might have escaped notice if the concept of partial conversion properties had not been introduced.

At about 74% conversion the partial conversion molecular weight changes sign again. The reason for this behavior is not absolutely clear since any of several possible factors could cause it. First of all, the nature of the cross-linking reaction might change. Cross-linking is a process which either joins together two distinct molecules or joins together two parts of the *same* molecule. As long as intermolecular cross-linking predominates, a net negative rate of molecule formation can result. Intramolecular cross-linking, on the other hand, does not produce a decrease in the number of molecules. Accordingly the formation of a few new molecules while the second type of cross-linking occurs is consistent with the observed reversal of sign for dN/dW.

Another process which can bring about the change in sign of the partial conversion molecular weight is degradation. Although degradation can occur, it is difficult to specify its extent quantitatively because of the numerous other simultaneous reactions. At about 77% conversion the molecular weight reaches a maximum of about 50,000. The decrease in molecular weight at higher conversions may be due to degradation at least as long as the polymer remains soluble. After gel begins to form it can be argued that the decrease in average molecular weight is due to the removal of the largest molecules as gel, thus leaving only lower molecular weight material to be studied experimentally. When gel formation becomes significant, the partial conversion molecular weights lose much of their meaning.

In addition to all the possible reactions heretofore mentioned, there should be added still another, namely, branching. Branching presumably occurs sooner than cross-linking, but it cannot be detected by partial conversion molecular weight studies. Branching will not alter the ratio of modifier to polymer molecules, and although it can increase molecular weights it cannot give rise to negative partial conversion values. The ways in which branching, cross-linking and degradation can occur have been discussed in some detail by Taylor and Tobolsky.[11]

Summary

Molecular weights of bottle-polymerized GR-S have been determined as functions of conversion. The partial conversion molecular weights are found to be negative between 61 and 74% conversion, thus indicating a net decrease in the number of polymer molecules with increasing weight conversion. This negative rate of molecule formation is attributed to intermolecular cross-linking. Above 74% conversion intramolecular cross-linking and degradation may become important.

(11) H. S. Taylor and A. V. Tobolsky, THIS JOURNAL, **67**, 2063 (1945).

URBANA, ILLINOIS RECEIVED JANUARY 13, 1947

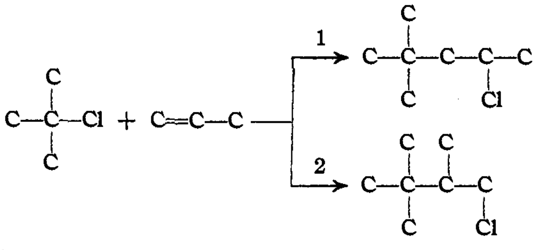
[RESEARCH LABORATORIES DIVISION OF GENERAL MOTORS CORPORATION]

The Aluminum Chloride-Catalyzed Addition of *t*-Butyl Chloride to Propylene

BY VERLE A. MILLER[1]

During the course of a general reaction study made in the search for a method of preparation of triptane (2,2,3-trimethylbutane), higher alkyl chlorides were found in a mixture of *t*-butyl chloride and propylene which had been left in a steel bomb at room temperature for several days. Since less reaction occurred in a glass pressure vessel with steel end-plates, the reaction catalyst may have been iron chloride. This conclusion was in agreement with the work of Schmerling on the catalyzed addition of alkyl halides to ethylene[1a] which was presented at about the same time.

Theoretically, two different methods of addition of *t*-butyl chloride to propylene are possible. According to analogous reactions, the heptyl chloride produced should be that from reaction 1. This has been prepared and characterized by Whitmore and Johnston,[2] but that from reaction 2 has not been described.



This paper presents the study of the structures of C_7 molecules obtained from the addition of *t*-butyl chloride to propylene in the presence of aluminum chloride.

Experimental Procedure

A 500-ml., three-necked flask was fitted with a mercury sealed stirrer, reflux condenser, thermometer and a coarse capillary gas inlet tube which extended well below the halide liquid level. A bubbler containing aqueous sodium hydroxide was inserted between the top of the condenser and a coil trap (which was cooled with acetone and Dry Ice) to serve as a guide for the control of the propylene addition rate.

When the desired reaction temperature was below the freezing point of *t*-butyl chloride, the stirred halide was

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(1) Present address: Firestone Tire and Rubber Company, Akron 17, Ohio.

