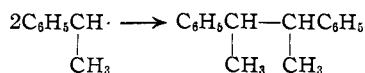


The (3-chloroallyl)-benzene was characterized by comparing its infrared spectrum with that of the product prepared by the reaction of benzene with 1,3-dichloropropene in the presence of aluminum chloride dissolved in nitromethane.

The reaction of toluene with trichloroethylene in the presence of di-*t*-butyl peroxide at 130–140° yielded a product believed to be (3,3-dichloroallyl)-benzene. The condensation with tetrachloroethylene under the same conditions produced what was apparently chiefly (2,3,3-trichloroallyl)-benzene; a lower yield was obtained when *t*-butyl perbenzoate was used as peroxide at 110–115°.

Chlorophenylbutenes were similarly formed from ethylbenzene and *trans*-dichloroethylene or trichloroethylene. 2,3-Diphenylbutane was isolated from the latter reaction product; its formation involved self-condensation of the intermediate methylbenzyl radical.<sup>2</sup>



When an attempt was made to condense benzene with trichloroethylene in the presence of di-*t*-butyl peroxide, the only reaction product which was isolated was the dimer of trichloroethylene, obtained in about 14% yield. This result indicates that hydrogen attached to an alkyl side chain is necessary for the chlorovinylation.

Indan also underwent the condensation reaction.

(2) M. S. Kharasch, E. V. Jensen and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945).

Compounds having the composition corresponding to 1-(2-chlorovinyl)-indan and 1-(2,2-dichlorovinyl)-indan were obtained by the reaction of indan with dichloro- and trichloroethylene, respectively.

Little reaction occurred when toluene was treated with 1,2-dibromoethylene in the presence of di-*t*-butyl peroxide. This apparently is due to the fact that bromine atoms are not good chain-carriers; they abstract hydrogen atoms from the side chains less readily than do chlorine atoms. It was previously shown<sup>3</sup> that the condensation of polybromomethylenes (unlike that of polychloroethylenes) with saturated hydrocarbons similarly occurs in low yield, if at all.

### Experimental

**Procedure.**—A glass liner containing the aromatic hydrocarbon, the chloroethylene and the peroxide was sealed into an Ipatieff-type rotating autoclave of 850-cc. capacity. Nitrogen was pressed in to a pressure of 50 atm. and the autoclave was then heated, the temperature being raised gradually during four hours from 130 to 140° when the peroxide was di-*t*-butyl peroxide and from 110 to 115° when it was *t*-butyl perbenzoate. The autoclave was permitted to stand overnight, the gas was discharged to the atmosphere, and the liquid product was washed with dilute alkali and with water, dried over potassium carbonate and distilled.

(3-Chloroallyl)-benzene.<sup>4</sup>—A solution of 50 g. of 1,3-dichloropropene in 80 g. of benzene was added during one hour to a stirred solution of 5 g. of aluminum chloride and 5 g. of nitromethane in 80 g. of benzene at 0°. The product was stirred for an additional one-half hour, washed with water and alkali, dried and distilled. There was obtained 32 g. of (3-chloroallyl)-benzene (47%); b.p. 50–51° (1.5 mm.), 208–209° (760 mm.),  $n_D^{20}$  1.5388.

The physical properties were in good agreement with those of the product obtained by the reaction of toluene with *trans*-dichloroethylene (b.p. 53–53° [2.0 mm.]; 208–208° [760 mm.];  $n_D^{20}$  1.5385). Infrared analysis indicated that the same major component was present in both samples with different and varying concentrations of impurity.<sup>5</sup>

(3) L. Schmerling and J. P. West, *THIS JOURNAL*, **71**, 2015 (1949).

(4) L. Bert, *Bull. soc. chim.*, [4] **37**, 880 (1925); P. Bert, *Compt. rend.*, **213**, 619 (1941).

(5) Infrared analysis by Mr. Edmond Baclawski, Physics Division, Universal Oil Products Company.

RIVERSIDE, ILLINOIS

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

## Condensation of Saturated Halides with Unsaturated Compounds. X. Condensation of *t*-Butyl Halides with Propene, 1-Butene and 2-Butene<sup>1</sup>

By LOUIS SCHMERLING AND E. E. MEISINGER

RECEIVED AUGUST 17, 1953

The addition of *t*-butyl chloride to propene in the presence of Friedel-Crafts catalysts yields 2-chloro-4,4-dimethylpentane together with 2- and 3-chloro-2,3-dimethylpentane, the proportion of the various isomers depending on the catalyst used. Pure 2-chloro-4,4-dimethylpentane may be readily obtained by treating the mixture of isomers with water at the reflux temperature to decompose the tertiary halides. The condensation of propene with *t*-butyl bromide and with *t*-butyl iodide takes place in analogous manner. The reaction of *t*-butyl chloride with 1-butene yields 3-chloro-5,5-dimethylhexane as the principal product, while the reaction with 2-butene produces 3-chloro-2,2,3-trimethylpentane and 2-chloro-3,4,4-trimethylpentane together with some chloro-2,3,4-trimethylpentane.

In a previous paper,<sup>2</sup> it was shown that condensation of *t*-butyl chloride or bromide with ethylene in the presence of a Friedel-Crafts metal halide catalyst yields halo-hexane consisting practically exclusively of 1-halo-3,3-dimethylbutane. It was

also indicated<sup>3</sup> that the reaction of *t*-butyl chloride with propene, on the other hand, yields not only the analogous 2-chloro-4,4-dimethylpentane (*i.e.*, the primary product formed by the addition of the alkyl group and the halogen atom to the double bond of the olefin, the halogen adding to the carbon

(1) Preceding paper in this series, *THIS JOURNAL*, **74**, 3592 (1952).

