

It should be noted that the acetate is very sensitive to hydrolysis, and during the preparation it is important to decompose the excess acetic anhydride in the cold otherwise the product will be contaminated with the hydroxy acid.

**$\beta$ -Dimethylaminoethyl 4-(*p*-Acetoxyphenyl)-cyclohexanecarboxylate Hydrochloride.**—To a refluxing solution of 1.23 g. of  $\beta$ -dimethylaminoethanol in 175 cc. of benzene was added a solution of the acid chloride, prepared<sup>2</sup> from 3.60 g. of the above acetate, in 180 cc. of benzene. The addition was carried out dropwise, with stirring, over a period of three hours. The mixture was then allowed to reflux for fifteen hours longer. Upon cooling, 4.30 g. of the crude hydrochloride crystallized, and an additional 0.14 g. was obtained by concentrating the mother liquor making the total yield 88% of colorless material melting at 164–168° (dec.). One gram of this product was purified by treating an aqueous solution with sodium bicarbonate to liberate the free base which was taken up in ether and washed well with water. After removal of the solvent, the residue was heated at 60° at the water pump to remove any remaining water and amino alcohol. The base was then dissolved in dry ether and treated with dry hydrogen chloride. In this way 0.92 g. of hydrochloride was obtained, m. p. 168–171° (dec.). Recrystallization from benzene raised the m. p. to 170.5–171.5° (dec.) with previous softening.

*Anal.* Calcd. for  $C_{19}H_{28}O_4ClN$ : C, 61.71; H, 7.63. Found: C, 61.81; H, 7.44.

**$\beta$ -Diethylaminoethyl 4-(*p*-Acetoxyphenyl)-cyclohexanecarboxylate Hydrochloride.**—This ester was prepared by the procedure described above. From 1.95 g. of  $\beta$ -diethylaminoethanol in 200 cc. of benzene and the acid chloride (from 4.76 g. of the acetate) in 200 cc. of benzene, there was obtained a total of 5.76 g. (80% yield) of hydrochloride melting at 205–209° (dec.).

One gram of material purified *via* the free base afforded 0.90 g. of hydrochloride melting at 211–213° (dec.). After recrystallization from benzene the m. p. was 212–213.5° (dec.).

*Anal.* Calcd. for  $C_{21}H_{32}O_4ClN$ : C, 63.38; H, 8.11. Found: C, 63.55; H, 7.96.

**$\beta$ -Piperidinoethyl 4-(*p*-acetoxyphenyl)-cyclohexanecarboxylate hydrochloride** was prepared by a slight modi-

fication of the above procedure, using 1.26 g. of  $\beta$ -piperidinoethanol, b. p. 86–87° (16 mm.), in 125 cc. of benzene, and the acid chloride (from 2.50 g. of the acetate) in 125 cc. of benzene. After the slow mixing of the reagents was complete the solution was allowed to reflux for one hour longer and then to stand overnight at room temperature. The yield of crude hydrochloride was 3.00 g. (77%); m. p. 168–181° (dec.). After purification *via* the free base, the product melted at 182–187° (dec.); yield 2.10 g. (54%). A sample further purified by two recrystallizations from benzene had the m. p. 192.5–195° (dec.).

*Anal.* Calcd. for  $C_{22}H_{32}O_4ClN$ : C, 64.46; H, 7.87. Found: C, 64.79; H, 7.99.

**$\gamma$ -(2-Methylpiperidino)-propyl 4-(*p*-acetoxyphenyl)-cyclohexanecarboxylate hydrochloride** was prepared by the procedure described in the preceding experiment; 1.51 g. of  $\gamma$ -(2-methylpiperidino)-propyl alcohol (supplied by the Eli Lilly Co.; b. p. after redistillation, 116–119° at 19 mm.) was used. Since the ester hydrochloride proved to be soluble in benzene the product was worked up by conversion to the free base and reconversion to the hydrochloride in dry ether solution. The material thus obtained melted at 159–165° (dec.); yield 2.00 g. (48%). Further purification was effected by treating a solution of the hydrochloride in benzene with ether. After three such precipitations it melted at 165–167.5° (dec.) with previous softening.

*Anal.* Calcd. for  $C_{24}H_{36}O_4ClN$ : C, 65.80; H, 8.29. Found: C, 65.93; H, 8.04.