(1a) L. Schmerling, THIS JOURNAL, **67**, 1152 (1945).

(2) Whitmore and Johnston, *ibid.*, **60**, 2265 (1938).

TABLE I

REACTION CONDITIONS AND PRODUCTS FROM REACTION OF 1 MOLE *t*-BUTYL CHLORIDE WITH 1.25 MOLES PROPYLENE

Run	Temperature, °C. Bath	Temperature, °C. Reaction	AlCl₃, g.	Propylene addition rate, liquid, ml./min.	Approx. % starting material recovered Propylene	Approx. % starting material recovered *t*-Butyl chloride	Volume of liquid reaction products, ml. at 0° B. p. above 57° at 744 mm.	B. p. 45–65° at 50 mm.	B. p. to 90° at 20 mm.	Residue[f]
12	Ice	....	13	0.99	..[a]	0	3	2	13	65
13	−20	....	10	.98	24	11.8	18	19	26	38
14	−26	....	5	.93	6.2	20.3[d]	27[d]	46	23	23
15	−26	....	2.5	1.05	9			38	32	17
16	−26	−21 to −23	1	0.78	29.5	71.7	0	20	11[e]	..
17	−36	−30	2	1.02	8.6	23	<5	77	15	12
18	−43	−37	2	1.02	8.6	25	...	79	18	12
19	..	−30 to −35	4[b]	1.15[c]	8	24	...	159[c]	36[c]	25[c]
20	..	−30 to −38	4[b]	2.29[c]	10.4	23.6	...	164[c]	27[c]	38[c]

[a] Fifty-five ml. unanalyzed liquid condensed in the cold trap as compared with 7 ml. in run 17. [b] Since double the usual quantity of all reagents was used, this is equivalent to 2 g. of catalyst in the other runs. [c] Divide by 2 to make this comparable with the smaller runs. [d] Average value from runs 14 and 15. [e] Includes the residue. [f] At room temperature.

cooled to −23°, the catalyst was added, and cooling was continued until solid started to separate. Propylene, from the bottom of a calibrated liquid storage vessel, was bubbled in slowly until the exothermic reaction started. The reaction temperature could then be lowered rapidly to the desired point before the propylene addition rate was increased. When the propylene addition was complete the reaction and bath temperature differential was decreased and stirring of the slightly yellow, opaque liquid was continued for thirty minutes.

The catalyst was destroyed by dropping in 25 ml. of water, removing the cooling bath, and stirring until the colorless product reached a temperature of about 0°. This was partially degassed, without stirring, on a water-bath until the temperature of the product reached a maximum of 30–35°. It was then cooled in an ice-bath before the water layer was separated. The product was dried over anhydrous potassium carbonate before the degassing was completed. This procedure prevented loss of low boiling constituents during separation of the water layer, but was mild enough to prevent hydrolysis of the alkyl halides present.

Analytical Procedure.—Low temperature distillation indicated that practically all of the gas fraction from the cold trap was unreacted propylene and no isobutylene was detected.

The dried, degassed liquid product was transferred to a modified Claisen flask, to which had been sealed an insulated 24-inch glass helices-packed side arm; this was provided with a total condensation head. The lower boiling liquid products were removed under reduced pressure and caught in a wide-mouthed trap which was cooled with acetone and Dry Ice. The remaining liquid was fractionally distilled under reduced pressure (50 mm.), in the presence of 2 g. of anhydrous potassium carbonate to combine with any liberated acid,[3] using a reflux ratio of at least 15 to 1. When the distillation temperature reached about 80° at 50 mm., equilibrium was reëstablished at 20 mm., and the distillation was continued until the temperature reached about 90°, or until the still pot was empty. No evidence of decomposition during distillation was observed.

The lower boiling liquid from the cold trap was combined with the residue from the gas distillation. This was redistilled at atmospheric pressure through a 915 × 12.7 mm. glass spiral vacuum-jacketed column, which was provided with a total condensation head. This distillation permitted the determination of the amount of unreacted *t*-butyl chloride, and also the product which boiled higher than the reactants, but lower than the heptyl chloride fraction.

The refractive index, density and chlorine content[4] of the various distillation cuts aided in their preliminary identification and segregation.

