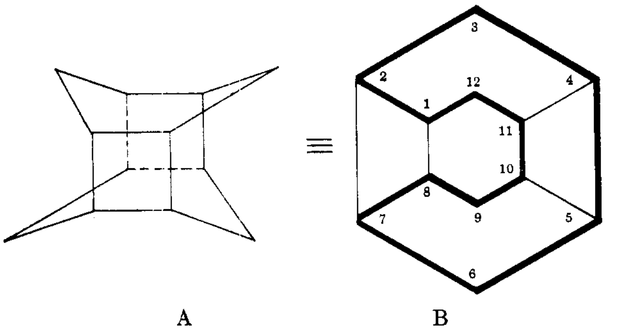

Figure 16.—(A) Pentacyclo[5.3.1.1^{2,6}.0^{3,10}.0^{5,8}]dodecane[18a] (incorrect); (b) pentacyclo[6.4.0.0^{2,7}.0^{4,11}.0^{5,10}]dodecane[18b] (correct).

sidering IUPAC rule A-2.2 which demands the placing of substituents at the lowest numbered carbon possible (the same rule which prevents the use of *4-chloropentane* for *2-chloropentane*), the appropriate name of "basketene" is, therefore, pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]-dec-9-ene[14,15] (Figure 11A).

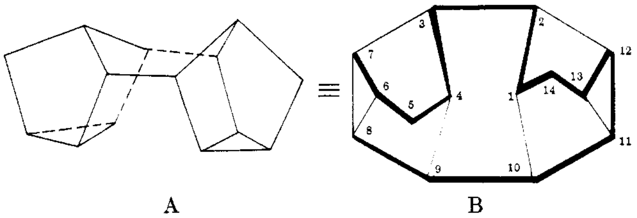

Figure 17.—(A) *endo,cis,endo*-Heptacyclo[5.3.1.1^{2,6}.1^{4,12}.1^{9,11}.-0^{3,5}.0^{8,10}]tetradecane[19] (incorrect); (B) *endo,cis,endo*-heptacyclo-[8.4.0.0^{2,12}.0^{3,7}.0^{4,9}.0^{6,8}.0^{11,13}]tetradecane (correct).

Further exemplification of this method which involves planar graphs can be shown in the naming of "congressane" and "triamantane." "Congressane" has been described as the "adamantalog" of adamantane.[4] It is easily numbered and named from its planar graph, as shown in Figure 12 (with the circuit exposed in heavy print). Bisadamantyladamantane ("triamantane"[5]) can also be named easily from its planar graph (Figure 13).

In Figures 14A–17A are examples of structures which have been incorrectly named in the literature. The structures have been redrawn in the form of planar graphs (Figures 14B–17B)[16–19] to show the basis for correct IUPAC designations.

[14] W. G. Dauben and G. L. Whalen (*Tetrahedron Letters*, 3743 (1966)) correctly named "basketene" as *pentacyclo*[*4.4.0.0^{2,5}.0^{3,8}.0^{4,7}*]*dec-9-ene* (Figure 11A).

[15] There are known to the present author three interpretations of rule A-32.31: d, each of which has its own merits, and each, quite often, leads to a different name for the same compound. In the first interpretation, used by the present author, the parent compound is given the name which has, at the first possible difference, the smallest possible number as the *first* member of a pair of superscripts. In the second interpretation, the parent compound is given the name which has the smallest possible number at the first possible difference as the first member of each pair of superscripts and the smallest possible numbers for the positions of substituents on the parent compound. This second interpretation would give precedence to the name in Figure 11C over that in Figure 11A. In the third interpretation, used by *Chemical Abstracts*, the parent compound is given the name which has the smallest possible number at the first possible difference in the superscripts, no matter whether it is the first or second member of a pair of superscripts. This third interpretation would give the compound in Figure 17 the name: *endo,cis,-endo*-heptacyclo[8.4.0.0^{2,7}.0^{3,5}.0^{4,8}.0^{9,13}.O^{12,14}]tetradecane.

Note: The sum of the superscripts for the above name is 77 and the sum of superscripts of the name in Figure 17 listed as "correct" is 75.

