# Capillary Gas Chromatography of Phenyldodecane Alkylation and Isomerization Mixtures[1]

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All six isomeric phenyl-*n*-dodecanes can be completely resolved by capillary gas chromatography, and the relative concentration of each phenyldodecane in a mixture can be estimated. The isomeric didodecylbenzenes formed during 1-dodecene alkylation or phenyldodecane isomerization are tentatively identified. The mechanisms of the alkylation and isomerization reactions are investigated and discussed.

We have found that the six isomeric phenyl-*n*-dodecanes can be completely resolved by capillary gas chromatography. Inasmuch as the alkylation of benzene with 1-dodecene and the isomerization of the reaction products gives mixtures of the five secondary phenyl-*n*-dodecanes, the application of this technique allows further insight into the mechanism of the reactions involved.

Fig. 1 shows chromatograms of such mixtures. Identification of the peaks as shown was confirmed by comparison with the pure synthetic isomers. Spacing between the isomers becomes progressively greater, and when the log retention time is plotted against phenyl position on a geometrically ex-
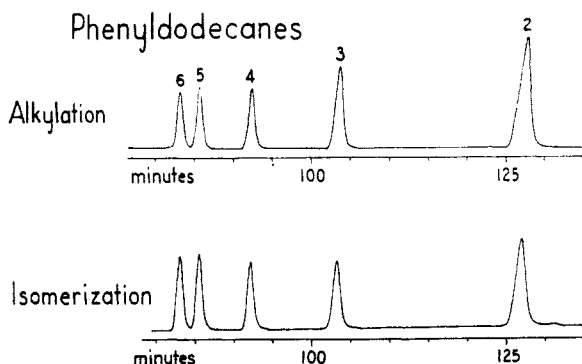


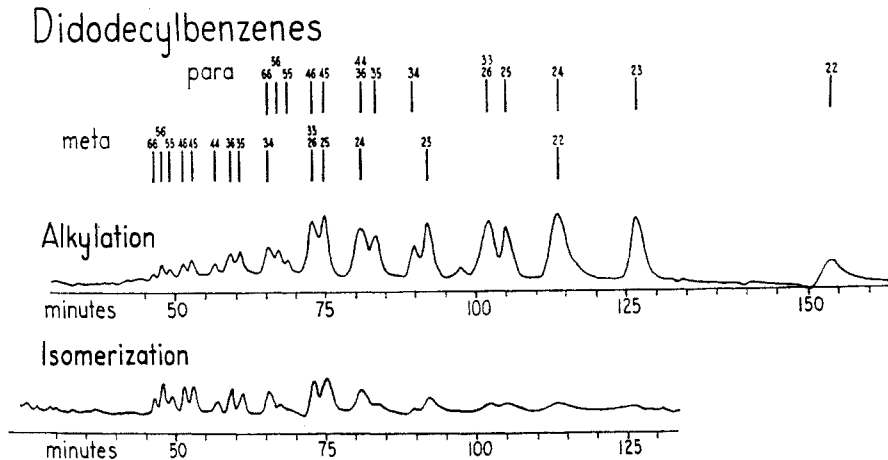Fig. 1.  Capillary gas chromatograms for phenyldodecane mixtures. 200-Foot column, Apiezon L, 170°



Fig. 2.  Capillary gas chromtograms of didodecylbenzene mixtures. 100-Foot column, Apiezon L, 240°

panded ordinate as in Fig. 3, a relatively smooth, almost straight line results.

Chromatograms of the didodecylbenzenes are shown in Fig. 2. In the absence of pure isomers for reference the identifications indicated in this figure[2] were tentatively made following several lines of

evidence. First, the didodecylbenzene peaks can be grouped into ten families on the basis of log retention time as shown in Figure 4, paralleling the five phenyldodecanes. Each family is made up of five isomers differing only in linkage to one of the dodecyl groups at the 6, 5, 4, 3, or 2 position. Secondly, with random attachment along the chain carbons there should be only half as much of the 66, 55, 44, etc., isomers as of their mixed neighbors. This is consistent with the assignment shown in Fig. 2. Thirdly, the ten families can be grouped into two sets, assumed to be the *meta* and the *para* derivatives, since the formation of *ortho*-isomers would

(1) Presented at the Frederick F. Blicke Symposium of the Division of Medicinal Chemistry at the 138th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1960.