Discussion

Determination of the Optimum Reaction Conditions.—When 1.25 moles of propylene is bubbled into 1 mole of *t*-butyl chloride plus 2 g. of aluminum chloride at −30°, at such a rate that the absorption of gas is complete, the chief reaction is one of addition to form a heptyl chloride fraction (about a 70% yield, based upon the reacted *t*-butyl chloride); some higher boiling ma-

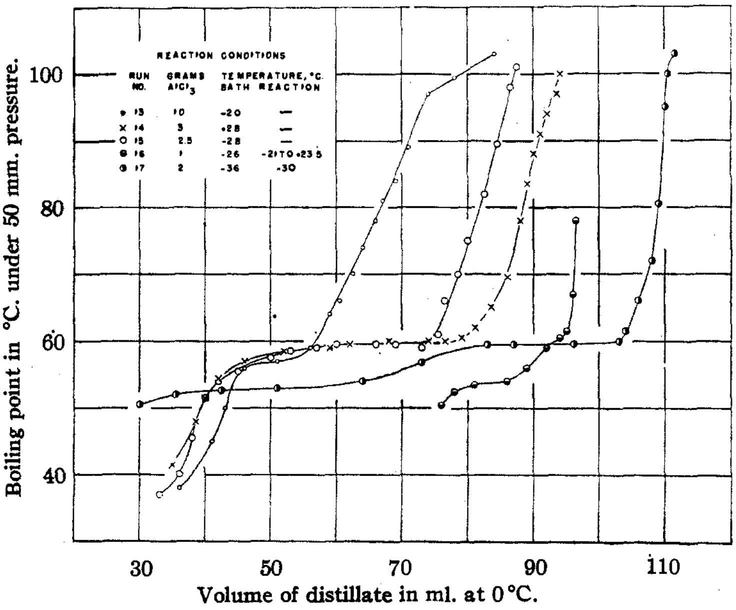

Fig. 1.—The effect of reaction temperature and quantity of catalyst upon the amount and composition of the heptyl chloride fraction.

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[3] Whitmore and Badertscher, THIS JOURNAL, 55, 1559 (1933).

[4] The author is indebted to Dr. P. K. Winter for the chlorine determinations.

terial, however, is also obtained. Under these conditions 8–10% of the propylene and 23–25% of the *t*-butyl chloride are recovered unchanged and practically no low boiling side reaction products are obtained.

A summary of the data obtained is given in Table I. The effect of changes in reaction temperature and quantity of catalyst upon the amount and composition of the heptyl chloride fraction obtained is shown graphically in Fig. 1.

t-Butyl chloride, cooled in ice, became orange-red when aluminum chloride was added. Quantities of hydrogen chloride were evolved before and during the propylene addition. Much condensable gas but no *t*-butyl chloride was recovered, and the liquid product was a heavy, viscous oil. At a bath temperature of −20°, the halide became only slightly yellow and much less hydrogen chloride was evolved during the propylene addition. At lower temperatures and with less catalyst, more propylene reacted to give more liquid product with a smaller proportion of high boiling oil. Decreasing the catalyst to 1 g./mole quite markedly lowered the reaction rate (run 16, Table I). Increasing the catalyst to 2 g./mole and lowering the reaction temperature to −30° (run 17), greatly increased the heptyl chloride fraction. Further lowering of the temperature (run 18) or decreasing the relative propylene addition rate in larger runs (19 and 20) failed to alter the proportion of reaction products. A second lower boiling heptyl chloride was obtained in runs 16 and 17 (Fig. 1) which was not present in any significant amount in runs made at higher temperature with more catalyst.

TABLE II

COMPOSITION OF THE REACTION PRODUCT

Volume[a]	Principal component	Final composition Volume[b]	%
286	Lower boiling heptyl chloride	222	35.0
204	Higher boiling heptyl chloride	272	43.0
106	Mixture of decyl chlorides	103	16.3
48	Residue	37	5.7

[a] Ml. at room temperature before refractionation. [b] Ml. at 0° after refractionation.

In runs 12–15, a small amount of product was obtained which boiled higher than *t*-butyl chloride, but lower than the heptyl chlorides. Its physical properties indicated that heptanes mixed with a small amount of alkyl halide probably were present. At the lower reaction temperature these side-reaction products disappeared almost entirely.

