

From 1,5-Dichloropentane.—Product XII showed nmr bands at 3.33 (t), 2.52 (t), and 2.6 (m); ms parent peak at 182; ir showed monosubstituted phenyl and primary chloride. Product XIII showed nmr bands at 3.32 (t), 2.58 (m), 1.63 (m), and 1.22 (d); ms parent peak at 182, large 105 peak, 167 peak; structure confirmed by ir. Products XIV and XV had ir spectra identical with those previously reported;<sup>9</sup> ms and nmr were consistent. Product XVI showed nmr bands at 2.47 (m), 1.5 (m), and 1.18 (d); ms parent peak at 224, 209 peak; it was consistent.

From 1,6-Dichlorohexane.—Product XVII was identical with purchased material (Ash Stevens Co.). Product XVIII showed nmr bands at 3.3 (t), 2.55 (q), 1.56 (m), and 1.17 (d); ms parent peak at 196, 181 peak; ir showed monosubstituted phenyl.

Products XXI, XIX, and XX had ir spectra identical with those previously reported;<sup>10</sup> nmr and ms were consistent.

**Registry No.**—Benzene, 71-43-2; 7-phenyl-1-chlorooctane, 15733-57-0; 6-phenyl-1-chlorooctane, 15733-58-1; III, 1081-75-0; VI, 4830-93-7; VII, 13556-61-1; IXa, 1610-39-5; XII, 15733-63-8; XIII, 15733-64-9; XVI, 6443-80-7; XVIII, 13556-57-5.

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## II. Solvent Effects in the Alkylation of Benzene with 1-Dodecene and *trans*-6-Dodecene in the Presence of Aluminum Chloride

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1-Dodecene and *trans*-6-dodecene alkylate benzene in the presence of aluminum chloride–hydrogen chloride at 35–37° to give similar isomer distributions of phenyldodecanes. At that temperature the alkylation reaction is accompanied by isomerization of the products to a certain equilibrium distribution that is different from the isomer distribution in the absence of product isomerization. Alkylation at 0° or below suppresses product isomerization and results in an isomer distribution that depends on the position of the double bond in the olefin. Attenuation of aluminum chloride with nitromethane prevents product isomerization even at the reflux temperature of benzene. Alkylation with both olefins in benzene solution in the presence of aluminum chloride–nitromethane results in widely different isomer distributions which approach each other if the alkylation reaction is carried out in nitromethane solution. These results are explained in terms of formation of secondary carbonium ions with relative stabilities and reactivities that are affected by the solvent and the mobility of the negative ion in the ion pair.

Alkylation of aromatic compounds with various alkylating agents in the presence of strong Friedel–Crafts catalysts such as aluminum chloride has long been known to be accompanied by isomerization and transalkylation.<sup>1–5</sup> This is especially important in the investigation of substrate selectivity and orientation of alkyl groups in di- and polyalkylation. The extent of this isomerization and disproportionation, which alters the product distribution, is determined by the severity of the reaction conditions, namely the strength and amount of the catalysts, the temperature, and the time of the reaction. The same question also occurs in the alkylation of benzene with long-chain  $\alpha$  olefins where the products initially formed undergo extensive isomerization in the presence of excess aluminum chloride.<sup>6,7</sup> Thus, Nenitzescu has concluded that the Friedel–Crafts alkylation leading to the formation of phenylalkanes is a kinetically controlled reaction, but the subsequent isomerization of phenylalkanes is a thermodynamically controlled reaction leading to the most stable isomer, which is not always identical with the phenylalkane formed from the most stable car-

bonium ion.<sup>8</sup> The situation is also somewhat complicated by the fact that isomerization of the initial products can be shifted beyond thermodynamic equilibrium by an excess of  $\text{BF}_3 \cdot \text{HF}$  or  $\text{AlCl}_3 \cdot \text{HCl}$  which often results in the formation of only the product whose intermediate complex with the catalyst is the most stable one.<sup>9</sup> Therefore, it is of interest to find out if the phenylalkanes obtained from the alkylation of benzene with a long-chain  $\alpha$  olefin such as 1-dodecene in the presence of aluminum chloride come to equilibrium as a result of their isomerization by the strong catalyst, and if this equilibrium distribution differs from the initial isomer distribution obtained in the absence of product isomerization. It is also of interest to find out if the intermediate carbonium ions also come to equilibrium before they attack benzene and if this equilibrium distribution differs from the final equilibrium distribution obtained as a result of isomerization of the products themselves.

### Results

Since alkylation with aluminum chloride proceeds rapidly only after an incubation period during which the so-called red oil forms,<sup>10</sup> the reaction was run in the presence of a small amount (about 20% of the catalyst) of a catalyst layer from a previous alkylation of the same system. At 35° and using 0.12 mol of the catalyst/mol of the olefin, both 1-dodecene and *trans*-6-dodecene afforded nearly identical isomer distribu-

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(2) K. L. Nelson, *J. Org. Chem.*, **21**, 145 (1956).

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(4) D. A. McCaulay in "Friedel–Crafts and Related Reactions," Vol. II, G. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 24.

