

of *n*-propylmagnesium bromide (0.9 mole in 600 ml. of anhydrous ether). The mixture was refluxed for two hours after the addition of the acid was completed and then poured onto a mixture of ice and an excess of concentrated hydrochloric acid. The layers were separated and the aqueous phase was extracted with several portions of ether. The combined ether extracts were washed several times with a saturated sodium bicarbonate solution to remove unreacted trifluoroacetic acid and then dried over Drierite. The solvent was removed and the residue distilled to give 12.7 g. (30.2%) of 1,1,1-trifluoro-2-pentanone (b.p. 65–67° at 731 mm., 2,4-dinitrophenylhydrazone, m.p. 75.0–75.5°<sup>6</sup> (from ethanol-water)) and 9.7 g. (22.7%) of 1,1,1-trifluoro-2-pentanol, b.p. 107–108° at 735 mm.<sup>8</sup>

(B) In *n*-Butyl Ether at 35°.—When the last reaction was repeated except that the Grignard reagent was prepared in *n*-butyl ether and the reaction was effected at 35°, there was obtained a mixture of 1,1,1-trifluoro-2-pentanone (21.8 g., 51.2%) and 1,1,1-trifluoro-2-pentanol (5.0 g., 11.8%).

**Reaction of Phenylmagnesium Bromide (Three Equivalents) with Trichloroacetic Acid (One Equivalent).**—Trichloroacetic acid (49.0 g., 0.3 mole), dissolved in 75 ml. of anhydrous ethyl ether, was added dropwise over a period of 2.5 hours to a rapidly stirred solution of phenylmagnesium bromide (0.9 mole in 1200 ml. of ether). The mixture was refluxed for an additional two hours and then poured onto a mixture of ice and excess hydrochloric acid. The layers were separated and the aqueous phase was extracted with several portions of ether. The combined ether extracts

were washed several times with saturated aqueous sodium bicarbonate solution. The bicarbonate-washed ether extracts were dried over Drierite, the solvent was removed and the residue was processed to give 28.3 g. of biphenyl (b.p. 85–95° at 2 mm., m.p. 68.5–69.5° alone and when mixed with an authentic sample) and 2.0 g. of diphenylacetic acid, m.p. 144.0–144.8° alone and when mixed with an authentic sample, amide m.p. 166.0–167.0°.<sup>23</sup> The sodium bicarbonate washings were acidified with hydrochloric acid, extracted several times with ether and the combined ether extracts were dried over Drierite. After removing the solvent the residue was distilled to give 14.5 g. of dichloroacetic acid (b.p. 95–96° at 18 mm., aniline salt m.p. 122.8–123.4°<sup>24</sup> alone and when mixed with an authentic sample) and 6.9 g. of phenylchloroacetic acid (b.p. 125–140° at 3 mm., m.p. 79.4–80.1°<sup>25</sup> (from 60–70° petroleum ether); amide m.p. 117.5–118.4°<sup>25</sup> (from benzene); alkaline hydrolysis of a sample of the phenylchloroacetic acid gave *dl*-mandelic acid, m.p. 118.7–119.0°.<sup>26</sup>

(23) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948.

(24) H. W. Doughty, *THIS JOURNAL*, **47**, 1095 (1925).

(25) H. A. Michaël and J. Jeanpretre, *Ber.*, **25**, 1680 (1892).

(26) S. M. McElvain, "The Characterization of Organic Compounds," revised edition, The Macmillan Co., New York, N. Y., 1953.

PITTSBURGH 13, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## The Formation of Vicinal Dichlorides in the Reaction of Alcohols with Phosphorus Pentachloride<sup>1</sup>

BY HARLAN L. GOERING AND FRED H. MCCARRON

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The reaction of phosphorus pentachloride with several secondary alcohols in chloroform at room temperature results in the formation of vicinal dichlorides together with the monochlorides. Cyclohexanol is converted to cyclohexyl chloride (50%) and *trans*-1,2-dichlorocyclohexane (28%); cyclopentanol and 3,3-dimethylcyclohexanol are similarly converted to the corresponding monochlorides and *trans*-1,2-dichlorides. Several acyclic secondary alcohols have been investigated and found to give vicinal dichlorides together with the monochlorides. The only primary alcohol investigated, *n*-octanol, is converted to *n*-octyl chloride and no evidence was obtained for the formation of a dichloride. The process by which the dichlorides are formed is stereospecific in the sense that only *trans*-vicinal dichlorides are formed from cycloalkanols and the vicinal dichloride obtained from optically active 3,3-dimethylcyclohexanol is optically active. The vicinal dichloride obtained from optically active 2-octanol has little if any optical activity. Control experiments demonstrate that the monochloride is not an intermediate in the formation of dichloride. It is proposed that the dichlorides result from a process similar to that involved in the conversion of tertiary bromides to vicinal dibromides by reaction with bromine.