(2) L. Schmerling, *ibid.*, **67**, 1152 (1945).

(3) L. Schmerling, *ibid.*, **67**, 1780 (1945).

TABLE I  
 CONDENSATION OF *t*-BUTYL HALIDES WITH PROPENE

Expt. Method	Reactants, g.		Catalyst MX	g.	Temp., °C.	Chief product				Higher boiling prod., g.		
	RX	C <sub>3</sub> H <sub>6</sub>				Compd.	B.p., <sup>a</sup> °C.	<i>n</i> <sub>D</sub> <sup>20</sup>	g.		Yield, %	
<i>t</i> -Butyl chloride and propene												
1	A	150 <sup>b</sup>	51	AlCl <sub>3</sub>	15	-40 to -32	I + II	130-140	1.428-1.431	70	43	31
2	C	680	190	FeCl <sub>3</sub>	35	-15 to -10	I + II	130-140	1.424-1.431	265	43	
							III	191-200	1.440-1.441	58	7	117
3	B	140	75	BiCl <sub>3</sub>	10	22	I + II	129-134 <sup>c</sup>	1.419-1.425	57	28	13
4	B	160	85	BiCl <sub>3</sub> <sup>d</sup>	10	22	I + II	128-140 <sup>c</sup>	1.419-1.431	102	44	
							III	190-200	1.445-1.447	14	5	22
5	B	50	26	ZnCl <sub>2</sub>	5	23	I + II	130-136	1.424-1.426	15	21	3
6	B	50	21	ZrCl <sub>4</sub>	10	22	I + II	127-136		12	18	14
7	B	50	25	TiCl <sub>4</sub>	7	50	I + II	138-140	1.426-1.430	21	29	17
8	A	100	26	BF <sub>3</sub>	8	10	I + II	130-140	1.426-1.429	52	63	13
<i>t</i> -Butyl bromide and propene												
9	B	70	21	FeCl <sub>3</sub>	6	30	IV	146-158	1.444-1.454	30	34	20
10	B	72	32	BiCl <sub>3</sub>	3	24	IV	147-148	1.443-1.445	46	49	21
11	C	200 <sup>b</sup>	60	BiCl <sub>3</sub>	6	30	IV	149-155	1.443-1.453	108	42	33
<i>t</i> -Butyl iodide and propene												
12	B	38	15	FeCl <sub>3</sub>	4	31	V	162-165	1.482-1.483	22	47	5

<sup>a</sup> Boiling range of major portion of product which was distilled under reduced pressure. The temperatures given are those at 760 mm. as determined by means of a nomograph prepared for hydrocarbon and halo-hydrocarbon conversions: Lippincott, *Ind. Eng. Chem.*, **38**, 320 (1946). <sup>b</sup> Also 50 g. of *n*-pentane used as diluent. <sup>c</sup> At least 50% boiling at 128-129°, *n*<sub>D</sub><sup>20</sup> 1.419-1.420. <sup>d</sup> Also 10 g. of alumina powder.

atom that holds the smaller number of hydrogen atoms) but also the products of its rearrangement, 2- and 3-chloro-2,3-dimethylpentane. Details of this reaction have since been discussed by Miller<sup>4</sup> who used aluminum chloride as catalyst; he concluded that the chloroheptane formed at -30° consists of about 45% of 2-chloro-4,4-dimethylpentane, the remainder being 3-chloro-2,3-dimethylpentane together with a smaller amount of 2-chloro-2,3-dimethylpentane. The present communication outlines the results with other catalysts as well as with *t*-butyl bromide and *t*-butyl iodide. Also, the reaction of *t*-butyl halides with 1- and with 2-butene is described.

As may be seen from the results summarized in Table I, the condensation of *t*-butyl chloride with propene was catalyzed by a number of halide catalysts, including aluminum chloride, ferric chloride, bismuth chloride, zinc chloride, zirconium chloride, titanium chloride and boron fluoride. The products differed somewhat in their boiling range which depended on the extent of the isomerization of the lowest boiling constituent, the primary product 2-chloro-4,4-dimethylpentane, to 2- and 3-chloro-2,3-dimethylpentanes. The highest proportion of 2-chloro-4,4-dimethylpentane was obtained when bismuth chloride was used as catalyst. Chlorodecanes, the structures of which were not determined, were usually formed as by-products, presumably by the condensation of the tertiary chloroheptanes with propene.

2-Bromo-4,4-dimethylpentane and isomeric bromoheptanes, presumably 2- and 3-bromo-2,3-dimethylpentane, were formed by the reaction of *t*-butyl bromide with propene in the presence of bismuth chloride or ferric chloride at room temperature. A smaller proportion of the tertiary bromides was obtained with the former catalyst.

(4) V. A. Miller, *ibid.*, **69**, 1764 (1947).

Condensation of *t*-butyl iodide and propene occurred in rather good yield in the presence of ferric chloride. The product decomposed to some extent on distillation even under reduced pressure; the distillate was red and opaque. Washing with dilute alkali yielded a pale yellow liquid which turned clear red on standing at room temperature.

The reaction of 1-butene with *t*-butyl chloride in the presence of aluminum chloride at -35 to -25° resulted in a 24% yield of chlorooctane which consisted of chlorodimethylhexanes, principally 3-chloro-5,5-dimethylhexane (Table II). Similar products were obtained in about 35% yield with ferric chloride at -15 to +15° and with bismuth chloride at room temperature.

