Isomerizations Accompanying Friedel-Crafts Alkylations of Benzene by Detergent Range Alkylating Agents

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ABSTRACT

The Friedel-Crafts alkylation of benzene with linear detergent range olefins and chloroparaffins in the presence of $AlCl_3$ and HF catalysts was investigated. Evidence is presented to support the argument that isomerization occurs both in the alkylating agent prior to alkylation and in the product arenes following alkylation. Data on product phenylalkane isomer distributions is presented. The alkylation of benzene with 2-hexyl-1-decene in the presence of $AlCl_3$ was shown to initially yield only one phenylhexadecane isomer, probably 7-methyl-7-phenylpentadecane, with subsequent product isomerization to other isomeric hydrocarbons.

INTRODUCTION

In the period following World War II, arene sulfonates with a high degree of alkyl sidechain branching (ABS) grew to dominate as the surfactant used in household detergents. When biodegradability became important ABS was replaced by linear alkylbenzene sulfonate (LAS).

Workers have realized that in LAS the physical properties of the arene sulfonate depend not only upon the molecular weight of the alkylate, but also upon the position of the phenyl group on the sidechain. For example, 5- and 6-phenyldodecane derived LAS has superior foam stability when compared with the 1-, 2-, 3- and 4-phenyldodecane derived isomers (1,2). To get the most effectiveness for a particular application it is desirable to be able to control the isomer distribution. The alkyl group normally becomes attached to the phenyl nucleus in an alkylation step involving benzene, an alkyl halide or an olefin, and a Lewis acid catalyst. The alkylation step then is an obvious area of investigation in an attempt to control the position of the phenyl group on the alkyl sidechain.

The distribution of isomers in the alkylation of benzene with assorted alkyl halides and olefins has been the subject of numerous publications; however only a small percentage of these are concerned with alkylating agents required to give arenes with linear sidechains in the detergent range. Olson (3,4) has reported that with 1-dodecene different product distributions are obtained using $AlCl_3$, HF and H_2SO_4 catalysts. Alul (5,6) and Alul and McEwan (7) have reported that for alkylations with 1-dodecene and 6-dodecene, the isomer distribution of the product alkylbenzene is dependent upon the strength and amount of catalyst, the solvent, and the position of the double bond in the starting olefin.

In Friedel-Crafts alkylations involving an alkyl halide or olefin, isomerization can occur either in the alkylating agent prior to alkylation or in the product alkylbenzene after alkylation (8). For example the product formed initially in the $AlCl_3$ catalyzed alkylation of benzene with 2-chloro-3-methylbutane is 3-methyl-3-phenylbutane (*tert*-pentylbenzene), a product of isomerization of the alkylating agent prior to alkylation. The thermodynamically favored product which ultimately predominates, however, is 2-methyl-3-phenylbutane, a product of isomerization of the *tert*-pentylbenzene after alkylation (9). Alul (5,6) observed both types of isomerizations in dodecene alkylations of benzene with $AlCl_3$ catalyst. Others (10,11) have observed similar rearrangements.

The object of the work reported here is (1) to furnish additional information on product distribution of detergent range alkylate from alkyl halide and olefin alkylations using $AlCl_3$ and HF catalysts and (2) to attempt to better understand the mechanism of the alkylation reaction, particularly as it pertains to isomerization before and after alkylation.

TABLE I

Isomerization of Phenyldodecanes[a] Using Aluminum Chloride Catalyst[b]

		Phenyldodecane isomers		
Starting material	Time, min	2-φ	3-φ	4-, 5-, and 6-φ
High 2-φ content[c] phenyldodecane, 80 C	0	65	25	10
	1	56	23	21
	2	50	22	28
	5	37	21	42
	10	35	21	44
	270	30	21	49
Low 2-φ content[d] phenyldodecane, 45 C	0	9	15	76
	5	10	---	74
	10	12	16	72
	30	22	18	59
	60	29	20	51
	120	30	20	50
	300	30	20	50

[a] Isomerizations run in excess benzene.

[b] Aluminum chloride 5% w/w based on arene; 4% water promoter based on aluminum chloride.

