing the glpc peak area ratios with the nmr methyl area ratios.

Effect of Reaction Temperature.—The effect of reaction temperature on the relative yields of 1-bromo-2-propanol and 2-bromo-1-propanol is shown in Table II. It can be seen that in order to limit the formation of 2-bromo-1-propanol to negligible amounts, reduced reaction temperatures are required such that the reaction rate would be prohibitively slow.[9]

TABLE II

PRODUCT DISTRIBUTION WITH VARYING TEMPERATURE

Reacn temp, °C	1-Bromo-2-propanol (1), %	2-Bromo-1-propanol (2), %	Reacn time, hr
60	73	27	41
60	70	30	41
80[a]	60	40	4
100	52	48	2

[a] Tube was at 60° for 1 hr and then 80° for 4 hr.

Isolation of Optically Active Propylene Bromohydrins 1 and 2.—Using the method described above, 20.1 g (0.248 mole) of anhydrous hydrogen bromide was bubbled into 19.1 g (0.251 mole) of (+)-(*S*)-1,2-propanediol, $[\alpha]^{25}D$ +14.92° (neat). The reaction mixture was heated at 60° for 43 hr. Distillation yielded 19.3 g (0.139 mole, 56%) of propylene bromohydrins **1** and **2**, bp 53–58° (15 mm), $[\alpha]^{25}D$ +2.61° (neat), which analyzed 70/30 1-bromo-2-propanol (**1**) to 2-bromo-1-propanol (**2**) by glpc and 66/34 by nmr. Samples of 0.25 ml of the mixture were injected on a 12 ft × 3/8 in. preparative glpc column packed with 20% diethylene glycol succinate on Chromosorb P at 110°, and gave almost complete separation of the two peaks whose retention times were 20 and 39 min from air. Both components were collected in Dry Ice–acetone cooled traps in approximately 50% yield, and were checked for chromatographic purity *via* the analytical glpc column.

Fraction 1 with the shorter retention time, (+)-(*S*)-1-bromo-2-propanol (**1**), had $n^{25}D$ 1.4776, d^{25}_4 1.5589, $[\alpha]^{25}D$ +4.96° (neat), and an nmr spectrum which exhibited a methyl doublet (3 H) with center at δ 2.17 (J = 7.0 cps), another doublet (2 H, CH_2Br) centered at δ 4.2 (J = 6.0 cps), a multiplet (1 H, HCO) centered at δ 4.65, and a singlet (1 H, OH) centered at δ 5.2.

Anal. Calcd for C_3H_7BrO: C, 25.92; H, 5.08; Br, 57.49; MR, 25.34. Found: C, 25.74; H, 5.12; Br, 57.32; MR, 25.24.

Fraction 2 with the longer retention time, 2-bromo-1-propanol (**2**), had $n^{25}D$ 1.4791, d^{25}_4 1.558, $[\alpha]^{25}D$ −2.59° (neat), and an nmr spectrum which exhibited a methyl doublet (3 H) centered at δ 1.8 (J = 6.0 cps), another doublet (2 H, CH_2O) centered at δ 3.95 (J = 5.5 cps), a multiplet (1 H, HCBr) centered at δ 4.5, and a singlet (1 H, OH) centered at δ 5.1.

Anal. Calcd for C_3H_7BrO: C, 25.92; H, 5.08; Br, 57.49; MR, 25.34. Found: C, 25.99; H, 4.93; Br, 57.07; MR, 25.34.

Propylene Oxides.—To 4 ml of stirred, 50% (by weight) aqueous potassium hydroxide was added rapidly at 60°, 2.79 g (20.1 mmoles) of the (+)-(*S*)-1-bromo-2-propanol (**1**) isolated above. Propylene oxide distilled immediately, after which the reaction mixture was subjected briefly to reduced pressure (150–200 mm). The Dry Ice–acetone trapped condensate was redistilled from potassium hydroxide pellets to give 0.92 g (15.8 mmole, 79%), bp 35°, $[\alpha]^{25}D$ −8.39° ($CDCl_3$). Its glpc chromatogram and nmr spectrum were identical with those of authentic propylene oxide.