(2) As an example of the nomenclature used, *para*-23 denotes the isomer in which the benzene ring is attached to the second carbon of one chain and to the third carbon of the other.

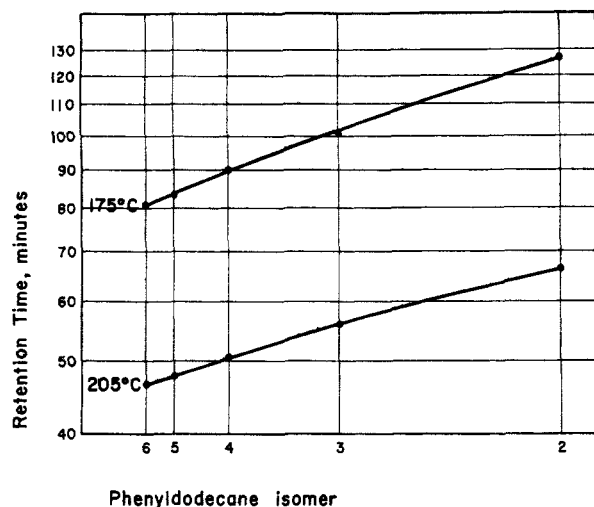Fig. 3. Retention times of phenyldodecanes. 200-Foot column, Apiezon L



Fig. 4. Retention times of didodecylbenzenes. 100-Foot column, Apiezon L

probably be minimized by steric effects. Fourthly, the set of isomers with the longer retention times is assigned the *para* structures because of their lesser stability toward aluminum chloride[3] as indicated by Fig. 2.[4]

Alkylation of benzene with 1-dodecene using aluminum chloride and hydrogen chloride as catalyst yielded all the phenyldodecanes except the 1-phenyl isomer. This is consistent with a carbonium ion mechanism. The absence of 1-phenyldodecane is due to the instability of the primary carbonium ion.

The nature of carbonium ion type intermediates in Friedel Crafts reactions has been the subject of many recent publications.[5-11] The concept of $\pi$ and $\sigma$ complexes has been elegantly demonstrated by Brown and co-workers, and Olah and Kuhn.[5-7] Thus, the 1-dodecene, benzene, aluminum chloride and hydrogen chloride form a 2-dodecyl complex (I), which may then rearrange along two paths,

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

(4) This assignment is also substantiated by unpublished work in this laboratory on the lower straight chain homologs from dihexyl- through dinonylbenzene (mixed isomers). In each case the set of isomers with longer retention time was more resistant to sulfonation, as would be anticipated for the *para* derivatives, and they showed proton magnetic resonance patterns consistent with *para* structures.

(5) H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, **74**, 3570 (1952).

(6) H. C. Brown and H. Jungk, *J. Am. Chem. Soc.*, **77**, 5579 (1955); *ibid.*, **78**, 2182 (1956).

(7) G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, **80**, 6535, 6541 (1958).

(8) R. L. Burwell, A. D. Shields, *J. Am. Chem. Soc.*, **77**, 2766 (1955).

(9) H. C. Brown, H. W. Pearsall, L. P. Eddy, W. J. Wallace, M. Grayson, and K. L. Nelson, *Ind. Eng. Chem.*, **45**, 1462 (1953).

(10) L. Schmerling and J. P. West, *J. Am. Chem. Soc.*, **76**, 1920 (1954).

