white solid which appeared toward the end of the reaction time was collected and washed with pentane. Dilution of the mother liquor with an equal volume of pentane caused more precipitation. The combined solids (3.6 g., 51% yield) on recrystallization from benzene afforded long white needles melting at 108–110° (Kofler).

Anal. Calcd. for $C_{16}H_{12}O_7$: C, 60.76; H, 3.83. Found: C, 60.77; H, 3.94.

The reaction of a benzene solution of this ozonide with 2–4 moles of a solution of triphenylmethyl in benzene gave, after a varying short induction period, a bright red color which faded after standing for several minutes. From such mixtures could be isolated by fractionation with pentane or chromatographic absorption on alumina (1) unchanged ozonide, (2) triphenylmethyl carbinol, m.p. 162°, (3) triphenylmethyl peroxide, m.p. 186°, (4) in one instance a very small amount of colorless needles, m.p. 91–98°, possibly a molecular complex or mixture of the ozonide with hexaphenylethane: infrared spectrum: 5.60, carbonyl of the ozonide, 6.10[8], phenyl band present in triphenylmethyl derivatives.

BETHESDA 14, MD.

[CONTRIBUTION FROM THE UNIVERSAL OIL PRODUCTS COMPANY]

The Mechanism of the Alkylation of Paraffins. III. The Reaction of Isobutane with 2-Chloro-4,4-dimethylpentane, 3-Chloro-5,5-dimethylhexane and 2- and 3-Chloro-3,4,4-trimethylpentane

BY LOUIS SCHMERLING AND J. P. WEST

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The hydrogen–chlorine exchange reaction of 2-chloro-4,4-dimethylpentane with isobutane in the presence of aluminum chloride yielded 2,3- and 2,4-dimethylpentane in approximately equal amount. Similarly, skeletal rearrangement accompanying the reaction of 3-chloro-5,5-dimethylhexane with isobutane resulted in the formation of octane consisting of 34% 2,3- and 66% 2,4- and 2,5-dimethylhexane. The analogous reaction of 2- and 3-chloro-3,4,4-trimethylpentane yielded a mixture of trimethylpentanes (61% 2,2,4-, 28% of 2,3,4- and 11% 2,3,3-trimethylpentane). The significance of these results which may be considered as further evidence in support of the chain mechanism for the alkylation of isobutane with propene, 1-butene and 2-butene, respectively, is discussed.

In previous papers[1] in this series, evidence was described in support of a chain mechanism for the catalytic alkylation of isoparaffins with olefins. Further confirmation and an answer to an objection which has been raised are presented in the present communication.

Described in molecular (rather than ionic) terms the alkylation of isobutane with propene in the presence of aluminum chloride and hydrogen chloride involves the conversion of the isobutane to *t*-butyl chloride, the condensation of the *t*-butyl chloride with propene to yield 2-chloro-4,4-dimethylpentane and its isomerization products, 2- and 3-chloro-2,3-dimethylpentane. The chloroheptanes are subsequently converted to dimethylpentanes (an approximately equimolar mixture of 2,3- and 2,4-dimethylpentane) by chlorine–hydrogen exchange with isobutane which is thereby converted to *t*-butyl chloride and a new cycle is started. Miller[2] has pointed out that no chloro-2,4-dimethylpentanes were found in the product of the condensation of *t*-butyl chloride with propene in the presence of aluminum chloride although 2,4-dimethylpentane is a product of the aluminum chloride catalyzed alkylation of isobutane with propene.[3] That this observation (which had also been made in these laboratories) is not at variance with the proposed mechanism was shown by determining the products of the reaction of 2-chloro-4,4-dimethylpentane with isobutane in the presence of aluminum chloride at −35 to −7°. Hydrogen–chlorine exchange[4] occurred yielding heptanes and *t*-butyl chloride. The product formed by the reaction of 0.16 mole of the chloroheptane with excess isobutane consisted of 0.003 mole of pentane, 0.083 mole of *t*-butyl chloride, 0.053 mole of 2,4-dimethylpentane, 0.052 mole of 2,3-dimethylpentane and a minor amount of higher boiling material (Table I). There was no evidence of the presence of 2,2-dimethylpentane. It is obvious that the 2-chloro-4,4-dimethylpentane undergoes complete rearrangement during the chlorine–hydrogen exchange and that formation of 2,4-dimethylpentane occurs under alkylation conditions. The isolation of only 0.083 mole of *t*-butyl chloride per 0.105 mole of dimethylpentane was presumably due to interaction of the chloride with the catalyst to form lower layer complex.