Treatment of 1.39 g (10.0 mmoles) of 2-bromo-1-propanol (**2**) with aqueous potassium hydroxide as above gave, on redistillation, 0.40 g (6.9 mmoles, 69%), bp 35°, $[\alpha]^{25}D$ −1.50° ($CDCl_3$). Again, its glpc chromatogram and nmr spectrum were identical with those of authentic propylene oxide.

Acknowledgment.—The authors are indebted to Mr. A. K. Russell for his very valuable technical assistance. We also wish to thank Dr. W. A. Thaler for his initial comments on our work when he, too, felt that exclusive primary carbon attack by HBr was highly suspect. In addition we also wish to acknowledge some very helpful comments by Dr. W. C. Baird, Jr., and Professor S. J. Cristol.

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[9] In a personal communication, Professor C. C. Price has informed us that their procedure for preparation of the bromohydrin (*cf.* ref 3) also involved addition of HBr at 0° followed by heating on a water bath for 1 hr. We are grateful to Professor Price for furnishing us with further experimental details.

Structural Stabilities of the Trimethylsilylmethyl and Neopentyl Groups in the Preparation of Phosphonyl Dichlorides

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Several investigators have reported the preparation of the diesters of trimethylsilylmethylphosphonic acid, $(CH_3)_3SiCH_2PO(OR)_2$, (I) using the Michaelis–Arbuzov procedure.[1–3] This method is somewhat limited by the availability and reactivity of trialkyl phosphites (or dialkyl phosphonates) and often requires prolonged refluxing of reactants.

We have synthesized a number of these esters (Table I) by alcoholysis of trimethylsilylmethylphosphonyl dichloride (III), prepared by the reaction shown below. This is a modification of Clay's method[4]

$$(CH_3)_3SiCH_2Cl + PCl_3 + AlCl_3 \longrightarrow \underset{\text{II}}{[(CH_3)_3SiCH_2PCl_3]^+[AlCl_4]^-}$$

$$\text{II} + 7H_2O \longrightarrow \underset{\text{III}}{(CH_3)_3SiCH_2P(O)Cl_2} + AlCl_3\cdot 6H_2O + 2HCl$$

used to prepare alkylphosphonyl dichlorides from alkyl halides. Kinnear and Perren[5] investigated this reaction and showed that when propyl or higher primary or secondary alkyl chlorides are used, only rearranged products are obtained. We observed no rearrangement of the "neopentyl" structure of chloromethyltrimethylsilane in this reaction at or below room temperature, even though this compound undergoes a Wagner–Meerwein-type rearrangement to chlorodimethylethylsilane when warmed with aluminum chloride alone.[6]

The reaction does not appear to be applicable to chlorosilanes ($\equiv$SiCl) since we observed no evidence of complex formation between chlorotrimethylsilane and $AlCl_3$–PCl_3 at room temperature. This observation is in general agreement with Eaborn's[7] conclusion that the siliconium ion is not formed under conditions in which analogous carbonium ions exist.

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TABLE I

TRIMETHYLSILYLMETHYLPHOSPHONATES

$(CH_3)_3SiCH_2P(O)R_2$, R =	Bp, °C (mm)	$n^{25}D$	Calcd, %			Found, %			Yield, %
			C	H	P	C	H	P	
OH	Mp 121°[a]	...	28.56	7.78	...	28.70	7.65	...	12 [b]
Cl	64 (1.4)[c]	1.4710	23.43	5.36	...	23.69	5.44	...	31
OCH_3	93 (7.0)[d]	1.4363	36.73	8.73	15.8	36.78	8.68	16.2	60
OC_2H_5	96–98(5.5)[e]	1.4302	42.84	9.43	13.8	43.04	9.14	13.8	50 (22)[f]
$O(CH_2)_2CH_3$	101–102 (2.3)[g]	1.4350	47.59	9.99	12.3	47.81	9.91	12.2	64
$O(CH_2)_3CH_3$	119 (2.0)[h]	1.4372	51.40	10.43	...	51.37	10.44	...	60
$O(CH_2)_5CH_3$	145–149 (2.0)	1.4422	...	...	...	[i]	...	...	71
$OCH_2CH(C_2H_5)(CH_2)_3CH_3$	157–158 (1.5)	1.4462	...	...	7.89	...	...	7.95	69
p-$OC_6H_4CH_3$	193–195 (2.0)	1.5262	62.04	7.23	...	62.05	6.98	...	40

