Isomeric Linear Phenylalkanes and Sodium Alkylbenzenesulfonates[1]

F. D. SMITH, A. J. STIRTON and M. V. NUNEZ-PONZOA, Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania

Abstract

Linear phenylalkanes made from 12, 14, 16 and 18 carbon α-olefins and benzene, with aluminum chloride or methanesulfonic acid as the condensing agent, were found by gas-liquid chromatography of the acetophenone homologs obtained by chromic acid oxidation to be a mixture of all possible internal position isomers.

Product distribution measured by the relative amounts of acetophenone homologs must be corrected in the case of the 2- and 3-phenylalkanes because of unequal oxidative scission and differing ease of oxidation. The 2-phenyl isomer, formed in largest amount and presumably the highest melting isomer, was separated by low temperature crystallization from acetone.

The phenylalkane product mixtures and the isolated 2-phenyl isomers were sulfonated and detergent and surface active properties were compared. The sodium *p*-alkylbenzenesulfonates from the 2-phenylalkanes were more biodegradable than the mixtures in the river water die-away test.

Introduction

LINEAR SODIUM ALKYLBENZENESULFONATES of known composition needed as controls in biodegradation studies of tallow-based detergents and surface active agents were prepared from benzene and 12, 14, 16 and 18 carbon α-olefins by the Friedel and Crafts reaction.

Since available gas-liquid chromatographic (GLC) equipment could not resolve a multicomponent mixture of linear phenylalkanes, a method found useful in showing the composition of arylstearic acids was employed (9). Resolution of acetophenone homologs obtained by chromic acid oxidation showed a maximum of the 2-phenyl isomer and a minimum of the 3-phenyl isomer, with distribution of the more internal isomers depending upon the catalyst and the chain length of the α-olefin. Use of reference 2-, 3-, and 6-phenyldodecanes[3] showed the values obtained for the 2- and 3-phenyl isomers must be corrected because of unequal oxidative scission and differing ease in oxidation. Although the need for such correction detracts from the value of the oxidation method, the amended distribution was then in general agreement with published data on linear phenylalkanes (6,8,11).

The 2-phenyl isomers and in one case the 3-phenyl isomer were isolated from the Friedel-Crafts reaction product by low temperature crystallization from acetone.

The linear phenylalkane mixtures and the isolated 2-phenylalkanes were sulfonated and the surface active properties and relative ease of biodegradation were compared. The sequence of reactions for octadecene-1 is shown in Figure 1. Identification of the lower molecular weight acetophenone homologs showed the point of attachment of the benzene ring.

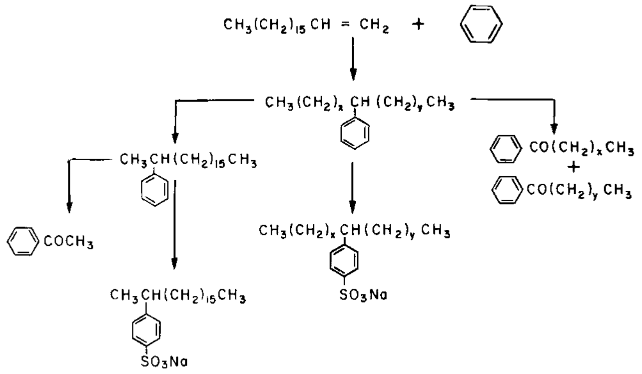

FIG. 1. Sequence of reactions.

Experimental

Phenylalkanes

α-Olefins. Commercial 95% α-olefins further purified by low temperature crystallization from acetone followed by distillation had the constants shown in Table I. Infrared analysis for *trans* olefin (characteristic adsorption at 965 cm^{-1}) showed the presence of less than 1%.

Friedel-Crafts Reaction. Hexadecene-1, 200g (0.892 moles) was added dropwise in 30 min to a stirred suspension of 6.4 g $AlCl_3$ (0.048 moles, 5.4% mole ratio) in 418 g benzene (5.35 moles), the temperature rising to 45C. The mixture was cooled, hydrolyzed on ice, washed acid free and distilled to give phenylhexadecane. The other $AlCl_3$ catalyzed reactions were similar except that it was necessary to supply heat to reach the final temperature in the case of phenyltetradecane.