The same complex reaction intermediate, $(CH_3)_3CCH_2CHCH_3^+(AlCl_4)^-$, is presumably involved as primary intermediate in the formation of 2,3- and 2,4-dimethylpentane by the reaction of isobutane with 2-chloro-4,4-dimethylpentane, and in the formation of 2-chloro-4,4-dimethylpentane and 2- and 3-chloro-2,3-dimethylpentane by the addition of *t*-butyl chloride to propene. The difference in skeletal structures of the products of the two reactions is due to a difference in the ease of the final step in each case.

Heptane is formed by the abstraction of a hydride ion from isobutane by a heptyl cation. Since this reaction occurs most readily with *t*-carbonium ions (II, IV and V), the heptane consists of 2,3- and 2,4-dimethylpentane mixed with little 2,2-dimethylpentane.

The chloroheptane is formed in part by dissociation of the complex, $C_7H_{15}^+AlCl_4^-$, but chiefly by the abstraction of a chloride ion from *t*-butyl chloride by a carbonium ion.[5] These are compara-

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[1] (a) L. Schmerling, THIS JOURNAL, **66**, 1422 (1944); (b) **67**, 1778 (1945); (c) **68**, 275 (1946).

[2] V. A. Miller, *ibid.*, **69**, 1764 (1947).

[3] (a) H. Pines, A. V. Grosse and V. N. Ipatieff, *ibid.*, **64**, 33 (1942); (b) L. Schmerling, *ibid.*, **68**, 275 (1946).

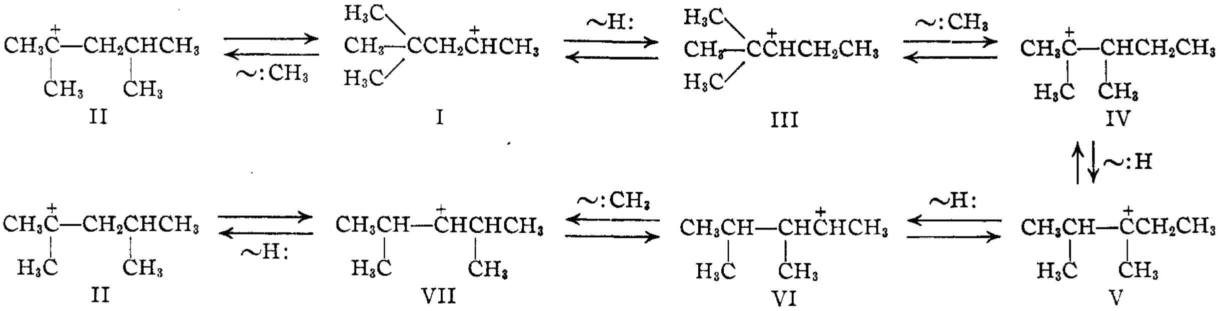
[4] P. D. Bartlett, F. E. Condon and A. Schneider, *ibid.*, **66**, 1534 (1944).

[5] *Cf.* L. Schmerling and J. P. West, *ibid.*, **74**, 3592 (1952).

$$(CH_3)_3CCl + AlCl_3 \rightleftarrows (CH_3)_3C^+(AlCl_4)^-$$

$$(CH_3)_3C^+(AlCl_4)^- + CH_2{=}CH{-}CH_3 \rightleftarrows (CH_3)_3CCH_2\overset{+}{C}HCH_3(AlCl_4)^-$$

I



tively rapid reactions (compared with abstraction of a hydride ion) and occur readily with the secondary alkyl ion (I) as well as the tertiary ions (IV and V) yielding, respectively, 2-chloro-4,4-dimethylpentane and 2- and 3-chloro-2,3-dimethylpentane. The absence of 2-chloro-2,4-dimethylpentane indicates that II forms too slowly to take part in the reaction with *t*-butyl chloride; furthermore, it seems to show that the direct formation of II from I by 1,3-shift is less probable than the sequence of 1,2-shifts involving VI and VII.

TABLE I

COMPOSITION OF THE PRODUCT OF THE REACTION OF 2-CHLORO-4,4-DIMETHYLPENTANE WITH ISOBUTANE

Fraction	B.p., °C.	Vol., cc.	Wt., g.	n^{22}_D	Composition[a], vol., % i-C_4H_{10}	C_5H_{12}	t-BuCl	2,4-DP[b]	2,3-DP[c]	Higher
A	<10	..	3.4	....	71	6	23			
1	50–55	4.2	3.6	1.3817			94	6		
2	55–65	4.2	3.5	1.3823			82	14	4	
3	65–79	1.4	1.0	1.3823			55	35	10	
4	79–89	10.6	7.3	1.3870			2	48	50	
5	89–93	1.9	1.3	1.3905				25	65	10
6	93–96	1.3	0.9	1.3937				20	62	18
Residue		2.0	1.5	1.4153						
Total, mole						0.003	0.083	0.053	0.052	

[a] By infrared absorption analysis, except fraction A which was analyzed by distillation through a low temperature Podbielniak column. The infrared analyst (Dr. W. S. Gallaway) indicated that fraction 1 might contain traces of 2,2- and 2,3-dimethylbutane, and that no 2,2,3-trimethylbutane, methylpentane or methylhexane was detected in any fraction (*i.e.*, these compounds were each present to the extent of less than 1%). [b] 2,4-Dimethylpentane. [c] 2,3-Dimethylpentane.