### Introduction

In the course of another investigation we were interested in a method for converting optically active 3,3-dimethylcyclohexanol into active 3,3-dimethylcyclohexyl chloride. Several standard methods for converting alcohols to chlorides were investigated including the method developed by Shoppee and co-workers<sup>2</sup> which involves the reaction of an alcohol with phosphorus pentachloride in dry chloroform at 0–25°. It has been shown<sup>2</sup> that under these conditions the reaction is stereospecific—the hydroxyl group is replaced by chlorine with inversion of configuration—and good yields are obtained in cases where thionyl chloride gives only unsaturated products.<sup>2a</sup> In the present work we have found that by this procedure optically active 3,3-dimethylcyclohexanol,  $[\alpha]^{25}_D 1.13^\circ$ ,<sup>3</sup> is indeed converted to

active 3,3-dimethylcyclohexyl chloride  $[\alpha]^{25}_D -2.37^\circ$ , in better yield (55%) than by any of the other methods investigated.<sup>4</sup> However, in addition to the 3,3-dimethylcyclohexyl chloride, considerable quantities (30%) of dichlorodimethylcyclohexane are also formed.

The formation of the dichloride was unexpected and apparently has not been observed previously under these conditions. For this reason it was of interest to investigate the reaction of various alcohols with phosphorus pentachloride in chloroform to determine if the formation of dichlorides is general.

### Results

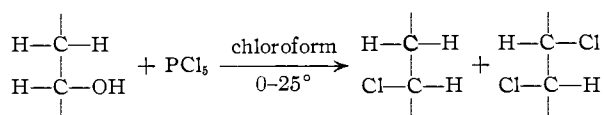
As shown in Table I all of the secondary alcohols investigated except isopropyl alcohol give appreciable quantities of 1,2-dichloride together with the monochloride as illustrated below.

(4) Thionyl chloride gave a maximum yield of 10%, phosphorus trichloride gave none of the desired product, and hydrochloric acid gave a 70% yield of 3,3-dimethylcyclohexyl chloride; however, the product was almost completely racemic.

(1) This work was supported by the Research Committee of the Graduate School with funds given by the Wisconsin Alumni Research Foundation.

(2) (a) R. J. Bridgewater and C. W. Shoppee, *J. Chem. Soc.*, 1709 (1953); (b) C. W. Shoppee and G. H. R. Summers, *ibid.*, 1790 (1952).

(3) All specific rotations are for pure liquid samples.



Only the monochloride was isolated from the reaction involving the only primary alcohol investigated, *n*-octanol. The structures of the dichlorides were determined by chemical composition and comparison of physical properties, including infrared spectra, with those of authentic samples.

TABLE I  
PRODUCTS FROM THE REACTION OF ALCOHOLS WITH PHOSPHORUS PENTACHLORIDE IN CHLOROFORM AT 0 TO 25°

Alcohol	Yield of monochloride, <sup>a,b</sup> %	Yield of dichloride, <sup>a</sup> %
3,3-Dimethylcyclohexanol	55 <sup>c</sup>	30 <sup>e,d</sup>
Cyclopentanol	50	8 <sup>e</sup>
Cyclohexanol	50	28 <sup>e</sup>
3-Pentanol	24	21 <sup>f</sup>
2-Pentanol	20	19 <sup>g</sup>
Isopropyl alcohol	20	0
<i>n</i> -Octanol	75	0
2-Octanol	51 <sup>c</sup>	7 <sup>h</sup>

<sup>a</sup> Yield based on alcohol. <sup>b</sup> In every case the structure of the monochloride corresponds to that of the alcohol from which it is derived. <sup>c</sup> This product is optically active if an optically active alcohol is used. <sup>d</sup> This is presumably a mixture of *trans*-1,2-dichloro-3,3-dimethylcyclohexane and *trans*-1,2-dichloro-4,4-dimethylcyclohexane. <sup>e</sup> Pure *trans*-1,2-dichlorocycloalkane. <sup>f</sup> 2,3-Dichloropentane. <sup>g</sup> This product is a mixture of 1,2- and 2,3-dichloropentane consisting of 9% of the 1,2-isomer. <sup>h</sup> This is presumably a mixture of 1,2- and 2,3-dichlorooctane.

The dichlorides obtained from cyclopentanol and cyclohexanol—isolated in such a way as to avoid fractionation of possible isomers—were identical with those obtained by the addition of chlorine to cyclohexene and cyclopentene. Thus it is clear that the dichlorides have the *trans* configuration. The dichloride obtained from 3-pentanol was identical with that obtained by the addition of chlorine to 2-pentene (prepared by dehydration of 3-pentanol).<sup>5</sup> The dichloride obtained from 2-pentanol was identified as a mixture of 1,2- and 2,3-dichloropentane consisting of 9% of the 1,2-isomer.

The dichlorodimethylcyclohexane obtained from optically active 3,3-dimethylcyclohexanol,  $[\alpha]^{25}_D 1.13^\circ$ , was optically active and had  $[\alpha]^{27}_D 0.32^\circ$ .<sup>3</sup> It is clear that this activity is not due to contamination with the optically active monochloride since the latter compound is levorotatory in both the pure form and when diluted with *dl*-dichlorodimethylcyclohexane. The chemical composition and physical properties (molecular refraction, constant boiling point and infrared spectrum) of the dichloride show that the activity is not due to contamination with unreacted alcohol. The dichloride was converted to 3,3-dimethylcyclohexane by dechlorination by zinc dust in alcohol followed by catalytic hydrogenation. Since *trans*-1,2-dichlorocycloalkanes are the only dichlorides obtained from cyclohexanol and cyclopentanol it appears that the dichloride derived from 3,3-dimethylcyclohexanol is

(5) M. L. Sherrill, B. Otto and L. W. Pickett, *THIS JOURNAL*, **51**, 3023 (1929).

a mixture of *trans*-1,2-dichloro-3,3-dimethylcyclohexane and *trans*-1,2-dichloro-4,4-dimethylcyclohexane.