(5) G. A. Olah, S. H. Flood, and M. E. Moffat, *J. Amer. Chem. Soc.*, **86**, 1060 (1964); G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **84**, 1685 (1962); G. A. Olah, J. C. Lapierre, and H. Schreier, *J. Org. Chem.*, **31**, 1268 (1966); G. A. Olah and J. A. Olah, *ibid.*, **32**, 1612 (1967).

(6) R. D. Swisher, E. F. Kaelble, and S. K. Liu, *ibid.*, **26**, 4066 (1961).

(7) A. C. Olson, *Ind. Eng. Chem.*, **52**, 833 (1960).

(8) C. D. Nenitzescu, *Rev. Roumaine de Chim.*, **9**, 5 (1964).

(9) D. A. McCaulay and A. P. Lien, *J. Amer. Chem. Soc.*, **74**, 6246 (1952).

(10) K. L. Nelson and H. C. Brown in "Chemistry of Petroleum Hydrocarbons," Vol. III, B. T. Brooks, Ed., Reinhold Publishing Corp., New York, N. Y., 1955, Chapter 56.

tions including about 32% 2-phenyldodecane and 31% 5 and 6 isomers. We define this as a distribution ratio of 32:31. However, a small amount of 2-phenyldodecane added along with the olefin showed extensive isomerization to its internal isomers, indicating that the phenyldodecanes could also have isomerized after their formation. Under similar conditions but at 0–5° for 30 min, the 2-phenyldodecane tracer remained unchanged indicating the absence of any product isomerization as well.<sup>11</sup> The  $\alpha$ -olefin product under these conditions had a significantly higher distribution ratio, 44:20, while the internal olefin was very much lower, 18:53. However, when stirring was continued for an additional hour at the same temperature, isomerization appeared in both the 2-phenyldodecane and the product phenyldodecanes and was essentially complete after another hour. Further lowering of the temperature (to –15°) completely prevented product isomerization even after several hours of stirring.<sup>12</sup> In spite of the low temperature, alkylation was essentially complete within a few minutes, as evidenced by the absence of the olefin in the glpc analysis of the mixture, but nevertheless extensive isomerization occurred at earlier stages in the reaction since all of the secondary phenyldodecanes were formed.

Product isomerization was also prevented at the higher temperature (35–37°) by alkylation with a recycled catalyst phase instead of fresh  $\text{AlCl}_3 \cdot \text{HCl}$ . This also resulted in widely different distribution ratios for 1-dodecene and *trans*-6-dodecene (42:25 and 26:43, respectively) indicating that the isomer distribution of the product depends on the position of the double bond in the starting olefin.

The alkylation reaction was also accompanied by the formation of some  $\text{C}_{12}$  paraffins which were isolated by distillation and analyzed by mass spectroscopy and gas-liquid partition chromatography. Their amount and type were found to depend on the temperature of the reaction. Thus at 0° only a 2% yield of dodecanes was obtained of which 67% was *n*-dodecane and 33% branched isomers. At 35° a 6% yield of the paraffin was obtained of which only 5.5% was *n*-dodecane and 94.5% was branched.<sup>13</sup> The greater formation of paraffins at the higher temperature resulted in a slight decrease in the yield of the product alkylbenzenes (83 vs. 87%). In addition to the paraffins, the reaction was also accompanied by the formation of a small amount of an unsaturated material (3.6%) whose analysis by mass spectroscopy showed it to have the molecular formula  $\text{C}_n\text{H}_{2n-8}$ .

Attenuation of aluminum chloride with nitromethane<sup>14</sup> also prevented product isomerization both in benzene and in nitromethane solutions. Even at the reflux temperature of benzene, no evidence for the isomerization of the secondary alkylbenzenes could be observed. This resulted in the same type of isomer distribution as was obtained from alkylation with aluminum chloride at low temperatures, or with a recycled

catalyst phase at 35°, where the position of the double bond was a factor in the isomer distribution of the product. The results of all these alkylations are recorded in Table I where it is seen that in benzene solution and in the absence of any product isomerization the  $\alpha$  olefin invariably afforded greater amounts of the 2 isomer (distribution ratio 44:20) while the internal olefin afforded greater amounts of the 5 and 6 isomers (distribution ratio 18:53). This difference in the behavior of the two olefins due to the position of the double bond was largely eliminated by alkylating in the presence of excess nitromethane where both reactants were present in solution in nitromethane (7:1). Under these conditions both olefins afforded almost identical distribution ratios (approximately 27:35) which were significantly different from the 32:31 ratio obtained from alkylation with aluminum chloride under conditions of product isomerization.

Alkylation with aluminum chloride–nitromethane in benzene solution was not accompanied by paraffin formation as was the case with aluminum chloride. The absence of paraffins, however, was not accompanied by a corresponding rise in the yield of alkylbenzenes. Instead, a small decrease was observed (78%) owing to a greater formation of a high-boiling material whose infrared analysis showed it to be primarily *p*- and *m*-di-alkylbenzenes (12.1 and 12.65  $\mu$ , respectively) in the ratio of 5:1. The yield of the product was further reduced (68%) by alkylation in nitromethane solution owing to the smaller concentration of benzene.