It would be helpful to have one interpretation of rule A-32.31: d approved for use by the IUPAC nomenclature committee.

[16] (a) W. H. F. Sasse, P. J. Collin, and G. Sugowdz, *Tetrahedron Letters*, 3373 (1965). (b) "Benzo" nomenclature is described in the IUPAC nomenclature rules for "*ortho*-fused" systems (rule A-21.3). This paper makes no attempt to cite ambiguities caused by the use of the "*ortho*-fused" nomenclature system; however, by dropping the "benzo" from the name of the compound in Figure 14B, the name becomes pentacyclo[6.4.0.0^{2,5}.0^{3,7}.0^{4,6}]-dodeca-1,9,11-triene.

[17] R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 3062 (1964).

[18] (a) *Chem. Abstr.*, **56**, 1609*S* (1962); (b) R. C. Cookson, D. A. Cox, and J. Hudec, *J. Chem. Soc.*, 4499 (1961).

[19] G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *J. Am. Chem. Soc.*, **88**, 4890 (1966).

Solvent Effects in the Alkylation of Benzene with 1-Dodecene and *trans*-6-Dodecene in the Presence of Hydrogen Fluoride

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1-Dodecene and *trans*-6-dodecene alkylate benzene in the presence of anhydrous hydrogen fluoride at 0 and 55° to give all five isomeric secondary phenyldodecanes. At both temperatures, the α-olefin affords greater amounts of the 2-phenylalkane and correspondingly smaller amounts of the 5- and 6-phenylalkanes. However, if the alkylation reaction is carried out in the presence of excess *n*-hexane, both olefins afford identical isomer distributions. A significant decrease in the 2-phenyl content of the products is observed at the lower temperature both in the presence and absence of *n*-hexane. In alkylations with either olefin at 55°, the absence of a separate liquid catalyst phase results in a substantial rise in the amount of the 2-phenyl isomer. An explanation for the above behavior is given based on alkylation in both phases of the two-phase reaction mixtures, competitive isomerization and alkylation reactions, and formation of carbonium ions with stabilities and reactivities which are affected by the solvent.

Earlier workers reported the formation of only one phenylalkane in the alkylation of benzene with long-chain α-olefins in the presence of Friedel–Crafts catalysts.[1,2] Subsequent investigations by many workers have definitely established that isomerization occurs and that all the possible phenylalkanes are obtained except the 1-phenyl isomer.[3,4] The generally accepted mechanism for Friedel–Crafts alkylations involves interaction of the olefin with the catalyst to form a carbonium ion, the corresponding ion pair, or a polarized complex. This undergoes

[1] W. S. Emerson, V. E. Lucas, and R. E. Heimsch, *J. Am. Chem. Soc.*, **71**, 1742 (1949).

[2] W. L. Lenneman, R. D. Hites, and V. I. Komarewsky, *J. Org. Chem.*, **19**, 463 (1954).

[3] A. C. Olson, *Ind. Eng. Chem.*, **52**, 833 (1960).

[4] R. D. Swisher, E. F. Kaelble, and S. K. Liu, *J. Org. Chem.*, **26**, 4066 (1961).

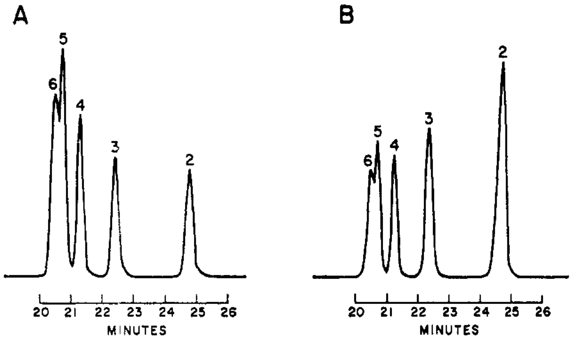

Figure 1.—Gas–liquid chromatograms for phenyldodecanes obtained from alkylation of benzene at 55° with (A) 1-dodecene or *trans*-6-dodecene in the presence of liquid HF and *n*-hexane and (B) 1-dodecene in the absence of both.

rapid isomerization in varying degrees and finally attacks benzene in what is considered to be the rate-determining step, to form the products.[5]