The samples of dichlorooctane, presumably a mixture of 1,2- and 2,3-dichlorooctane, isolated from the reaction of (+) and (-)-2-octanol with phosphorus pentachloride had low optical activity, e.g.,  $[\alpha]^{27}_D \pm 0.18$  to  $0.33^\circ$ .<sup>3</sup> However, in every case the sign of the rotation was the same as that for the highly active co-product, 2-chlorooctane, and the observed rotations may be due to contamination with 1% or less of the monochloride.

Control experiments were carried out in order to determine if the dichloride could possibly be formed by chlorination of the initially formed monochloride. There are several examples in the literature in which phosphorus pentachloride acts as a chlorinating agent. However, more drastic conditions appear to be required than those employed in the present work. An aromatic nucleus can be chlorinated by phosphorus pentachloride at high temperatures (no solvent)<sup>6</sup> and nitriles<sup>7</sup> and imino chlorides<sup>8</sup> are chlorinated in the  $\alpha$ -position under similar conditions.

When cyclohexyl chloride was treated with phosphorus pentachloride in dry chloroform at room temperature, *i.e.*, conditions under which cyclohexanol gives a 28% yield of *trans*-1,2-dichlorocyclohexane, no 1,2-dichlorocyclohexane could be detected in the reaction mixture. In order to determine if any species is present during the reaction which is capable of chlorinating an initially formed monochloride, reactions of alcohols with phosphorus pentachloride were carried out in the presence of an alkyl halide. Thus, the reaction of 3,3-dimethylcyclohexanol with phosphorus pentachloride was carried out in the presence of cyclopentyl chloride. The only chlorides isolated from this experiment were 3,3-dimethylcyclohexyl chloride, dichlorodimethylcyclohexane and cyclopentyl chloride; there was no indication that any *trans*-1,2-dichlorocyclopentane was formed. In the converse experiment the reaction of cyclopentanol with phosphorus pentachloride was carried out in the presence of 3,3-dimethylcyclohexyl chloride. Cyclopentyl chloride, *trans*-1,2-dichlorocyclopentane and 3,3-dimethylcyclohexyl chloride were isolated and no dichlorodimethylcyclohexane could be detected in the reaction mixture. These experiments demonstrate that the monochloride is not an intermediate in the formation of the dichloride.

## Discussion

The results of the present investigation show that the reaction of secondary alcohols with phosphorus pentachloride in chloroform generally gives vicinal dichlorides together with the expected alkyl chloride. With some of the alcohols investigated the amount of dichloride produced is substantial and approaches 50 mole % of the product. Evidently the formation of dichlorides under the conditions

(6) E. Seyfferth, *J. prakt. Chem.*, **34**, 241 (1886); S. M. Kupchan and R. C. Elderfield, *J. Org. Chem.*, **11**, 136 (1946); W. Autenrieth, *Ber.*, **30**, 2369 (1897), and W. Autenrieth and P. Mühlinghaus, *ibid.*, **39**, 4098 (1906).

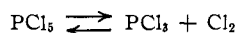
(7) C. L. Stevens and T. H. Coffield, *THIS JOURNAL*, **73**, 103 (1951).

(8) C. L. Stevens and J. C. French, *ibid.*, **76**, 4398 (1954).

used in the present work has not been observed previously and it appears that there are only a few isolated cases in which dichlorides have been detected as a product of this reaction. Mousseron and co-workers<sup>9</sup> have reported that 3-methylcyclohexanol gives mainly 3-methylcyclohexyl chloride together with small amounts of dichloromethylcyclohexane when treated with phosphorus pentachloride in benzene. Shoppee and Summers<sup>10</sup> have observed that cholestane-6 $\beta$ -ol is converted to 5 $\alpha$ ,6 $\beta$ -dichlorocholestane under similar conditions.

It has been proposed<sup>11,12</sup> that the reaction of an alcohol with phosphorus pentachloride involves the initial formation of an alkoxyphosphorus chloride (ROPCl<sub>4</sub> and/or (RO)<sub>2</sub>PCl<sub>3</sub>) with retention of configuration, followed by conversion of this intermediate to alkyl chloride with inversion of configuration. Presumably the second step is an S<sub>N</sub>2-type replacement and thus it is not surprising that primary alkoxyphosphorus chlorides are converted to the corresponding monochloride in good yields. Evidently, with secondary alkoxyphosphorus chlorides, a competing process is involved which results in the formation of vicinal dichlorides.

