haloaralkenes. This alkylation again takes preference over the third possible Friedel–Crafts reaction, e.g., dehydrochlorination of the α-haloaralkene to the corresponding styrene derivative, which then in turn could undergo polymerization in the presence of the acid catalyst.

As the starting α-haloaralkanes can generally be easily and quantitatively obtained from the appropriate styrene derivatives by hydrogen halide addition or by side-chain halogenation of the alkylbenzenes, this method represents a suitable preparative way to combine styrene with practically any simple olefin and obtain (with recovery in the dehydrohalogenation step of the hydrogen halide first added to styrene) a variety of new aralkanes.

Experimental

All of the olefins used in present investigation were commercial products of highest available purity. The prepared α-haloalkylbenzenes were characterized, besides their physical characteristics and analyses, through their infrared and n.m.r. spectra, giving good agreement with those of samples of the known pure compounds.

α-Chloroethylbenzene.—Styrene (1 mole) was placed in a 250-ml. flask and cooled to near the freezing point (−30°). HCl gas was then introduced and the temperature of the mixture was gradually decreased to −80° (the freezing point decreases as HCl is introduced). After 1.05 moles of HCl was introduced, the temperature of the mixture was slowly raised to room temperature. Excess HCl was removed by passing dry N_2 through the mixture, followed by washing with water. After drying, the resulted mixture was fractionated in vacuo. A 95% yield of α-chloroethylbenzene, b.p. 64–65° (8 mm.), was obtained.

Anal. Calcd. for C_8H_9Cl: Cl, 25.2. Found: Cl, 25.0.

α-Bromoethylbenzene, α-chlorocumene, and p-methyl- and p-t-butyl-α-chloroethylbenzene were prepared by the same method: α-bromoethylbenzene, b.p. 106° (31 mm.), yield 92% (C_8H_9Br, % Br calculated 43.2, found 42.9); p-methyl-α-chloroethylbenzene, b.p. 85° (10 mm.), yield 97% ($C_9H_{11}Cl$, % Cl calculated 22.9, found 22.6); p-t-butyl-α-chloroethylbenzene, b.p. 96–97° (3 mm.), yield 96% ($C_{12}H_{17}Cl$, % Cl calculated 18.0, found 17.7); α-chlorocumene, b.p. 64° (3 mm.), yield 90% ($C_9H_{14}Cl$, % Cl calculated 22.9, found 23.3).

α-Chloro-n-propylbenzene and α-Chloro-n-butylbenzene.—n-Propylbenzene (2 moles, 240 g.) and 3 g. of PCl_5 were placed in 500-ml. flask equipped with drying tube and dry Cl_2 gas was introduced into the mixture. An exothermic reaction takes place and the temperature gradually went up to 40°. The tem-

perature was kept at 40° with external cooling and the introduction of chlorine was continued until the weight of the mixture increased by 45 g. After cooling, the mixture was washed three times with water, dried over $CaCl_2$, and fractionated.

Unchanged n-propylbenzene (130 g.) and 120 g. of α-chloro-n-propylbenzene, b.p. 105–106° at 16 mm., were obtained ($C_9H_{11}Cl$, % Cl calculated 22.9, found 22.5).

α-Chloro-n-butylbenzene, b.p. 89–90° (6 mm.), was prepared by a similar method with a 79% yield ($C_{10}H_{13}Cl$, % Cl calculated 21.0, found 20.7).

α-Fluoroethylbenzene.—α-Bromoethylbenzene (1 mole, 185 g.) was fluorinated with 190 g., (1.5 moles) of AgF in 300 ml. of acetonitrile as solvent. The reaction was exothermic and the temperature of the reaction mixture was maintained between 20 and 40°. To get a smooth reaction, the solution of the fluoride was added to the α-chloroethylbenzene in five–six portions. After 2 hr. the silver chloride formed was filtered; the organic layer was washed three times with water, dried, and distilled; b.p. 50° (5 mm.), $n^{25}D$ 1.4972, yield 44.7%.

Anal. Calcd. for C_8H_9F: C, 77.39; H, 7.3; F, 15.31. Found: C, 77.21; H, 7.23; F, 15.56.

4-t-Butyl-α-fluoroethylbenzene[6] was prepared in a similar manner to α-fluoroethylbenzene, starting from 4-t-butyl-α-bromoethylbenzene; yield 51%, b.p. 78–80° (4 mm.), $n^{25}D$ 1.4880.

Anal. Calcd. for $C_{12}H_{17}F$: C, 79.95; H, 9.51; F, 10.54. Found: C, 79.80; H, 9.38; F, 10.82.