In the reaction of benzene with an α-olefin such as 1-dodecene in the presence of hydrogen fluoride, it is evident that the intermediate carbonium ion undergoes a series of fast hydride shifts to produce the isomeric ions. However, evidence has been obtained which suggests that hydride transfers, though rapid, are not instantaneous[6,7] and therefore some of the carbonium ions may react with the aromatic hydrocarbons before undergoing rearrangement.[8] Therefore, it is of interest to find out if isomerization of the carbonium ions is fast enough to allow the isomeric ions to attain the equilibrium distribution before they attack benzene. If so, the position of the double bond in the starting olefin will have no effect on the alkylbenzene isomer distribution and the two isomeric olefins 1-dodecene and *trans*-6-dodecene should afford identical products under the same experimental conditions. If, on the other hand, the rate of alkylation can effectively compete with the rate of isomerization, then the isomer distributions of the products will differ according to the position of the double bond in the starting olefin. Anhydrous hydrogen fluoride is particularly useful for this study since it does not isomerize the products under the described alkylation conditions.

Results

At 0 and at 55°, 1-dodecene and *trans*-6-dodecene alkylate benzene in the presence of a large amount of anhydrous hydrogen fluoride (molar ratio of HF–olefin ≈16:1) to give all the possible secondary alkylbenzenes. At both temperatures, 1-dodecene gives larger amounts of the 2-phenyl isomer and correspondingly smaller amounts of the internal ones.

The reaction was also run at 55° in the absence of a separate liquid catalyst phase. This was accomplished by reducing the HF content to an amount which gave a total pressure slightly below the equilibrium pressure of a mixture of benzene and HF. Under these conditions the catalyst in the system was present either in solution in benzene or in the vapor phase. When benzene was alkylated with 1-dodecene and *trans*-6-dodecene under these conditions, the reaction products from both olefins showed a significant rise in the amount of the 2 isomer and a corresponding decrease in the amount of the internal ones. Still, however, 1-dodecene continued to afford much larger amounts of the 2-phenyldodecane than the internal olefin (37.3 *vs.* 22.0%), indicating that the position of the double bond in the starting olefin is a factor in isomer distribution. The results of these alkylations are summarized in Table I which records the amount of each alkylbenzene as obtained by glpc analysis.[9]

TABLE I

	Alkylation in the presence of separate liquid catalyst phase, %				Alkylation in the absence of separate liquid catalyst phase, %	
	0°		55°		55°	
Compd	1-Dod	6-Dod	1-Dod	6-Dod	1-Dod	6-Dod
2-Phenyl	18.5	10.6	25.2	14.8	37.3	22.0
3-Phenyl	15.5	12.7	16.9	14.5	19.0	15.0
4-Phenyl	18.3	17.9	17.4	16.6	15.2	15.3
5- and 6-phenyl	47.7	58.6	40.6	54.1	28.5	47.7

Dilution of benzene and the olefin with an inert solvent such as *n*-hexane[10] (10:1) in the presence of liquid anhydrous hydrogen fluoride results in a significant change in the isomer distribution of the products from both olefins, especially the terminal one for which the 2-phenyl product is greatly reduced. This is summarized in Table II where it is seen that at 55° both 1-dodecene and *trans*-6-dodecene afford, within the experimental error, nearly identical isomer distributions.

TABLE II

DILUTION OF REACTANTS WITH *n*-HEXANE

	Alkylation in the presence of separate catalyst phase, %				Alkylation in the absence of separate liquid phase, %	
	0°		55°		55°	
Compd	1-Dod	6-Dod	1-Dod	6-Dod	1-Dod	6-Dod
2-Phenyl	11.4	11.1	13.7	13.6	25.1	13.6
3-Phenyl	14.0	13.8	15.1	15.8	15.8	13.0
4-Phenyl	18.6	18.3	16.8	17.3	14.9	19.6
5- and 6-phenyl	56.0	56.8	54.4	53.6	44.2	53.8