Methanesulfonic acid was used as the catalyst following a procedure described for oleic acid (4) except that the reaction temperature was raised to 60C. A small amount of olefin was recovered in CH_3SO_3H catalysis and polymeric still residues were formed with $AlCl_3$. Yield and constants are shown in Table II.

Isolation of 2- and 3-Phenyl Isomers. The 2-phenyl isomer was isolated from the phenylalkane mixture by repeated crystallization from acetone, 5 cc/g, at −58C.

Phenyltetradecane, 92 g, gave 9.6 g 2-phenyltetradecane after 5 crystallizations from acetone. The acetone mother liquor from the isolation of 2-phenyltetradecane was concentrated to 250 ml, cooled to −58C and a small amount of solid containing mainly the 2-phenyl isomer was separated. The filtrate was concentrated again to 125 ml, cooled to −58C and the precipitate crystallized 5 times from acetone to give 3-phenyltetradecane.

TABLE I
α-Olefins

	f.p. °C	bp °C/mm	Iodine value		n^{20}_D
			Found	Theo.	
Dodecene-1	−27	150/120	149.6	150.8	1.4301
Tetradecene-1	−12.5	163/60	128.4	129.3	1.4363
Hexadecene-1	+ 4	181/40	112.2	113.1	1.4413
Octadecene-1	+18	201/32	100.5	100.5	1.4448

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[2] E. Utiliz. Res. Dev. Div., ARS, USDA.
[3] The 3- and 6-phenyl isomers supplied by R. D. Swisher, Monsanto Co.

TABLE II
Linear Phenylalkane Reaction Products

Phenylalkane	Yield %		Distillation range bp °C/0.2 mm	n_D^{20}
	$AlCl_3$	CH_3SO_3H		
Phenyldodecane	65	79	108–14	1.4817
Phenyltetradecane	57	70	118–22	1.4811
Phenylhexadecane	77	65	143–8	1.4800
Phenyloctadecane	83	64	145–52	1.4796

Table III shows the purity and physical constants of the isolated 2- and 3-phenyl isomers of different chain length. Two component phenylalkane mixtures were found to be separable by the same GLC equipment used in the analysis of acetophenone homologs. The close agreement in percent purity analyzed both as the ketones and the hydrocarbons shows the chromic acid oxidation method is sufficiently accurate under these conditions.

Chromic Acid Oxidation. Chromic acid, 3 g, was added to a solution of 2 g phenyloctadecane in 50 ml glacial acetic acid. The mixture was refluxed 30 min, cooled, the condenser was rinsed with 30 ml ethyl ether and the mixture was decanted into a separatory funnel containing 200 ml of saturated Na_2SO_4 solution and 50 ml ether. The ether solution was washed, separated, washed with 100 ml Na_2SO_4 solution, then with 100 ml 5N NaOH, washed free of alkali, evaporated with an air jet to 3 ml volume, dried with anhydrous Na_2SO_4 and analyzed by GLC.

Analysis by GLC. The instrument was an F & M dual column programmed temperature gas chromatograph Model 720. Either an 8 ft stainless steel column containing 10% Silicone Rubber SE-30 on 45–60W, or a 6 ft column containing 10% Apiezon L on 60–80W, was equally suitable in most cases. A 6 ft 20% Carbowax 20 M column was found useful for observing the relative amounts of butanophenone and nonanophenone from phenyldodecane. The alkyl aryl ketones were recognized by comparison with reference acetophenone homologs. Figure 2 shows the separation of acetophenone homologs from the oxidation of phenyloctadecane. The peak numbers are the points of attachment of the benzene ring on the aliphatic chain.