### Summary

A synthesis of 4-(*p*-hydroxyphenyl)-cyclohexanecarboxylic acid from *p*-methoxybiphenyl is described. Acetylation of the ether followed by hypobromite oxidation gives 4-(*p*-methoxyphenyl)-benzoic acid which is selectively reduced with sodium and amyl alcohol and then demethylated. The preparation of four dialkylaminoalkyl esters of this acid also is described.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

## Condensation of Saturated Halides with Unsaturated Compounds. II. The Condensation of Alkyl Halides with Monohaloölefins<sup>1</sup>

BY LOUIS SCHMERLING

It has long been known that polychloroalkanes (particularly chloroform and carbon tetrachloride) can be condensed with chloroölefins (such as vinyl chloride and dichloroethylene) in the presence of aluminum chloride to yield polychloroalkanes of higher molecular weight. The reaction, which is usually referred to as the Prins reaction, was studied quite extensively by Prins<sup>2</sup> and has been the subject of several United States and foreign patents.<sup>3</sup> The condensation of monohaloalkanes

(*i. e.*, alkyl halides) with haloölefins was, however, not described; in fact, Prins has stated<sup>2c</sup> that the reaction does not occur, his conclusion being based on experiments with methyl and ethyl chlorides. On the other hand, the present investigation has shown that propyl and alkyl halides of higher molecular weight can be condensed with ölefins and haloölefins in the presence of metal halide catalysts to yield halides of higher molecular weight. The reaction with ethylene was described in the first paper of this series.<sup>4</sup> The reaction with monochloro- and monobromoölefins will be discussed in the present paper.

The condensation of the alkyl halide with the haloölefins proceeds *via* the addition of the alkyl group and the halogen atom to the double bond

(1) Presented before the Division of Organic Chemistry of the American Chemical Society, Atlantic City, April, 1946.

(2) (a) J. Böeseken and H. J. Prins, *K. Akad. Wetenschappen*, **19**, 776 (1910); *C. A.*, **5**, 2845 (1911); (b) H. J. Prins, *J. prakt. Chem.*, **89**, 414, 425 (1914); (c) H. J. Prins, *Rec. trav. chim.*, **51**, 1065 (1932); (d) **54**, 249 (1935); (e) **56**, 779 (1937); (f) **57**, 659 (1938).

(3) (a) H. J. Prins, German Patent 261,689 (1912); (b) J. Sixt (to Consortium fuer elektrochemische Industrie G. m. b. H.) U. S. Patent 2,068,772 (Jan. 26, 1937); (c) F. W. Kirkbride (to Imperial Chemical Industries, Ltd.) U. S. Patent 2,297,564 (Sept. 29, 1942).

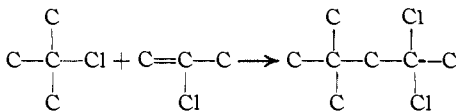
(4) L. Schmerling, *THIS JOURNAL*, **67**, 1152 (1945).

of the haloölefin, the halogen adding to the carbon atom that holds the smaller number of hydrogen atoms. The reaction is catalyzed by metal halides of the type which are often called "Friedel-Crafts type halides." Aluminum chloride, ferric chloride and bismuth chloride have been found to be especially useful. In this respect the reaction differs markedly from the Prins reaction which is catalyzed by aluminum chloride only.<sup>5</sup>

Condensation of vinyl chloride with isopropyl chloride, *t*-butyl chloride and *t*-amyl chloride yields, respectively, 1,1-dichloro-3-methylbutane, 1,1-dichloro-3,3-dimethylbutane and 1,1-dichloro-3,3-dimethylpentane. Hydrolysis of the dichlorides yields the corresponding aldehydes.

The reaction of the *t*-alkyl chlorides with 2-chloropropene offers a convenient means of preparing 2,2-dichloro-4,4-dimethylalkanes and their derivatives, including the hydrolysis products, methyl neoalkyl ketones. Similarly, the reaction of the *t*-alkyl chlorides or bromides with allyl chloride or bromide, respectively, yields 1,2-dihalo-4,4-dimethylalkanes which may be converted to *gem*-dimethylalkenes by treatment with zinc and an alcohol. In this manner, the reaction of *t*-amyl chloride with allyl chloride makes possible the synthesis of pure 3,3-dimethylhexene-1 and, thence, of pure 3,3-dimethylhexane.

When the condensation of *t*-butyl chloride with 2-chloropropene was carried out in the presence of aluminum chloride, there was obtained not only 2,2-dichloro-4,4-dimethylbutane (III, 42-49% yield) but also a trichlorodecane (IIIA, 19% yield) presumably 2,2,4-trichloro-4,6,6-trimethylheptane.



2-Chloro-4,4-dimethyl-1-pentene (IIIB) was obtained as a by-product of the reaction of *t*-butyl chloride and 2-chloropropene in the presence of bismuth chloride at 50°. Its formation by the dehydrochlorination of the primary product, 2,2-dichloro-4,4-dimethylpentane, is interesting and is analogous to previous observations<sup>6</sup> concerning the relative lability of the hydrogen atoms in the terminal methyl group and in the methylene of the neopentyl radical.