Condensation of *t*-butyl chloride with 2-butene in the presence of ferric chloride at temperatures below 0° resulted in 55-65% yields of chlorooctane (chiefly 2-chloro-3,4,4-trimethylpentane and 3-chloro-2,2,3-trimethylpentane) boiling at a somewhat higher temperature than the 1-butene product and having a higher refractive index. Similar results were obtained with other catalysts (Table II). It is particularly significant to note that a solution of aluminum chloride in ether catalyzed the condensation, chlorooctane being obtained in 11% yield at a reaction temperature of 26° and in 30% yield at 50°. Solutions of aluminum chloride in excess ethyl ether are inactive for most hydrocarbon condensation reactions which are catalyzed by undissolved aluminum chloride, e.g., the alkylation of benzene.

Condensation of *t*-butyl chloride with 2-butene in the presence of zinc chloride at 60° (Expt. 22) resulted in a 39% yield of chlorooctane and a 36% yield of octenes. Hydrogenation of the latter yielded a mixture of octanes shown by infrared spectral analysis to consist of about 59% 2,2,3-, 29% 2,3,4- and 12% 2,3,3-trimethylpentane; no

TABLE II  
CONDENSATION OF *t*-BUTYL HALIDES WITH 1- AND 2-BUTENE

Expt.	Method	Reactants, g.		Catalyst MX	g.	Temp., °C.	Chief products				Higher boiling prod., g.	
		RX	C <sub>4</sub> H <sub>8</sub>				Compd.	B. p., <sup>a</sup> °C.	<i>n</i> <sub>D</sub> <sup>20</sup>	g.		%
<i>t</i> -Butyl chloride and 1-butene												
13	T	98	59	FeCl <sub>3</sub>	2	-15 to +35	VI	153-156	1.429	88	56	20
14	B	90	45	BiCl <sub>3</sub>	10	22	VI	152-156	1.430	45	38	8
15	A	100 <sup>b</sup>	58	AlCl <sub>3</sub>	4	-35 to -25	VI	154-155	1.430	38	25	
							VII	231-232	1.449	26	12	40
<i>t</i> -Butyl chloride and 2-butene												
16	A	150 <sup>b</sup>	76	FeCl <sub>3</sub>	5	-35 to -25	VIII	159-161	1.442	130	65	12
17	T	105	65	FeCl <sub>3</sub>	2	-30 to 0	VIII	159-160	1.443	87	55	12
18	B	90	45	BiCl <sub>3</sub>	18	25	VIII	158-161	1.442	29	25	8
19	A	151	78	AlCl <sub>3</sub>	3	-45 to -35	VIII	159-160	1.442	36	18	15
20	B	101	62	AlCl <sub>3</sub> <sup>c</sup>	10	50	VIII	160-162	1.442	48	30	15
21	B	50	36	ZnCl <sub>2</sub> <sup>d</sup>	3	24	VIII	158-162	1.443	22	28	10
22	B	100	50	ZnCl <sub>2</sub>	10	60 <sup>e</sup>	VIII	157-159	1.442	52 <sup>f</sup>	39	18
<i>t</i> -Butyl bromide and 2-butene												
23	A <sup>g</sup>	80	40	FeCl <sub>3</sub>	2	<sup>g</sup>	IX	179-182	1.467	42	37	16

<sup>a</sup> See footnote a, Table I. <sup>b</sup> Also 50-100 g. of *n*-pentane used as diluent. <sup>c</sup> Dissolved in 10-12 g. of ethyl ether; the catalyst was soluble in the reactants. <sup>d</sup> 10 g. of alumina impregnated with 25% by weight of zinc chloride. <sup>e</sup> Preceded by 1 hour at room temperature. <sup>f</sup> Also 22 g. of *s*-butyl chloride and 36 g. of octenes (59% 2,2,3-, 29% 2,3,4- and 12% 2,3,3-trimethylpentene). <sup>g</sup> A stirred mixture of the reactants and the catalyst was slowly warmed from -55 to -13°. A vigorous reaction occurred causing the temperature to rise to +23° in less than one minute and resulting in the loss of 20 g. of material from the reaction flask.

2,2,4-trimethylpentane was detected. Dehydrochlorination of the primary product, 2-chloro-3,4,4-trimethylpentane, and its isomers under the condensation conditions is indicated.

A mixture of *t*-butyl bromide and 2-butene reacted very vigorously at about -10° in the presence of less than 2% by weight of ferric chloride. The temperature rose to 23° in less than one minute. Bromooctane, presumably principally 2-bromo-3,4,4-trimethylpentane and 3-bromo-2,2,3-trimethylpentane was obtained in at least 37% yield.

**Dehydrochlorination and Identification of the Chloroalkanes.**—The lower-boiling chloroheptane was shown to be 2-chloro-4,4-dimethylpentane by conversion to known derivatives. The higher-boiling chloroheptane fraction was identified as a mixture of 2- and 3-chloro-2,3-dimethylpentane by comparing its infrared spectrum with those of the synthetic compounds. Its composition was also established by comparing the infrared spectrum of the mixture of alcohols obtained by its hydrolysis with those of 2,3-dimethyl-2-pentanol and 2,3-dimethyl-3-pentanol.

Dehydrohalogenation and hydrolysis of the *t*-heptyl chlorides takes place very readily even at room temperature, 2,3-dimethylpentenes, mixed with more or less heptanol depending on the conditions, being formed. The secondary chloride, on the other hand, undergoes little reaction at the reflux temperature. This offers a means for preparing pure 2-chloro-4,4-dimethylpentane; heating mixtures of this chloride and the 2- and 3-chloro-2,3-dimethylpentane with water at the reflux temperature converts the tertiary halides to heptenes while the secondary chloride is largely unaffected.