Similarly, the fact that the condensation of *t*-butyl chloride with ethylene in the presence of aluminum chloride yields 1-chloro-3,3-dimethylbutane[6] while the reaction of this chlorodimethylbutane with isobutane in the presence of the same catalyst yields 2,3-dimethylbutane (and only a minor amount of 2,2-dimethylbutane)[1b] may also be explained as inherent in the difference in ease of abstraction of chlorine from *t*-butyl chloride and of hydrogen from isobutane.

Complete skeletal rearrangement accompanied the hydrogen transfer reaction which occurred when 3-chloro-5,5-dimethylhexane was treated with isobutane and aluminum chloride catalyst at room temperature; the octane consisted of 35% 2,3- and 65% 2,4- and 2,5-dimethylhexane (Table II). This is related to the fact that the alkylation of isobutane with 1-butene yields 2,3-, 2,4- and 2,5-dimethylhexane and very little or no 2,2-dimethylhexane. For example, the alkylation of isobutane with 1-butene in the presence of aluminum chloride monomethanolate at 55° yields an alkylate consisting of 60% dimethylhexane (28% 2,3-, 59% 2,3- and 2,4-, and 13% 3,4-dimethylhexane) and 9.5% trimethylpentane (presumably formed *via* isomerization of part of the 1-butene to 2-butene).[3b]

Similarly, the fact that 2,2,3-trimethylpentane is formed in only a very small amount by the alkylation of isobutane with 2-butene is explained by the observation that the reaction of a mixture of 2-

TABLE II

COMPOSITION OF THE PRODUCT OF THE REACTION OF 3-CHLORO-5,5-DIMETHYLHEXANE WITH ISOBUTANE

Fraction	B.p., °C.	Vol., cc.	Wt., g.	n^{20}_D	Composition,[a] vol. % t-BuCl	Dimethylhexanes 2,3-	2,4- and 2,5-
A	[b]	2.7	1.9		40		
1	42–57	5.3	4.1	1.3790	50[c]		
2	57–103	4.2	3.1	1.3842	35[c]		
3	103–106	2.9	2.0	1.3942		30[d]	70[e]
4	106–108	3.7	2.6	1.3958		25	75
5	108–113	12.5	8.8	1.3978		35	65
6	113–121	3.8	2.7	1.4009		50	50
7	121–133	1.2	0.8	1.4088			
Residue		..	3.5[f]	1.4232			
Total, mole					0.046	0.050	0.091

[a] By infrared absorption analysis. [b] Residue obtained by permitting the recovered isobutane to evaporate. [c] Dr. W. S. Gallaway reported that the fractions contained too much *t*-butyl chloride to permit complete analysis of these fractions. [d] The higher value for 2,3-dimethylhexane in this fraction as compared to fraction 4 is probably due to the presence of 2,3-dimethylbutane or 2,3-dimethylpentane. A split is not reliable here (W. S. G.). [e] Dr. Gallaway estimated that the 2,5-isomer made up about 30–40% of the mixture of 2,4- and 2,5-dimethylhexane; up to 5% of 2,2-dimethylhexane may have been present. Trimethylpentanes were not present in measurable amount. [f] Alkyl chloride.

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

TABLE III

COMPOSITION OF THE PRODUCT OF THE REACTION OF 2- AND 3-CHLORO-3,4,4-TRIMETHYLPENTANE WITH ISOBUTANE

Fraction	B.p., °C.	Vol., cc.	Wt., g.	$n^{20}\mathrm{D}$	Composition,[a] vol. %				
					t-BuCl	Trimethylpentane 2,2,4-	2,3,4-	2,3,3-	Higher boiling
1	53–57	4.0	3.3	1.3846	91	6	3		
2	57–70	2.9	2.4	1.3850	87	9	4		
3	70–95	2.1	1.6	1.3882	49	40	7	4	
4	95–104	7.1	4.9	1.3956	2	69	21	8	
5	104–112	5.7	4.0	1.3998		52	33	15	
6	112–113	1.4	1.0	1.4023		30	45	20	5
Residue			3.0	1.4193					
Total, mole					0.067	0.058	0.027	0.011	

[a] By infrared absorption analysis. Dr. W. S. Gallaway indicated that "for the early fractions, it is difficult to be certain that the small components are octanes and not hexanes or heptanes; it is believed that they are octanes. The later fractions may contain small amounts of dimethylhexanes, but their presence was not established: 2,2,3-trimethylpentane appears to be absent or present in too low concentration to be determined."