### Discussion

It is evident from the above experimental facts that alkylation of benzene with any long-chain olefin in the presence of aluminum chloride at 35° or higher produces the same isomer distribution regardless of the position of the double bond in the original olefin. This is, however, the result of the rapid and efficient isomerization of the products themselves rather than the intermediate carbonium ions coming to equilibrium. Thus at 0° or below, and in the absence of any product isomerization, 1-dodecene and *trans*-6-dodecene give widely different isomer distributions depending on the position of the double bond in the chain. This is similar to alkylation with anhydrous hydrogen fluoride in the absence of *n*-hexane where the alkylation reaction appeared to be too fast to permit the intermediate carbonium ions to come to equilibrium. One major difference from HF alkylations is that addition of *n*-hexane at 0 or 35° made no difference in the isomer distribution of the product, indicating that the reaction takes place exclusively in the catalyst phase. Consequently, the intermediate carbonium ions could not be brought to equilibrium by this method.<sup>15</sup>

Alkylation with  $\text{AlCl}_3 \cdot \text{CH}_3\text{NO}_2$  produces essentially the same results as alkylation with aluminum chloride at lower temperatures in that the products under these conditions do not undergo any isomerization<sup>16</sup> and, therefore, they reflect the concentration of the secondary carbonium ions prior to alkylation. Consequently, the isomer distribution of the final product depends on

(11) Product isomerization can also be suppressed by use of smaller amounts of aluminum chloride.<sup>6</sup>

(12) Normal hexane was added to the reaction mixture to prevent the benzene from freezing.

(13) Reduction of the alkylating agent to paraffin has also been observed in the alkylation of benzene with decyl, dodecyl, and hexadecyl chloride in the presence of aluminum chloride at 70°: T. Mazonski and A. Hopfinger, *Przemysl Chem.*, **40**, 453 (1961); *Chem. Abstr.*, **62**, 3957f (1965).

(14) L. Schmerling, *Ind. Eng. Chem.*, **40**, 2072 (1948).

(15) H. R. Alul and G. J. McEwan, *J. Org. Chem.*, **32**, 3365 (1967).

(16) Aluminum chloride–nitromethane is also incapable of effecting isomerization of cymenes: G. A. Olah, S. H. Flood, S. J. Kuhn, M. E. Moffat, and N. E. Overchuck, *J. Amer. Chem. Soc.*, **86**, 1046 (1964).

TABLE I

1-Dodecene	Amount, mol			Nitro- methane	AlCl <sub>3</sub> <sup>a</sup>	Temp, °C	Total time, min	2-Phenyl	3-Phenyl	4-Phenyl	5-, 6-Phenyl
	<i>trans</i> -6- dodecene	2-Phenyl- decane	Benzene								
0.3			3.0		0.037	35-37	45	31.8	20.8	17.2	30.2
	0.15	0.01	3.0		0.02	35-37	45	31.9	18.5	17.6	32.0
								38.5 <sup>b</sup>	22.0	19.5	20.0 <sup>c</sup>
0.3		0.01	3.0		0.037	0-5	30	44.0	22.1	14.2	19.7
							90	100.0 <sup>b</sup>	...	...	...
							90	36.9	20.9	16.8	25.4
							150	55.8 <sup>b</sup>	16.8	15.7	11.7
							150	31.0	20.6	18.9	29.5
							150	39.5 <sup>b</sup>	21.4	22.8	16.3
	0.15	0.01	3.0		0.02	0-5	30	18.1	12.3	16.9	52.7
								100.0 <sup>b</sup>	...	...	...
0.3		0.01	3.0		0.037	-15 <sup>d</sup>	360	43.0	21.9	14.5	20.6
								100.0 <sup>b</sup>	...	...	...
0.3		0.01	3.0		0.037 <sup>e</sup>	35-37	30	41.7	19.8	13.2	25.3
								100.0 <sup>b</sup>	...	...	...
	0.15	0.01	3.0		0.037 <sup>e</sup>	35-37	30	26.0	15.4	15.6	43.0
								100.0 <sup>b</sup>	...	...	...
0.15			3.0	0.08 <sup>f</sup>	0.037	35-37	60	40.9	20.7	14.4	24.0
0.15		0.01	3.0	0.08 <sup>f</sup>	0.037	65	90	42.9	19.1	15.0	23.0
								100.0 <sup>b</sup>	...	...	...
							78	41.8	20.6	14.7	22.9
								100.0 <sup>b</sup>	...	...	...
	0.15	0.01	3.0	0.08 <sup>f</sup>	0.037	35-37	60	23.2	17.3	17.8	41.3
								100.0 <sup>b</sup>	...	...	...
0.15		0.01	0.5	4.0 <sup>e</sup>	0.037	35-37	60	27.9	19.5	18.6	34.0
								100.0 <sup>b</sup>	...	...	...
	0.15		0.5	4.0 <sup>e</sup>	0.037	35-37	60	26.1	18.3	19.1	36.5
0.15			3.0		0.074 <sup>g</sup>	35-37	120	57.0	21.5	9.0	12.5

<sup>a</sup> In addition, 20% by weight of red oil from a previous alkylation of the same system was added. <sup>b</sup> Analysis of the added 2-phenyl-decane to detect product isomerization. <sup>c</sup> Amount of the 5 isomer only since the 6 isomer is not possible with the phenyldecane. <sup>d</sup> *n*-Hexane was added to prevent the benzene from freezing. <sup>e</sup> Only a recycled catalyst phase from a previous alkylation of the same system was used in this experiment. <sup>f</sup> No red oil was added when nitromethane was used. <sup>g</sup> The catalyst used in this experiment was AlCl<sub>3</sub>·HSO<sub>4</sub>.