Dehydrochlorination of the 2-chloro-4,4-dimethylpentane did occur when it was heated with water at 200°. There was obtained a practically quantitative yield of heptenes consisting of 28%

2,2-dimethylpentenes, 50% 2,3-dimethylpentenes and 22% 2,4-dimethylpentenes. Under alkaline conditions, relatively little rearrangement to the 2,4-dimethylpentene took place. The reaction of the chloride with an aqueous suspension of magnesium oxide at 200° yielded (besides a small amount of heptanol) heptenes consisting of 59% 2,2- and 41% 2,3-dimethylpentene. When the chloroheptane was passed over soda-lime at 260°, it was converted to a mixture of 44% 2,2-, 53% 2,3- and less than 3% 2,4-dimethylpentene.

The chlorooctene prepared from *t*-butyl chloride and 1-butene was dehydrochlorinated by heating with water at 225°. Hydrogenation of the resulting olefins yielded an octane mixture shown by infrared analysis to consist principally of 2,2- and 2,3-dimethylhexane together with a small amount of 2,4-dimethylhexane. By analogy with the reaction of *t*-butyl chloride with propene, it may be concluded that the chlorooctane was 3-chloro-5,5-dimethylhexane (VI) mixed with a small

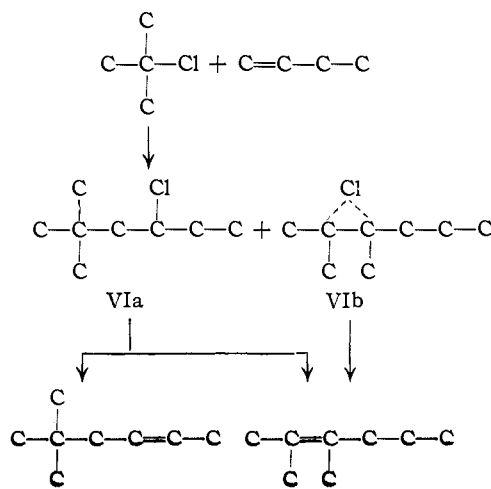


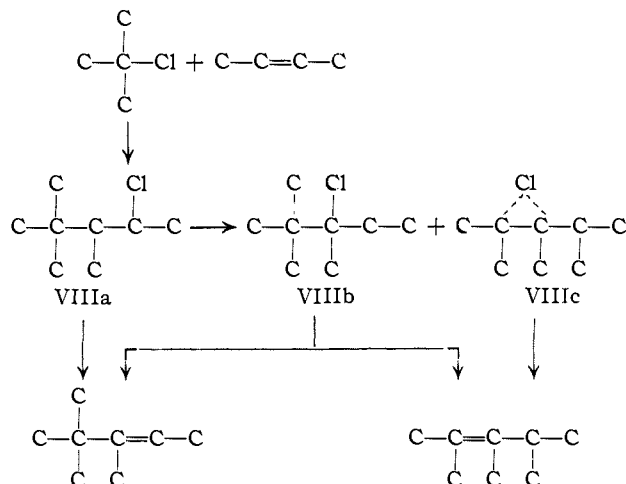
TABLE III  
 PROPERTIES OF THE CONDENSATION PRODUCTS<sup>a</sup>

Compd.	Formula <sup>c</sup>	B.p.,		B.p. at 760 mm., °C.	<i>n</i> <sub>D</sub> <sup>20</sup>	<i>d</i> <sub>4</sub> <sup>20</sup>	Mol. refr.		Analyses, <sup>b</sup> %					
		°C.	Mm.				Calcd.	Obsd.	C	Calcd. H	X	C	Found H	X
I	(CH <sub>3</sub> ) <sub>2</sub> CCH <sub>2</sub> CHClCH <sub>3</sub> <sup>d</sup>	45-45	39	128-128	1.4192	0.8603	39.27	39.48	62.42	11.23	26.35			
II	C <sub>7</sub> H <sub>15</sub> Cl <sup>e</sup>	66-67	70	137-139	1.4275	.8735	39.27	39.56	62.42	11.23	26.35	62.81	11.39	25.73
III	C <sub>10</sub> H <sub>21</sub> Cl <sup>f</sup>	68-69	6	199-200	1.4465	.8736	53.06	53.99						
IV	(CH <sub>3</sub> ) <sub>2</sub> CCH <sub>2</sub> CHBrCH <sub>3</sub> <sup>g</sup>	59-61	36	149-151	1.4433						44.64			44.85
V	(CH <sub>3</sub> ) <sub>2</sub> CCH <sub>2</sub> CHICH <sub>2</sub>	60-63	20	162-165	1.4830	1.3199	45.28	48.44						
VI	(CH <sub>3</sub> ) <sub>2</sub> CCH <sub>2</sub> CHClC <sub>2</sub> H <sub>5</sub>	49-50	15	155-156	1.4284	0.8699	43.85	43.99	64.61	11.53	23.86	65.24	11.55	23.49
VII	C <sub>12</sub> H <sub>25</sub> Cl	77-78	3	231-232	1.4484	.8821	62.26	62.21	70.38	12.31	17.31	70.66	12.28	16.98
VIII	(CH <sub>3</sub> ) <sub>2</sub> CC(CH <sub>3</sub> )ClC <sub>2</sub> H <sub>5</sub> <sup>h</sup>	58-59	21	159-160	1.4420	.8913	43.85	44.07	64.61	11.53	23.86	64.70	11.42	24.09
IX	(CH <sub>3</sub> ) <sub>2</sub> CC(CH <sub>3</sub> )BrC <sub>2</sub> H <sub>5</sub> <sup>i</sup>	56-57	7	181-182	1.4674	1.1359	46.80	47.20						