(11) D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **75**, 2407, 2411 (1953).
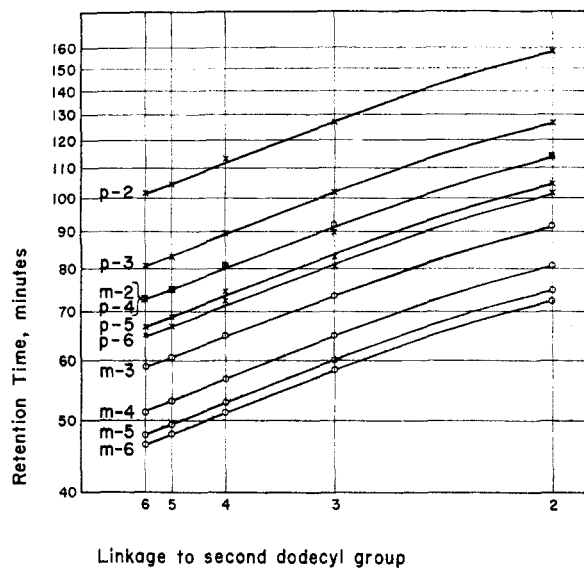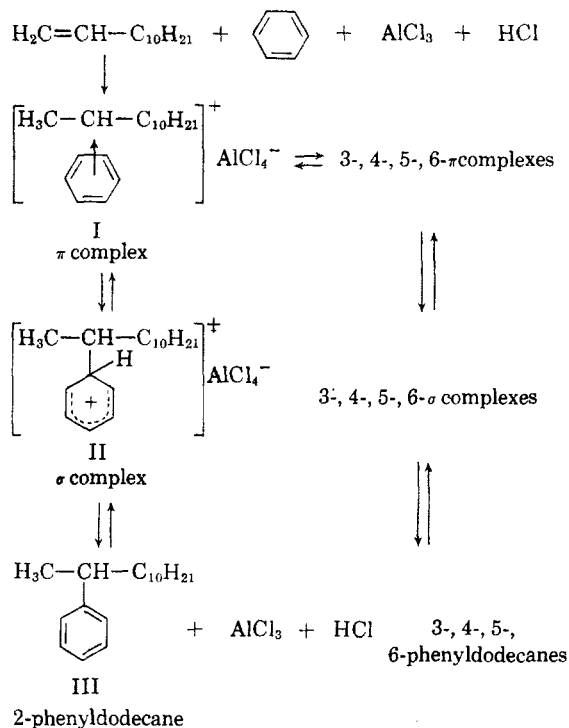
either to isomeric $\pi$ complexes or to a 2-dodecyl $\sigma$ complex (II), which then yields the corresponding 2-phenyldodecane (III).

$$H_2C{=}CH{-}C_{10}H_{21} \;+\; \langle\bigcirc\rangle \;+\; AlCl_3 \;+\; HCl$$

$$\left[\begin{array}{c} H_3C{-}CH{-}C_{10}H_{21} \\ \langle\bigcirc\rangle \end{array}\right]^{+} AlCl_4^{-} \;\rightleftarrows\; 3\text{-}, 4\text{-}, 5\text{-}, 6\text{-}\pi\text{complexes}$$

I
$\pi$ complex

$$\left[\begin{array}{c} H_3C{-}CH{-}C_{10}H_{21} \\ {}_{\backslash}H \\ \langle\bigcirc\rangle_{+} \end{array}\right]^{+} AlCl_4^{-} \qquad 3\text{-}, 4\text{-}, 5\text{-}, 6\text{-}\sigma \text{ complexes}$$

II
$\sigma$ complex

$$H_3C{-}CH{-}C_{10}H_{21}$$
$$\langle\bigcirc\rangle \;+\; AlCl_3 \;+\; HCl \qquad 3\text{-}, 4\text{-}, 5\text{-}, 6\text{-phenyldodecanes}$$

III
2-phenyldodecane

It appears from the data in Table I that the overall rates along these two paths are of the same order of magnitude. For example, in Run No. 1, the distribution of phenyldodecane isomers at the end of olefin addition (fifteen minutes) showed a higher proportion of 2-phenyl to 6 phenyl (about 3:1) as compared to those after prolonged aging or isomerization (about 2:1). Thus, the equilibrium was not reached during the alkylation but only after