The fact that in the presence of *n*-hexane and a separate HF phase both olefins give the same isomer distribution indicates that under these conditions the position of the double bond in the olefin is immaterial (Figure 1). In other words, it makes no difference as to the point at which the proton enters the olefin. The same type of effect was observed in the absence of a separate HF phase (Table II) where the 2-phenyl isomer was sharply reduced in both cases when *n*-hexane was present. However, the effect was not so complete since *trans*-6-dodecene gave greater amounts of the internal secondary alkylbenzenes and smaller amounts of the 2 isomer than 1-dodecene, indicating that the absence of liquid hydrogen fluoride is similar to the

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[5] S. H. Patinkin and B. S. Friedman in "Friedel–Crafts and Related Reactions," G. Olah, Ed., Vol. II, Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 14, p 3.

[6] E. Renk and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 878 (1961).

[7] M. Saunders, P. von R. Schleyer, G. A. Olah, *ibid.*, **86**, 5680 (1964).

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

[9] Since the internal alkylbenzenes have slightly lower boiling points than the ones near the end of the chain, the crude mixture was analyzed to avoid any discrepancy due to distillation.

[10] J. H. Simons, *Advan. Catalysis*, **2**, 218 (1950).

absence of *n*-hexane in that the position of the double bond in the starting olefin affects the isomer distribution of the products.

At 0°, alkylation of benzene with 1-dodecene and *trans*-6-dodecene in the presence of a separate HF phase invariably resulted in greater amounts of the internal isomers (5- and 6-phenyl) than at 55° (Table II). In the case of 1-dodecene in the absence of *n*-hexane, the amount of 2-phenylalkane was reduced from 25 to 18%. Low temperature, however, was not sufficient to nullify the effect of the position of the double bond on the isomer distribution and *trans*-6-dodecene continued to give smaller amounts of the 2 isomer than 1-dodecene (18 *vs.* 11%). Dilution of the reactants with *n*-hexane at 0° brought the isomer distribution from both olefins to the same value which was considerably lower in the 2-phenyl content than at 55° (11.2 *vs.* 13.7%). Therefore, a separate HF phase, low alkylation temperature, and dilution with *n*-hexane result in the greatest amounts of the internal secondary alkylbenzenes regardless of the position of the double bond in the dodecene employed. It is interesting to note that, under the proper conditions of alkylation, 1-dodecene can be made to afford greater amounts of internal alkylbenzenes than *trans*-6-dodecene under other alkylating conditions.

Since 1-dodecene has recently been reported to rearrange to the various methylundecanes in the presence of HF and isopentane (or isobutane),[11] it became necessary to determine whether the products contain any of the tertiary alkylbenzenes. All the peaks in the chromatograms were unambiguously identified as secondary alkylbenzenes by the use of authentic samples of phenyldodecanes.[12] In addition, the product from one alkylation at 55° was separated into the individual isomers (except the 5- and 6-phenyl which could not be resolved) by a combination of distillation in a 40-plate column and a preparatory glpc apparatus. The individual isomers were then analyzed by nmr spectroscopy which established their structures as secondary alkylbenzenes. However, when the reactants were diluted 50:1 with *n*-hexane, a small peak ($\approx 2\%$ of the total product) appeared in the chromatogram and was tentatively identified as 2-methyl-2-phenylundecane by use of an authentic sample in separate columns coated with SE 30 silicon gum rubber, Carbowax silver nitrate, and poly-*m*-phenyl ether (seven ring).

Discussion

Since the products from alkylation of benzene with 1-dodecene in the presence of hydrogen fluoride at 55° contain greater amounts of the 2-phenyl isomer than those from *trans*-6-dodecene, it must be concluded that under these conditions the intermediate carbonium ions from 1-dodecene do not come to equilibrium before they attack benzene. In other words, the rate of the alkylation step is not sufficiently slow to allow isomerization of the intermediates to proceed to the most stable distribution. Dilution of the reactants with *n*-hexane apparently slows down the alkylation step sufficiently to allow the intermediate ions to isomerize to the equilibrium distribution since 1-dodecene and *trans*-6-dodecene afford the same alkylbenzene mixture composition.