<sup>a</sup> Refractionated analytical samples. <sup>b</sup> Microanalyses by Dr. T. S. Ma, formerly of the University of Chicago, and by Mr. C. W. Beazley, Micro-Tech Laboratories, Skokie, Ill. <sup>c</sup> Probable formula of principal isomer. <sup>d</sup> Whitmore, *et al.*, THIS JOURNAL, **63**, 2028 (1941), report for 2-chloro-4,4-dimethylpentane: b.p. 63-65° at 85 mm. (corresponds to 125-128° at 760 mm.), *n*<sub>D</sub><sup>20</sup> 1.4178-1.4187. <sup>e</sup> Mixture of 2- and 3-chloro-2,3-dimethylpentane. Miller, *ref. 4*, reports: b.p. 58-60° at 50 mm. (corresponds to 137-140° at 760 mm.), *n*<sub>D</sub><sup>20</sup> 1.428-1.432. <sup>f</sup> Miller reports b.p. 85-93° at 20 mm. (corresponds to 196-205° at 760 mm.), *n*<sub>D</sub><sup>20</sup> 1.440-1.449. <sup>g</sup> That IV was chiefly the secondary alkyl bromide was indicated by the fact that very little hydrolysis occurred when it was stirred with water at room temperature for 48 hours. Whitmore, *et al.*, *ref. d*, report for 2-bromo-4,4-dimethylpentane, b.p. 56-60° at 29-34 mm. (corresponds to about 150° at 760 mm.), *n*<sub>D</sub><sup>20</sup> 1.4460. Kharasch, *ibid.*, **56**, 244 (1934), reports b.p. 59.4° at 34 mm., corresponding to 150° at 760 mm.; *n*<sub>D</sub><sup>20</sup> 1.4463. <sup>h</sup> And isomer. <sup>i</sup> Melting point, -33 to -30°.

amount of 2- and/or 3-chloro-2,3-dimethylhexane (VI). That the amount of the chloro-2,3-dimethylhexanes was not high was indicated by the small amount of the chlorooctane which was decomposed when treated with water at 100°. The product of such treatment was shown to be chiefly VI by converting it to the corresponding ketone which was characterized as 5,5-dimethyl-3-hexanone and to octane which was found to be pure 2,2-dimethylhexane. The presence or absence of 2-chloro-5,5-dimethylhexane was not established.

The chlorooctane derived from 2-butene consisted of chlorotrimethylpentanes; conversion to octane *via* dehydrochlorination to octene yielded a product shown by infrared analysis to be a mixture of 2,2,3- and 2,3,4-trimethylpentane in approximately equal amount.<sup>5</sup>



Infrared analysis indicated that the chlorooctane consisted of about 40% 3-chloro-2,2,3-trimethylpentane (VIIIb) mixed with an isomer,

(5) It is significant to note that the octenes (76% yield) obtained by the copolymerization of *s*- and *t*-butyl alcohols consisted of 53% 3,4,4-trimethyl-2-pentene and 47% 2,3,4-trimethyl-2-pentene; F. C. Whitmore, K. C. Laughlin, J. F. Matuszeski and J. D. Surmatis, THIS JOURNAL, **63**, 756 (1941). The products of both the dehydrochlorination and the copolymerization may best be explained by carbonium ion mechanisms.

probably the primary product VIIIa, which contains chlorine attached to a carbon atom adjacent to a tertiary carbon atom holding hydrogen. Isomerization of VIIIa is analogous to the formation of 2-chloro-2-methylbutane in the reaction of 3-methyl-2-butanol with hydrochloric acid. The presence of some VIIIc was indicated by the fact that hydrolysis of the Grignard reagent of the chlorooctane yielded 2,2,3-trimethylpentane mixed with a lesser amount of 2,3,4-trimethylpentane.

### Experimental

**Condensation of *t*-Butyl Halides with Olefins.**—The procedures were similar to those previously described for the condensation of alkyl halides with ethylene<sup>6</sup> and with haloolefins.<sup>6</sup> They will be outlined briefly here.

In method A, olefin was bubbled through a stirred mixture of *t*-butyl chloride, *n*-pentane diluent (if used) and the catalyst in a three-necked flask equipped with an inlet tube, a mercury-sealed stirrer and a reflux condenser (cooled with Dry Ice-acetone mixture).

In method B, the *t*-butyl halide and the liquefied olefin, cooled to about -78°, were weighed into a glass liner and the catalyst was added. The liner was sealed into an Ipatieff-type rotating autoclave of 850-cc. capacity which was then charged to 30-50 atm. pressure with nitrogen.

The autoclave was rotated at the desired temperature (usually room temperature) for 4 hours and then permitted to stand at room temperature overnight before it was opened.

In method C, the catalyst was sealed into an autoclave equipped with a very efficient stirrer (a "turbomixer").

The autoclave was cooled to a temperature somewhat below the desired reaction temperature, evacuated, and the *t*-butyl halide and diluent (if used) sucked in. The stirrer was started and the olefin was added gradually, as a liquid, from a calibrated charger.

In method T, the catalyst was added to the reactants in a large "test-tube" cooled to about -65° and the mixture then allowed to warm up to the reaction temperature while being shaken manually.

**Identification of the Chloroheptanes.** The Lower-boiling Chloroheptane.—The structure of the lower-boiling chloroheptane (b.p. 127-128°) was established as 2-chloro-4,4-dimethylpentane in the same manner as that subsequently described by Miller<sup>4</sup>: by way of the Grignard reagent, it was converted to the previously reported methylnepentylacetanilide,<sup>8</sup> m.p. 118-119°, and 4,4-dimethyl-2-pentanol, which

(6) L. Schmerling, *ibid.*, **63**, 1650 (1946).

(7) G. L. Hervert, U. S. Patent 2,377,937.