The reaction of *t*-amyl chloride with 2-chloropropene in the presence of ferric chloride yielded not only the expected dichloroöctane, 2,2-di-

(5) Ref. 2c, p. 1078.

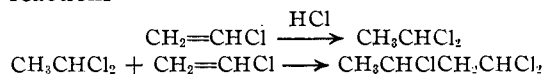
(6) F. C. Whitmore, C. S. Roland, S. N. Wrenn and G. W. Kilmer, THIS JOURNAL, 64, 2970 (1942).

chloro-4,4-dimethylhexane, but also a dichloroheptane, namely, 2,2-dichloro-4,4-dimethylpentane, which is the same product that is obtained by the reaction of the chloropropene with *t*-butyl chloride. The intermediate formation of the butyl chloride from the amyl chloride is thus indicated. A similar side reaction occurs in the condensation of *t*-amyl chloride with ethylene.<sup>4</sup>

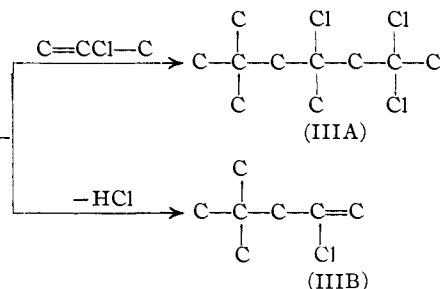
When *t*-butyl chloride and allyl chloride reacted at -10 to -20° in the presence of aluminum chloride, there was obtained a 48% yield of 1,2-dichloro-4,4-dimethylpentane and an 18% yield of an isomeric, higher-boiling dichloroheptane, the structure of which was not determined.

The major product of the reaction of a *t*-alkyl bromide with a chloroölefin is a chlorobromoalkane. Some halogen disproportionation occurs resulting in the formation of the analogous dichloro- and dibromo-alkane.

Methyl and ethyl chlorides could not be condensed with chloroölefins. In most cases practically all of the alkyl chloride was recovered unchanged. When a mixture of ethyl chloride and vinyl chloride was heated at 50° in the presence of aluminum chloride, a small amount of higher-boiling material was obtained. This was not, however, the interaction product of the ethyl chloride and vinyl chloride, namely, 1,1-dichlorobutane. Instead, it was 1,1,3-trichlorobutane formed from the vinyl chloride by the sequence of reactions



The hydrogen chloride is formed by dehydro-



chlorination of the ethyl chloride or vinyl chloride polymer. This mechanism was confirmed by heating vinyl chloride and hydrogen chloride in the presence of aluminum chloride; 1,1-dichloroethane and 1,1,3-trichlorobutane were obtained. The preparation of the trichlorobutane by the condensation of 1,1-dichloroethane with vinyl chloride is the subject of a United States patent.<sup>3b</sup>

### Experimental<sup>7</sup>

**Condensation of Alkyl Halides with Monohaloölefins:**  
**Method A.**—The experiment was carried out in a three-necked flask which was equipped with a glycerol-sealed stirrer, a Dry Ice-cooled condenser and an opening for introducing the reactants and the catalyst. The flask was

(7) Microanalyses by Dr. T. S. Ma, University of Chicago.