and 3-chloro-3,4,4-trimethylpentane[7] with isobutane at −20 to −8° yielded a mixture of trimethylpentanes consisting of 61% 2,2,4-, 28% 2,3,4- and 11% 2,3,3-trimethylpentane (Table III). The alkylate obtained by the reaction of isobutane with 2-butene at 28° in the presence of aluminum chloride monomethanolate included 65% of trimethylpentanes (43% 2,2,4-, 34% 2,3,4-, 22% 2,3,3- and less than 1% 2,2,3-trimethylpentane) and 4% dimethylhexanes.[3b]

A higher temperature was required for the reaction of isobutane with the 3-chloro-5,5-dimethylhexane than with the mixture of chlorotrimethylpentanes. This is analogous to the fact that a higher temperature was required for the alkylation of isobutane with 1-butene than with 2-butene in the presence of aluminum chloride monomethanolate as catalyst.[3b]

Experimental

Preparation of Chloroalkanes.—2-Chloro-4,4-dimethylpentane[8] was prepared by the condensation of *t*-butyl chloride with propene in the presence of bismuth chloride at room temperature. It was heated with water under reflux for 16 hours in order to remove the *t*-alkyl chlorides, 2- and 3-chloro-2,3-dimethylpentane. The purified product had a constant b.p., 45°, at 39 mm. (128° at 760 mm.); $n^{20}\mathrm{D}$ 1.4192.

3-Chloro-5,5-dimethylhexane[8] was synthesized by the reaction of *t*-butyl chloride with 1-butene in the presence of ferric chloride. It was freed of contaminating isomers by heating with water at the reflux temperature for 16 hours; b.p. 60–61° at 26 mm. (156–157° at 760 mm.); $n^{20}\mathrm{D}$ 1.4268.

A mixture of 2- and 3-chloro-3,4,4-trimethylpentane[8] (which may have contained a minor amount of chloro-2,3,4-trimethylpentane) was obtained by the reaction of *t*-butyl chloride and 2-butene in the presence of ferric chloride at −25 to −35°. The redistilled product boiled at 58–59° at 20 mm. (160–161° at 760 mm.); $n^{20}\mathrm{D}$ 1.4427.

Reaction of 2-Chloro-4,4-Dimethylpentane with Isobutane.—To a well-stirred mixture of 110 g. (1.9 moles) of isobutane and 3 g. of aluminum chloride (20 mesh) in a three-necked flask immersed in a bath at about −35°, there was gradually added, during 35 minutes, 21.5 g. (0.16 mole) of 2-chloro-4,4-dimethylpentane. The reaction temperature was maintained at −20° during the addition of the chloride and then was permitted to rise slowly to −7° during the next 90 minutes. The product was cooled to −35° and the liquid upper layer was decanted from the 5 g. of catalyst layer into a trap containing ice, and then stabilized at room temperature to separate unreacted isobutane. The 22.5 g. of dried residue was distilled and the fractions were analyzed by means of infrared absorption analysis. The data are summarized in Table I.

Reaction of 3-Chloro-5,5-dimethylhexane with Isobutane.—A mixture of 30 g. (0.20 mole) of the 3-chloro-5,5-dimethylhexane, 103 g. (1.8 moles) of isobutane and 2 g. of aluminum chloride was sealed into an Ipatieff-type rotating autoclave, 50 atmospheres of nitrogen was pressed in and the mixture was rotated at room temperature for six hours and then permitted to stand overnight. The gaseous product was discharged through a soda-lime tower which gained 1 g. The liquid product was then separated from the 7.5 g. of amber semi-solid catalyst layer and stabilized; the soda-lime tower gained an additional 3 g. The residue (35 g.) was washed with water, dried, and the 30.5 g. of product was distilled and analyzed (Table II).

Reaction of 2- and 3-Chloro-3,4,4-trimethylpentane with Isobutane.—Twenty-three grams of the chloroöctane (0.15 mole) was added to a stirred mixture of 116 g. (2.0 moles) of isobutane and 3 g. of aluminum chloride at −20° during one hour. Since there was little reaction, the stirred mixture was warmed to −8° during 40 minutes. The product was cooled to −30° and the 134 g. of water-white upper layer was decanted from the 3.5 g. of orange semi-solid catalyst layer into ice-water and stabilized. The dried residue (23.5 g.) was distilled and analyzed as shown in Table III.

Acknowledgment.—The writers are indebted to the Physics Division, Universal Oil Products Company, for the infrared analysis of the reaction products.

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[7] The latter is, of course, more properly named 3-chloro-2,2,3-trimethylpentane.

[8] L. Schmerling and E. E. Meisinger, THIS JOURNAL, in press.