[c] The starting alkylate was concentrated in 2-phenyldodecane by fractional distillation.

[d] The starting alkylate diminished in 2-phenyldodecane content by fractional distillation.

TABLE II

Alkylation of Benzene With Alkyl Chlorides[a] Using $AlCl_3$[b] and HF[c] Catalysts

			Phenylalkane isomers			
Alkyl chloride[d]	Catalyst	Temperature, C	2-ϕ	3-ϕ	4-ϕ	Internal isomers
Chlorododecane	$AlCl_3$	65	30	19	17	34
Chlorotetradecane	$AlCl_3$	65	27	15	14	44
Chloropentadecane	$AlCl_3$	10	23	15	13	49
Chloropentadecane	$AlCl_3$	95	24	13	13	49
Chloropentadecane	HF	100	20	16	17	47
Chloropentadecane	HF	60	No reaction		No reaction	

[a] Alkyl chlorides from 20 mole % chlorination of appropriate paraffin.

[b] $AlCl_3$ level throughout was 5 wt % based upon alkyl chloride.

[c] HF level throughout equal to or greater than the weight of alkyl chloride.

[d] Mole ratio of benzene to alkyl chloride was 8:1.

EXPERIMENTAL PROCEDURES

Isomerization of Phenyldodecanes Using $AlCl_3$ Catalyst

The high and low 2-isomer phenyldodecanes used in these experiments were obtained by fractional distillation of the mixed phenyldodecanes from the alkylation of benzene with 1-dodecene. In the isomerization reactions benzene (10 moles, 780 g) and the phenyldodecane (1.0 mole, 246 g) were placed in a creased flask fitted with mechanical stirrer, thermometer and condenser. The reactants were heated to the desired temperature and the $AlCl_3$ (0.092 moles, 12.3 g) and 0.5 g water promoter were added. Five ml aliquots were withdrawn with time, quenched with water, washed, dried, and analyzed directly by gas chromatography (GC). Results are presented in Table I. A 15 ft x 0.055 in. ID copper column packed with 10% SE-30 silicone gum rubber on 70-80 mesh Anachrom ABS was used for all analyses of isomeric phenylalkanes.

Alkylation of Benzene With Alkyl Chlorides

Alkyl chlorides were obtained by chlorination of the appropriate *n*-alkane to a 20 mole % level. Chlorine gas was bubbled into the alkane at 125 C; after the appropriate amount of chlorine had been consumed, the reaction mass was purged free of HCl and unchanged chlorine with nitrogen. Analysis for chlorine content was done by X-ray fluorescence. Dodecane, for example, gave a chlorinated paraffin containing 4.23% chlorine. The alkyl chlorides were used without removal of excess paraffin.

Using $AlCl_3$ Catalyst: Benzene (5.0 moles, 390 g) and the appropriate chlorinated alkane (1.0 mole as alkyl chloride) were placed in a flask similar to that described in the isomerization section. The temperature was adjusted to the desired level and the $AlCl_3$ (5 wt % based on alkyl chloride) was added. The reactions were run for 1 hr, at which time they were poured onto dilute NaOH, washed with water, dried, and analyzed by GC. Results are presented in Table II.

Using HF Catalyst: Benzene (2.5 moles, 195 g) and the appropriate chlorinated alkane (0.50 mole as alkyl chloride) were placed in a one liter autoclave. The autoclave was cooled to 5 C and 200 g of liquid HF was added. The autoclave was then closed and heated to the desired reaction temperature, held for 1 hr, and cooled. The HF layer was split off. The products were poured into dilute NaOH, washed with water, dried, and analyzed by GC. Results are presented in Table II.

Alkylation of Benzene With Linear Olefins

The α-olefins used were obtained from Gulf. The mixed tridecenes and pentadecenes were obtained from dehydrohalogenation of the appropriate chlorinated *n*-alkane. Pentadecene will be used as an example. *n*-Pentadecane chlorinated to 20 mole % (as described above) was heated to 250 C in the presence of 1% alumina and 1% calcium oxide for 8 hr. The resultant product was filtered, washed, dried, and distilled through a simple still. The distillate contained 20 mole % isomeric pentadecenes which by GC analysis was 94.1% mixed 3-, 4-, 5- and 6-pentadecene and 5.9% 2-pentadecene.