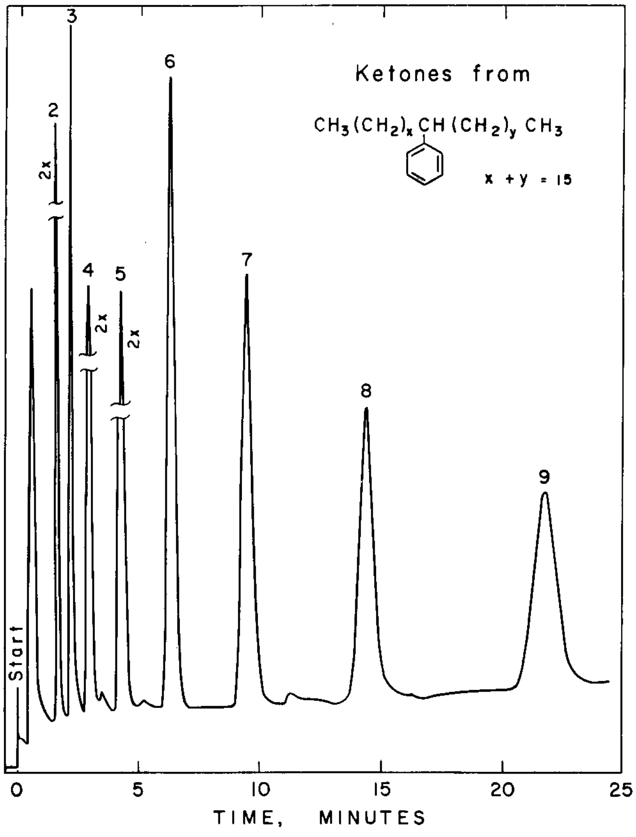

FIG. 2. Separation of acetophenone homologs from the chromic acid oxidation of phenyloctadecane.

TABLE III
Isolated 2- and 3-Phenyl Isomers

	Purity %		Freezing point °C	n_D^{20}
	Analysis of ketones[a]	Analysis of hydrocarbons[b]		
2-Phenyldodecane	99.3	99.2	−12.3	1.4816
2-Phenyltetradecane	98.9	99.1	2.5	1.4808
3-Phenyltetradecane	99.1[c]	98.9	0.2	1.4808
2-Phenylhexadecane	98.6	98.7	6.5	1.4800
2-Phenyloctadecane	99.0	99.0	17.2	1.4797

[a] GLC analysis of ketones from CrO_3 oxidation. The impurity is the corresponding 3- or 2-phenyl isomer.
[b] GLC analysis of the hydrocarbon.
[c] Presence of a trace amount (0.1%) of 4-phenyltetradecane.

Scission of Phenylalkanes. The optimum conditions for CrO_3 oxidation produce a mixture of alkyl aryl ketones containing also unreacted phenylalkanes which prevent recognition of the higher molecular weight ketones in some cases. Both ketones can be identified, however, when the proper column is used for a given pair of ketones or when a single phenylalkane is used. The 2-, 3-, and 6-phenyldodecanes gave the following pairs, respectively: 61.7% $PhCOCH_3$ + 38.3% $PhCOC_{10}H_{21}$; 22.35% $PhCOC_2H_5$ + 77.65% $PhCOC_9H_{19}$; 50.4% $PhCOC_5H_{11}$ + 49.6% $PhCOC_6H_{13}$. Oxidation of a mixture containing 4- and 5-phenyldodecane gave 54.1% $PhCOC_3H_7$ + 45.9% $PhCOC_8H_{17}$ and 52.4% $PhCOC_4H_9$ + 47.6% $PhCOC_7H_{15}$. Oxidative scission is therefore unequal for the 2- and 3-phenyldodecanes but is approximately equal for the more internal isomers.

Selective Oxidation. Analysis of a known mixture of 62.2% 2-, 19.5% 3-, and 20.0% 6-phenyldodecane after CrO_3 oxidation showed residual hydrocarbons present in the neutral ketone fraction in the proportion 16.2% 2-, 42.2% 3-, and 41.6% 6-phenyldodecane. The 2-phenyl isomer therefore differs from the others in being more susceptible to CrO_3 oxidation.

Treatment of Data. Two factors operate to give erroneous high values for the 2-phenyl isomer when analysis of phenylalkanes is based upon the lower molecular weight acetophenone homologs produced by oxidation. These are: (I) unequal scission favoring acetophenone; (II) greater ease of oxidation compared to other position isomers.

Known mixtures of 2-, 3-, and 6-phenyldodecane in proportions 1:1:1, 1:1:3, 2:1:1, and 3:1:1 were analyzed by GLC both as the phenylalkanes and as the lower molecular weight acetophenone homologs. The results were plotted to give the two straight lines of Figure 3 from which the values of Table IV, based on the ketones were corrected.