[a] Lit.[2] mp 119–121. [b] Total purified products from hydrolysis of complex. Based on $(CH_3)_3SiCH_2Cl$. [c] Lit.[1] bp 102.8–103.5° (51 mm). [d] Lit.[3] bp 111–114° (21.5 mm). [e] Bp 118–121° (22 mm) reported by A. R. Gilbert, U. S. Patent 2,768,193 (1956). [f] Lower yield obtained from ethanolysis of complex. All other esters by phosphonyldichloride–alcohol reaction. [g] Lit.[3] bp 125–128° (10 mm). [h] Lit.[2] bp 154–158° (17 mm). [i] Not obtained analytically pure.

When neopentyl chloride was substituted for chloromethyltrimethylsilane and complex formation was carried out at −10°, only the isomerized product (*t*-pentylphosphonyl dichloride) was obtained. This pronounced difference between neopentyl chloride and its silicon analog might be explained on the basis of the relative stabilities of the initial carbonium ion intermediates. Rearrangement of $(CH_3)_3CCH_2^+$ is apparently much more rapid than its reaction with the complexing species whereas the structure $(CH_3)_3SiCH_2^+$ would be stabilized to some extent by the positive inductive effect of the trimethylsilyl group.

Structures of the products were verified by nmr spectra and agreement of the physical properties of the phosphonic acids with reported values. Gas chromatography and mass spectral analysis gave supporting evidence as to the purity and structure of *t*-pentylphosphonyl dichloride.

Experimental Section

Chloromethyltrimethylsilane and neopentyl chloride were obtained from commercial sources and distilled through an efficient fractionating column prior to use. Melting and boiling points are uncorrected.

Trimethylsilylmethylphosphonyl Dichloride (III).—A mixture of 133.4 g (1.0 mole) of anhydrous aluminum chloride and 137.4 g (1.0 mole) of phosphorus trichloride in 300 ml of methylene chloride was prepared under dry nitrogen. Chloromethyltrimethylsilane (122.7 g, 1.0 mole) was added dropwise with stirring over a 1-hr period while the reaction temperature was maintained at 25–28° by external cooling. The mixture was stirred for 1 additional hr at 25° to give a clear solution of the complex salt. An equal volume of methylene chloride was added and the solution was cooled to −30° in Dry Ice–acetone. Water (162 ml) was then added dropwise with rapid stirring over a 1-hr period. The temperature was kept below −20° during hydrolysis of the complex to minimize hydrolysis of the phosphonyl dichloride. Precipitated aluminum salt was removed on a filter and washed with methylene chloride. The filtrate was dried over calcium chloride at 0°. After removal of solvent, the crude product was distilled through an efficient column to give 64 g of trimethylsilylmethylphosphonyl dichloride, bp 64° (1.4 mm). Treatment of the distillation residue with boiling water gave 20 g of the corresponding phosphonic acid, mp 121° from water.

Trimethylsilylmethylphosphonyl dichloride was rapidly hydrolyzed by boiling water to the corresponding acid. Physical constants and analytical data were in agreement with reported values[2] for this acid. The structure was confirmed by nmr analysis.

Dialkyl Trimethylsilylmethylphosphonates.—To a solution of 0.08 mole of the alcohol and 7.3 g (0.06 mole) of N,N-dimethylaniline in 100 ml of benzene was added 6.15 g (0.03 mole) of trimethylsilylmethylphosphonyl dichloride. The mixture was stored at room temperature for 24 to 48 hr and filtered to remove amine hydrochloride. The filtrate was washed with 5% hydrochloric acid, followed by water, and finally treated with solid sodium bicarbonate and dried over calcium sulfate. The esters were distilled at reduced pressure through an efficient column. Properties are listed in Table I.

