Infrared analysis of the product showed no absorption in the C–D stretching region (~2290 cm.$^{-1}$). Two earlier attempts were made to induce exchange of the ring protons of **10** under milder conditions (70° for 10 hr., 90° for 24 hr.).

Preparation of 4-Pyrone-3,5-d_2 (7) by Exchange[1].—4-Pyrone (**1**) (1.82 g., 0.022 mole) and ~90% deuterium oxide (7.13 g., 0.36 mole) were heated together in a 50-ml. flask fitted with a reflux condenser and protected by a calcium chloride drying tube on an oil bath at 95° for 19 hr. The exchanged pyrone was then separated from the solvent by vacuum distillation. The infrared spectrum of the product showed absorption in both the C-H stretching region (3084 cm.$^{-1}$) and in the C–D stretching region (2289 cm.$^{-1}$). An n.m.r. spectrum of the partially deuterated material showed a large singlet at δ = 7.60 p.p.m. superimposed on the remains of a doublet at δ = 7.58 p.p.m. and a weak high field doublet at δ = 6.18 p.p.m. Integration indicated that the exchange was nearly 60% complete at this stage.

Acknowledgment.—We wish to thank the Smith, Kline and French Laboratories for a grant which supported part of this investigation.

Selective Friedel–Crafts Reactions. II.[1a] Alkylation of Olefins and Vinylbenzenes with α-Haloalkylbenzenes

GEORGE A. OLAH,[1b] S. J. KUHN, AND D. G. BARNES

Contribution No. 118, Exploratory Research Laboratory, Dow Chemical of Canada, Limited, Sarnia, Ontario, Canada

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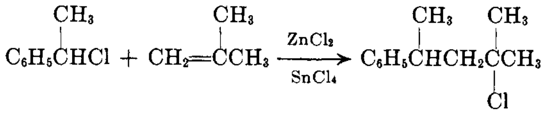
Olefins and vinylbenzenes react with α-haloalkylbenzenes in the presence of weak Friedel–Crafts catalysts such as $ZnCl_2$ or $SnCl_4$ by addition of the haloalkylbenzenes onto the olefinic double bond and not through alkylation of the aromatic ring. Subsequent dehydrohalogenation allows the preparation of α-aralkylated olefins or vinylbenzenes with high yields.

Lewis acid halide catalyzed addition of haloalkanes onto halo olefins have been first investigated by Boeseken and Prins.[2] The so-called Prins reaction has been applied by many other investigators for reactions of polyhaloalkanes with alkenes. It was, however, generally considered that mono- or polyhaloalkanes cannot be added by this reaction to simple olefins. It was Schmerling[3] who in a series of investigations studied the interaction of haloalkanes and olefins and arrived at the conclusion that in the presence of aluminum chloride and a number of less active Lewis acid halides the addition of haloalkanes onto olefins can be carried out with very satisfactory results.

At the time of our investigations no data were available from the literature on the behavior of haloaralkanes with olefins other than indicating usual ring alkylations complicated by side reactions due to dehydrohalogenation of the haloalkane. After our work was disclosed in the patent literature,[4] a paper appeared by Paushkin and Mirgaleev[5] in which the interaction of α-chloroethylbenzene with propylene in the presence of $H_3PO_3 \cdot BF_3$ has been described producing unexpectedly 2-chloro-2-phenyl-3-methylbutane instead of 2-phenyl-4-chloropentane as was obtained in our work.[4]

Results and Discussion

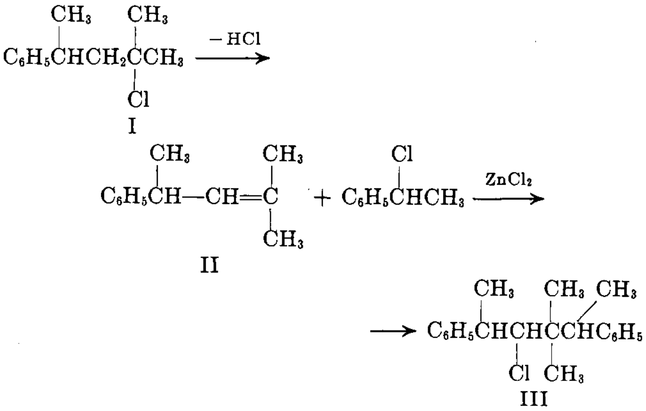
While attempting to ring alkylate α-haloalkylbenzenes with olefins in the presence of Friedel–Crafts catalysts, we have observed that strong acid catalyst such as sulfuric acid or aluminum halides cause dehydrohalogenation and subsequent polymerization of the α-haloalkylbenzene instead of ring alkylation. Weaker catalysts, such as zinc and stannic halides do not catalyze ring alkylation of the α-haloalkylbenzene with olefins, but addition of the α-haloalkylbenzene onto the olefins takes place, as is illustrated in the reaction of α-chloroethylbenzene with isobutylene yielding 2-methyl-2-chloro-4-phenylpentane (I).