TABLE I  
 CONDENSATION OF ALKYL HALIDES WITH HALOÖLEFINS

Expt.	Method of prepn.	Reactants				Catalyst		Temp., °C.	Chief product			Higher-boiling prod., g.
		Alkyl halide RX	g.	Haloölefin Formula <sup>a</sup>	g.	MX	g.		Comp. no.	g.	%	
1	A <sup>b</sup>	<i>i</i> -PrCl	36	ViCl	18	AlCl <sub>3</sub>	2	-30 to -20	I	14	34	4
2	B	<i>i</i> -PrCl	78	ViCl	38	FeCl <sub>3</sub>	5	R. T. <sup>c</sup>	I	20	23	6
3	B	<i>t</i> -BuCl	100	ViCl	55	FeCl <sub>3</sub>	10	R. T.	II	105	77	8
4	B	<i>t</i> -BuCl	65	ViCl	42	BiCl <sub>3</sub>	5	90	II	15	14	5
5	A	<i>t</i> -BuCl	92	2ClPr	71	AlCl <sub>3</sub>	4	-10 to -5	III	66	42	
									IIIA	22	19	8
6	T	<i>t</i> -BuCl	93	2ClPr	76	AlCl <sub>3</sub>	2	-12 to +6	III	82	49	
									IIIA	23	19	6
7	B	<i>t</i> -BuCl	47	2ClPr	48	BiCl <sub>3</sub>	5	50	III	9	10	
									IIIB	14	11	5
8	A <sup>d</sup>	<i>t</i> -BuCl	92	ACl	76	AlCl <sub>3</sub>	4	-20 to -10	IV	80	48	
									IVA	30	18	10
9	B	<i>t</i> -BuCl	50	ACl	40	FeCl <sub>3</sub>	5	R. T.	IV	26	29	16
10	B	<i>t</i> -BuCl	50	ACl	50	BiCl <sub>3</sub>	5	60	IV	6	7	2
11	T	<i>t</i> -AmCl	54	ViCl	32	AlCl <sub>3</sub>	2	-20 to 0	V	31	38	6
12	A	<i>t</i> -AmCl	105	2ClPr	75	AlCl <sub>3</sub>	7	-14 to -10	VI	16	10	28
13	T	<i>t</i> -AmCl	40	2ClPr	31	FeCl <sub>3</sub>	4	0 to 32	VI	10	15	
									III	5	8	7
14	A	<i>t</i> -AmCl	100	ACl	75	AlCl <sub>3</sub>	8	-8 to +7	VII	40	23	28
15	A	<i>t</i> -BuBr	71	ABr	60	AlCl <sub>3</sub>	5	-30 to -30	VIII	72	56	8
16	A	<i>t</i> -AmBr	75	ABr	60	AlCl <sub>3</sub>	5	-30 to -30	IX	45	34	14
17	B	<i>t</i> -BuBr	42	ViCl	21	BiCl <sub>3</sub>	5	50	X	20	33	2
18	e	<i>t</i> -BuBr	80	ViCl	40	FeCl <sub>3</sub>	5	*	X	82	71	5
19	T	<i>t</i> -BuBr	165	2ClPr	76	AlCl <sub>3</sub>	3	0 to 15	XI	80	37	30

<sup>a</sup> ViCl = vinyl chloride; 2ClPr = 2-chloropropene; ACl = allyl chloride; ABr = allyl bromide. <sup>b</sup> The usual procedure of Method A was modified in Expt. 1 in that the vinyl chloride was bubbled into the well-stirred mixture of isopropyl chloride and aluminum chloride during twenty minutes. The product, a clear deep red-orange liquid, was stirred for an additional ten minutes and then poured into ice water, taken up in pentane, washed, dried and distilled. This modification of the usual procedure was made necessary by the fact that isopropyl chloride reacts very vigorously with vinyl chloride in the presence of aluminum chloride. A preliminary attempt was made to carry out the reaction by Method T. A mixture of 51 g. (0.65 mole) of isopropyl chloride and 40 g. (0.65 mole) of vinyl chloride in the large test-tube was cooled to -70° and 1 g. of powdered, resublimed aluminum chloride was added. The mixture was allowed to warm up with shaking. The catalyst gradually dissolved and was in solution when the temperature reached -25°; no further change occurred up to 5°. A test sample showed the presence of little condensation product. The solution was cooled to -40° and 1 g. additional aluminum chloride was added. The temperature rose to -35° in thirty seconds and then to +35° in the next thirty seconds despite the fact that the test tube was immersed in the Dry Ice-acetone bath. The reaction was so vigorous that 55 g. of material was blown from the tube. The remaining 38 g. of product was worked up in the usual manner. There was obtained, besides the unreacted chlorides, 18 g. of crude 1,1-dichloro-3-methylpentane, b. p. 127-132°, *n*<sub>D</sub><sup>20</sup> 1.4351. If the mechanical loss is taken into account and if it is assumed that the lost product had the same composition as that saved, the yield of dichloroisopentane was about 45-50% of the theoretical. <sup>c</sup> R. T. = room temperature. <sup>d</sup> An experiment similar to Expt. 8 but carried out at -10 to 0° gave 88 g. (53%) of IV and 25 g. of IV-A. In a third experiment, the aluminum chloride was added to the stirred mixture of *t*-butyl chloride and allyl chloride which was cooled to only -40° instead of to -70° as was usually done in Method A. A vigorous reaction occurred on the addition of the first portion (about 2 g.) and much of the catalyst was blown from the inlet tube. The temperature rose to +40° in less than one minute. Addition of the remainder of the aluminum chloride had little effect, the reaction apparently having already gone to completion. The liquid product was decanted from the red-brown catalyst sludge and washed, dried and distilled. There was obtained 73 g. (44%) of IV and 25 g. of IV-A. <sup>e</sup> In Expt. 18 an attempt was made to carry out the reaction following Method B. The liner containing the *t*-butyl bromide was cooled in a bath at -78° (part of the bromide crystallized and the ferric chloride was added). Vinyl chloride (also cooled to -78°) was then poured into the liner. There was an immediate reaction and part of the vinyl chloride (about 9 g.) boiled off. The mixture was permitted to warm to room temperature and then to stand for four hours. No further loss of condensable gas occurred. Distillation of the washed liquid product showed that it contained over 85% by volume of the chlorobromide boiling at 65-67° at 25 mm. and only 7% of higher boiling material.