The effect of dilution on the isomer distribution suggests another important phenomenon, namely, that a significant part of the alkylation reaction occurs in the organic phases. Careful investigation of the behavior and products of heterogeneous aluminum chloride alkylations has led to the conclusion that they proceed in the catalyst phase.[13] It has also been observed that alkylation with aluminum chloride proceeds at a very rapid rate only after an incubation period during which the so-called red oil forms. Since aluminum chloride is very soluble in the oil, it was suggested by Nelson and Brown[14] that these σ complexes also provide a highly polar medium in which the ionic or polar intermediates may form and react. The solubility of HF in benzene, though limited, is apparently sufficient to allow formation of the intermediate ions (or ion pairs) in the organic phase and alkylation of benzene by these intermediates in the same phase. The formation of alkylbenzene in better than 90% yield under conditions where a separate liquid catalyst phase does not exist supports such a conclusion. Of course, it can be argued that the ionic or polar intermediates are forced out of solution to a separate phase as soon as they are formed in a manner similar to that of aluminum bromide, hydrogen bromide, and benzene. This would provide a separate polar phase for the alkylation reaction. However, it would then be difficult to explain the large differences in the isomer distribution in the presence and absence of a separate catalyst phase. It would also be difficult to explain the role of *n*-hexane under both sets of conditions except on the basis that it affects the rates of the processes which take place in the phase where it exists, which is the organic phase.

The big change in the isomer distribution due to the presence of a large and separate liquid catalyst phase indicates that a substantial part of the alkylation reaction occurs in that phase also. Since the catalyst phase is a highly polar medium, the alkylation intermediates are likely to be more stable in the catalyst phase and, therefore, less reactive toward benzene than if they were in the organic phase. In addition, the concentration of benzene in the catalyst phase is smaller than in the organic phase, which results in a slower alkylation rate. The over-all mechanism probably involves alkylation in both phases with greater isomerization of the intermediate carbonium ions taking place in the catalyst phase than in the organic phase where they are probably closer to "intimate ion pairs."[15] The isomer distribution of the alkylbenzenes from *trans*-6-dodecene in the presence of liquid HF with or without *n*-hexane shows the amount of internal isomers (*i.e.*, the 5- and 6-phenyldodecanes) to be nearly twice as great as the 2-phenylalkane, suggesting that the internal secondary carbonium ions are slightly

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

[12] We are indebted to Drs. R. D. Swisher and S. K. Liu for supplying the phenyldodecanes.

[13] A. W. Francis, *Chem. Rev.*, **43**, 257 (1948).

[14] K. L. Nelson and H. C. Brown, *Chem. Petrol. Hydrocarbons*, **3**, 472 (1955).

[15] S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Am. Chem. Soc.*, **78**, 328 (1956); S. Winstein, P. E. Klinedinst, Jr., and E. Clippinger, *ibid.*, **83**, 4986 (1961).

more stable than those near the end of the chain. This difference in their stability is magnified at 0° where lower amounts of the 2-phenylalkane are obtained. The effect of *n*-hexane on the isomer distribution of the product from *trans*-6-dodecene is consistent with this observation. Since the proton enters the olefin at the point where the carbonium ions are most stable, they start out closer to the equilibrium distribution than those from 1-dodecene and the *n*-hexane has less effect on the alkylation products.

The behavior of *trans*-6-dodecene in the absence of a separate HF phase is a bit involved. By analogy with the behavior of 1-dodecene at 55°, one would expect the product to contain greater amounts of the internal isomers than in the presence of a separate HF phase. Instead, the product contains greater amounts of the 2-phenylalkane. This behavior is probably due to the solvation of the intermediates by benzene. The involvement of the solvent in certain free-radical reactions involving the selectivity of chlorine atoms has been observed by Russel,[16] who stressed the importance of stabilization of the reagent through complex formation with the solvent. Stock and Brown[17] have suggested that this applies equally well to electrophilic reagents in aromatic substitution reactions and Nenitzescu[8] has recently explained the reaction of benzyl benzenesulfonate with benzene in terms of ion pairs included in a cage of solvent molecules. Other examples involving change in the reactivity of the reagent due to interaction with the solvent have been observed in connection with the reaction of molecular chlorine and benzene[18] and also nitration of phenol with N_2O_4.[19] In the alkylation of benzene with *trans*-6-dodecene in the absence of a separate HF phase, the solvation of the intermediates by the benzene molecules apparently reduces the differences in their stabilities which results in greater formation of 2-phenyldodecane. Addition of large amounts of *n*-hexane removes the benzene from the vicinity of the intermediate ion pairs and magnifies the differences in their stabilities. This effect of solvation of the reactive intermediates by the benzene molecules is also in accord with the behavior of 1-dodecene in the absence of liquid HF where at 55° the amount of the 2-phenyl isomer is 37.3%. The solvation of the carbonium ions immediately formed by the benzene molecules slows down their rate of isomerization to the internal ones as it increases their reaction rate toward benzene. Therefore, addition of excess *n*-hexane not only reduces the rate of attack of the carbonium ions on benzene but also promotes greater isomerization to the more stable internal isomers by removing the solvation effect of benzene.