$$C_6H_5\overset{CH_3}{C}HCl + CH_2{=}\overset{CH_3}{C}CH_3 \xrightarrow[SnCl_4]{ZnCl_2} C_6H_5\overset{CH_3}{C}HCH_2\underset{Cl}{\overset{CH_3}{C}}CH_3$$

I

It has been observed that even if the reaction temperature is kept as low as 30° the haloalkylbenzene I formed loses, at least partially, HCl to form the corresponding olefin II, which then could react with excess α-haloalkylbenzene present to form III and the reaction can proceed accordingly to yield higher alkylates.



$$\underset{\text{I}}{C_6H_5\overset{CH_3}{C}HCH_2\underset{Cl}{\overset{CH_3}{C}}CH_3} \xrightarrow{-HCl}$$

$$\underset{\text{II}}{C_6H_5\overset{CH_3}{C}H{-}CH{=}\underset{CH_3}{\overset{CH_3}{C}}} + C_6H_5\overset{Cl}{C}HCH_3 \xrightarrow{ZnCl_2}$$

$$\longrightarrow \underset{\text{III}}{C_6H_5\overset{CH_3}{C}H\underset{Cl}{C}H\underset{CH_3}{\overset{CH_3}{C}}\overset{CH_3}{C}HC_6H_5}$$

The α-haloalkylbenzenes usable in the present reaction include substituted α-haloethylbenzenes, α-chlorocumene, α-chloro-*n*-propylbenzene, α-chloro-*n*-butylbenzene, etc. Benzyl chloride failed to give the reaction. Suitable olefins in the reaction are alkenes containing at least three carbon atoms such as propylene, butenes, pentenes, hexenes, octenes, diisobutylene, styrene, vinyltoluene, etc. Zinc halides have been

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(1) (a) Part I: G. A. Olah and S. J. Kuhn, *J. Org. Chem.*, **29**, 2317 (1964). (b) To whom correspondence should be addressed at The Dow Chemical Co., Eastern Research Laboratory, Framingham, Mass.

(2) J. Boeseken and H. J. Prins, *Koninkl. Ned. Akad. Wetenschap., Proc.*, **13**, 685 (1911); **19**, 776 (1911).

(3) L. Schmerling, *J. Am. Chem. Soc.*, **67**, 1152 (1954); **68**, 1650, 1655 (1946); **69**, 1121 (1947); **71**, 753 (1949); **74**, 2855, 3592 (1952).

(4) G. A. Olah, S. J. Kuhn, and D. G. Barnes (to The Dow Chemical Co.), U. S. Patent 2,996,554 (1961).

(5) Y. M. Paushkin and I. G. Mirgaleev, *Neftekhimiya*, **2**, 784 (1962); *Chem. Abstr.*, **58**, 11,243 (1963).