the position of the double bond in the chain and, therefore, on the point at which the proton enters the alkylating agent. The condition of equilibrium among the carbonium ions is almost achieved by alkylating in nitromethane solution where the alkylation reaction is sufficiently slowed down to permit greater isomerization in the alkylating agent. However, complete equilibrium in nitromethane was apparently not quite achieved and 1-dodecene continued to give slightly greater amounts of the 2 isomer than *trans*-6-dodecene (27.9 vs. 26.1%) and slightly smaller amounts of the 5 and 6 isomers (34.0 vs. 36.5%). This is in contrast to the effect of *n*-hexane on alkylations with hydrogen fluoride where complete equilibrium was readily achieved resulting in the same isomer distribution regardless of the point at which the proton enters the chain.<sup>15</sup> This is probably due to the solvation of the intermediate ions by the polar solvent, nitromethane, which affects their relative stabilities and their rates of isomerization across the chain.

The product from alkylation with both olefins at or near equilibrium conditions in nitromethane solution shows about the same amount for all the isomers except the 2-phenyl isomer which is invariably greater than the 3 isomer. At lower temperatures the inherent stability of the 5 and 6 isomers (which was also observed in hydrogen fluoride alkylations) becomes more magnified, and their amount rises to 52.7%.<sup>15</sup> Still, however, the amount of the 2 isomer is greater than the 3 isomer which probably indicates that the 2-carbonium ion reacts with benzene more rapidly than the 3-car-

bonium ion. The excess of the 2 isomer over the 3 isomer was also observed in some hydrogen fluoride alkylations, but it disappeared upon lowering the polarity of the medium by addition of *n*-hexane.<sup>15</sup> Apparently solvation of the intermediates by a polar solvent such as benzene or nitromethane reduces the differences in their stabilities and concentrations which permits greater formation of the 2-phenylalkane. Removal of this stabilization by addition of *n*-hexane magnifies the differences in these stabilities which raises the concentrations of the internal isomers sufficiently to nullify the steric advantages of the 2 isomer.

The excess of the 2 isomer over the internal phenylalkanes also occurs under conditions of product isomerization such as aluminum chloride-hydrogen chloride and benzene at 35-37°. Under these conditions the phenyldecane is at equilibrium as evidenced by the fact that both 1-dodecene and *trans*-6-dodecene afford the same isomer distribution as the equilibrium distribution reported by Swisher, *et al.*<sup>6</sup> The amount of 2-phenylalkane at equilibrium is twice the amount of the 5 or 6 isomers and 50% greater than the 3 isomer. This is probably due to greater solvation of the intermediate alkylarenonium ion by the extremely polar phase (the red oil) of the reaction mixture. In the alkylbenzenonium ion derived from the 2-phenylalkane, the positive charge of the ion is located near the end of the chain which permits more efficient solvation by the catalyst phase. As the charge enters the middle of the chain, the ion is more efficiently shielded from the solvent by its alkyl groups. Therefore, alkylation of

benzene with 1-dodecene results in greater amounts of the 2-phenylalkane both in the absence as well as presence of product isomerization. In the first case, it is due to greater reactivity of the intermediate carbonium ion toward benzene, and in the second case, it is due to greater solvation of the intermediate alkylarenium ion by the catalyst phase.

Although the isomer distribution of the primary product obtained with  $\text{AlCl}_3 \cdot \text{HCl}$  at  $35^\circ$  is altered by the concurrent isomerization of the phenylalkanes, it appears that the intermediate carbonium ions do not come to equilibrium prior to their reaction with benzene at that temperature. Thus, when a recycled catalyst phase is used instead of fresh aluminum chloride, product isomerization is prevented and the two olefins, 1-dodecene and *trans*-6-dodecene, no longer afford the same isomer distribution.

Comparison of the product from alkylation in the presence of hydrogen fluoride with those from alkylation in the presence of aluminum chloride at  $0^\circ$  shows the first to be closer to equilibrium conditions.<sup>15</sup> Thus 1-dodecene and *trans*-6-dodecene afford 18.5 and 10.6%, respectively, of the 2 isomer in the presence of hydrogen fluoride and 44.0 and 18.1%, respectively, in the presence of aluminum chloride. This is probably due to the effect of the negative ion of the ion pair on the rate of isomerization of the positive ion across the chain.<sup>17</sup> This effect of the mobility of the negative ion on the rate of isomerization was also observed by alkylation of benzene with 1-dodecene in the presence of  $\text{AlCl}_3 \cdot \text{HSO}_4$  which resulted in the highest distribution ratio obtained in this series of alkylations (57:13).<sup>18</sup> Further work on this point is in progress in this laboratory.

Since intermolecular hydride abstractions occur more readily with stronger acids such as aluminum chloride-hydrogen chloride,<sup>19</sup> one may also expect them to occur more readily in intramolecular abstractions where the carbonium ion abstracts a hydride from a carbon atom at some distance from the positive charge which, if it occurs to any significant degree, would result in greater isomerization. The fact that greater isomerization occurs at  $0^\circ$  with 1-dodecene and hydrogen fluoride than with aluminum chloride argues against such long-range isomerization occurring to a significant degree. In any event the rate of isomerization of the interme-

mediate cations is not sufficient to bring them to equilibrium under ordinary conditions.