One possible way in which the secondary alkoxyphosphorus chloride could be converted to a vicinal dichloride is a two stage process involving an E<sub>1</sub>-type elimination to form olefin followed by *trans* addition of chlorine. This corresponds to the suggestion of Shoppee and Summers<sup>10</sup> that the conversion of cholestane-6 $\beta$ -ol to 5 $\alpha$ ,6 $\beta$ -dichlorocholestane by phosphorus pentachloride involves dehydration to give cholest-5-ene, followed by *trans* addition of chlorine derived from the reaction



This suggestion merits careful consideration since in every case the dichlorides that were isolated (*i.e.*, the position isomers) are the ones that would be expected from the *trans* addition of chlorine to the expected dehydration products. Moreover, it has been observed that alkenes<sup>13</sup> and cycloalkenes<sup>14</sup> are converted to vicinal dichlorides by reaction with phosphorus pentachloride.<sup>15</sup> We have also observed that cyclohexene and 2-pentene are converted to *trans*-1,2-dichlorocyclohexane and 2,3-dichloropentane in good yields when treated with phosphorus pentachloride in chloroform at room temperature, *i.e.*, conditions under which secondary alcohols are converted in part to vicinal dichlorides.

The only observation in the present work that is not consistent with this process is that an opti-

(9) M. Mousseron, R. Granger and J. Valette, *Bull. soc. chim. France*, 244 (1946).

(10) C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, 1786 (1952).

(11) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *ibid.*, 1252 (1937).

(12) W. Gerrard and R. J. Phillips, *Chem. and Ind.*, 540 (1952).

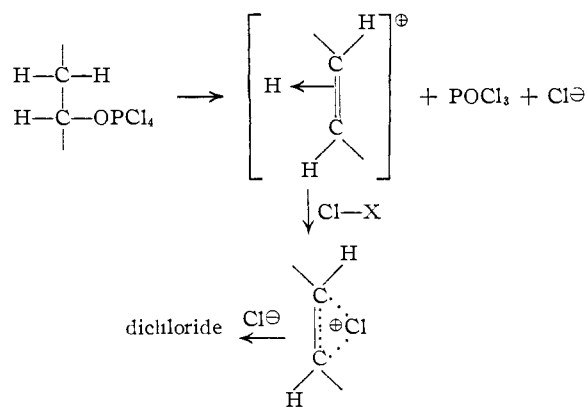
(13) (a) L. Spiegler and J. M. Tinker, *THIS JOURNAL*, 61, 940 (1939); (b) E. Bergmann and A. Bondi, *Ber.*, 64, 1455 (1931).

(14) M. Mousseron and R. Jacquier, *Bull. soc. chim. France*, 648 (1950); F. Pirrone, *Gazz. chim. ital.*, 62, 63 (1932); *C. A.*, 26, 3260 (1932)

(15) Frequently the reaction of phosphorus pentachloride with olefins, especially those containing terminal double bonds, does not give vicinal dichlorides but gives phosphorus containing adducts instead. See reference 13b and G. M. Kosolapoff and W. F. Huber, *THIS JOURNAL*, 68, 2540 (1946).

cally active dichloride is formed from optically active 3,3-dimethylcyclohexanol. This clearly shows that in this case the dichloride is not formed exclusively by the reaction of chlorine (or any other optically inactive chlorinating agent present in the medium) with a dehydration product, 3,3- or 4,4-dimethylcyclohexene since neither of these are optically active. However, the formation of an optically active dichloride does not necessarily rule out the possibility that *gem*-dimethylcyclohexene is an intermediate. It is conceivable that optically active chlorinating agents are present during the reaction, *e.g.*, alkoxyphosphorus chlorides, and if such species are involved in the first stage of the *trans* addition an optically active dichloride might be formed.

Another possible mechanism for the conversion of secondary alkoxyphosphorus chlorides to dichlorides is the one recently proposed by Russell and Brown<sup>16</sup> for the conversion of tertiary bromides to vicinal dibromides by reaction with bromine in carbon tetrachloride. This mechanism, which appears to be consistent with all of the available data, is applied to the present reaction below. According to this scheme, the secondary alkoxyphosphorus chloride is converted to a "high energy  $\pi$ -complex form of the carbonium ion"<sup>16</sup> which is subsequently converted to the chloronium ion by reaction with an unspecified chlorinating agent (X-Cl). This, then, is converted to the dichloride (*trans*-addition product) by reaction with chloride ion. In the 3,3-dimethylcyclohexyl system these intermediates, as well as an ion-pair intermediate presumably involved in the ionization step,<sup>16</sup> are asymmetric, and presumably an optically active product could be formed from an optically active reactant.



### Experimental

**Materials.**—The vicinal dichlorides used for comparison were obtained by the addition of chlorine to the corresponding alkene or cycloalkene.

*trans*-1,2-Dichlorocyclohexane, b.p. 87.5–88° (30 mm.),  $n_D^{25}$  1.4888,  $d_4^{25}$  1.180 (lit.<sup>17</sup> 78.1° (20 mm.),  $n_D^{25}$  1.4879,  $d_4^{25}$  1.179), was prepared by the addition of chlorine to cyclohexene.<sup>17</sup>

*trans*-1,2-Dichlorocyclopentane, b.p. 53–53.5° (25 mm.),  $n_D^{25}$  1.4781,  $d_4^{25}$  1.200;  $M_D$  32.80 (calcd. 32.84), was prepared in a similar manner from cyclopentene. Because of discrepancies in the observed and reported<sup>9</sup> physical prop-

(16) G. A. Russell and H. C. Brown, *ibid.*, 77, 4025 (1955).

(17) B. Carroll, D. G. Kubler, H. W. Davis and A. M. Whaley, *ibid.*, 73, 5382 (1951).

erties for the dichloride the chemical composition of the product was determined.