The diethyl ester was also prepared by the dropwise addition of 161 g of absolute ethanol to 0.5 mole of the preformed complex in 500 ml of methylene chloride. After addition, the mixture was refluxed for 3 hr and then hydrolyzed with 250 ml of water, keeping the temperature below 25° by external cooling. The methylene chloride layer was removed and dried over calcium chloride. Distillation at reduced pressure gave 60 g of distillate boiling between 60 and 77° (2–5 mm). Fractionation of this cut gave 25 g of diethyl trimethylsilylmethylphosphonate, bp 72–73° (2.0 mm), $n^{25}D$ 1.4302.

Di-*p*-tolyl Trimethylsilylmethylphosphonate.—A solution of 15 g (0.14 mole) of *p*-cresol and 10.3 g (0.05 mole) of trimethylsilylmethylphosphonyl dichloride in 50 ml of bromobenzene containing 0.1 g of freshly calcined magnesium chloride was refluxed for 6 hr. Dry nitrogen was passed through the mixture during this time to remove hydrogen chloride. Solvent and excess *p*-cresol were removed at reduced pressure and the product distilled, bp 193–195° (2.0 mm).

***t*-Pentylphosphonyl Dichloride.**—Neopentyl chloride (51 g, 0.48 mole) was added over a 1-hr period to a mixture of 69 g (0.5 mole) of phosphorus trichloride and 67 g (0.5 mole) of anhydrous aluminum chloride in 200 ml of methylene chloride. The temperature was held at −5 to −10° during this time. An additional 100 ml of methylene chloride was added to dissolve the complex. The solution was then cooled to −30° and hydrolyzed by the careful addition of 80 ml of water, keeping the temperature below −20°. The reaction mixture was worked up as before and the product was fractionated to give 48 g (51%) of a C_5 phosphonyl dichloride, bp 76.5° (5.0 mm), $n^{25}D$ 1.4750.

Anal. Calcd for $C_5H_{11}Cl_2OP$: C, 31.77; H, 5.87; P, 16.39. Found: C, 32.03; H, 5.89; P, 16.62.

Gas chromatographic analysis showed a single peak. The nmr spectrum (60 Mc, neat) was consistent with a *t*-pentyl structure. The β-methyl groups appear as a doublet centered at $\delta = 1.38$ ppm (spin coupled to P, $J = 26$ cps). The ethyl group appears characteristically as a quartet ($\delta = 2.00$ ppm) and a triplet ($\delta = 1.07$ ppm), with the methylene quartet coupled to P ($J = 23$ cps).

Mass spectral analysis is consistent also with the *t*-pentyl structure, showing a sizable peak for the loss of an ethyl (parent minus 29) group.

The chloride was refluxed with water (2.7 g/50 ml) for 2 hr. Water was removed and the residue was dried *in vacuo*, over P_2O_5. The white prisms obtained after two recrystallizations from ligroin melted at 136° (lit.[8] *t*-pentylphosphonic acid mp 139–141°.)

Anal. Calcd for $C_5H_{13}O_3P$: neut equiv, 152.1. Found, neut equiv, 151.7.

Chlorotrimethylsilane with PCl_3–$AlCl_3$.—A mixture of 34 g (0.25 mole) of phosphorus trichloride and 33 g (0.25 mole) of anhydrous aluminum chloride in 100 ml of methylene chloride

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[8] P. C. Crofts and G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 3379 (1953).

was treated with 27 g (0.25 mole) of chlorotrimethylsilane at 25°. No temperature rise was observed, and after 48 hr the reaction mixture remained unchanged.

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Reaction of Butadiene with Ethylene. II.[1] New Catalytic Systems in Synthesis of 1,4-Hexadiene

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1,4-Hexadiene is of commercial interest because of its utility as the third monomer for sulfur-curable ethylene propylene rubber. Recently, the preparation of the diene by a catalytic reaction of butadiene with ethylene has been reported by Hata[2] and by Alderson, *et al.*[3] Thermally initiated reaction of acetylene with 1-butene also yielded the diene.[4] The present work was undertaken in order to explore catalysts for the synthesis of 1,4-hexadiene from butadiene and ethylene. We have found that the catalytic systems consisting of an iron halide, an organoaluminum compound, and a ditertiary phosphine exert excellent selectivity in the formation of the diene.