The formation of the paraffins occurs under conditions which permit disproportionation and *trans*-alkylation. Evidence has been obtained to show that it occurs after the formation of alkylbenzene.<sup>20</sup> This is in accord with the fact that the alkylation reaction is much faster than hydride abstraction<sup>21</sup> so that almost all the carbonium ions are converted into alkylbenzene. At higher temperatures and in the presence of the strong acid aluminum chloride-hydrogen chloride the product is converted to the alkylarenium ion (I) which may equilibrate with a localized  $\pi$  complex (II)<sup>10,22-24</sup> or dissociate to an alkyl cation (III) and benzene. The  $\pi$  complex isomerizes to the other  $\pi$  complexes,<sup>25</sup> which rearrange to the  $\sigma$  complexes and finally lose a proton to form the rearranged phenylalkanes.<sup>6</sup> The alkyl cations (III) also isomerize by rapid hydride shifts and either realkylate benzene or, to a much smaller extent, abstract the tertiary hydrogen of a molecule of alkylbenzene. The new phenylalkyl cation (IV) rearranges to VI by way of a phenonium-type intermediate<sup>26</sup> (V) which then either abstracts another hydride to form the rearranged alkylbenzene or alkylates benzene to form a high-boiling product. These reactions are summarized in Chart I written for the 2-phenyldodecane isomer.

Some of the alkyl cations (III) undergo skeletal isomerization in a manner similar to that reported by Peterson, *et al.*,<sup>27</sup> and subsequently appear as isoparaffins. The failure to observe *t*-alkylbenzene in the gas-liquid chromatogram is due to its vulnerability to attack by the strong acid.<sup>28</sup> Under the influence of  $\text{AlCl}_3 \cdot \text{HCl}$  the alkyl cations (III) may abstract a hydride ion from a carbon atom of an alkylbenzene molecule other than the benzylic one.<sup>19</sup> This is more likely to occur with the internal phenyldodecanes where the tertiary hydrogen atom is surrounded by two large alkyl groups. The new phenylalkyl cation undergoes isomerization and then cyclization to form the indanes and tetralines ( $\text{C}_n\text{H}_{2n-8}$ ) which have frequently been observed<sup>29,30</sup> or postulated<sup>20</sup> as by-products of these reactions.

## Experimental Section

**Materials.**—1-Dodecene, *trans*-6-dodecene, and benzene were obtained as described previously.<sup>15</sup> Aluminum chloride was Fisher reagent grade and nitromethane was obtained from Eastman Organic Chemicals. 2-Phenyldecane was obtained from Dr. R. D. Swisher of the Monsanto Co.

**Alkylation with Aluminum Chloride.**—The alkylation reaction was carried out at  $35\text{--}37^\circ$  by adding 0.3 mol of 1-dodecene to 3.0 mol of dry benzene which had previously been saturated with dry hydrogen chloride and mixed with 0.037 mol of an-

(17) From the point of view of their catalytic activity in these reactions the most important differences between HF and  $\text{AlCl}_3 \cdot \text{HCl}$  are (a) the difference in their acidity and (b) the difference in the mobility of  $\text{F}^-$  and  $\text{AlCl}_4^-$  ions. The Hammett acidity function,  $H_0$ , for anhydrous HF is  $-10$  and that for  $\text{AlCl}_3 \cdot \text{HCl}$  is about  $-15$ , which makes the latter a much stronger acid. The acidity of hydrogen fluoride, however, can be varied over a very wide range (6 powers of 10) by addition of certain Lewis acids such as  $\text{BF}_3$ ,  $\text{NbF}_5$ , or  $\text{SbF}_5$  which raise the acidity of the solvent. Also the addition of certain salts such as NaF or KF lowers its acidity. This property of hydrogen fluoride solutions permits the study of the effect, if any, of the acidity of the medium on the isomerization of the positive charge across the chain of the secondary carbonium ion. Experiments with various catalyst systems such as  $\text{HF} \cdot \text{BF}_3$ ,  $\text{HF} \cdot \text{KF}$ , and  $\text{HF} \cdot \text{KBF}_4$  failed to show any relation between the acid strength of the catalyst and the isomer distribution of the product if the reaction is carried out under conditions which do not permit product isomerization. The results of this work will be reported in the near future.

(18) It is interesting to note that *n*-propyl chloride has been reported to alkylate benzene in the presence of dichloroaluminum sulfate with no isomerization of the *n*-propyl group: A. V. Topchiev, B. A. Krentsel, and L. N. Andreen, *Dokl. Akad. Nauk SSSR*, **92**, 781 (1953); *Chem. Abstr.*, **49**, 3039 (1955). Subsequent work on the alkylation of benzene with 8-methyl-1-nonene showed that under these conditions of minimum isomerization the positive charge barely reaches the eighth carbon atom of the chain, while under conditions of maximum isomerization<sup>15</sup> it winds up almost exclusively on it. The result of this work will be reported in a future communication.

(19) H. Pines and N. E. Hoffman, *ref 4*, Chapter 28, p 1215.