General Method of α-Aralkylation of Olefins and Vinylbenzenes.—One mole of α-haloalkylbenzene and 2 g. of $ZnCl_2$ (or related halide catalyst in amounts of 0.5 to 3%) were placed in a reaction flask and 1 mole of olefin (vinylbenzene) was added to the stirred mixture. The rate of addition of the olefin depends on the reactivity of the system. In reactions with isobutylene the olefin was introduced in a fast stream and by external cooling the temperature was kept below 50°. With less reactive olefins, such as propylene, external heating was required to carry out the reaction (see data of Table I). Gaseous olefins were introduced as such. Liquid olefins were added through a dropping funnel and the stirring was continued for an additional hour after the addition of the olefin. The haloaralkylated intermediates were generally not isolated, but were directly dehydrohalogenated.

In some cases simple steam distillation was sufficient to remove the hydrogen halides. In most of the cases, however, to complete dehydrohalogenation the reaction mixtures obtained were refluxed with 50% excess pyridine or anhydrous Na_2CO_3 or K_2CO_3 for 6–8 hr. After the removal of the hydrogen halide the reaction mixtures were washed with water, dried, and fractionated.

The olefins obtained were characterized, besides their elementary analyses (see Table I), through their infrared and proton magnetic resonance spectra, showing the characteristics of monoaryl-substituted olefins.

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Friedel–Crafts Isomerization.   X.[1a]   Aluminum Chloride Catalyzed Isomerization of the Di-t-butylbenzenes

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The isomerization of o-, m-, and p-di-t-butylbenzene with water-promoted aluminum chloride was investigated. The isomer distributions were established using gas–liquid chromatography. The equilibrium mixture starting from any of the isomers contains about 52% m- and 48% p-di-t-butylbenzene, with no ortho isomer present. The acid-catalyzed isomerization of o-di-t-butylbenzene is exceedingly fast, in all probability helped by the relief of steric stress. Fast, kinetically controlled ortho–para conversion going through probably a π-complex-type intermediate, is followed by much slower 1,2-shift leading to the equilibrium. The isomerization of m- and p-di-t-butylbenzene proceeds by an apparent 1,2-shift mechanism, which however could be either intra- or intermolecular, in the latter case again involving a π-complex-type intermediate.

The acid-catalyzed isomerization of di-t-butylbenzenes has not been investigated so far. The recent

availability of o-di-t-butylbenzene[2] made it possible to extend our investigations of the Friedel–Crafts isomeri-

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TABLE I

ISOMERIZATION OF p-DI-t-BUTYLBENZENE WITH WATER-
PROMOTED ALUMINUM CHLORIDE IN CARBON DISULFIDE
SOLUTION

Time, min.	Di-t-butylbenzene			% t-butyl-benzene	% 1,3,5-tri-t-butyl-benzene
	% ortho[a]	% meta[a]	% para[a]		
0.25		0.5	99.5	0.3	0.3
0.5		1.4	98.6	0.9	0.7
1		1.9	98.1	1.6	5.8
1.5		4.0	96.0	3.5	7.1
2.5	21.0		79.0	5.9	11.0
4	37.5		62.5	11.8	15.9
6	42.8		57.2	12.6	12.6
10	52.3		47.7	16.8	22.4
15	51.7		48.3	16.9	19.0
25	53.5		46.5	17.6	16.8
40	53.5		46.5	17.3	12.7
60	53.5		46.5	18.5	13.6
300	52.8		47.2	19.3	11.3
2880	51.6		48.4	21.2	13.4

[a] Normalized.

TABLE II

ISOMERIZATION OF m-DI-t-BUTYLBENZENE WITH WATER-
PROMOTED ALUMINUM CHLORIDE IN CARBON DISULFIDE
SOLUTION

Time, min.	Di-t-butylbenzene			% t-butyl-benzene	% 1,3,5-tri-t-butyl-benzene
	% ortho[a]	% meta[a]	% para[a]		
0.25		100		0.5	0.7
0.5		98.7	1.3	1.6	3.3
1		97.4	2.6	4.2	9.7
1.5		93.9	6.1	8.3	13.8
2		88.6	11.4	6.3	21.0
2.5		83.8	16.2	7.8	21.8
3		79.0	21.0	7.5	27.9
4		74.1	25.9	8.2	22.9
6		63.7	36.3	9.3	23.8
10		53.7	46.3	9.8	24.7
25		53.8	46.9	14.3	18.2
60		54.3	45.7	18.5	18.9
120		53.8	46.2	18.4	19.4
300		51.7	48.3	26.1	18.5
484		52.7	47.3		

[a] Normalized.

zation of disubstituted benzenes to all three isomeric di-t-butylbenzenes.