TABLE I

PHENYLDODECANE ISOMER DISTRIBUTION IN ALKYLATION AND ISOMERIZATION AT 37°

| Run No. | | 1-Dodecene mole | Phenyldodecane | | Benzene Mole | AlCl₃ Mole | Total Time Min. | Phenyldodecane, % | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Isomer | Mole | | | | 2- | 3- | 4- | 5- | 6- |
| 1 | A | 0.60 | — | — | 3.60 | 0.027 | 15ᵃ | 40 | 19 | 13 | 15 | 13 |
| | B | | | | | | 25 | 36 | 19 | 16 | 15 | 14 |
| | C | | | | | | 45 | 32 | 19 | 16 | 17 | 16 |
| 2 | | — | 3- | 0.20 | 1.00 | 0.035 | 45 | 33 | 19 | 15 | 17 | 16 |
| 3 | | — | 2- | 0.016 | 0.22 | 0.005 | 45 | 32 | 18 | 16 | 18 | 16 |
| 4 | | — | 6- | 0.016 | 0.22 | 0.005 | 45 | 31 | 18 | 16 | 18 | 17 |
| 5 | A | 0.50 | 3- | 0.10 | 3.50 | 0.027 | 15ᵃ | 33 | 31 | 12.5 | 12.5 | 11 |
| | B | | | | | | 45 | 34 | 30 | 12 | 13 | 11 |
| | C | | Calculated distribution with no isomerizationᵇ | | | | | 32.5 | 34.1 | 10.6 | 12.2 | 10.6 |

ᵃ The addition of olefin was completed in 15 min. Alkylation was essentially complete as indicated by bromine number determination. ᵇ Based on distribution found in Run 1 A.

aging. If the isomerization of the 2-dodecyl π complex to the other π complexes were very much slower than its conversion to the 2-dodecyl σ complex, a preponderance of 2-phenyldodecane would be expected in the product, whereas, the maximum proportion we have observed is around 40%. In the opposite situation, the alkylation should always have given the equilibrium proportion with around 30% of 2-phenyldodecane.

Isomerization of phenyldodecanes under the influence of aluminum chloride and hydrogen chloride appears to be more complicated. Starting from pure 2- or 3- or 6-phenyldodecane, it was possible to achieve an equilibrium distribution of phenyldodecanes. However, the single pure phenyldodecane showed only traces of isomerization with aluminum chloride at the alkylation level. By doubling the aluminum chloride only a few percent rearranged. At four times the alkylation aluminum chloride level, rapid isomerization took place and the equilibrium mixture was obtained.

The reaction mixture from a 3-phenyldodecane isomerization run was fractionally distilled and analyzed by gas chromatography. A comparison of the components from this mixture with that from 1-dodecene alkylation (Table II) showed that the phenyldodecane contents were about the same but in the isomerization, the amount of didodecylbenzene was significantly less while the lower boiling or

TABLE II

PRODUCTS OF ALKYLATION AND ISOMERIZATION

| Reactants, Mole | Alkylation | Isomerization |
|---|---|---|
| 1-Dodecene | 1.00 | — |
| 3-Phenyldodecane | — | 0.20 |
| Benzene | 5.50 | 1.00 |
| AlCl₃ | 0.044 | 0.035 |
| Phenyldodecane yield | 0.85ᵃ | 0.67ᵇ |
| Product distribution, % | | |
| Low boiler | 2.5 | 7.8 |
| Phenyldodecanes | 87.5 | 84.6 |
| Didodecylbenzenes (high boiler) | 10.0 | 7.6 |

ᵃ Mole per mole 1-dodecene. ᵇ Mole per mole 3-phenyldodecane.

cracking products were greater. This is a direct consequence of the higher aluminum chloride level necessary for the isomerization reaction, as is the lower yield obtained.