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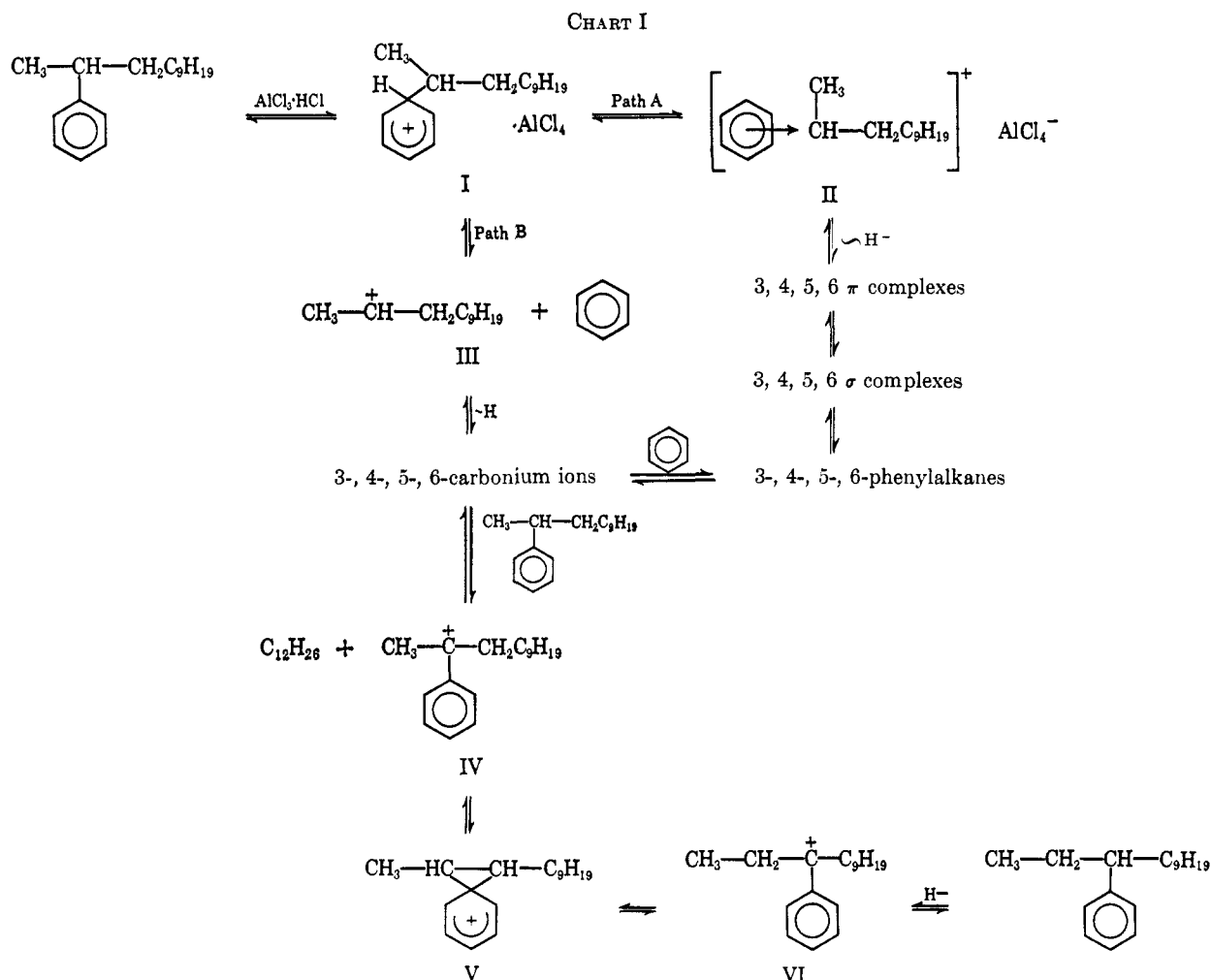
(26) Reference 4, p 1065.

(27) A. H. Peterson, B. L. Phillips, and J. J. Kelly, *Ind. Eng. Chem.*, **4**, 261 (1965).

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(29) P. W. Flanagan, M. C. Hamming, and F. M. Evans, *J. Amer. Oil Chemists' Soc.*, **44**, 30 (1967).

(30) A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **31**, 89 (1966).



hydrous aluminum chloride and about 1 ml of a red oil from a previous alkylation. After separation of the catalyst complex phase from the alkylated liquor, the latter was quenched by adding water, washed with 5% NaOH solution followed by water, and dried. A small sample was analyzed by gas-liquid chromatography using a Barber-Colman Model 20 chromatograph equipped with Sargent SR recorder with a coupled integrator. The column used for the analysis was 150 ft  $\times$  0.02 in. stainless steel coated with SE-30 silicon gum rubber. Another column of the same dimensions but coated with *m*-bis[*m*-(*m*-phenoxyphenoxy)phenoxy]benzene<sup>31</sup> was also used. The excess benzene was removed on a water bath, and the rest of the mixture was distilled in a 2-ft packed column under vacuum. After a small amount of benzene ( $n_D^{25}$  1.4930) had been removed, the first fraction boiled at 85–115° (15 mm),  $n_D^{25}$  1.4335 (2.8 g or 6%). It was passed through a column of silica gel to remove any unsaturated impurities and then examined by glpc rapid scan mass spectrometry. The spectrometer used was Consolidated Electro-dynamics Corp. (CEC) conventional mass spectrometer, model 21-130, modified for rapid scanning. The glpc separation was made on a 200 ft  $\times$  0.02 in. d capillary column coated with 10% didecyl phthalate (DDP). Six major peaks appeared and accounted for about 95% of the entire chromatogram. The boiling points of the various components were computed from their retention times and were found to lie between 205 and 215° (*n*-dodecane bp 215°). The effluent from the glpc column was passed through the continuous capillary inlet of the mass spectrometer where each of the six peaks was found to be a paraffin with the molecular formula  $\text{C}_{12}\text{H}_{26}$ . The last peak (5.5% of the chromatogram) showed a fragmentation pattern similar to published data.<sup>32</sup> It had a parent peak (P) at  $m/e$  170 ( $\text{C}_{12}\text{H}_{26}$ ) in addition to groups of peaks differing by 14 ( $\text{CH}_2$ ) mass units.