The 3-phenyl isomer appears to oxidize just about as readily as the more internal isomers but since oxidative scission favors decanophenone over propiopheneone, erroneous low values are obtained. Analysis of known mixtures of the three reference phenyldodecanes in different proportions gave a constant factor, 2.15; multiplication by this gave the corrected values of Table IV.

After correcting the values for the 2- and 3-phenyl isomer a further small correction ranging from 0.5

TABLE IV

Product Distribution, Isomeric Phenylalkanes, Mole %[a]

Isomer	Phenyldodecane[b]		Phenyltetradecane[b]		Phenylhexadecane[b]		Phenyloctadecane[b]		Phenyldodecane[c]	
	Found	Corrected	Found	Corrected	Found	Corrected	Found	Corrected	Found	Corrected
2-Ph	53.2	41.2	37.9	24.5	53.6	42.0	60.2	49.2	41.2	28.0
3-Ph	9.2	19.8	9.1	19.6	9.3	20.0	9.1	19.6	9.8	21.1
4-Ph	11.4	12.8	11.8	14.7	9.8	10.7	9.8	10.3	13.3	15.2
5-Ph	14.5	14.5	13.2	13.2	9.5	9.5	8.0	8.0	19.4	19.4
6-Ph	11.7	11.7	12.2	12.2	6.7	6.7	4.4	4.4	16.3	16.3
7-Ph			15.8	15.8	5.4	5.4	2.9	2.9		
8-Ph					5.7	5.7	2.6	2.6		
9-Ph							3.0	3.0		

[a] "Found" determined by GLC of acetophenone homologs; "corrected" by use of reference 2-, 3-, and 6-phenyldodecanes.
[b] $AlCl_3$ catalyst
[c] CH_3SO_3H catalyst

to 3% was made in the value for the 4-phenyl isomer to bring the total to 100%. The corrected values for distribution of isomers of phenyldodecane, phenylhexadecane, and phenyloctadecane are now in general agreement with other reported values (6,8,11). In the case of phenyltetradecane the smaller amount of the 2-phenyl isomer and larger amounts of the more internal isomers (Table IV) may result from the fact that the reaction mixture remained at a lower temperature (30–40C) for a longer time.

Product distribution based on acetophenone homologs is compared to corrected distribution in the curves of Figure 4. The corrected distribution for phenyldodecane, phenylhexadecane and phenyloctadecane, with $AlCl_3$ as the catalyst, is shown in Figure 5. The $AlCl_3$ and CH_3SO_3H catalysts are compared in Figure 6; there is a minimum of the 4-phenyl isomer in each case. Methanesulfonic acid is a less vigorous catalyst and the amounts of each isomer are more nearly equal.

Sodium Alkylbenzenesulfonates

Sulfonation. Concentrated H_2SO_4, 100 ml, mole ratio to phenylalkane 27, was added with stirring to 18.5 phenyltetradecane. The sulfonation mixture was heated and stirred 1 hr at 70–80C and the two phases were hydrolyzed separately on cracked ice. The aqueous H_2SO_4 layer was extracted with ethyl ether and the ether extract was used to extract the organic sulfonic acid layer, to give a total volume of 500 ml ether extract from which water was carefully separated. After washing with 25 ml of water the ether solution was evaporated, dissolved in 100 ml of 50% ethanol and neutralized by passing through a Dowex 50W X-8 column. The aqueous ethanol solution of the sodium salt was evaporated and dried in a vacuum oven for 6 hr at 60C to give sodium *p*-tetradecylbenzenesulfonate, yield 96%. Infrared spectra showed the presence of a small amount of the *o*-sulfonate with characteristic absorption at 762 cm^{-1} (5).

The 2-phenylalkanes were sulfonated in the same manner, neutralized with aqueous NaOH and recrystallized from aqueous ethanol at room temperature. Infrared spectra showed the presence of a small amount of *o*-sulfonate only in the case of the product from 2-phenyltetradecane. Analyses for Na on all of the alkylbenzenesulfonates agreed with theoretical values with an average deviation of 0.04% Na.

Surface Active Properties

Surface active and related properties were measured by methods used in previous publications (1,2,7,10,13). The results are shown in Table V. The surface and interfacial tension values for the linear sodium alkylbenzenesulfonate mixtures decrease with increase in molecular weight. Properties of the sulfonated phenyltetradecane mixture may not be strictly comparable because of differences in relative amounts of the various position isomers.