Results and Discussion

The isomerization of o-, m-, and p-t-butylbenzene with water-promoted aluminum chloride was investigated in carbon disulfide solution at room temperature (~25°). The isomer distributions were determined using gas–liquid chromatography.

The results obtained are displayed in Table I–III. The isomerization of o-di-t-butylbenzene was found to be extremely fast. In order to achieve isomerization with measurable rate a substantially higher dilution of the reaction system was used in the case of o-di-t-butyl-benzene than in the case of the meta and para isomers. Starting with any of the isomers the isomerization leads to an equilibrium mixture of about 52% meta and 48% para isomer. No o-di-t-butylbenzene is present in the equilibrium mixture.

TABLE III

ISOMERIZATION OF o-DI-t-BUTYLBENZENE WITH WATER-
PROMOTED ALUMINUM CHLORIDE IN CARBON DISULFIDE
SOLUTION (HIGH DILUTION)

Time, min.	Di-t-butylbenzene			% t-butyl-benzene	% 1,3,5-tri-t-butyl-benzene
	% ortho[a]	% meta[a]	% para[a]		
0.33	94.7	0.4	4.9	0	0
0.67	81.4	4.3	14.3	0.3	0.5
1	68.2	27.4	24.4	0.6	0.8
1.33	55.8	10.5	33.7	0.8	1.4
1.67	42.4	14.7	42.9	2.3	1.7
2	13.4	23.6	63.0	3.3	3.1
2.5		28.8	71.2	4.1	5.6
3		28.6	71.4	6.1	6.7
4		27.6	73.4	8.0	10.5
5.5		28.5	71.5	12.5	14.8
7		32.5	67.5	13.2	17.9
9		48.5	51.5	14.2	19.6
11		49.8	50.2	15.8	14.7
15		51.6	48.4	27.3	18.7
20		52.4	47.6	28.6	15.6

[a] Normalized.

In the isomerization of all isomeric di-t-butylbenzenes, products of disproportionation (t-butylbenzene and 1,3,5-tri-t-butylbenzene) were found, besides unidentified higher boiling materials. The amount of disproportionation products amounted at equilibrium to 50% of the reaction mixture, but had no effect on the isomeric di-t-butylbenzene composition.

The isomerization of o-di-t-butylbenzene, as seen from data of Table III, proceeds in a very fast (even in high dilution), mostly kinetically controlled formation of p- (and m-) di-t-butylbenzene. In a reaction time of about 2.5 min., a composition of 28% meta and 72% para isomer is reached. During this phase of the isomerization the para–meta isomer ratio stays relatively constant (para–meta, 3:2.). Subsequent isomerization to the final equilibrium of about 52% meta and 48% para isomer is slower and is reached in about 20 min.

In the over-all isomerization of o-di-t-butylbenzene, the concentration of the para isomer goes through a maximum. The mainly kinetically controlled part of the isomerization can be described in the following way.
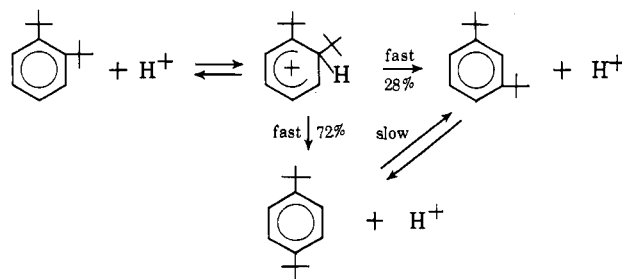
The situation is reminescent of that observed in the isomerization of o-t-butyltoluene[3] and o-bromotoluene.[4] As discussed previously,[3] it is not necessary to postulate complete detachment of the migrating t-butyl group during isomerization. A π-complex-type transition state is in accordance with the observed high rate of the isomerization even under the high dilution conditions used, where a dealkylation–realkylation

(3) G. A. Olah, M. W. Myer, and N. A. Overchuk, J. Org. Chem., in press.
(4) G. A. Olah and M. W. Meyer, ibid., 27, 3464 (1962).

mechanism, with complete detachment of the migrating alkyl group as a trimethylcarbonium ion, would be expected to show much slower reaction rates.

The absence of *ortho* isomer from the equilibrium mixture and the high speed of isomerization of *o*-di-*t*-butylbenzene is obviously influenced by steric factors. No *t*-butylation *ortho* to an alkyl group, and in particular *ortho* to a *t*-butyl group, is possible. The substantial steric stress involved in *o*-di-*t*-butylbenzene is relieved during migration of the *t*-butyl group to the *para* and *meta* position, thus contributing to the ease of migration.

Experimental

Starting Materials.—*p*- and *m*-Di-*t*-butylbenzene were obtained by preparative-scale vapor phase chromatographic separation of a reaction mixture obtained through aluminum chloride catalyzed *t*-butylation of *t*-butylbenzene with isobutylene. The purity of these isomers was better than 99%.