Identification of Products

Since the proportion of reaction products was essentially the same in runs 17–20 (Table I), the comparable distillation cuts from these runs were combined to produce four samples (Table II) for refractionation. The data obtained are given in Table III.

The carbon skeletal structures of the higher- and lower-boiling heptyl chlorides were identified as those of 2,3- and 2,2-dimethylpentane, respectively, by reducing the Grignard reagent made from distillation cuts 11–19 (Table III) and fractionation of the resulting paraffin mixture in a 100-plate Podbielniak column. This fractionation showed the paraffin to contain 59% of 2,3-dimethylpentane and the remainder to be 2,2-dimethylpentane (Table IV), while the original halide mixture, based on its refractive index, was composed of about 62% of the higher boiling chloride.

Identification of the Lower Boiling Heptyl Chloride.—Only one of the four possible chloro-2,2-dimethylpentanes (2-chloro-4,4-dimethylpen-

TABLE III

REDISTILLATION OF COMBINED FRACTIONS FROM RUNS 17, 18, 19 AND 20

The density and % chlorine determinations were made on individual cuts only, instead of on the combined cuts as listed in the table. Thus *a* was made on cut 5 only and is not an average value for cuts 2–5. The other determinations were made on individual cuts as follows: *b*-8, *c*-21, *d*-24, *e*-25, *f*-31, *g*-33, *h*-35, *j*-38, *k*-40, *m*-42 and *n*-43.

Distillation cut	Volume, ml. at 0°	Boiling point, °C., end of cut Under 50 mm.	Under 20 mm.	n^{20}_D	d^{20}_4	% Chlorine
1	10	50		1.4183		
2–5	64	50.3–51.3		1.4191–1.4192	0.8600*a*	26.2*a*
6–8	75	51.4–51.6		1.4194–1.4197	.8603*b*	
9–10	50	51.8–52.5		1.4198–1.4201		
11	25	56.1		1.4224		
12–19	66	58.6–59.6		1.4279–1.4304		
20–21	50	59.8		1.4308–1.4310	.8881*c*	26.3*c*
22–24	77	60.1–60.4		1.4313–1.4318	.8894*d*	
25–27	58	60.6–62.8		1.4321–1.4322	.8896*e*	
28	13	74.2		1.4322		
29	7	94.4		1.4349		
30–31	14		85.1–86.1	1.4403–1.4424	.866*f*	
32–33	14		87.8	1.4434–1.4444	.873*g*	19.5*g*
34–40	49		88.7–91.2	1.4451–1.4484	0.875*h*–0.878*j*,*k*	19.0*j*–18.7*k*
41–44	25		91.3–93.4	1.4489–1.4499	.877*m*– .871*n*	16.7*n*
Residue	37 ml. at (room temperature)			1.4611	.874	12.8

TABLE IV

IDENTIFICATION OF THE HEPTYL CHLORIDE CARBON SKELETAL STRUCTURES[c]

Podbielniak still charge: 50.5 ml. sample + 16 ml. added methylcyclohexane

Distillation cut	Volume, ml.	B. p., °C., end of cut	n^{20}_{D}
1–3	3.5	76.62–78.08	1.3844–1.3829
4–5	3.7	78.26–78.43	1.3826–1.3824
6–8	11.1	78.54	1.3823[a]
9	1.6	78.74	1.3824
10–13	6.0	80.54–88.63	1.3831–1.3914
14–17	9.4	88.98–89.10	1.3919–1.3920
18–22	12.1	89.10–89.18	1.3921[b]
23	1.3	89.39	1.3924
24–27	3.0	91.05–97.06	1.3939–1.4100
Residue	15.5		1.4225

[a] The refractive index of pure 2,2-dimethylpentane was reported as 1.3823 by Edgar and Calingaert, THIS JOURNAL, **51**, 1540 (1929). [b] That of pure 2,3-dimethylpentane was reported as 1.3921 by Smittenberg, Hoog and Henkes, *ibid.*, **60**, 17 (1938). [c] The author is indebted to C. R. Begeman for this distillation.

tane, d^{20}_{4} 0.855; n^{20}_{D} 1.4180) has been described[2] but three of the corresponding alcohols are known. A 65.4% yield of crude alcohol was obtained from the oxidation of the Grignard reagent made from the lower boiling heptyl chloride. This yield indicated that this was a secondary chloride.[2] The boiling point, 3,5-dinitrobenzoate, α-naphthyl- and phenylurethans (Table V) identified this alcohol as 4,4-dimethyl-2-pentanol. This was derived from 2-chloro-4,4-dimethylpentane[5] which was obtained from the addition of *t*-butyl chloride to propylene according to reaction 1.