*Anal.* Calcd. for  $C_6H_8Cl_2$ : C, 43.19; H, 5.80. Found: C, 43.21; H, 6.00.

2,3-Dichloropentane, b.p. 59–59.5° (43 mm.),  $n^{25}_D$  1.4448,  $d^{25}_4$  1.076 (lit.<sup>18</sup> b.p. 58° (50 mm.),  $n^{20}_D$  1.4464,  $d^{20}_4$  1.079), was prepared in a similar manner from 2-pentene.<sup>5</sup> 1,2-Dichloropentane, b.p. 146.5–147°,  $n^{25}_D$  1.4457,  $d^{25}_4$  1.082 (lit.<sup>19</sup> b.p. 146.0–146.2,  $n^{25}_D$  1.4453,  $d^{25}_4$  1.077), was prepared by the addition of chlorine to 1-pentene.<sup>20</sup>

The alcohols shown in Table II were purified by fractionation, and in all cases the physical properties are in close agreement with published values.

TABLE II  
PHYSICAL PROPERTIES OF ALCOHOLS

Alcohol	B.p., °C.	$n^{25}_D$	$d^{25}_4$
Cyclohexanol	157.3–158	1.4658	0.945
Cyclopentanol	59–62 (27 mm.)	1.4513	.942
2-Pentanol	114.5–115.5	1.4069	.812
3-Pentanol	114–116	1.4061	.812
Isopropyl alcohol	82	1.3759	.782
<i>n</i> -Octanol	105–105.5 (27 mm.)	1.4275	.821
<i>dl</i> -2-Octanol	83–83.5 (18 mm.)	1.4247	.817

*dl*-2-Octanol was resolved according to the directions of Ingersoll,<sup>21</sup> giving (+)2-octanol, b.p. 72–73° (9 mm.),  $n^{25}_D$  1.4238,  $d^{25}_4$  0.817,  $[\alpha]^{25}_D$  9.10° (*l* 1 dm., neat); and (–)2-octanol, b.p. 72–73° (9 mm.),  $n^{25}_D$  1.4239,  $d^{25}_4$  0.816,  $[\alpha]^{25}_D$  –9.23° (*l* 1 dm., neat).

*dl*-3,3-Dimethylcyclohexanol, b.p. 88–92° (25 mm.), was prepared in 82% yield from 5,5-dimethyl-1,3-cyclohexanedione by a modification of the procedure of Doering and Beringer.<sup>22</sup> The modification involved the addition of the 5,5-dimethyl-1,3-cyclohexanedione in one instead of three portions.

The alcohol was purified by converting it to the acid phthalate and dissolving the latter in sodium carbonate solution. This aqueous solution was extracted with benzene, and the acid phthalate was hydrolyzed with alkali with simultaneous steam distillation of the alcohol by the previously described procedure for hydrolyzing acid phthalates.<sup>23</sup> The alcohol layer of the distillate was separated and the aqueous layer extracted twice with benzene. After removal of the benzene by distillation, the product was distilled and 3,3-dimethylcyclohexanol, b.p. 80–81° (16 mm.),  $n^{25}_D$  1.4569,  $d^{25}_4$  0.904 (lit.<sup>24</sup>  $n^{15}_D$  1.4606,  $d^{15}_4$  0.912), was obtained.

Resolution of the *dl*-3,3-dimethylcyclohexanol was accomplished by four recrystallizations of the brucine salt of 3,3-dimethylcyclohexyl acid phthalate from acetone-methanol. Hydrolysis of the brucine salt, followed by saponification of the optically active acid phthalate, m.p. 93.8–94.2°,  $[\alpha]^{25}_D$  4.3° (*c* 0.12,  $CHCl_3$ ), gave (+)3,3-dimethylcyclohexanol, b.p. 97.3–98.5° (31 mm.),  $n^{25}_D$  1.4572,  $d^{25}_4$  0.906,  $[\alpha]^{25}_D$  1.13° (*l* 1 dm., neat).

**Reaction of Alcohols with Phosphorus Pentachloride.**—With the following exceptions, the general procedure was the same as that reported by Shoppe and co-workers<sup>2</sup>: (a) technical grade instead of "dried" chloroform was used as the solvent. Control experiments showed that the same results were obtained with technical grade chloroform as with purified (dried and fractionated) chloroform. (b) Approximately 1 l. of solvent ( $CHCl_3$ ) per mole of phosphorus pentachloride was used instead of 5 l. per mole. (c) The phosphorus pentachloride was not sublimed.

**A. (*dl*-3,3-Dimethylcyclohexanol).**—A mixture of 100 g. (0.78 mole) of *dl*-3,3-dimethylcyclohexanol, 440 g. (4.4 mole)

of calcium carbonate and 3.7 l. of chloroform in a 5-l. flask was cooled to 0–5° in an ice-bath, and 720 g. (3.45 mole) of phosphorus pentachloride (Merck Reagent Grade) was added over a period of approximately 25 min. to the stirred solution. After the mixture was stirred for 3 hr. at ice-bath temperature and 18 hr. at room temperature, it was cooled to 0–5° and 1.2 l. of water was added slowly. The cold mixture was stirred until it became clear, after which stirring was continued for 18 hr. at room temperature.