(8) F. C. Whitmore, C. I. Noll, J. W. Heyd and J. D. Surmatis, THIS JOURNAL, **63**, 2028 (1941).

was characterized as the 3,5-dinitrobenzoate,<sup>9</sup> m.p. 94.5–95.5°, and the  $\alpha$ -naphthylurethan,<sup>9</sup> m.p. 86–87°.

**The Higher-boiling Chloroheptane.** A. **Synthesis of 2,3-Dimethyl-2- and 3-Pentanol.**—2,3-Dimethyl-2-pentanol (contaminated with mesityl oxide) was prepared by the reaction of acetone with *s*-butylmagnesium chloride<sup>10,11</sup>; b.p. 51–52° (20 mm.), 137–138° (760 mm.),  $n_D^{20}$  1.4276–1.4304. It yielded a 3,5-dinitrobenzoate (pyridine used as solvent), m.p. 77–78°, and the  $\alpha$ -naphthylamine addition compound which melted at 105–106°.

2,3-Dimethyl-3-pentanol was obtained by the reaction of methyl ethyl ketone with isopropylmagnesium chloride<sup>11</sup>; b.p. 50–52° (20 mm.), 137–138° (760 mm.),  $n_D^{20}$  1.4295–1.4309; 3,5-dinitrobenzoate (by pyridine method) nacreous flakes, m.p. 87°;  $\alpha$ -naphthylamine addition compound, m.p. 107°.

A sample of the higher-boiling chloride (13 g., b.p. 139–140°,  $n_D^{20}$  1.4302) obtained by the condensation of *t*-butyl chloride with propene in the presence of ferric chloride (expt. 2) was heated under reflux for 20 hours with a suspension of 5 g. of magnesium oxide in 100 cc. of water. The product was steam distilled and the organic layer was separated, washed, dried and distilled. There was obtained, besides about 3 g. of heptene, 5 g. of heptanol (b.p. 134–136°,  $n_D^{20}$  1.4260) which yielded (by the pyridine method) a 3,5-dinitrobenzoate, m.p. 70–71°;  $\alpha$ -naphthylamine addition compound, m.p. 100°. A mixture of the dinitrobenzoate with the 3,5-dinitrobenzoate of 2,3-dimethyl-2-pentanol melted at 73–74°. A mixture of the  $\alpha$ -naphthylamine addition compound with the analogous derivative of 2,3-dimethyl-2-pentanol melted at 101–102°, with the derivative of 2,3-dimethyl-3-pentanol at 92–93°.

Comparison of the infrared spectrum of the alcohol obtained by hydrolysis of the chloride with those of the synthesized dimethylpentanols indicated that the alcohol was a mixture of the two isomers. The 3,5-dinitrobenzoate of the 2,3-dimethyl-3-pentanol apparently was formed less readily than that of the 2,3-dimethyl-2-pentanol.

**B. Synthesis of Chloroheptanes.**—A mixture of 10 cc. of the 2,3-dimethyl-2-pentanol and 30 cc. of concentrated hydrochloric acid was shaken for 5 minutes and then permitted to set over a week-end. The product was washed with water followed by sodium bisulfite (to remove mesityl oxide originally present in the heptanol), dried and distilled. There was obtained 4 g. of 2-chloro-2,3-dimethylpentane, b.p. 49–50° (30 mm.), 140–141° (760 mm.),  $n_D^{20}$  1.4290.

The reaction of 10 cc. of 2,3-dimethyl-3-pentanol with 25 cc. of hydrochloric acid under similar conditions yielded 5.5 g. of 3-chloro-2,3-dimethylpentane, b.p. 50° (30 mm.), 141° (760 mm.),  $n_D^{20}$  1.4317–1.4320.

The infrared spectrum of the higher-boiling chloroheptane (b.p. 51–52° at 30 mm.) obtained in expt. 1 showed that it contained 30% 2- and 60% 3-chloro-2,3-dimethylpentane, the remainder being unidentified.

**Purification of 2-Chloro-4,4-dimethylpentane.**—A sample (27 g., 0.20 mole, b.p. 129–133°,  $n_D^{20}$  1.4200–1.4225) of the lower-boiling fractions of the chloroheptane obtained in expt. 3 was heated with 250 g. of water under reflux for 8 hours. Titration of the aqueous layer indicated that 0.038 mole of hydrogen chloride had been liberated. Distillation of the organic layer (25.5 cc.) yielded the following fractions: 6.5 cc., b.p. 92–123°,  $n_D^{20}$  1.4160; 17.5 cc., b.p. 127–128° (745 mm.),  $n_D^{20}$  1.4186; 1.5 cc. residue,  $n_D^{20}$  1.4220.

**Dehydrochlorination of 2-Chloro-4,4-dimethylpentane.** (A) **With Water.**—A sealed tube containing 18 g. (0.14 mole) of 2-chloro-4,4-dimethylpentane and 125 g. of water was heated at 200° for 5 hours. There was recovered 12.5 g. (0.13 mole) of heptene, b.p. 80–95°. Hydrogenation of this material at room temperature in the presence of 2 g. of U.O.P. nickel-kieselguhr under 100 atm. initial hydrogen pressure yielded heptane, b.p. 81–87°,  $n_D^{20}$  1.3881. Infrared absorption analysis indicated that it consisted of 28% 2,2-dimethylpentane, 50% 2,3-dimethylpentane and 22% 2,4-dimethylpentane.

(B) **With Water and Magnesium Hydroxide.**—A sealed tube containing 20 g. (0.15 mole) of the chloride, 8 g. (0.20 mole) of magnesium oxide and 100 g. of water was heated at 200° for 5 hours in an Ipatieff-type rotating autoclave.