Solubility and Krafft Point. The sodium alkyl-

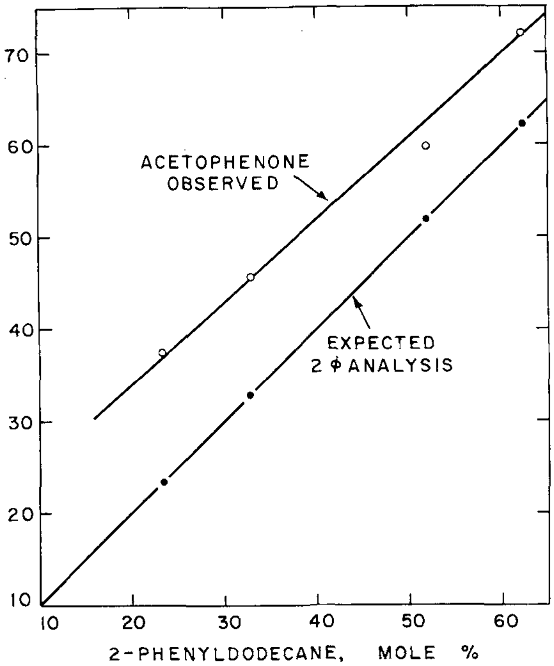

FIG. 3. Corrected analysis for 2-phenylalkane.

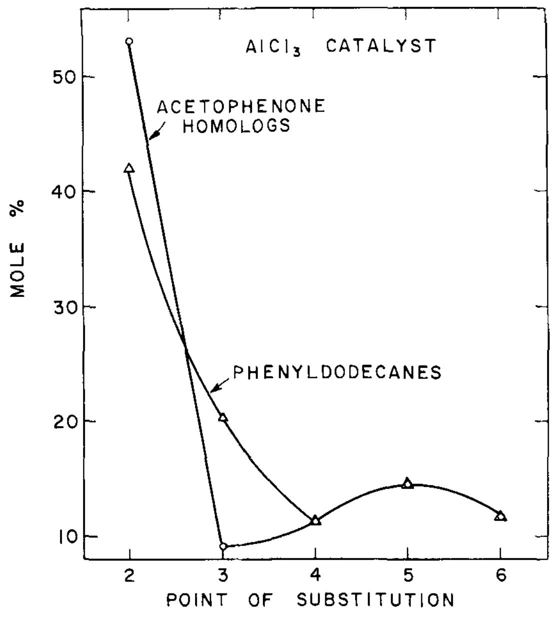

FIG. 4. Corrected distribution of phenyldodecanes, $AlCl_3$ catalyst.

TABLE V

Linear Sodium Alkylbenzenesulfonates

Number of aliphatic C atom	Surface and interfacial tension 0.1%, dynes/cm		Krafft point, °C	Ca^{++} stability (13) ppm $CaCO_3$	Lime soap dispersing power % (1)	Detergency[a] 60C, 300 ppm, ΔR		Foam height (7) 60C, 300 ppm, mm		Wetting time (2) 0.1%, seconds		Biodegradability[c] Days to 80% degradation
	S.T.	I.T.				0.25%	0.05% + 0.2% builder[b]	0.25%	0.05% + 0.2% builder	Distilled water	300 ppm	
					Sulfonation of Phenylalkane Mixtures							
12	36.8	9.1	......	620	20	22	26	230	235	5.1	8.4	4
14	34.9	6.6	......	560	20	23	28	205	210	10.2	78	16
16	34.4	5.9	......	500	30	18	25	20	150	86	> 300	10
18	33.3	5.5	......	620	40	7	27	0	5	>300	> 300	16
					Sulfonation of 2-Phenylalkanes							
12	.... d	.... d	31.5	.... d	.... d	21	27	245	220	10.3	80	3
14	.... d	.... d	46.0	.... d	.... d	21	28	80	220	30	> 300	4
16	.... d	.... d	54.2	.... d	.... d	21	25	10	105	155	> 300	5
18	.... d	.... d	60.8	.... d	.... d	11	26	0	5	>300	> 300	17

[a] Detergency measured as ΔR, increase in reflectance after washing standard soiled cotton (3) in a Terg-O-Tometer. For comparison the values for Na dodecyl sulfate are 18.0 and 17.7.