The absence of any tertiary alkylbenzene in the products under moderate dilution (10:1) indicates that the rate of skeletal isomerization of the intermediate ions is much slower than the rate of the alkylation step which in turn is slower than the rate of the hydride shifts which result in isomerization across the chain. Actually, skeletal isomerization of 1-dodecene in the presence of HF at 75° has recently been observed.[11] Apparently under conditions of moderate dilution such an isomerization is not fast enough to compete with the rate of the alkylation step. However, the identification of 2-methyl-2-phenylundecane in the alkylation product under conditions of greater dilution (50:1) indicates that the alkylation step has been sufficiently slowed down to permit the carbonium ions to undergo some, although small, skeletal isomerization.

On the basis of the present data, one cannot rule out the possibility of long-range isomerization within the reactive intermediate in which the positive ion abstracts a hydrogen anion from a carbon atom other than the adjacent one. Recent work on deamination of 1-propylamine indicates that 1,3-hydride shifts are considerably more common than had originally been thought.[20] However, in the present system of alkylation, the reactive intermediates exist as ion pairs and since long-range hydride shifts require greater charge separation and therefore greater energy than 1,2-hydride shifts, these long-range isomerizations are not likely to occur to any significant degree. Although it is difficult to rule out intramolecular reactions due to the absence of intermolecular reactions,[21] the fact that the rate of attack on benzene has been estimated to be nearly 350 times faster than the abstraction of a hydride ion from an isoparaffin,[22] which is more reactive than a *n*-paraffin, argues against long-range isomerization.

Experimental Section

Materials and Apparatus.—1-Dodecene was obtained from Aldrich Chemical Co. and *trans*-6-dodecene was obtained from Farchan Research Laboratories, Cleveland, Ohio. Benzene was dried by azeotropic distillation and *n*-hexane was used without further purification. Anhydrous hydrogen fluoride was obtained from Matheson Co. and was used as received.

The alkylation reactions were carried out in a 2-l. stainless steel reactor equipped with agitator, thermocouple, cooling coil, pressure gauge, and various inlet ports for introducing catalyst and olefin, sampling the reaction mixture, venting the apparatus, and withdrawing the products. All the inlets were provided with stainless steel valves.

Alkylation by 1-Dodecene in the Presence of a Separate Catalyst Phase.—Anhydrous benzene (3.9 moles) was charged to the reactor and cooled to 5–7° with ice water circulated through the cooling coil. Anhydrous hydrogen fluoride (10 moles), cooled to about −30° with Dry Ice, was then added. All the valves were closed and heating was started by circulating hot water through the coil. When the temperature reached 55°, agitation was started and the pressure had risen to 38 psig. The temperature was maintained at 55 ± 2° while 0.6 moles of 1-dodecene in 1.3 moles of benzene was pumped into the reactor over a 10-min period, using a Research Appliance Co. microbellows pump. The reaction mixture was aged for 10 min at the same temperature after which time completion of the alkylation was verified by standard bromine number determination of unsaturation.[4] The mixture was then settled for 1 hr to allow separation of the two phases while it cooled slowly. Glpc analysis of the mixture before and after the settling period gave identical results, indicating that no further changes in the isomer distribution of the product occurred during the settling period.