Distillation of the 13 g. of organic product yielded 10 g. (0.10 mole) of heptenes, b.p. 76–95°, and about 2 g. of 4,4-dimethyl-2-pentanol, characterized as the 3,5-dinitrobenzoate, m.p. and "mixed m.p." 95–96°. Hydrogenation of the heptene yielded heptane, b.p. 80–85°,  $n_D^{20}$  1.3860, the infrared absorption spectrum of which indicated that it consisted of 59% 2,2-dimethylpentane and 41% 2,3-dimethylpentane; about 1–2% of 2,4-dimethylpentane *might* have been present (the determination of such small quantities in this mixture is difficult).

(C) **With Soda-lime.**—2-Chloro-4,4-dimethylpentane (14 g.) was passed over 50 cc. of 4–8 mesh soda-lime heated to 260° in a 10 mm. i.d. glass tube in a vertical furnace. The chloride was added dropwise during 80 minutes. There was recovered 13 cc. of organic product, fractionation of which yielded 10.1 cc., b.p. 79–92°,  $n_D^{20}$  1.4041; 1.1 cc., b.p. 92–93°; 1.3 cc. residue. Hydrogenation of the combined distillate yielded octane shown by infrared analysis to be a mixture of approximately 44% 2,2-dimethylpentane, 53% 2,3-dimethylpentane and 3% of 2,4-dimethylpentane and 2- and 3-methylhexane.

**Purification and Identification of 3-Chloro-5,5-dimethylhexane.**—A mixture of 55 g. (0.37 mole) of the product of expt. 13 (b.p. 36–39° at 8.5 mm.,  $n_D^{20}$  1.4268) and 750 cc. of water was refluxed for 16 hours. The aqueous product contained 0.077 mole of hydrogen chloride indicating that about 20% of the chlorooctane had been dehydrochlorinated. Distillation of the organic layer yielded 39 g. (0.26 mole, 70%) of 3-chloro-5,5-dimethylhexane, b.p. 60–61° (26 mm.),  $n_D^{20}$  1.4268.

The purified chlorodimethylhexane was converted to the corresponding alcohol (5,5-dimethyl-3-hexanol) by way of the Grignard reagent; b.p. 56–60° (10 mm.),  $n_D^{20}$  1.4262.

*Anal.* Calcd. for  $C_8H_{18}O$ : C, 73.78; H, 13.93. Found: C, 74.26; H, 13.93.

The 3,5-dinitrobenzoate of the alcohol melted at 73–74°.

*Anal.* Calcd. for  $C_{15}H_{26}N_2O_6$ : N, 8.63. Found: N, 8.73.

Oxidation of the alcohol by heating 4.5 g. of the material with a solution of 1 g. of sodium dichromate and 1 g. of sulfuric acid in 50 cc. of water at 52–56° yielded 5,5-dimethyl-3-hexanone, characterized as the semicarbazone,<sup>12</sup> m.p. 157–158°, which did not depress the melting point of an authentic specimen (m.p. 162°) obtained from Prof. E. B. Reid. The somewhat low melting point of the semicarbazone seemed to indicate the presence of a small amount of another ketone (e.g., 5,5-dimethyl-2-hexanone) formed from 2-chloro-5,5-dimethylhexane present in VI.

The *gem*-dimethylhexane structure of the chlorooctane was confirmed by hydrolyzing the Grignard reagent; infrared analysis of the resulting octane showed that it was pure 2,2-dimethylhexane.

**Identification of 3-Chloro-2,2,3-trimethylpentane.**—A sample of 3-chloro-2,2,3-trimethylpentane prepared by the reaction of 2,2,3-trimethyl-3-pentanol with dry hydrogen chloride was obtained from Prof. H. C. Brown and its infrared spectrum was compared with that of VIII (the products of expts. 16 and 19, the spectra of which were practically identical). It was estimated that VIII contained about 40% of 3-chloro-2,2,3-trimethylpentane. That most of the remainder of VIII also had the 2,2,3-trimethylpentane structure (and was presumably 2-chloro-3,4,4-trimethylpentane) was shown by converting a sample of the chlorooctane to the octane *via* the Grignard reagent; infrared analysis indicated that the paraffin consisted of 2,2,3-trimethylpentane mixed with a minor amount of 2,3,4-trimethylpentane.

**Dehydrochlorination of Chlorooctanes.** (A) **Product from 1-Butene.**—A mixture of 100 cc. of water and 30 g. of the chlorooctane (b.p. 52–53° at 20 mm.,  $n_D^{20}$  1.4290) obtained by the reaction of *t*-butyl chloride and 1-butene in the presence of bismuth chloride (expt. 14) was heated in a sealed tube in a rotating autoclave at 225° for 4 hours. Distillation of the reaction product yielded 16 g. of octene, b.p. 107–118°,  $n_D^{20}$  1.4089–1.4176; residue, 5 g., containing some alkyl chloride. Hydrogenation of the octene gave octane boiling at 106–114°,  $n_D^{20}$  1.3927–1.4002; infrared analysis indicated that it consisted of approximately 60% 2,2-dimethylhexane, 35% 2,3-dimethylhexane and 5% 2,4-dimethylhexane.

(9) F. C. Whitmore and A. H. Homeyer, *ibid.*, **55**, 4194 (1933).

(10) G. Edgar, G. Callngaert and R. E. Marker, *ibid.*, **51**, 1486 (1929).

(11) F. H. Norton and H. B. Hass, *ibid.*, **58**, 2148 (1936).

(12) E. B. Reid and R. B. Fortenbaugh, *J. Org. Chem.*, **16**, 33 (1951).