Using $AlCl_3$ Catalyst: Benzene (10 moles, 780 g) and $AlCl_3$ (5.0 wt % based on olefin) were placed in the reactor and the temperature adjusted to the desired level. The olefin (1.0 mole) was added dropwise over a 30 min period followed by a 1 hr post stir. Workup was the same as for the other $AlCl_3$ catalyzed alkylations. The results of the GC analyses are presented in Table III.

Using HF Catalyst: Benzene (10 moles, 780 g) was added to a polyethylene flask and cooled to 5-10 C. Liquid HF, weight equal to that of the olefin used, was then added. The reaction temperature was held at 10 C as the

TABLE III

Alkylation of Benzene With Olefins[a] Using $AlCl_3$[b] and HF[c] Catalysts

			Phenylalkane isomers			
Olefin	Catalyst	Temperature, C	2-ϕ	3-ϕ	4-ϕ	Internal isomers
1-decene	$AlCl_3$	45	38	19	23	38
1-dodecene	$AlCl_3$	45	31	19	16	33
1-dodecene	$AlCl_3$	10	46	21	14	19
n-pentadecene, mixed[d]	$AlCl_3$	45	25	15	11	49
n-pentadecene, mixed[d]	HF	10	10	12	16	62

[a] Mole ratio of benzene to olefin was 8:1.

[b] $AlCl_3$ level throughout was 5%, w/w, based on olefin.

[c] HF level throughout was equal to or greater than the weight of olefin.

[d] The mixed olefins came from dehydrochlorination of 20 mole % chlorinated paraffins.

TABLE IV

Alkylation of Benzene With 2-Hexyl-1-decene Using $AlCl_3$ Catalyst[a]

Time, min[b]	Isomer purity of alkylate, %[c]
0.5	100
1	92
3	69
10	63
30	51
60	35
120	30
240	30

[a] The olefin was added slowly to the benzene-$AlCl_3$ mixture at 30 C. Mole ratio of benzene-olefin-$AlCl_3$ was 8:1:0.085.

[b] Reaction aliquots removed, quenched with water and analyzed directly.

[c] As determined by GC. No attempt was made to identify isomers.

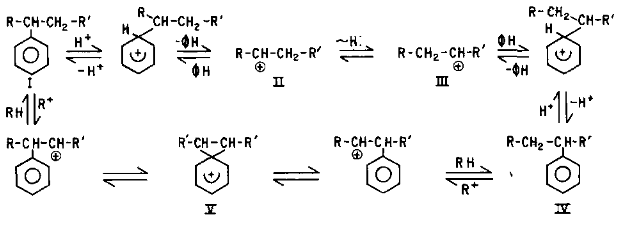

FIG. 1. Mechanism for isomerization of phenylalkanes.

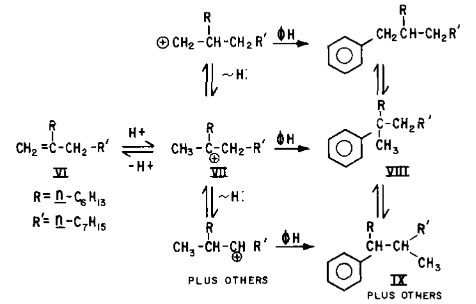

FIG. 2. Alkylation of benzene with 2-hexyl-1-decene.

desired olefin (1.0 mole) was added dropwise over a 30 min period. The reaction was post stirred 1 hr and the HF was then allowed to evaporate. The reactants were quenched with 5% NaOH, washed, dried, and analyzed by GC. The results are presented in Table III.

Alkylation of Benzene With 2-Hexyl-1-decene

The reaction procedure was the same as that described for the other olefin alkylations using $AlCl_3$ catalyst. Benzene (4.0 moles, 312 g), olefin (0.50 moles, 112 g) and $AlCl_3$ (0.043 moles, 5.7 g) were used. The reaction temperature was maintained at 30 C. Aliquots were withdrawn at intervals, worked up as described before, and analyzed by GC. The results are presented in Table IV. The 2-hexyl-1-decene was prepared by aluminum alkyl catalyzed dimerization of 1-octene (12).