The peak at  $m/e$  155 (P -  $\text{CH}_3$ ) was absent, which is characteristic of straight-chain paraffins.<sup>33</sup> The identification of this component as *n*-dodecane was further supported by the use of an authentic sample of the straight-chain paraffin. The other five components which eluted before *n*-dodecane also showed parent peaks of *n*-dodecane, as well as a strong peak at  $m/e$  155 (P -  $\text{CH}_3$ ). Some of the components showed prominent peaks at even mass numbers (142, 126, 112, 98) which is characteristic of two side chains and a higher degree of branching.<sup>33</sup> These branched dodecanes, however, could not be assigned individual structures due to the lack of model compounds. The same result was confirmed by simple glpc analysis using an 18 ft  $\times$  0.25 in. id column packed with Carbowax-silver nitrate. The *n*-dodecane peak was well resolved and was identified by use of an authentic sample. The other peaks eluted before the *n*-dodecane but were less well resolved.

The main fraction of the product boiled at 128–136° (2 mm) ( $n_D^{25}$  1.4807), and the yield was 62 g or 83% of theoretical. A sample of the product was analyzed by conventional mass spectrometry using the major ion fragments to represent various isomer species, *i.e.*,  $m/e$  105 (2-phenyl), 119 (3-phenyl), 133 (4-phenyl), 147 (5-phenyl), and 161 (6-phenyl).<sup>34</sup> The parent molecular ion peak (P) for all the above isomers was observed at  $m/e$  246. The spectrum also contained a small amount (3.6%) of a component whose P appeared at  $m/e$  244 ( $\text{C}_7\text{H}_{2n-8}$ ).<sup>20,29,30</sup>

When the reaction was carried out at 0°, small samples from the reaction mixture were withdrawn at definite intervals, quenched with water, washed with 5% sodium hydroxide solution and water, and finally analyzed by gas-liquid partition chromatography for the isomer distribution of both the phenyldecanes, present to detect product isomerization, and the product phenyl-dodecanes. The column, SE-30 silicon gum rubber, and the procedure were as above. The yield of this reaction was 87% of

(31) Commonly known as poly-*m*-phenyl ether (seven-ring) and obtained from Monsanto Research Corp., Dayton, Ohio.

(32) "Mass Spectral Data," American Petroleum Institute Research Project No. 44; Spectral No. 404, 981, 1028, 1598.

(33) J. H. Beynon, "Mass Spectrometry and Its Application to Organic Chemistry," Elsevier, Amsterdam, 1960, p 329.

(34) Reference 32, Spectral No. 1743-1747.

theoretical. At temperatures below 0° about 100 ml of *n*-hexane was added to prevent the benzene from freezing.<sup>35</sup>

The same procedure was followed for the alkylation of benzene with *trans*-6-dodecene. The olefin (0.15 mol) was mixed with 0.01 mol of 2-phenyldecane, and the alkylation reaction was completed as above. The mixture was worked up as usual and the analysis of the product appears in Table I. The yields were similar to those obtained with 1-dodecene.

**Alkylation in the Presence of Aluminum Chloride-Nitromethane.**—Benzene (2.5 mol) was added to the yellowish solution prepared by dissolving 0.037 mol of anhydrous aluminum chloride in 0.08 mol of nitromethane. The temperature was kept at 35–37°, and a mixture of 0.15 mol of 1-dodecene and 0.01 mol of 2-phenyldecane in 0.5 mol of benzene was added over a period of 15 min. The mixture was stirred for 45 more minutes and was quenched with water and washed with dilute HCl, 10% NaOH solution, and water. The product was analyzed by glpc and distilled as usual. The yield was 28.5 g or 78%. Infrared analysis of the residue (7.3 g) showed it to be mainly *p*- and *m*-dialkylbenzene in the ratio of 5:1 (12.1 and 12.65  $\mu$ , respectively).

The same procedure was followed for the alkylation reactions in nitromethane solution. A mixture of 0.15 mol of 1-dodecene, 0.01 mol of 2-phenyldecane, and 0.1 mol of benzene was added to a solution of 0.037 mol of anhydrous aluminum chloride in 4.0 mol of nitromethane and 0.4 mol of benzene maintained at 35–37°. Stirring was continued for 1 hr, and the reaction mixture was quenched with 10 g of ice and extracted three times

with 200 ml of *n*-hexane. The combined hexane extracts were washed with dilute hydrochloric acid, water, 10% sodium hydroxide solution, and finally water. The solution was dried with anhydrous magnesium sulfate, and the solvent was removed on a water bath. The product was analyzed for isomer distribution and then distilled as above. The yield was 68% of theoretical.