immersed in a Dry Ice-acetone-bath. The alkyl halide and the haloölefin were placed in the flask, stirring was begun and the catalyst was added when the mixture had cooled to about -70°. The temperature of the bath was then permitted to rise to the point necessary for reaction. This point was estimated by observation of changes in the physical nature of the catalyst as well as by determining (in a test-tube) the boiling point range of 0.5-1.0 cc. of washed sample. The bath was maintained at this temperature until little further reaction occurred; this usually required from one-half to one hour. The temperature was then lowered to about -40 or -50°, the product was de-

canted from the viscous catalyst layer, taken up in ether or pentane if necessary, washed with water, dried over reflux fractionation column.<sup>8</sup>

**Method B.**—The alkyl halide and the haloölefin were weighed into a glass liner, the resulting solution was cooled to about -78°, and the catalyst was then added. The liner was sealed into an Ipatieff-type rotating autoclave of 850 cc. capacity, nitrogen was charged to a pressure of 50

(8) C. L. Thomas, H. S. Bloch and J. Hoekstra, *Ind. Eng. Chem. Anal. Ed.*, **10**, 153 (1938).

TABLE II  
 PROPERTIES OF THE HALOALKANES

Compd.	Formula	B. p., °C.	B. p. at 760 mm., °C. <sup>a</sup>	<i>n</i> <sub>D</sub> <sup>20</sup>	<i>d</i> <sub>4</sub> <sup>20</sup>	Mol. refr.		Analyses, %						
						Calcd.	Obs.	Calcd.			Found			
								C	II	X	C	H	X	
I	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CHCl <sub>2</sub> <sup>b</sup>	58-59	70	127-128	1.4344			42.56	7.15	50.29	42.18	7.11	50.95	
II	(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> CHCl <sub>2</sub>	57-57	81	148-148 <sup>c</sup>	1.4389	1.0262	39.6	39.7	46.50	7.75	45.75	46.70	7.89	45.08
III	(CH <sub>3</sub> ) <sub>2</sub> CCH <sub>2</sub> CCl <sub>2</sub> CH <sub>3</sub>	59-60	20	160-161 <sup>d</sup>	1.4470	1.012	44.2	44.6			41.96			42.06
IIIA	C <sub>10</sub> H <sub>19</sub> Cl <sub>2</sub>	96-97	4	245-246	1.4314	1.117	63.0	62.6	48.87	7.80	43.33	49.06	7.67	43.50
IIIB	(CH <sub>3</sub> ) <sub>2</sub> CCH <sub>2</sub> CCl=CH <sub>2</sub>	40-40	37	124-124	1.4302	0.8814	38.9	38.9	63.37	9.88	26.75	63.37	9.36	27.03
IV	(CH <sub>3</sub> ) <sub>2</sub> CCH <sub>2</sub> CHClCH <sub>2</sub> Cl	58-59	12	173-175	1.4489	1.0259	44.2	44.1	49.70	8.34	41.96	49.67	8.77	41.98
IVA	C <sub>7</sub> H <sub>14</sub> Cl <sub>2</sub>	76-77	12	194-195	1.4613	1.0518	44.2	44.1	49.70	8.34	41.96	49.67	8.18	42.42
V	C <sub>2</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CHCl <sub>2</sub>	50-50	7	175-175	1.4500	1.0321	44.2	44.0	49.70	8.34	41.96	49.70	8.54	42.19
VI	C <sub>2</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CCl <sub>2</sub> CH <sub>3</sub>	63-65	8	187-189	1.4565	1.0248	48.8	48.6			38.74			38.99
VII	C <sub>2</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CHClCH <sub>2</sub> Cl	53-54	3	197-198	1.4572	1.029	48.8	48.6	52.45	8.81	38.74	52.40	8.42	39.36
VIII	(CH <sub>3</sub> ) <sub>2</sub> CCH <sub>2</sub> CHBrCH <sub>2</sub> Br	54-56	3	198-200	1.4962	1.502	50.1	50.2			61.96			61.61
IX	C <sub>2</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CHBrCH <sub>2</sub> Br	74-75	3	224-225	1.5003	1.4689	54.7	54.5	35.80	5.93	58.77	35.83	5.89	58.65
X	(CH <sub>3</sub> ) <sub>2</sub> CCH <sub>2</sub> CHBrCl	65-67	25	161-163	1.4640	1.2638	42.5	43.5	36.10 <sup>e</sup>	6.06 <sup>f</sup>		38.32	6.60	
XI	(CH <sub>3</sub> ) <sub>2</sub> CCH <sub>2</sub> CBrClCH <sub>3</sub>	48-57	7	170-180	1.4735	1.25	49.2	48.4						