Concurrent Alkylation and Isomerization

Two experiments were done. The first involved the addition of 7-tetradecene to a mixture of benzene, phenyldecane (low 2-phenyl content from fractional distillation of a 1-decene alkylation of benzene), and $AlCl_3$. In the second 1-tetradecene was added to a mixture of benzene, phenyldecane (high 2-phenyl content from fractional distillation of a 1-decene alkylation of benzene), and $AlCl_3$. In both experiments benzene (10 moles, 780 g) and phenyldecane (0.59 moles, 129 g) were placed in the reaction flask. The temperature was adjusted to 30 C and the $AlCl_3$ (0.096 moles, 12.9 g) was added. Tetradecene (1.0 moles, 196 g) addition began immediately and continued over a 30 min period followed by a 30 min post stir. Aliquots were withdrawn at intervals, quenched, washed, dried, and analyzed by GC for phenyldecane and phenyltetradecane isomer distribution. The results are presented in Figures 3 and 4.

RESULTS AND DISCUSSION

In Friedel-Crafts alkylations there exists the possibility of isomerization of the alkylating agent prior to alkylation as well as the possibility of isomerization of the product arene once formed. The isomerization of phenyldodecane at elevated temperatures is quite facile (Table I). When an isomeric mixture containing 65% 2-phenyldodecane was treated with $AlCl_3$ at 80 C, the product distribution changed quite rapidly to one containing 30% 2-phenyldodecane. The same final product distribution was obtained when an isomer mixture initially containing 9% 2-phenyldodecane was treated with $AlCl_3$ at 45 C although isomerization was slower. At 80 C a significant drop in 2-phenyl content from 65-56% was noted in only 1 min. A similar equilibrium isomer distribution has been reported by others for treatment of phenyldodecanes with $AlCl_3$ (3-5,7). This isomerization is believed to occur by either or both of the mechanisms described in Figure 1. The upper route in Figure 1 involves dealkylation of the arene isomer I to the cation II. Cation II isomerizes via a hydride shift to III which subsequently realkylates benzene to yield another arene isomer IV. The second mechanism suggested for isomerization involves the abstraction of a hydride ion from I. Isomerization occurs via the phenonium ion V with subsequent hydride transfer to IV.

The chloroalkanes used in the alkylations of benzene described in Table II came from thermally initiated chlorination of the appropriate *n*-paraffin. These chlorinations were carried out to a low conversion, 20 mole %, to minimize the formation of dichloroparaffin. The dichlorides would be expected to yield diphenylalkanes from intermolecular dialkylation of benzene and alkyl substituted tetralins from intramolecular cyclialkylation (13,14) of the intermediate phenylchloroalkane. The chloroalkanes were used without any attempt to remove excess *n*-paraffin, which means these alkylations were done in a four molar excess of paraffin over chloroalkane. The alkylations conducted at 65 C and 95 C using $AlCl_3$ catalyst would be expected to give equilibrium distributions resulting from isomerization of the product arenes. The chlorododecane alkylation gave the same product distribution as that reported in Table I for phenyldodecane isomerization. The chlorotetradecane alkylation gives the same product distribution as obtained by Alul (5) for the alkylation of benzene with 1-tetradecene at 35 C, a product distribution he attributed to product isomerization.