Samples of *o*-di-*t*-butylbenzene were graciously provided by Professors E. M. Arnett and L. R. C. Barclay. The purity of *o*-di-*t*-butylbenzene used, based on gas chromatographic and infrared analyses, was about 95%.

General Process of Isomerization.—Reactions were carried out in stoppered vessels with magnetic stirring. In the case of the isomerization of *p*- and *m*-di-*t*-butylbenzene, 0.02 mole of aluminum chloride was used per 0.1 mole of aromatic, and 2 drops of water was added as promoter; the reactions were carried out in 100 ml. of purified carbon disulfide. In the case of the isomerization of *o*-di-*t*-butylbenzene, 0.001 mole of the aromatic was dissolved in 10 ml. of carbon disulfide and 0.0001 mole of aluminum chloride was added, without any measured amount of water. Owing to the high dilution of the system and the difficulty

in handling the small amount of catalyst under absolutely anhydrous conditions, it was assumed that a sufficient amount of moisture as cocatalyst was present in the system. Samples were drawn periodically, the reaction was stopped with water, and the organic material was extracted with ether. Dried ether extracts were analyzed by gas–liquid chromatography.

In the tables, the amounts of *o*-, *m*-, and *p*-di-*t*-butylbenzenes are given as normalized per cent. Per cent given for the products of disproportionation represent mole per cent of total aromatic present.

Gas–Liquid Chromatographic Analysis.—The analyses were carried out on a Perkin-Elmer Model 154-D vapor fractometer equipped with Golay-type capillary column and hydrogen flame ionization detector. Peak areas were calculated using a Perkin-Elmer Model 194 printing integrator. The capillary column used was 150 ft., coated with polypropylene glycol operated at 104° with a He carrier-gas pressure of 20 p.s.i. Characteristic retention times of *t*-butylbenzene, di-*t*-butylbenzenes and 1,3,5-tri-*t*-butylbenzene observed are summarized in Table IV.

TABLE IV

RETENTION TIMES OF *t*-BUTYLBENZENE, DI-*t*-BUTYLBENZENES
AND 1,3,5-TRI-*t*-BUTYLBENZENE

Compound	Time, min.
t-Butylbenzene	7
p-Di-*t*-butylbenzene	26
m-Di-*t*-butylbenzene	16
o-Di-*t*-butylbenzene	44
1,3,5-Tri-*t*-butylbenzene	33

A Comparison of Alkylpotassium and Alkylsodium Reagents in Metalation of α-Olefins

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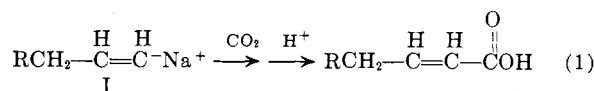
Metalation of 1-dodecene with *n*-butylpotassium differs from metalation with *n*-butylsodium in three respects. The variation in ratio of α,β- to β,γ-unsaturated carbonation products with time is much less marked in the potassium system. At short reaction time the β,γ-products arising from an allyl intermediate predominate, whereas α,β-unsaturated acid was the major product with *n*-butylsodium under these conditions. Olefin recovered from the potassium system is unchanged, while extensive isomerization was noted in the sodium case. Preparation of 1-potassio-1-dodecene from 1-bromo-1-dodecene shows that this precursor to the α,β-unsaturated acid undergoes rearrangement to the allyl intermediate. These results are explained on the basis of competitive metalation at the vinyl and allyl positions.

Recent studies[1,2] of the metalation of alkylbenzenes, using alkylsodium and alkylpotassium reagents, apparently clarify earlier discrepancies[3–6] as to the position of metalation in these systems. Benkeser, *et al.*, suggest that in both cases there is a kinetically favored reaction at a ring position followed by equilibration to the thermodynamically favored α-position and they account for differences in product distribution with the two reagents by more rapid equilibration reactions in the potassium case.

We have reported[7] earlier that when 1-dodecene is metalated with *n*-pentylsodium[8] a large proportion of

α,β-unsaturated acid is isolated if the reaction mixture is carbonated after short reaction time. This product is thought to arise from a vinylsodium intermediate (reaction 1). At longer reaction times the expected[9,10]

$$RCH_2—\overset{H}{C}=\overset{H}{C}-Na^+ \xrightarrow{CO_2} \xrightarrow{H^+} RCH_2—\overset{H}{C}=\overset{H}{C}-\overset{O}{\overset{\|}{C}}OH \quad (1)$$

I

β,γ-products from carbonation of an allyl intermediate predominate (reaction 2). This variation in compo-

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