<sup>a</sup> Calculated from boiling point under reduced pressure using nomograph prepared for hydrocarbon boiling-point conversions. This was found by experience to give accurate results for halogenated hydrocarbons. <sup>b</sup> Ebersbach, *Ann.*, **106**, 265 (1858). <sup>c</sup> M. p. -56°. <sup>d</sup> M. p. -35 to -34°. <sup>e</sup> Calcd. for C<sub>6</sub>H<sub>12</sub>Br<sub>2</sub>, 29.52; for C<sub>6</sub>H<sub>12</sub>Cl<sub>2</sub>, 46.50. <sup>f</sup> Calcd. for C<sub>6</sub>H<sub>12</sub>Br<sub>2</sub>, 4.90; for C<sub>6</sub>H<sub>12</sub>Cl<sub>2</sub>, 7.75.

atm., and the autoclave was rotated at the desired temperature for four hours. It was then allowed to stand overnight after which the gaseous products were discharged through a soda lime tower followed by a trap immersed in Dry Ice-acetone. The liquid product remaining in the autoclave was separated from the semi-solid catalyst layer, washed, dried and distilled.

In all these experiments, especially in those in which the autoclave was rotated at room temperature, it is quite possible that at least part of the reaction occurred before the contents reached the temperature noted in Table I.

**Method T.**—The experiments were carried out in large "test-tubes" (50 mm. × 350 mm., actually glass liners for the rotating autoclave used in Method B). The size of the test-tubes was such that they could readily be cooled by immersion in a Dry-Ice-acetone-bath in a quart Dewar jar. A low-temperature thermometer was suspended in the test-tube by means of a wire. The solution of alkyl halide and the haloolefin was cooled to about -60° and the catalyst was added. The test-tube was removed from the bath and allowed to warm up while being shaken manually. When the evolution of tiny bubbles of gas indicated that reaction was taking place, the test-tube was immersed in the bath until the temperature had dropped a few degrees after which it was again removed and permitted to warm up to the reaction temperature. The intermittent cooling and warming was repeated until there was little sign of reaction at a temperature at least 10° higher than the original reaction temperature. This usually required from one-half to two hours. The liquid product was then decanted from the catalyst, washed, dried and distilled.

**Reaction of Ethyl Chloride with Vinyl Chloride.**—A mixture of 38 g. (0.59 mole) of ethyl chloride and 37 g. (0.59 mole) of vinyl chloride in a glass liner was cooled to -70° and 3 g. of aluminum chloride was added. The mixture was allowed to warm up slowly while being shaken. No reaction occurred up to a temperature of -3°; at this point the liquid began to boil. The mixture was therefore sealed into an autoclave which was rotated at room temperature for two hours and then at 50° for two hours. The product consisted of 7 g. of deep red liquid, 47 g. of condensable gas (a mixture of vinyl and ethyl chlorides and 15 g. of catalyst sludge. Distillation of the liquid product yielded 4 g. of 1,1-dichloroethane (b. p. 55-60°, *n*<sub>D</sub><sup>20</sup> 1.4160) and 3 g. of trichlorobutane<sup>2b</sup> (b. p. 150°, *n*<sub>D</sub><sup>20</sup> 1.4598, 1,1,3-trichlorobutane). No 1,1-dichlorobutane was obtained.

**Reaction of Hydrogen Chloride with Vinyl Chloride.**—A glass liner containing 70 g. (1.12 moles) of vinyl chloride and 3 g. of aluminum chloride was sealed into an autoclave and 11 g. (0.30 mole) of anhydrous hydrogen chloride was pressed in. The autoclave was rotated at room temperature for two hours and then at 50° for two hours. There was obtained besides unreacted vinyl chloride, 16 g.

(54% of the theoretical) of 1,1-dichloroethane (b. p. 55-56°, *n*<sub>D</sub><sup>20</sup> 1.4150) and 4 g. (8% of the theoretical) of trichlorobutane (b. p. 149-150°, *n*<sub>D</sub><sup>20</sup> 1.4550).

#### Identification of the Products

**General Procedure for the Hydrolysis of the Dichlorides.**—Most of the products were identified by hydrolysis to a ketone or aldehyde. The dichloride, water and, in some cases, magnesium oxide were heated for four hours in a sealed glass tube in a rotating autoclave. Water was placed in the autoclave outside the tube in order to nearly equalize the pressure and prevent breakage. The reaction product was separated from the aqueous layer (often by steam distillation), dried and distilled.