TABLE V

IDENTIFICATION OF THE 2,2-DIMETHYLPENTANOL

Pentanol	B. p., °C.	Mm.	3,5-Dinitrobenzoate	α-Naphthyl urethan	Phenylurethan
2,2-Dimethyl-1-	...	..	....	....	....
2,2-Dimethyl-3-	135	(737)[a]	92.5–93[d]	107–108[d]	83[f]
4,4-Dimethyl-2-	137	(736)[b]	95.2–95.7[b]	86.5–87[b]	
4,4-Dimethyl-1-	158	(737)[c]	66–67[e]	80.5–81[c]	51–52[e]
Reaction product	138	(757)	94	86	52–53[g]

[a] James, Publication 641, University Microfilms, Ann Arbor, Michigan. [b] Whitmore and Homeyer, THIS JOURNAL, **55**, 4194 (1933). [c] Whitmore and Homeyer, *ibid.*, **55**, 4555 (1933). [d] Stevens and McCoubrey, *ibid.*, **63**, 2847 (1941). [e] Bartlett and Rosen, *ibid.*, **64**, 543 (1942). [f] Leroide, *Ann. chim.*, (9) 16, 367 (1921). [g] New compound.

TABLE VI

HEPTYL CHLORIDES AND ALCOHOLS WITH A 2,3-DIMETHYLPENTANE CARBON SKELETAL STRUCTURE

Heptyl chlorides	B. p., °C.	Mm.	n^{20}_{D}	α-Naphthalide
2-Chloro-2,3-dimethylpentane	59	(50)[a]	1.4291[a]	125.5–126[a]
3-Chloro-2,3-dimethylpentane	60.5	(50)[a]	1.4318[a]	174–174.5[a]
1-Chloro-3,4-dimethylpentane	53	(20)[b]	1.4299[b]	
Reaction product	60–61	(50)	1.4308–1.4322	176–177[c]

Heptyl alcohols	B. p.				
	°C.	Mm.	°C.	Mm.	n^{20}_{D}
2,3-Dimethyl-1-pentanol	....		75	(17)[d]	....
2,3-Dimethyl-2-pentanol	129–130.5[e]		65	(50)[f]	1.4252[a]
2,3-Dimethyl-3-pentanol	139.4–139.9[g]		68.5	(50)[h]	1.4287[i]
3,4-Dimethyl-2-pentanol	149–150.5	(719)	....		....
3,4-Dimethyl-1-pentanol	160–162	(740)[k]	....		1.4288[b]
2-*i*-Propyl-1-butanol	....		....		....
Reaction product	137.5	(744)	67.5–68.5	(50)	1.4283–1.4290

[a] James, Publication 641, University Microfilms, Ann Arbor, Michigan. [b] Schmerling, THIS JOURNAL, **67**, 1438 (1945). [c] A very small amount of naphthalide melting at 125–126.5° was isolated from the recrystallization filtrates. This showed the presence of a small percentage of 2-chloro-2,3-dimethylpentane along with the 3-chloro-2,3-dimethylpentane. [d] Levene and Marker, *J. Biol. Chem.*, **91**, 405 (1931). [e] Edgar, Calingaert and Marker, THIS JOURNAL, **51**, 1483 (1929). [f] From vapor pressure curve of 2,3-dimethyl-2-pentanol as determined by a plot of the available literature data. [g] Chavanne and de Graef, *Bull. soc. chim. Belg.*, **33**, 366 (1924). [h] From vapor pressure curve of 2,3-dimethyl-3-pentanol as determined by a plot of the available literature data. [i] Whitmore and Evers, THIS JOURNAL, **55**, 812 (1933). [j] Willstätter and Hatt, *Ann.*, **418**, 148 (1919). [k] Huston and Agett, *J. Org. Chem.*, **6**, 123 (1941).