(B) **Product from 2-Butene.**—The chlorooctane (b.p. 58–59° at 21 mm.,  $n_D^{20}$  1.4427–1.4491) obtained by the condensation of *t*-butyl chloride with 2-butene in the presence of ferric chloride (expt. 17) was converted to octene by heating with water at 200°. Experiments in which 90–135 g. of the chloride was heated with 150 cc. of water in a sealed tube yielded 65–100 g. of product which still contained chlorine; distillation of a sample indicated that about 15% of the product was unreacted. The material was therefore further dehydrochlorinated by heating at 225° with an aqueous suspension of calcium hydroxide: two runs were made in each of which 220–240 cc. of the olefin-chlorooctane mixture was treated with 10 g. of calcium oxide and 50 cc. of water. The product which contained only traces of chlorine boiled chiefly at 103–112°,  $n_D^{20}$  1.4195–1.4265. Hydrogenation yielded octane boiling at 110–112°,  $n_D^{20}$  1.4036–1.4051. It was shown by infrared analysis to consist of 52% 2,2,3- and 48% 2,3,4-trimethylpentane.

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(13) Beckman Instrument, Incorporated, South Pasadena, California.

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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

## Studies in the Terpene Series. XVII.<sup>1</sup> The Thermal Isomerization of Pinane at High Pressure<sup>2,3</sup>

BY V. N. IPATIEFF,<sup>4</sup> WILLIAM D. HUNTSMAN<sup>5</sup> AND HERMAN PINES

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Pinane was isomerized at 400° and 815 atmospheres. The major product appeared to be 1-*trans*-2-dimethyl-*cis*-3-isopropenylcyclopentane. The yield of this compound and double bond isomers of it totaled 34% of the pinane converted. In addition, an unidentified isomeric bicyclic hydrocarbon, other alkenylcyclopentanes and higher boiling hydrocarbons were formed.

The non-catalytic isomerization of terpenes and hydroterpenes at high temperatures has been the subject of a number of investigations.<sup>6</sup> However, the effect of pressure on these reactions has not been reported. For that reason, a study of the isomerization of pinane at 815 atmospheres was undertaken.

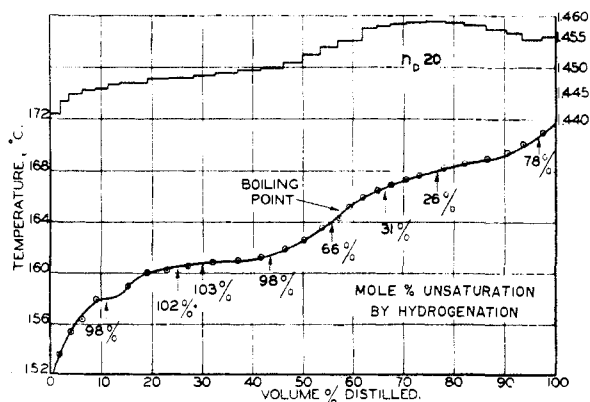


Fig. 1.

(1) For the previous paper of this series, see V. N. Ipatieff, F. J. Pavlik and H. Pines, *THIS JOURNAL*, **75**, 3179 (1953).

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(3) Presented before the Organic Division of the American Chemical Society Meeting at Los Angeles, Calif., March 16–19, 1953.

(4) Deceased, November 29, 1952.

(5) Postdoctoral Research Associate, 1950–1951.

(6) (a) B. A. Arbuzov, *Ber.*, **67B**, 1946 (1934); (b) G. Dupont and R. Dulou, *Compt. rend.*, **201**, 219 (1935); (c) R. E. Fuguit and J. E. Hawkins, *THIS JOURNAL*, **67**, 242 (1945); (d) L. A. Goldblatt and S. Palkin, *ibid.*, **63**, 3517 (1941); **66**, 655 (1944); (e) L. Rummelsburg, *ibid.*, **66**, 1718 (1944); (f) T. R. Savich and L. A. Goldblatt, *ibid.*, **67**, 2027 (1945).

The reaction was carried out in a copper tube packed with copper pellets, which has been shown to exhibit no catalytic activity. A temperature of 400° was found to be adequate for reaction at 815 atmospheres, although pinane underwent no appreciable change at 400° and atmospheric pressure.

The product, obtained in 99% yield, comprised a mixture of liquid hydrocarbons of which about 3% distilled below 152°, 69% distilled at 152–172°, and the remainder boiled above 172°. The 152–172° fraction was investigated in some detail.

A fractionation curve of this material is shown in Fig. 1, where the percentage unsaturation for several of the fractions, as determined by hydrogenation, is also shown. A well-defined plateau is indicated at 160–162° and, in fact, infrared spectra of first, center and last cuts in this boiling range were identical. This material absorbed hydrogen equivalent to one double bond per mole and its infrared spectrum had a strong band at 880  $\text{cm}^{-1}$  indicative of a disubstituted terminal double bond,  $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$ .<sup>7</sup> It was identified as 1-*trans*-2-dimethyl-*cis*-3-isopropenylcyclopentane (I) by chemical degradation to known hydrocarbons shown.

Ozonization gave formaldehyde and a ketone,  $\text{C}_9\text{H}_{16}\text{O}$  (III), which gave a positive iodoform test. Oxidation of the ketone with sodium hypobromite gave an acid,  $\text{C}_8\text{H}_{14}\text{O}_2$  (IV). Reduction of this acid with lithium aluminum hydride yielded a primary alcohol,  $\text{C}_8\text{H}_{16}\text{O}$  (V). Hydrogenolysis of this primary alcohol at 160–180° in the presence of nickel-kieselguhr<sup>8</sup> gave practically pure 1-*trans*-2-dimethylcyclopentane.

(7) H. W. Thompson and O. H. Whiffen, *J. Chem. Soc.*, 1412 (1948).

(8) V. N. Ipatieff, G. J. Czajkowski and H. Pines, *THIS JOURNAL*, **73**, 4098 (1951).