Requirement of a higher aluminum chloride level for isomerization was verified in another experiment (Table I, Run 5). A measured amount of 3-phenyldodecane was pre-mixed with benzene and aluminum chloride. The 1-dodecene was added as in normal alkylation. At the end of olefin addition, completion of the alkylation was verified by standard bromine number determination of unsaturation. The resulting phenyldodecane mixture was analyzed by gas chromatography. The percentage of 3-phenyl isomer was much higher than the equilibrium value and this did not change significantly upon aging. The composition of the product (5A, B) corresponded closely to that from the alkylation reaction (1A) with relatively little isomerization of the added 3-phenyldodecane (compare with 5C). Thus, it appears that the formation of all five phenyldodecanes in the alkylation must mainly be a consequence of isomerization of the intermediate π complex (I). Once they are formed there is relatively little isomerization of the phenyldodecanes under minimum alkylation conditions.

Failure of the phenyldodecanes to isomerize to their equilibrium mixture at low catalyst level, even in the presence of the alkylation reaction, may result from a low rate constant for reversion to the σ and π complexes plus occurrence of side reactions destroying the catalyst activity.

Since our preliminary presentation of this work,[1] Olson has published his isomerization results on pure phenyldodecane[12] using aluminum chloride and water as catalyst. The aluminum chloride level required is lower than reported here; this however may be attributed to the differences between aluminum chloride-hydrogen chloride and aluminum chloride-water systems.[13,14]

(12) A. C. Olson, Ind. Eng. Chem., 52, 833 (1960).
(13) L. Schmerling, Ind. Eng. Chem., 45, 1447 (1953).
(14) C. D. Nenitzescu, Experientia, 16, 333 (1960).

EXPERIMENTAL

*Capillary gas chromatography.* A Barber-Colman Model 20 chromatograph equipped with a radium-226 ionization detector was used. The columns were 0.01-inch I.D., $^1/_{16}$-inch O.D. stainless steel capillaries coated with Apiezon Grease L. The use of capillary columns and ionization detectors in gas chromatography has been previously described.[15-21]

Capillary columns, in which the stationary phase is coated directly on the inside wall of the tube, provide extremely high separating efficiencies. Their low capacity, however, requires a highly sensitive detector. The radium-226 ionization detector used in this work is reported to be sensitive to $10^{-13}$ moles of most organic compounds. The small radioactive source in the detector ionizes some atoms of the argon carrier gas and excites others to a metastable but unionized state. The metastable argon atoms in turn ionize molecules of sample components whose ionization potentials are lower than the excitation potential of argon (as are the ionization potentials of most organic compounds). The ionization current is amplified and recorded and serves as an extremely sensitive means of detecting the elution of sample components from the column. The steady voltage developed across the input resistance of the amplifier by the ionization current of pure argon is balanced out by applying an equal and opposite voltage so that a zero reading is obtained when no compound is being eluted.

The capacity of a capillary column is so small that even the smallest sample size which can be conveniently handled is many times too large. Therefore, a sample splitting device is built into the chromatograph allowing the major portion of the injected sample to be discarded.

With a 200-foot column at 170° and an inlet argon pressure of 25 psig., complete resolution of the six isomeric phenyl *n*-dodecanes was achieved in about 2 hr. Partial separation of the corresponding dialkylbenzenes was achieved at 240° in several hours. With a 100-foot column at 200° and 25 p.s.i.g., the retention time of the phenyldodecanes was cut to about 20 min., but the 5- and 6-phenyl isomers were only partially resolved.

The detector cell was operated at about 240° throughout and the flash heater at 290°. The flow rate of the effluent from the sample splitter was normally kept at 50 ml. per min. Flow rate through the column was of the order of 1 ml. per min., so that about 98% of the injected sample was normally discarded. The volume of sample injected ranged from 0.5 to 10 microliters, depending on the number of components present in the sample. Injection was made with a 10-microliter syringe.

The usual flow rate of scavenging gas to the detector was 80 ml. per min. The amplifier gain was varied between $1 \times 10^{-6}$ and $3 \times 10^{-8}$ amps. full scale to accommodate the range of peak sizes. Full current output at any gain setting delivered a 50-millivolt output to the recorder, which had a 1-second pen speed.