The alkylation with chloropentadecane gave the same isomer distribution at 10 C and 95 C. At 95 C one would expect a distribution determined by product isomerization. However at 10 C product isomerization should be very slow if occurring at all, none was seen at 0-5 C (5). Assuming equal alkylation rates by each of the isomeric secondary alkyl chlorides, one would expect a product with the same phenyl isomer distribution as the chloro isomer distribution present in the starting chloroalkane. The thermal chlorination of *n*-pentadecane gives 15.4% of each of the 2- through 7-isomers and 7.7% of the 8-isomer (15,16). These are statistically determined percentages based upon the number of hydrogen atoms on each carbon atom and have in this case been normalized to 100% excluding the primary chlorides. The isomerization of the secondary alkyl chlo-

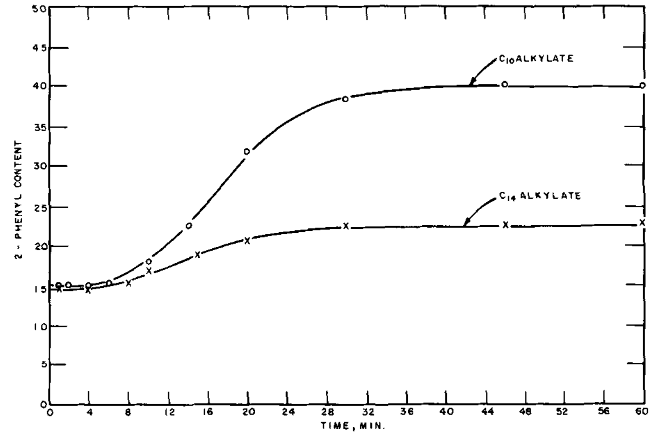

FIG. 3. Alkylation of benzene with 7-tetradecene in the presence of phenyldecane.

rides by the $AlCl_3$ would be of no significance and for that matter unobservable since by using individual chloroparaffin isomers it has been shown that one obtains the same statistically determined chloroparaffin isomer distribution as from thermal chlorination (17,18). However a significantly higher 2-phenylpentadecane content of 23% was obtained for the alkylation at 10 C (Table II). This could then be the result of a faster rate of alkylation by the 2-cation (or cation-catalyst complex) over the more sterically hindered internal cations. It may also arise from the small amount of 1-chloropentadecane present in the chloroparaffin.

The HF catalyzed alkylation with chloropentadecane did not go at 60 C (Table II). However it did go at 100 C and gave a product distribution significantly higher in 2-phenyl content than was obtained from a similar alkylation with pentadecene at 10 C (Table III). We suggest at this time that at the harsh 100 C reaction temperature, the high 2-phenyl content is the result of isomerization of the arene once formed, not solely a result of isomerization of the alkylating agent prior to alkylation. We have observed such arene isomerizations in HF at 100 C and plan to report these findings in a subsequent paper.

Competition between alkylation and isomerization of the alkylating agent prior to alkylation was observed in the alkylation with 1-dodecene at 10 C using $AlCl_3$ catalyst (Table III). A product significantly higher in 2-phenyl content (46%) was observed over the 30% obtained when this competition is masked by product isomerization.

The alkylation of benzene with 2-hexyl-1-decene (Table IV) presents the interesting possibilities outlined in Figure 2. The alkylating agents may interconvert although the tertiary cation, or cation-catalyst complex, should be expected to be much more stable. The product arenes may also interconvert. The results in Table IV show that initially the product phenylhexadecane had an isomeric purity of 100% (only one phenylhexadecane isomer present in GC trace). The isomeric purity rapidly degenerated with time. An explanation compatible with these results is initial alkylation by the tertiary cation VII to form 7-methyl-7-phenylpentadecane with subsequent isomerization to other phenylhexadecanes under the reaction conditions. These views are supported by the reported (9) analogous alkylation of either 1-chloro-2-methylbutane, 2-chloro-2-methylbutane, or 2-chloro-3-methylbutane to initially form *tert*-pentylbenzene (structure VIII in Figure 2 with $R=CH_3$, $R'=CH_3$) with subsequent product isomerization to 2-methyl-3-phenylbutane (structure IX in Figure 2 with $R=CH_3$ and $R'=CH_3$).