[b] Builder was a mixture of $Na_5P_3O_{10}$, Na_2SO_4, $Na_4P_2O_7$, and Na_2SiO_3 and CMC.

[c] River water die-away test (12).

[d] This group of compounds was not soluble enough for the test conditions.

benzenesulfonates from phenylalkane mixtures are easily soluble and readily form clear 1% solutions, which however, partially precipitate on standing in the case of sodium hexadecyl- and octadecylbenezenesulfonates. The Krafft point, the temperature at which a 1% aqueous dispersion forms a clear solution on gradual heating, is a convenient method of expressing solubility. The individual sodium *p*-(1-methylalkyl)-benzenesulfonates from the 2-phenylalkanes are less soluble than the alkylbenzenesulfonate mixtures and have Krafft points which increase markedly with increase in molecular weight.

Lime Soap Dispersion. Since values of 10 or less are desirable for an efficient lime soap dispersing agent (11) the values for dodecyl- and tetradecylbenzenesulfonate mixtures indicate they are only moderately effective, but superior to the 16 and 18 carbon homologs.

Detergency, Foam Height and Wetting. Built solutions of the alkylbenzenesulfonates have about equal detergency in hard water (ΔR=25–28). In distilled water the sulfonation products from octadecene-1 have the lowest detergency.

The sulfonation products from the phenyldodecane mixture and from 2-phenyldodecane, followed by the products from tetradecene-1, have the best foaming and wetting properties.

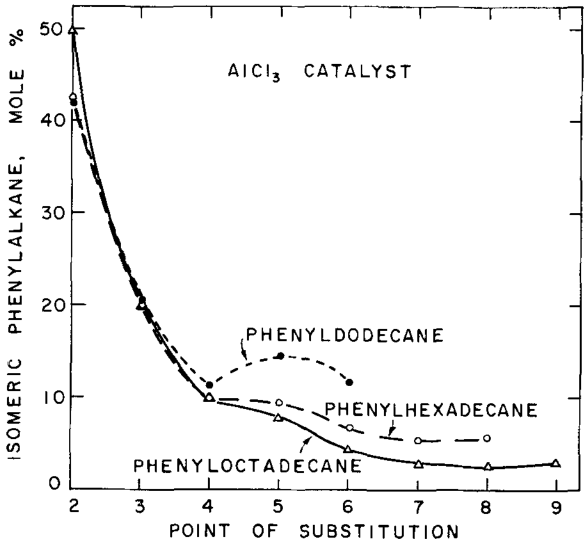

FIG. 5. Corrected distribution of phenylalkanes, $AlCl_3$ catalyst.

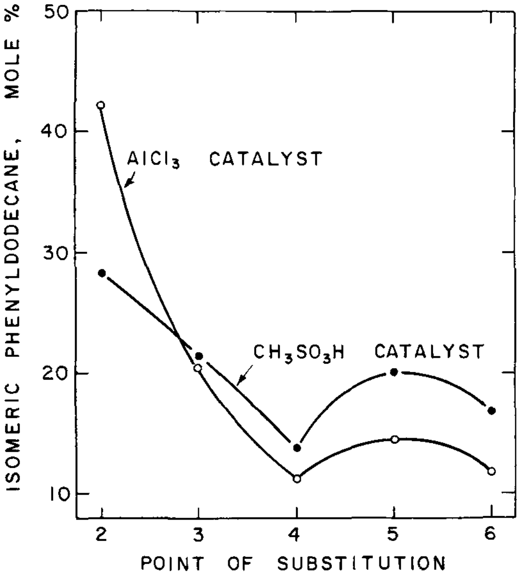

FIG. 6. Comparison of $AlCl_3$ and CH_3SO_3H catalysts.

Biodegradability. The die-away test in Schuylkill River water (12) showed the sulfonated phenylalkane mixtures of 14, 16 and 18 C atoms were more resistant to biodegradation than linear sodium dodecylbenzenesulfonate. The sulfonated 2-phenylalkanes were more biodegradable than the mixtures except for the difficultly soluble sodium *p*-(1-methylheptadecyl)-benzenesulfonate.

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