Identification of the Higher Boiling Heptyl Chloride.—Only three of the six possible chloro-2,3-dimethylpentanes have been described, but five of the corresponding alcohols are known (Table VI). A 31.7% yield of alcohol was obtained from the oxidation of the Grignard reagent made from the higher boiling heptyl chloride. The yield indicated that this was a tertiary chloride.[2] Elimination of 1-chloro-3,4-dimethylpentane was accomplished since its boiling point is higher than that of the reaction product. Of the other two known chlorides of this structure (2-chloro- and 3-chloro-2,3-dimethylpentane), the boiling point and refractive index of the 3-chloro isomer agree better with the data from the reaction product (Table VI). The boiling point of the alcohol obtained ruled out three of the five known structures, and again the physical constants of the unknown agreed more closely with those of 2,3-dimethyl-3-pentanol than with those of 2,3-dimethyl-2-pentanol.

The higher boiling heptyl chloride was further characterized by the preparation of a large sample of α-naphthalide, the melting point of which agreed with that from 3-chloro-2,3-dimethylpentane (Table VI). From the recrystallization filtrates a very small amount of a second naphthalide was isolated. The melting point of this agreed with that from 2-chloro-2,3-dimethylpentane.

Thus, 45% of the heptyl chloride fraction was composed of the primary addition product, 2-chloro-4,4-dimethylpentane. The remainder was the rearranged product, 3-chloro-2,3-dimethyl-

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(5) Whitmore and Johnston[2] converted this halide to the corresponding alcohol without rearrangement.

pentane which was mixed with a quite small amount of 2-chloro-2,3-dimethylpentane.[6]

In the alkylation mechanism proposed by Schmerling,[6] which involves the addition of an alkyl chloride to the olefin, it is postulated that the rearrangement of the carbon skeletal structure occurs during the hydrogen-chlorine exchange reaction. The data presented here show that rearrangement of the carbon skeletal structure of the halide may also occur before it is reduced to the paraffin.

No chloro-2,4-dimethylpentanes were found, although a mixture of 2,3- and 2,4-dimethylpentanes is produced in the alkylation of isobutane with propylene.[7]

Investigation of the Higher Boiling Product.—The halide content of the distillate obtained under 20 mm. pressure (cuts 29–44, Table III) was approximately that of a decyl chloride. The properties of the purified paraffin obtained by reduction of the Grignard reagent made from this fraction, when distilled through a one-foot Stedman-packed vacuum-jacketed column, fell within the range of those of the decanes (b. p. 151–157° (738 mm.); n^{20}D 1.4144–1.4220).

Experimental

Identification of the Lower Boiling Heptyl Chloride.—When the Grignard reagent made from cuts 1–10 (Table III) was oxidized,[8] although the rapid initial reaction rate dropped sharply after thirty minutes, and the reaction mixture became so thick after one and one-half hours that it stopped the stirrer, the oxygen addition was continued overnight. Redistillation of the low boiling constituents of the hydrolyzed product gave 18 ml. of chiefly paraffinic material which boiled at 70–80° (738 mm.); n^{20}D 1.3875–1.3881. This represents about 11–12% of the starting halide.

The 115 ml. of crude alcohol obtained (b. p. 68–69° (50 mm.), n^{20}D 1.4221–1.4245) was contaminated with a product which contained halide.[9] The 12-ml. residue also contained halide (n^{20}D 1.4343). Various derivatives of this alcohol identified it as 4,4-dimethyl-2-pentanol (Table V).

Anilide of 2-Chloro-4,4-dimethylpentane.—The anilide of the lower boiling halide was purified by extracting it with carbon tetrachloride, in which the contaminating diphenylurea is not appreciably soluble, evaporating to dryness, and recrystallizing the residue from high boiling petroleum ether, m. p. 118.5°.[10]

Identification of the Higher Boiling Heptyl Chloride.—The rapid absorption of oxygen by the Grignard reagent made from cuts 20–28 (Table III) ceased after only fifteen minutes, and again the thickening reaction mixture stopped the stirrer after one and one-half hours. This oxidation produced more (65 *vs.* 18 ml.) low boiling product of higher olefinic content,[11] as shown by its higher refractive index (b. p. 83–89° (748 mm.); n^{20}D 1.3978–1.3990). This represents about 37% of the starting halide.