**1,1-Dichloro-3-methylbutane (I).**—A solution of twelve grams of the compound in 15 cc. of *n*-pentane was heated with 6 g. of magnesium oxide and 150 g. of water at 200-230°. There was obtained, after distilling off the pentane, 4.8 g. of product boiling at 83-93°, *n*<sub>D</sub><sup>20</sup> 1.4070. Isovaleraldehyde boils at 92° but forms a hydrate boiling at 82°. Both the lower-boiling and the higher-boiling material yielded 2,4-dinitrophenylhydrazones melting at 123° which is the melting point reported<sup>10</sup> for isovaleraldehyde 2,4-dinitrophenylhydrazone.

**1,1-Dichloro-3,3-dimethylbutane (II).**—Hydrolysis of 14 g. of the dichloride by heating with 30 cc. of water at 300° resulted in a 60% yield of *t*-butylacetaldehyde, b. p. 102-103°; *n*<sub>D</sub><sup>20</sup> 1.4150; 2,4-dinitrophenylhydrazone,<sup>11</sup> m. p. 146-147°; dimedon derivative,<sup>11</sup> m. p. 162-163°. There was also obtained high-boiling material, presumably condensation product of the aldehyde.

**2,2-Dichloro-4,4-dimethylpentane (III).**—A sealed tube containing 20 g. of the dichloroheptane and 100 cc. of water was heated at 200° for four hours. There was recovered 13 g. (96% of the theoretical) of crude 4,4-dimethyl-2-pentanone, b. p. 120-122°, *n*<sub>D</sub><sup>20</sup> 1.4130<sup>12</sup>; 2,4-dinitrophenylhydrazone,<sup>13</sup> m. p. 100°; semicarbazone,<sup>13</sup> m. p. 176°.

**2-Chloro-4,4-dimethyl-1-pentene (IIIB).**—Hydrolysis of 2.3 g. of the chloroheptene by heating at 250° with 100 g. of water in a sealed tube yielded 1.4 g. of 4,4-dimethyl-2-pentanone, b. p. 121-123°, *n*<sub>D</sub><sup>20</sup> 1.4041; 2,4-dinitrophenylhydrazone,<sup>13</sup> m. p. 100°, semicarbazone<sup>13</sup>, 176°.

The position of the double bond in the chloroheptene was established by comparing its infrared spectrum<sup>14</sup> with

(9) Nef, *Ann.*, **318**, 162 (1901).

(10) C. F. H. Allen, *This Journal*, **52**, 2957 (1930).

(11) H. Brunner and E. H. Farmer, *J. Chem. Soc.*, 1044 (1937).

(12) The high refractive index (pure ketone 1.4030) probably indicates the presence of the chloroheptene, IIIB.

(13) F. C. Whitmore, *et al.*, *This Journal*, **63**, 2040 (1941).

(14) The writer is indebted to Dr. W. S. Gallaway of the Physics Division of Universal Oil Products Company for the infrared analyses mentioned in this paper.

those of the products obtained by adding *t*-butyl chloride to methylacetylene and to allene, respectively.<sup>15</sup> The compound was shown to be the same as the major product of the reaction with allene, proving that the compound was 2-chloro-4,4-dimethyl-1-pentene and not 2-chloro-4,4-dimethyl-2-pentene (the product obtained with methylacetylene). The probable method of formation of this compound (namely, by dehydrochlorination of 2,2-dichloro-4,4-dimethylpentane) confirms this structure; the methylene hydrogens are less likely to be involved in the dehydrochlorination than are those of the primary methyl group.

**1,2-Dichloro-3,4-dimethylpentane (IV).**—The proof of the structure of this dichloroheptane was described previously.<sup>16</sup> A 45% yield of heptene was obtained by the reaction of 18 g. of the compound with 8 g. of zinc dust and 40 g. of 95% ethyl alcohol in a sealed tube at 120°. The heptene boiled at 71–71.5°;  $n_D^{20}$  1.3921. These values are in agreement with the best literature values<sup>17</sup> for 4,4-dimethyl-1-pentene: b. p. 71.8°,  $n_D^{20}$  1.3922.

**1,1-Dichloro-3,3-dimethylpentane (V).**—Hydrolysis of 13 g. of the dichloride by heating in a sealed tube with 7 g. of sodium bicarbonate and 100 g. of water yielded 7 g. (80% of the theoretical) of 3,3-dimethylpentanal, b. p. 131–134°;  $n_D^{20}$  1.4292; 2,4-dinitrophenylhydrazone,<sup>18</sup> m. p. 101–102°.