Areas under the peaks were measured by carefully tracing the peaks onto constant thickness tracing paper and then cutting out and weighing the tracings. Replicate measurements on the same peak showed the standard deviation of this operation to be 1.6 parts per hundred.

Replicate chromatograms displayed wide variations in total instrument response. The variations were greater than could be attributed to imprecision of sample injection and were concluded to be due to nonreproducibility of the sample splitter. For this reason, the area per cent of a peak rather than its absolute area was used as a measure of concentration. Appropriate corrections were applied when the amplifier gain was changed between peaks of a chromatogram. Based on replicate chromatograms of synthetic three-component mixtures, the standard deviation of area per cent measurements at the 20% concentration level was found to be 0.6 percentage points or 3 parts per hundred.

Chromatograms of 5 synthetic mixtures of 2-, 4-, and 6-phenyldodecane were obtained. The concentrations of the 2- and 6-phenyl isomers ranged from 5 to 80 weight per cent, while that of 4-phenyldodecane was constant at 15%, and this isomer served as internal standard. Area ratios of the 2- and 6-phenyldodecane peaks to the 4-phenyldodecane peaks were calculated. The 2- and 6- phenyl isomers were found to give equal response in the instrument. As these isomers represent the extremes in retention times of the five phenyldodecanes occurring in alkylation and isomerization mixtures, it was concluded that the response of the intermediate isomers was also the same.

Plots of area ratio *versus* weight per cent were somewhat nonlinear. The weight per cent was approximately proportional to the 1.1 power of the area ratio. Thus, the weight per cent of a major component is somewhat larger than the observed area per cent, while that of a minor component is somewhat smaller than the area per cent. If the concentration range is not large, the correction is less than experimental error. Area per cents encountered in the alkylation mixtures studied ranged from 11 to 41%. The nonlinearity correction was neglected, and area per cents are reported directly as weight per cents.

*Alkylation.* The alkylation was carried out at 35-37° by adding 0.6 mole of 1-dodecene to 3.60 moles of dry benzene which had previously been saturated with dry hydrogen chloride gas and mixed with 0.027 mole of anhydrous aluminum chloride. The addition was completed in about 15 min. The reaction mixture was stirred for additional time up to 30 min. After separation of any catalyst complex phase from the alkylated layer, the latter was quenched by adding water.

*Isomerization.* One-tenth mole of pure phenyldodecane was mixed with 0.5 mole of dry benzene and 0.0175 mole of aluminum chloride. The solution was saturated with hydrogen chloride, and a continuous and steady sweep of the gas was maintained throughout the reaction. The temperature was maintained at 35-37°. Samples were withdrawn from time to time without interrupting either the stirring or the gas flow.

*Materials.* 1-Dodecene was Aldrich commercial grade, used without further purification. Aluminum chloride was Fisher reagent grade. Benzene was commercial grade, from which water had previously been removed by azeotropic distillation. Pure phenyldodecane isomers were synthesized by well established methods in the literature *via* the Grignard reaction, dehydration and hydrogenation. Their purity was verified by gas chromatography.

(15) A. J. P. Martin, in *Vapour Phase Chromatography*, ed. by D. H. Desty and C. L. A. Harbourn, p. 1, Butterworth, London, 1957.

(16) M. J. E. Golay, in *Gas Chromatography*, ed. by V. J. Coates, p. 1, Academic Press, New York, 1958.

(17) M. J. E. Golay, Second Symposium on Gas Chromatography, Amsterdam, May 20, 1958.

(18) J. E. Lovelock, *J. Chromatogr.*, 1, 35 (1958).

(19) A. Zlatkis and J. E. Lovelock, *Anal. Chem.*, 31, 620 (1959).

(20) S. R. Lipsky, R. A. Landowne, and J. E. Lovelock, *Anal. Chem.*, 31, 852 (1959).

(21) R. D. Condon, *Anal. Chem.*, 31, 1717 (1959).