Among the effective organoaluminum compounds are triethylaluminum, triisobutylaluminum, diisobutylaluminum hydride, and diethylaluminum chloride. As an iron halide component, ferric chloride and ferric bromide are suitable. Some ditertiary phosphines are used as the third component in these systems and it is considered that the phosphines affect the conversion and the selectivity of 1,4-hexadiene. Bis(diphenylphosphino)ethane, bis(diphenylphosphino)propane, bis(diphenylphosphino)ethylene (*cis* and *trans* isomers), and *o*-phenylenebis(diphenylphosphine) were found to be effective as the third component. The catalysts were prepared by mixing the three components in a solvent in an inert atmosphere. According to the results shown in Table I, the effectiveness of each component was in the following order: organoaluminum compound, $(C_2H_5)_3Al > (i\text{-}C_4H_9)_3Al > (i\text{-}C_4H_9)_2AlH > (C_2H_5)_2AlCl$; iron halide, $FeCl_3 > FeBr_3 > FeI_2$; ditertiary phosphine,[5] DPP $\geq$ DPE $>$ *cis*-DPET $>$ *trans*-DPET $>$ PDP $>$ DPM.

In the system containing triethylaluminum, ferric chloride, and DPE, the amount of nondistillable material (shown as residue in Table I) tended to increase and the selectivity of 1,4-hexadiene tended to decrease as the charged butadiene increased. A high conversion based on the charged butadiene was obtained at 80 to 100°. The molar ratio of the phosphine to ferric chloride remarkably affected the process. The proper ratio was within the limits of 0.5 to 1.

Chatt and Hayter[6] have prepared the complex of $[FeCl_2(diphosphine)_2][FeCl_4]$ type from an equimolar mixture of ferric chloride and diphosphine. Then the complex has been reduced with lithium aluminum hydride to give $FeH_2(diphosphine)_2$ in a minor yield. It is not clear whether the definite complex such as that obtained by Chatt and Hayter was formed or not in the ternary systems of this work. Ferric chloride is obviously reduced with triethylaluminum to a lower valent species. Simultaneously, diphosphine coordinates to the lower valent iron atom as a chelate ligand and stabilizes the catalytically active iron complex by forming a dative π bond between the iron atom and phosphorus atom.[7] As it blocks at least two of the coordination positions on the iron atom, the reactants approaching the iron atom, that is the catalytic site, should be limited and orientated.

The formation of 1,4-hexadiene must involve a hydrogen shift from ethylene to butadiene. In a linear dimerization of butadiene, the hydrogen shift *via* metal–hydrogen bonding has been assumed by Otsuka.[8] Cobalt and iron compounds, especially as carbonyl and hydridocarbonyl compounds, are used as hydrogen carrier.[9] These facts and the formation of iron hydrido complex described previously suggest some postulates on the reaction mechanism. One of them is as follows: an iron hydridodiphosphine complex is formed by the reaction of the catalyst components and the complex reacts with butadiene to give π-butenyl complex such as the complex derived from butadiene and hydridocobalt tetracarbonyl.[10] One hydrogen atom of the coordinated ethylene is pulled out by the iron atom of the complex and the residual group of the ethylene molecule simultaneously attacks the π-allyl part of the butenyl group, then 1,4-hexadiene leaves the catalytic site and the hydridodiphosphine complex is regenerated. An alternate postulate is as follows: the iron hydrido complex reacts with butadiene to give σ-butenyl complex and after ethylene coordinates with the complex, the butenyl group adds to the ethylene to form a σ-hexenyliron complex. This complex then disproportionates to give 1,4-hexadiene and the iron hydrido complex. The fact that butadiene and ethylene react so easily by means of these iron catalyst is strong evidence for a coordination mechanism. 3-Methyl-1,4-pentadiene is one of the possible products in the former mechanism, but it was not detected in any

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[4] N. F. Cywinski, *J. Org. Chem.*, **30**, 361 (1965).

[5] Bis(diphenylphosphino)ethane, bis(diphenylphosphino)propane, *cis*-bis(diphenylphosphino)ethylene, *trans*-bis(diphenylphosphino)ethylene, *o*-phenylenebis(diphenylphosphine), and bis(diphenylphosphino)methane are abbreviated to DPE, DPP, *cis*-DPET, *trans*-DPET, PDP, and DPM, respectively.

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