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[16] G. Russel, *J. Am. Chem. Soc.*, **80**, 4987, 4997, 5002 (1958).

[17] L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 49 (1963); H. C. Brown, C. J. Kim, and S. E. Scheppele, *J. Am. Chem. Soc.*, **89**, 376 (1967).

[18] L. M. Stock and A. Himoe, *Tetrahedron Letters*, No. 13, 9 (1960).

[19] J. Podkowka and A. Tarnawski, *Monatsh. Chem.*, **90**, 179 (1959).

[20] O. A. Reutov and T. N. Shatkina, *Tetrahedron*, **18**, 237 (1962). A more recent investigation of the same reaction, however, favors 1,2-hydride shifts within a protonated cyclopropane: C. C. Lee and K. E. Kruger, *J. Am. Chem. Soc.*, **87**, 3986 (1965).

[21] M. J. S. Dewar in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 295.

[22] F. E. Condon and M. P. Matuszak, *J. Am. Chem. Soc.*, **70**, 2539 (1948).

The mixture was cooled further to 5–10° and the reactor was carefully vented to release excess pressure. After settling, the catalyst was drained onto crushed ice, neutralized, and discarded. The alkylate layer was either quenched with ice and neutralized or placed in a monel still where all the HF and most of the benzene were removed under suction. The crude alkylbenzene was examined by glpc using a Barber–Coleman Mode 120 chromatograph equipped with a Sargent SR recorder with a coupled integrator. The stainless steel column was 150 ft × 0.02 in. and was coated with SE 30 silicon gum rubber. Another column of the same dimensions but coated with *m*-bis[*m*-(*m*-phenoxyphenoxy)phenoxy]-benzene[23] was also used. The crude product, except for that used for glpc analysis, was distilled in a glass apparatus and the fraction boiling at 128–134° (2 mm) (n^{25}_{D} 1.4805) was collected. The yield was 131.5 g or 90% of theoretical.

When alkylation was carried out in the presence of *n*-hexane, the hexane (800 cc) was charged to the reactor along with the benzene (2.5 moles) and hydrogen fluoride (10 moles). The olefin (0.6 moles) was diluted with 200 cc of *n*-hexane and pumped into the alkylator. The rest of the procedure was exactly as above. The yield of this reaction (89%) as well as all the subsequent alkylations was consistently high (87–92% of theoretical).

Alkylation by 1-Dodecene in the Absence of a Separate Catalyst Phase.—Anhydrous benzene (3.9 moles) and anhydrous hydrogen fluoride (2 moles) were charged to the reactor and heated to 55°. Agitation was started and the reactor was carefully vented to 30 psig at the same temperature.[24] A mixture of 0.6 moles of 1-dodecene in 1.3 moles of benzene was pumped into the reactor and the reaction was completed as above.

The same procedure was followed for alkylation in *n*-hexane solution except that the benzene (2.5 moles) and the dodecene (0.6 moles) were diluted with *n*-hexane (800 and 200 cc, respectively) before being charged to the reactor.

Alkylation with *trans*-6-Dodecene.—The same procedure was followed for alkylation of benzene with *trans*-6-dodecene, but the scale was only one-fifth that for 1-dodecene. When the reaction was run at 0°, stirring was continued for 30 min before the mixture was allowed to settle.

Check for Isomerization of the Phenylalkanes during Alkylation.—Two experiments were run in order to check for product isomerization under the prescribed alkylating conditions. In the first, a reaction was carried out in which benzene (1.3 moles) was alkylated at 55° in the presence of hydrogen fluoride (3 moles) with a mixture of 1-dodecene (0.2 moles) and 2-phenyldecane (0.03 mole). Analysis of the products by glpc failed to show any isomerization of the 2-phenyldecane.

In another experiment, the 2-phenyl isomer of the products from several alkylations was concentrated to 70% by distillation in a 15-plate column. The high 2-phenyl material was divided into equal parts. One was added to the olefin during alkylation and the other was added to an equal amount of a reaction mixture after alkylation was completed and the hydrogen fluoride had been completely removed. The products were analyzed by glpc and were found to contain the same isomer distribution.