The layers were separated, and the aqueous layer was extracted once with chloroform. After removing the chloroform by distillation, the product was distilled, and 62.3 g. (55%) of *dl*-3,3-dimethylcyclohexyl chloride, b.p. 56–61° (14 mm.) and 42.6 g. (30%) of dichlorodimethylcyclohexane, b.p. 96–99° (14 mm.), were obtained. The 3,3-dimethylcyclohexyl chloride was redistilled and had b.p. 70° (24 mm.),  $n^{25}_D$  1.4588,  $d^{25}_4$  0.954,  $M_D$  42.0 (calcd. 41.8).

*Anal.* Calcd. for  $C_6H_{10}Cl$ : C, 65.51; H, 10.31; Cl, 24.18. Found: C, 65.23; H, 10.16; Cl, 24.40.

After redistillation the dichlorodimethylcyclohexane had b.p. 93–93.2° (9 mm.),  $n^{25}_D$  1.4832,  $d^{25}_4$  1.110;  $M_D$  46.62 (calcd. 46.70).

*Anal.* Calcd. for  $C_6H_{14}Cl_2$ : C, 53.05; H, 7.79; Cl, 39.16. Found: C, 52.97; H, 8.05; Cl, 39.29.

When the reaction was repeated using optically active 3,3-dimethylcyclohexanol,  $[\alpha]^{25}_D$  1.13° (*l* 1 dm., neat), there was obtained (–)3,3-dimethylcyclohexyl chloride, b.p. 49.4–50° (8 mm.),  $n^{25}_D$  1.4580,  $[\alpha]^{25}_D$  –2.37° (*l* 1 dm., neat) and (+)dichlorodimethylcyclohexane, b.p. 92–93° (8 mm.),  $n^{25}_D$  1.4831,  $[\alpha]^{27}_D$  0.32° (*l* 1 dm., neat). The identity of this active dichlorodimethylcyclohexane was established by its chemical composition and by comparison of its infrared spectrum with that of authentic inactive material. A solution of 13 mole % of (–)3,3-dimethylcyclohexyl chloride in *dl*-dichlorodimethylcyclohexane has  $[\alpha]^{25}_D$  –0.21° (*l* 1 dm.) which shows that the observed activity cannot be due to contamination of the dichlorodimethylcyclohexane with (–)3,3-dimethylcyclohexyl chloride.

**B. (3-Pentanol).**—Treatment of 3-pentanol with phosphorus pentachloride under the conditions described in part A gave 20 g. (24%) of 3-chloropentane, b.p. 95–100°,  $n^{25}_D$  1.4090,  $d^{25}_4$  0.884 (lit.<sup>25</sup> b.p. 97.8°;  $n^{20}_D$  1.4104,  $d^{20}_4$  0.880) and 23 g. (21%) of 2,3-dichloropentane, b.p. 48.5–52.5° (28 mm.),  $n^{25}_D$  1.4450,  $d^{25}_4$  1.075. The infrared spectrum of the dichloride was indistinguishable from that of an authentic sample of 2,3-dichloropentane and it had the correct chemical composition.

**C. (2-Pentanol).**—Treatment of 2-pentanol with phosphorus pentachloride under the conditions described in part A gave 17 g. (20%) of 2-chloropentane, b.p. 95–96°,  $n^{25}_D$  1.4062;  $d^{25}_4$  0.866 (lit.<sup>25</sup> b.p. 96.8–96.9°,  $n^{20}_D$  1.4069;  $d^{20}_4$  0.870) and 21 g. (19%) of a mixture of 1,2- and 2,3-dichloropentane, b.p. 43–45° (24 mm.),  $n^{25}_D$  1.4452,  $d^{25}_4$  1.076,  $M_D$  34.89 (calcd. 35.16). This binary mixture was found to consist of 9% of the 1,2-isomer by comparing the transmission at 12.34  $\mu$  (band present in the 2,3-isomer but not in the 1,2-isomer) with that of synthetic mixtures.

**D. (Cyclopentanol).**—Treatment of cyclopentanol with phosphorus pentachloride under the conditions described in part A gave 41 g. (50%) of cyclopentyl chloride, b.p. 39–45° (56 mm.),  $n^{25}_D$  1.4505,  $d^{25}_4$  1.011 (lit.<sup>26</sup>  $n^{20}_D$  1.4510,  $d^{20}_4$  1.005) and 8 g. (7%) of *trans*-1,2-dichlorocyclopentane, b.p. 50–55° (25 mm.),  $n^{25}_D$  1.4779,  $d^{25}_4$  1.198. The infrared spectrum of the dichloride was indistinguishable from that of an authentic sample of *trans*-1,2-dichlorocyclopentane.

**E. (Cyclohexanol).**—Treatment of cyclohexanol with phosphorus pentachloride under the conditions described in part A gave 46 g. (50%) of cyclohexyl chloride, b.p. 48–50° (27 mm.),  $n^{25}_D$  1.4610,  $d^{25}_4$  0.998 (lit.<sup>27</sup>  $n^{20}_D$  1.4626,  $d^{20}_4$  1.000) and 33 g. (28%) of *trans*-1,2-dichlorocyclohexane, b.p. 80–85° (27 mm.),  $n^{25}_D$  1.4879,  $d^{25}_4$  1.178. The infrared spectrum of the dichloride was indistinguishable from that of an authentic sample of *trans*-1,2-dichlorocyclohexane.