**2,2-Dichloro-4,4-dimethylhexane (VI).**—Hydrolysis of 8 g. of the dichloride by heating with 50 g. of water at 225° yielded a ketone boiling at 149–150°,  $n_D^{20}$  1.4186. It yielded a 2,4-dinitrophenylhydrazone, m. p. 75°, and a semicarbazone, m. p. 170°. Drake, Kline and Rose<sup>19</sup> report the following properties for 2,2-dimethyl-4-hexanone, b. p. 154.4° at 768 mm.,  $n_D^{20}$  1.4183; 2,4-dinitrophenylhydrazone, 146.5–147°; semicarbazone, 169.5°. On the other hand, Laucius<sup>18</sup> gives 75° for the melting point of the 2,4-dinitrophenylhydrazone, citing "Wheeler, This Laboratory," and listing Drake's value also.

**1,2-Dichloro-4,4-dimethylhexane (VII).**—A solution of 14 g. of the dichlorooctane in 40 cc. of *n*-propyl alcohol was refluxed at 98° over 10 g. of zinc dust for eight hours. The product was distilled until addition of water to the distillate no longer yielded an appreciable amount of water-insoluble material. There was obtained 8.3 cc. of octene, boiling chiefly at 105–107°;  $n_D^{20}$  1.4111. Hydrogenation yielded a product boiling at 108–109°;  $n_D^{20}$  1.4009. Infrared analysis of this material showed that it consisted of 90–95% 3,3-dimethylhexane, the remainder being the unhydrogenated olefin.

**1,2-Dibromo-4,4-dimethylpentane (VIII).**—A solution of 20 g. of the dibromide in 45 cc. of 95% ethyl alcohol was refluxed over 6 g. of zinc dust. The reaction was complete

in less than ten minutes at 60–65° reflux temperature. Heptene (b. p. 71–72°,  $n_D^{20}$  1.3921) was obtained in better than 90% yield. Hydrogenation yielded heptane, b. p. 79°,  $n_D^{20}$  1.3820. This was pure 2,2-dimethylpentane. Infrared analysis showed that the maximum amount of impurity was less than 1%.

**1,2-Dibromo-4,4-dimethylhexane (IX).**—This dibromide was converted to octane in the analogous manner to that used for converting 1,2-dibromo-4,4-dimethylpentane (VIII) to heptane. Infrared analysis of the octane showed that it was 3,3-dimethylhexane of at least 98% purity.

**1-Chloro-1-bromo-3,3-dimethylbutane (X).**—The chlorobromide was converted to *t*-butylacetaldehyde by heating 10 g. of the compound with 50 cc. of 10% potassium hydroxide at 200°. The aldehyde boiled at 104–105° and yielded a 2,4-dinitrophenylhydrazone,<sup>11</sup> m. p. 145–146°.

**2-Chloro-2-bromo-4,4-dimethylpentane (XI).**—Sixteen grams of the chlorobromoheptane was heated at 200° with 4 g. of magnesia and 100 g. of water. There was recovered 10 cc. of yellowish upper layer which was dried and distilled. It boiled mainly at 119–122° ( $n_D^{20}$  1.4250<sup>12</sup>) and consisted of a mixture of 2-chloro-4,4-dimethyl-1-pentene (III B) and 4,4-dimethyl-2-pentanone (characterized by its 2,4-dinitrophenylhydrazone,<sup>13</sup> m. p. 100°).

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### Summary

1. The condensation of alkyl chlorides and bromides with monochloro- and bromoolefins in the presence of metal chlorides of the Friedel-Crafts type yields higher molecular weight dihaloalkanes. The reaction proceeds via the addition of the alkyl group and the halogen atom of the alkyl halide to the double bond of the haloolefin, the halogen adding to the carbon atom that holds the smaller number of hydrogen atoms.

2. The reaction of a number of alkyl halides (isopropyl, *t*-butyl, and *t*-amyl chlorides and *t*-butyl and *t*-amyl bromides) with some of the more readily available haloolefins (vinyl chloride, 2-chloropropene, allyl chloride and allyl bromide) is described.

3. The condensation products obtained from the *t*-alkyl halides are new compounds. They serve as intermediates for the synthesis of aldehydes, ketones, and olefins (and the corresponding paraffins) containing quaternary carbon atoms.

4. Ethyl chloride could not be condensed with vinyl chloride.

(15) L. Schmerling, unpublished results.

(16) L. Schmerling, *THIS JOURNAL*, **67**, 1438 (1945).

(17) G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939.

(18) J. F. Laucius, Ph.D. Thesis, Pennsylvania State College, 1940, tabulation, pp. 161–165.

(19) N. L. Drake, G. M. Kline and W. G. Rose, *THIS JOURNAL*, **56**, 2076 (1934).