Vacuum distillation of the remaining product gave 55 ml. of halide-free alcohol (b. p. 67.5–68.5° (50 mm.); n^{20}D 1.4283–1.4290). The residue (8 ml.) contained halide (n^{20}D 1.4510). These physical constants, along with those of the halide and its α-naphthalide, identified this structure (Table VI).

Phenyl Urethan of 2,3-Dimethyl-3-pentanol.—No derivative of this tertiary alcohol has been reported. It was synthesized from isopropyl Grignard reagent and methyl ethyl ketone and the phenyl urethan was prepared by the method of Tarbell, Mallatt and Wilson.[12] The urethan was separated from diphenyl urea by extraction with carbon tetrachloride and purified by vacuum distillation (b. p. about 145° (2 mm.)). It is extremely soluble in organic solvents and all attempts to crystallize it from aqueous alcohol failed. It finally was recrystallized from a very small amount of petroleum ether at −20°, m. p. 48.5–49°.

Anal. Calcd. for $C_{14}H_{21}NO_2$: N, 5.96. Found[13]: N, 5.93.

The phenyl urethan, prepared from the alcohol obtained from the higher boiling heptyl chloride, melted in the same general range as did the urethan from the synthetic alcohol, but it was contaminated with a somewhat higher melting substance. Repeated recrystallization failed to purify this material because of its very high solubility and the quite similar solubility of the impurity present.

Phenyl Urethan of 4,4-Dimethyl-2-pentanol.—It was desirable to know whether the higher melting impurity in the phenyl urethan from the 2,3-*dimethyl*-3-*pentanol* fraction was the unreported urethan of 4,4-dimethyl-2-pentanol. This would be possible if complete separation of the two heptyl chlorides had not been obtained.

The phenyl urethan from reaction product 4,4-dimethyl-2-pentanol solidified after it was purified by vacuum distillation (b. p. about 132° (1 mm.)). The product crystallized slowly, from petroleum ether and then from aqueous alcohol, at 0° after the solution had been seeded, m. p. 52–53°. This melting point is lower than that of the impurity present in the urethan from the 2,3-dimethyl-3-pentanol fraction.

Anal. Calcd. for $C_{14}H_{21}NO_2$: N, 5.96; Found[14]: N, 5.72.

Summary

1. The condensation of *t*-butyl chloride with propylene at −30° in the presence of 2 g. of aluminum chloride per mole alkyl halide produces a 70% yield of heptyl chlorides.

2. Under these conditions about 45% of the heptyl chloride fraction is composed of the primary addition product, 2-chloro-4,4-dimethylpentane, and the remainder is the rearranged product, 3-chloro-2,3-dimethylpentane, which is mixed with a quite small amount of 2-chloro-2,3-dimethylpentane.

3. The principal fraction of the higher boiling mixture obtained is composed chiefly of decyl chlorides which were not further identified.

4. At higher reaction temperatures and when more catalyst was used, the reaction was more complex: (a) the amount of heptyl chloride fraction decreased and the primary addition product was converted almost entirely into the rearranged product; (b) the amount of higher boiling product obtained increased; (c) the amount of lower boiling side-reaction products increased from a negligible to a significant amount.

5. Two new phenyl urethans are reported.

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[6] These data are in agreement with those from the concurrent investigation of Schmerling, which were mentioned, THIS JOURNAL, **67**, 1778 (1945), in support of a proposed reaction mechanism.

[7] Pines, Grosse and Ipatieff, THIS JOURNAL, **64**, 33 (1942).

[8] By the method of Whitmore and Lux, THIS JOURNAL, **54**, 3448 (1932).

[9] Whitmore and Homeyer, THIS JOURNAL, **55**, 4194 (1933), report a refractive index of 1.4188 for pure 4,4-dimethyl-2-pentanol.

[10] Whitmore and co-workers, THIS JOURNAL, **63**, 2028 (1941), report a m. p. of 117.5° for this compound made from the acid.

[11] Whitmore and Johnston[2] showed that the lower yield of carbinols from tertiary chlorides was due to olefin formation.

[12] Tarbell, Mallatt and Wilson, THIS JOURNAL, **64**, 2229 (1942).

[13] Nitrogen analysis by Miss Patricia Craig.

[14] Nitrogen analysis by Dr. P. K. Winter.