In order to get a better understanding of the competing isomerization of the alkylating agent and product arenes, two experiments were conducted in which a nonequilibrium isomer distribution of phenyldecane was present during alkylation with either 1- or 7-tetradecene. In the first of these (Figure 3) 7-tetradecene was added to a mixture of benzene and phenyldecane containing 15% of the 2-phenyl isomer. In the first 6 min of reaction no isomerization of the phenyldecane was noted. At this time the product phenyltetradecane contained 15% of the 2-phenyl isomer. There is therefore initially isomerization of the alkylating agent occurring in the absence of isomerization of the product phenylalkanes. As the reaction progressed isomerization of the phenyldecane to an equilibrium 2-phenyl content of 40% was observed. Similarly by the termination of the reaction, the 2-phenyl content of the phenyltetradecane attained the equilibrium distribution of 26%, the result of isomerization of the phenylalkene once formed. The results obtained for the experiment using 1-tetradecene and a phenyldecane containing 77% of the 2-phenyl isomer are similar (Figure 4). Both isomerization of the alkylating agent prior to alkylation and isomerization of the phenyltetradecanes once formed was observed.

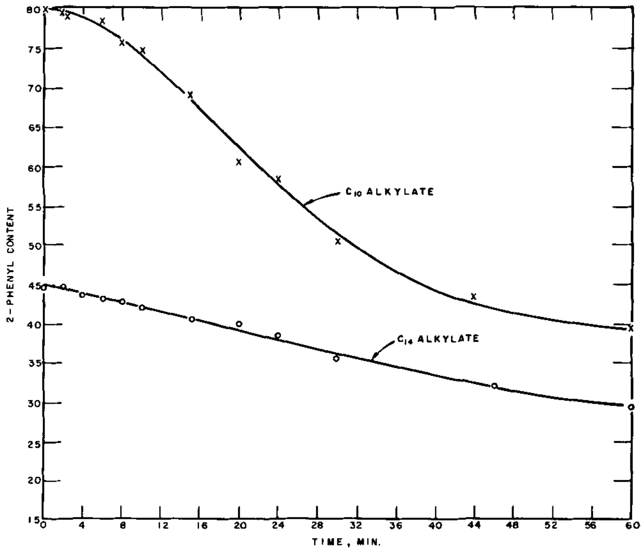

FIG. 4. Alkylation of benzene with 1-tetradecene in the presence of phenyldecane.

REFERENCES

1. Rubinfield, J., E.M. Emery and H.D. Cross, AOCS Meeting, April 1954, New Orleans, Louisiana.
2. Rubinfield, J., E.M. Emery and H.D. Cross, Div. of Ind. and Eng. Chem., 148th National Meeting American Chemical Society, August 1964.
3. Olson, A.C., Amer. Chem. Soc. Petr. Chem. Div. Preprint 4(3):89 (1959).
4. Olson, A.C., Ind. Eng. Chem. 52:833 (1960).
5. Alul, H.R., Ibid. 7(1):7 (1968).
6. Alul, H.R., J. Org. Chem. 33:1522 (1968).
7. Alul, H.R., and G.J. McEwan, Ibid. 32:3365 (1967).
8. Nenitzescu, C.D., Rev. Reumaine de Chim 9:5 (1964).
9. Roberts, R.M., and S.E. McGuire, J. Org. Chem. 35:102 (1970).
10. Friedman, B.S., and F.L. Morritz, J. Amer. Chem. Soc. 78:2000 (1956).
11. Schmerling, L., and J.P. West, Ibid. 76:1917 (1954).
12. Ziegler, K., H.G. Gellert, K. Zosel, E. Holzkamp, J. Schneider, M. Soll and W.R. Kroll, Ann. 629:121 (1960).
13. Khalaf, A.A., and R.M. Roberts, J. Org. Chem. 31:89 (1966).
14. Barclay, L.R.C., B.A. Ginn and C.E. Milligan, Can. J. Chem. 42:579 (1964).
15. Morrison, R.T., and R.N. Boyd, "Organic Chemistry," Second Edition, Allyn and Bacon, Inc., Boston, Mass., 1966, p. 121.
16. Asinger, F., "Paraffins–Chemistry and Technology," First Edition, Pergamon Press, New York, 1968, p. 266-267.
17. McGuire, S.E., Ph.D. Thesis, University of Texas, 1967, p. 54.
18. Stinger, R.A., Ph.D. Thesis, University of Wisconsin, 1962. See Dissertation Abstracts 22:3412 (1962).

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