TABLE I

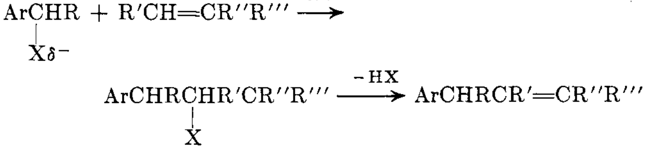
α-ARALKYLATION OF OLEFINS AND VINYLBENZENES

Olefin or vinylbenzene	α-Haloalkylbenzene	Aralkene	Yield, %	Reaction temp., °C.	B.p., °C. (mm.)	n^{25}_D	% C Calcd.	% C Found	% H Calcd.	% H Found
Propene	α-Chloroethyl-	4-Phenylpentene-2	40	20–80	68–70 (4)	1.5709	90.42	90.49	9.58	9.64
Propene	α-Fluoroethyl-	4-Phenylpentene-2	47	20–50						
Butene-1	α-Chloroethyl-	5-Phenylhexene-3	85	20–50	75–80 (4)	1.5262	90.00	90.10	10.0	9.96
Isobutylene	α-Chloroethyl-	2-Methyl-4-phenylpentene-2	95	20–50	70 (3)	1.5069	90.00	90.00	10.0	10.00
Isobutylene	α-Bromoethyl-	2-Methyl-4-phenylpentene-2	89							
2-Methylbutene-2	α-Chloroethyl-	2,3-Dimethyl-4-phenylpentene-2	90	20–50	78–82 (3)	1.5180	89.66	89.68	10.34	10.30
Octadecene-1	α-Chloroethyl-	2-Phenyleicosene-3	65	30–70	160–165 (3)	1.4602	87.64	87.70	12.36	12.30
Styrene	α-Chloroethyl-	1,3-Diphenylbutene-1	70	45–60	158 (5)	1.5654	92.30	92.35	7.70	17.65
Styrene	2-Methyl-α-chloroethyl-	1-Phenyl-3-(2′-methylphenyl)-butene-1	73	35–60	144 (2)	1.5831	91.90	91.94	8.10	8.06
2-Methylstyrene	2-Methyl-α-chloroethyl-	1,3-Di(2′-methylphenyl)butene-1	68	45–60	159 (3)	1.5754	91.53	91.40	8.47	8.60
2-Methylstyrene	α-Chloroethyl-	1-(2′-Methylphenyl)-3-phenylbutene-1	50	45–60	153 (3)	1.5763	91.90	91.85	8.10	8.15
α-Methylstyrene	α-Chloroethyl-	2,4-Diphenylpentene-2	57	45–60	155 (4)	1.5769	91.90	91.93	8.10	8.06
4-Chlorostyrene	α-Chloroethyl-	1-(4′-Chlorophenyl)-3-phenylbutene-1	40	50–60	176–178 (3)	1.5858	79.60	79.52	6.20	6.17
Isobutylene	4-*t*-Butyl-α-chloroethyl-	2-Methyl-4-(4′-*t*-butylphenyl)-pentene-2	90	20–50	110–115 (5)		88.89	88.76	11.11	11.30
Isobutylene	4-*t*-Butyl-α-fluoroethyl-	2-Methyl-4-(4′-*t*-butylphenyl)-pentene-2	92	20–50						
2-Methylbutene-2	4-*t*-Butyl-α-chloroethyl-	2,3-Dimethyl-4-(4′-*t*-butylphenyl)-pentene-2	86	20–50	110–115 (5)	1.5085	88.70	88.79	11.30	11.20
Isobutylene	α-Chloroisopropyl-	2,4-Dimethyl-4-phenylpentene-2	80	20–50	93–96 (6)		89.66	89.91	10.34	10.27
2,5-Dichlorostyrene	α-Chloroethyl-	1-(2′,5′-Dichlorophenyl)-3-phenylbutene-1	62	45–60	177–182 (5)		69.31	69.18	5.05	5.12
Isobutylene	α-Chloro-*n*-propyl-	2-Methyl-4-phenylhexene-2	78	20–50	95–99 (6)		89.66	89.7	10.34	10.40
Isobutylene	α-Chloro-*n*-butyl-	2-Methyl-4-phenylheptene-2	76	20–50	98–103 (6)		89.37	89.28	10.63	10.72
2,4, 4-Trimethylpentene-2	α-Chloroethyl-	2-Methyl-3-*t*-butyl-4-phenylpentene-2	75	20–60	110–115 (5)		88.88	88.75	11.11	11.22

found the most suitable catalysts. However, $SnCl_4$ and in some cases $FeCl_3$, $BiCl_3$, or BCl_3 can also be used.

The experimental conditions for carrying out the alkylations are quite simple. Approximately 1% $ZnCl_2$ (or related catalyst) is added to the α-haloalkylbenzene in a reaction flask and slowly the olefin is introduced into the vigorously stirred mixture. In many instances the reaction is exothermic and external cooling is needed to keep the temperature in the generally most suitable range of 20–60°. With the less reactive, longer chain α-olefins sometimes heating is needed to carry out the reactions, but the reaction temperatures even in these cases seldom need to be higher than 80°. In most of the cases investigated, the intermediate haloalkylates were not isolated in pure form, owing to partial dehydrohalogenation taking place already during the alkylations. The reaction mixtures obtained were either thermally dehydrohalogenated to the corresponding olefins or treated with potassium carbonate or pyridine and the aralkenes then were isolated by distillation. Table I summarizes the results of the over-all alkylations together with the yields and physical properties of the products.

The mechanism of the reaction is that of an electrophilic addition of the reactive α-haloaralkene, polarized by the catalyst, onto the olefin, followed by dehydrohalogenation. As such, the reaction represents an example of selectivity in polyfunctional Friedel–Crafts systems. No alkylation of the aromatic ring by the olefins is observed when the above-mentioned "mild" Friedel–Crafts catalysts are used. Thus, these catalysts are not sufficiently reactive to activate the olefinic double bond in order to promote ring alkylation. At the same time they are sufficiently reactive to activate alkylation of the olefin itself by the more reactive α-



$$\underset{\substack{|\\ X\delta^-}}{\overset{\delta^+}{\text{ArCHR}}} + \text{R'CH}{=}\text{CR''R'''} \xrightarrow{\text{cat.}}$$

$$\text{Ar}\underset{\substack{|\\ X}}{\text{CHR}}\text{CHR'CR''R'''} \xrightarrow{-\text{HX}} \text{ArCHRCR'}{=}\text{CR''R'''}$$

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 temperature 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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[6] G. A. Olah and S. J. Kuhn, U. S. Patent 2,998,460 (1961).

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

George A. Olah,[1b] Charles G. Carlson, and Joan C. Lapierre

Contribution No. 121, Exploratory Research Laboratory, Dow Chemical of Canada, Limited, Sarnia, Ontario, Canada

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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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[1] (a) Part IX: *J. Org. Chem.*, **29**, 2315 (1964). (b) To whom correspondence should be addressed at The Dow Chemical Co., Eastern Research Laboratory, Framingham, Mass.

[2] C. Hoogzand and W. Hübel, *Angew. Chem.*, **73**, 680 (1961); E. M. Arnett and M. E. Strem, *Chem. Ind.* (London), 2008 (1961); L. R. C. Barclay, C. E. Milligan, and N. D. Hall, *Can. J. Chem.*, **40**, 1664 (1962).