When the calcium carbonate was omitted from the reaction mixture 48 g. (52%) of cyclohexyl chloride and 33 g.

(18) M. C. Hoff, K. W. Greenlee and C. E. Boord, *THIS JOURNAL*, **73**, 3329 (1951).

(19) C. F. Koelsch and S. M. McElvain, *ibid.*, **51**, 3390 (1929).

(20) M. A. Kirrman, *Bull. soc. chim. France*, **39**, 988 (1926).

(21) A. W. Ingersoll, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 376.

(22) W. von E. Doering and F. M. Beringer, *THIS JOURNAL*, **71**, 2221 (1949).

(23) H. L. Goering and J. P. Blanchard, *ibid.*, **76**, 5405 (1954).

(24) G. Chavanne, M. O. Miller and M. Cornet, *Bull. soc. chim. Belg.*, **40**, 673 (1931).

(25) F. C. Whitmore and F. A. Karnatz, *THIS JOURNAL*, **60**, 2536 (1938).

(26) N. D. Zelinski, *Ber.*, **41**, 2627 (1908).

(27) E. Krause and R. Pohlard, *ibid.*, **57**, 532 (1924).

(28%) of *trans*-1,2-dichlorocyclohexane were obtained. Thus it appears the presence of calcium carbonate has no effect on the course of the reaction.

**F. (Isopropyl Alcohol).**—Treatment of isopropyl alcohol with phosphorus pentachloride under the conditions described in Part A gave 12.5 g. (20%) of isopropyl chloride, b.p. 31–34.5°,  $n_D^{25}$  1.3752,  $d_4^{25}$  0.847 (lit.<sup>28</sup> b.p. 34.8°,  $n_D^{15}$  1.3811,  $d_4^{15}$  0.868). Propylene chloride could not be isolated from the residue by careful fractionation, and the infrared spectrum of this residue indicated that propylene chloride was not present.

**G. (*n*-Octanol).**—Treatment of *n*-octanol with phosphorus pentachloride under the conditions described in part A gave 88 g. (75%) of *n*-octyl chloride, b.p. 83–87° (33 mm.),  $n_D^{25}$  1.4285,  $d_4^{25}$  0.881 (lit.<sup>29</sup>  $n_D^{20}$  1.4306,  $d_4^{20}$  0.875). 1,2-Dichlorooctane could not be isolated from the residue by careful fractionation.

**H. (2-Octanol).**—Treatment of *dl*-2-octanol with phosphorus pentachloride under the same conditions as described in part A, except in one-fifth quantities, gave 12 g. (51%) of 2-chlorooctane, b.p. 55–60° (14 mm.),  $n_D^{25}$  1.4253,  $d_4^{25}$  0.871 (lit.<sup>30</sup>  $n_D^{20}$  1.4295,  $d_4^{20}$  0.865) and 1.9 g. (7%) of dichlorooctane, b.p. 84–86° (14 mm.),  $n_D^{25}$  1.4496,  $d_4^{25}$  1.007,  $M_D$  48.90 (calcd. 48.83).

When the reaction was repeated using (+)2-octanol,  $[\alpha]_D^{25}$  9.10° (*l* 1 dm., neat), 10 g. (45%) of (–)2-chlorooctane, b.p. 64–68° (17 mm.),  $n_D^{25}$  1.4255,  $d_4^{25}$  0.872,  $[\alpha]_D^{27}$  –32.6° (*l* 1 dm., neat) and 1.9 g. (7%) of dichlorooctane, b.p. 88–88.5° (16 mm.),  $n_D^{25}$  1.4500,  $d_4^{25}$  1.010,  $[\alpha]_D^{27}$  –0.33° (*l* 1 dm., neat) were isolated. (–)2-Octanol,  $[\alpha]_D^{26}$  –9.23° (*l* 1 dm., neat), gave 12 g. (50%) of (+)2-chlorooctane, b.p. 63° (17 mm.),  $n_D^{25}$  1.4254,  $d_4^{25}$  0.866,  $[\alpha]_D^{27}$  34.1° (*l* 1 dm., neat) and 1.9 g. (7%) of dichlorooctane which had b.p. 87.5–87.8° (17 mm.),  $n_D^{25}$  1.4492,  $d_4^{25}$  1.009,  $[\alpha]_D^{27}$  0.18° (*l* 1 dm., neat).

**Conversion of Dichlorodimethylcyclohexane to 1,1-Dimethylcyclohexane.**—Treatment of 17.4 g. (0.1 mole) of dichlorodimethylcyclohexane (obtained by procedure A above) with zinc dust and alcohol<sup>31</sup> gave 8 g. (76%) of dimethylcyclohexane, b.p. 114–116°;  $n_D^{25}$  1.4400,  $d_4^{25}$  0.797,  $M_D$  36.4 (calcd. 36.5).

(28) J. Timmermans and F. Martin, *J. chim. phys.*, **25**, 411 (1928).

(29) A. I. Vogel, *J. Chem. Soc.*, 636 (1943).

(30) R. H. Clark and H. R. L. Streight, *Trans. Roy. Soc. Can.*, **23**, 77 (1929).