**Alkylation with Dichloroaluminum Sulfate.**—This catalyst was prepared according to the directions of Topchiev, *et al.*<sup>36</sup> Ground  $\text{AlCl}_3 \cdot \text{HSO}_4$  (0.074 mol) and anhydrous benzene (3.0 mol) were placed in the alkylation flask. The temperature was raised to 35°, and a mixture of 0.15 mol of 1-dodecene and 0.01 mol of 2-phenyldecane was added. Stirring was continued for 2 hr after which time an oily layer appeared at the bottom of the flask. The mixture was allowed to stand overnight before it was quenched with water and acidified with dilute HCl. The organic layer was washed successively with dilute HCl, water, dilute alkali, and finally water. The product was then analyzed by glpc and distilled as usual. The yield was 27.5 g or 75%.

**Registry No.**—Benzene, 71-43-2; 1-dodecene, 112-41-4; *trans*-6-dodecene, 7206-17-9; aluminum chloride, 7446-70-0.

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(35) Special alkylations were carried out at 0 and 35° in which *n*-hexane, in contrast to hydrogen fluoride alkylations, was shown to have no effect on the isomer distribution of the product.

(36) A. V. Topchiev, S. V. Zavgorodnii, and V. G. Kryuchkova, "Alkylation with Olefins," Elsevier Publishing Co., Amsterdam, 1964, p 141.

## The Synthesis and Properties of 1- and 2-(Dichloromethyl)heptamethyltrisilane and Related Compounds<sup>1</sup>

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The first carbon-functional organotrisilanes, 1- and 2-(dichloromethyl)heptamethyltrisilane, have been prepared from the corresponding chloroheptamethyltrisilanes with  $\alpha$ -dichloromethylolithium. 1-(Chloromethyl)heptamethyltrisilane as well as (chloromethyl)pentamethyldisilane were also prepared by *in situ* coupling of bromochloromethane with the corresponding chlorosilanes. Aluminum chloride catalyzed reactions of 1- and 2-(dichloromethyl)heptamethyltrisilane were examined. Both compounds undergo intramolecular rearrangement followed by a redistribution reaction. Nmr spectral data are reported for several chloromethyl- and dichloromethyl-substituted silanes.

Recently considerable attention has been directed toward a study of the organopolysilanes.<sup>2</sup> However, no carbon-functional organotrisilane except vinylheptamethyltrisilanes<sup>3</sup> has been known to date. We now report the synthesis and aluminum chloride catalyzed rearrangement of the first examples of the carbon-functional organotrisilanes, 1- and 2-(dichloromethyl)heptamethyltrisilane.

Many procedures for preparing carbon-functional silanes or disilanes<sup>4</sup> cannot be extended to higher polysilanes because of extensive silicon-silicon bond cleavage. These procedures involve halogenation or other

substitution reactions on carbon. Alternatively, nucleophilic substitution reaction on a silicon atom would be a preferred route to the carbon-functional organopolysilanes. The (dichloromethyl)heptamethyltrisilanes were thus prepared by the reaction of the corresponding chloroheptamethyltrisilanes with  $\alpha$ -dichloromethylolithium.

Recently the reaction of polychloromethane with *n*-butyllithium in tetrahydrofuran at low temperature has been shown to lead to the formation of a new class of organolithium reagents, the  $\alpha$ -chloroalkyllithium compounds.<sup>5</sup> It was reported that the action of *n*-butyllithium on methylene chloride at -65° afforded dichloromethylolithium in high yield and this reagent served as an intermediate in the preparation of some dichloromethyl-substituted compounds.<sup>6</sup>

(1) (a) Aluminum Chloride-Catalyzed Reactions of Organosilicon Compounds. V. (b) For part IV, see H. Sakurai, K. Tominaga, T. Watanabe, and M. Kumada, *Tetrahedron Lett.*, 5493 (1966).

(2) For pertinent reviews, see (a) H. Gilman, W. H. Atwell, and F. K. Cartledge, *Advan. Organometal. Chem.*, 4, 1 (1966); (b) M. Kumada and K. Tamao, *ibid.*, in press; (c) H. Sakurai, *J. Soc. Org. Syn. Chem. Jap.*, 25, 555, 642 (1967).

(3) H. Sakurai, K. Tominaga, and M. Kumada, *Bull. Chem. Soc. Jap.*, 39, 1279 (1966).

(4) C. Eaborn, "Organosilicon Chemistry," Butterworth and Co. Ltd., London, 1960, p 377.

(5) (a) H. Heaney, *Organometal. Chem. Rev.*, 1, 27 (1966); (b) G. Köbrich, *et al.*, *Angew. Chem.*, 79, 15 (1967); (c) D. F. Hoeg, D. L. Lusk, and A. L. Crumbliss, *J. Amer. Chem. Soc.*, 87, 4147 (1967), and references cited therein.

(6) G. Köbrich, K. Flory, and W. Drischel, *Angew. Chem.*, 76, 536 (1964).