Separation of the Phenyldodecane Isomers.—The product (0.65 mole) was fractionated through a 40-plate column between 128 and 135° (2 mm). Twelve different and approximately equal fractions were obtained. The first one contained 92% 5- and 6-phenyldodecanes and 8% 4-phenyldodecane. The latter was removed by passing through an F & M chromatograph, Model 720A, equipped with a 16 ft × 10 in. column coated with Chromosorb W (81%), Carbowax (18%), and silver nitrate (1%). The seventh fraction contained 60% 3-phenyldodecane and 40% 4-phenyldodecane. These were separated by the same preparatory glpc method. The last fraction of the distillate was pure 2-phenyldodecane. Nmr (CCl_4) of the individual isomers and the 5- and 6-phenyldodecanes mixture showed 2.35–2.65 (broad multiplet, 1 H, benzyllic) and 6.95–7.15 ppm (5 H, aromatic). Only the 2-phenyl isomer showed 1.18 ppm identified as the β-methyl group.[25]

Identification of 2-Methyl-2-Phenylundecane in the Product.—A solution of benzene (0.40 mole) in 1500 ml of *n*-hexane was alkylated with 1-dodecene (0.10 mole) in the presence of HF (3.0 moles) at 55° as described above. The organic layer was washed with water and NaOH as usual and then concentrated on a water bath to about 30 ml. Glpc analysis with the Carbowax–silver nitrate column or the polyphenyl ether (seven-ring) column showed a small band ($\approx 2\%$ of the product) between the 3- and the 2-phenyl isomers. This small band gave a single peak with an authentic sample of 2-methyl-2-phenylundecane. With the SE 30 silicon gum rubber column, the small band disappeared as did also the 2-methyl-2-phenylundecane band which overlapped with 3-phenyldodecane band.

Registry No.—Benzene, 71-43-2; 1-dodecene, 112-41-4; *trans*-6-dodecene, 7206-17-9; hydrogen fluoride, 7664-39-3.

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[23] This compound is commonly known as poly-*m*-phenyl ether (seven ring) and was obtained from Monsanto Research Corp., Dayton, Ohio.

[24] In a number of previous runs it had been established that this procedure (in which excess HF is charged and then partially vented to a certain pressure) gives an amount of HF in the reactor which is reproducible enough to avoid any variation in the product distribution.

[25] M. M. Crutchfield, private communication. The spectra of 2-methyl-2-phenyldecane and 4-methyl-4-phenylundecane show the β-methyl groups at 1.25–1.30 ppm. The signal for the benzyllic proton is absent.

Ozonolysis. IX. The Alkene Ozonation Oligomer

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The ozonation products from the geometric isomers of 2-butene, 2-pentene, and 3-hexene have been determined. The *cis*-alkenes gave excellent yields of ozonide and minor amounts of aldehyde and oligomer. With the *trans*-alkenes oligomer was the major product; in *n*-pentane solvent little aldehyde and a minor amount of ozonide were formed. In methylene chloride solvent *trans*-3-hexene gave a markedly increased amount of aldehyde but the same yield of ozonide as in pentane solvent. However, in ether solvent this alkene gave about twice as much ozonide as in pentane or methylene chloride solvent. The ozonation temperature exerted a minor effect on the relative amounts of products. The evidence does not support any of the structures that have been suggested for the oligomer and a new structure is proposed.

From the time that the ozonation of alkenes has been a practical laboratory process, it has been recognized[3] that substances which were polymeric[4] could be formed in this reaction. Indeed, it was a study of these substances that led Staudinger[5] to postulate that a molozonide must be the first product of an alkene–ozone reaction. Although some peroxidic oligomer would appear to be formed in most, if not all, alkene ozonations, these substances have received little attention. Fre-

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[2] Participant, summer 1965, NSF Research Participation for College Teachers Program.

[3] C. Harries and R. Seitz, *Ann.*, **410**, 21 (1915); C. Harries and H. Wagner, *ibid.*, **410**, 29 (1915).

[4] Actually, these substances should be designated as oligomers and not polymers, for they are of low molecular weight.

[5] H. Staudinger, *Ber.*, **58**, 1088 (1925).