(31) A. W. Crossley and N. Renouf, *J. Chem. Soc.*, 1487 (1905).

*Anal.* Calcd. for  $C_8H_{14}$ : C, 87.19; H, 12.81. Found: C, 86.84; H, 12.61.

Hydrogenation of 4 g. (0.04 mole) of the above dimethylcyclohexene using 0.4 g. of 10% palladium-on-charcoal at atmospheric pressure gave 1,1-dimethylcyclohexane, b.p. 117.5–118°,  $n_D^{25}$  1.4261,  $d_4^{25}$  0.774 (lit.<sup>32</sup> b.p. 118.5–120°,  $n_D^{15}$  1.4342,  $d_4^{15}$  0.782). The infrared spectrum of this material was indistinguishable from the published spectrum of 1,1-dimethylcyclohexane.<sup>33</sup>

**Reaction of 3,3-Dimethylcyclohexanol with Phosphorus Pentachloride in the Presence of Cyclopentyl Chloride.**—3,3-Dimethylcyclohexanol was treated with phosphorus pentachloride under the same conditions described in part A with the exception that 41 g. (0.39 mole) of cyclopentyl chloride was added with the solvent. The products were isolated as described above, and 17 g. (42%) of recovered cyclopentyl chloride, 59 g. (51%) of 3,3-dimethylcyclohexyl chloride and 46 g. (33%) of dichlorodimethylcyclohexane were obtained. The appropriate fraction, b.p. 59–94° (79 mm.), was carefully refractionated to determine whether any *trans*-1,2-dichlorocyclopentane was present. None of these fractions had bands at 7.8 or 11.2  $\mu$  where the spectrum of *trans*-1,2-dichlorocyclopentane has strong bands.

**Reaction of Cyclopentanol with Phosphorus Pentachloride in the Presence of 3,3-Dimethylcyclohexyl Chloride.**—Cyclopentanol was treated with phosphorus pentachloride under the same conditions as described in part A with the exception that 45 g. (0.31 mole) of 3,3-dimethylcyclohexyl chloride was added with the solvent. From this experiment 45 g. (100%) of recovered 3,3-dimethylcyclohexyl chloride, 29 g. (36%) of cyclopentyl chloride and 10 g. (9.6%) of *trans*-1,2-dichlorocyclopentane were isolated. Distillation of the residue gave no indication of the presence of any dichlorodimethylcyclohexane which would distill at a higher temperature than any of the chlorides isolated.

**Reaction of Cyclohexene and 2-Pentene with Phosphorus Pentachloride.**—Treatment of 64 g. (0.78 mole) of cyclohexene with phosphorus pentachloride under the same conditions as described above for the alcohols, gave 91 g. (77%) of *trans*-1,2-dichlorocyclohexane. Under similar conditions 2-pentene was converted to 2,3-dichloropentane in 76% yield.

(32) N. D. Zelinsky, *Ber.*, **56**, 1716 (1923).

(33) National Bureau of Standards, American Petroleum Institute Research Project 44, Washington, D. C., No. 370.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

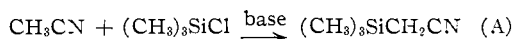
## The Anomalous Silico-alkylation of Acetonitrile

BY MAURICE PROBER

RECEIVED SEPTEMBER 21, 1955

The reaction of trimethylchlorosilane with acetonitrile and sodium yields trimethylsilyl cyanide and a high boiling fraction which consists of two silico-alkylated compounds—a nitrile  $[(CH_3)_3Si]_2CHCN$ , and the unusual ketenimine,  $(CH_3)_2SiCH=C=NSi(CH_3)_3$ . Minor reaction products are tetramethylsilane and cyanomethyltrimethylsilane. The ketenimine is thermally stable but rearranges easily to the nitrile in the presence of water—a rearrangement not hitherto observed. Benzyl cyanide also undergoes silico-alkylation to form nitrile and ketenimine.

In connection with a program on nitrile-containing organosilicon compounds, the synthesis of cyanomethyltrimethylsilane was of interest.<sup>1</sup> The alkylation of the nitrile carbanion is a well-known procedure<sup>2</sup> and the silico-alkylation of acetonitrile was attempted.



While this work was in progress the silico-alkyla-

(1) M. Prober, *THIS JOURNAL*, **77**, 3224 (1955).

(2) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 599.

tion of an ester carbanion was described.<sup>3</sup>

The silico-alkylation was carried out by the reaction of equal molar quantities of trimethylchlorosilane, sodium and acetonitrile. Sodium and acetonitrile form the desired carbanion along with other products.<sup>4,5</sup>

(3) C. R. Hance and C. R. Hauser, *THIS JOURNAL*, **75**, 994 (1953). The silico-alkylation of sodioacetoacetic ester has been carried out, H. Gilman and R. N. Clark, *ibid.*, **69**, 967 (1947), but the structure of the reaction product is in doubt; F. C. Whitmore, L. H. Sommer, J. Gold and R. E. Van Strien, *ibid.*, **69**, 1551 (1947).

(4) R. Holzwart, *J. prakt. Chem.*, **147**, 230 (1889).

(5) H. Adkins and C. M. Whitman, *THIS JOURNAL*, **64**, 152 (1942).