p-Alkylstyrenes.—The dehydration of the carbinols was carried out according to the general method described in reference 5c. In all cases, the styrenes were removed by distillation from the reaction mixture. For the higher boiling styrenes, it was necessary to use pressures of 1 to 2 mm. during dehydration. *p*-Alkyl C_2, C_4, C_6, C_8, C_9, C_{10}, C_{12} and C_{14} styrenes were purified by successive distillations, *p*-C_{16} and C_{18} styrenes were recrystallized from petroleum ether (b.p. 28–36°). Monomers were stored with inhibitor, usually *p*-*t*-butylcatechol and purified by removing inhibitor with dilute sodium hydroxide followed by distillation or recrystallization before analysis and polymerization. The styrenes are described in Table III.

Preparation of Polymers.—The polymerization of the C_2, C_4, C_6, C_8 and C_{10} styrenes was carried out in the following way. In a standard test-tube were placed 2 g. of the monomer and 0.1% by weight of benzoyl peroxide. The air in the test-tube was displaced with carbon dioxide and the tube sealed. The tubes were then heated in a water-bath at 70° until no flow could be observed. The approximate time required for polymerization varied from 30 hours for *p*-ethylstyrene to 72 hours for the *n*-decylstyrene. The polymers were dissolved in benzene and the filtered solution added slowly with rapid stirring into a large excess of methanol. After 5 such precipitations, the polymers were dried in a vacuum desiccator for several days.

The C_9, C_{14}, C_{16} and C_{18} alkylstyrenes were polymerized in a similar manner under nitrogen except that only 1 to 3 mg. of benzoyl peroxide was used and the monomers were exposed to ultraviolet light. The approximate temperature under the light was 70°. Precipitation of the benzene solution was carried out with different solvents (Table IV).

Properties of Polymers.—Analyses of the purified polymers are listed in Table IV. Intrinsic viscosities (four concentrations) were determined at 20° in toluene with an Ubbelohde viscometer. The determination of the transition temperatures is outlined in the discussion.

Acknowledgment.—The senior author wishes to express his appreciation to Dr. T. Alfrey of the Dow Chemical Company for many helpful discussions. We also wish to thank the Office of Naval Research for the loan of the special refractometer used on the determination of the transition temperatures.

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Friedel–Crafts Reactions between Gaseous Benzene and Ethyl Chloride on Solid Aluminum Chloride

BY MONTE BLAU AND JOHN E. WILLARD

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It has been shown that gaseous ethyl chloride and benzene at a few cm. pressure and 0 to 25° react rapidly to form ethylbenzenes when in contact with solid aluminum chloride. The rate is proportional to the pressure of each reactant and the over-all activation energy is about 4 kcal./mole. Infrared analysis, radiocarbon analysis and titration of hydrogen chloride have been used to follow the reaction. The products include ethylbenzene, the three diethylbenzenes and more complex compounds.

Introduction

It has been found earlier: (1) that exchange of chlorine between aluminum chloride and carbon tetrachloride requires the presence of a surface of solid aluminum chloride[1]; (2) that solid aluminum chloride can exchange chlorine with gaseous organic chlorides[2] and with hydrogen chloride[3] at room temperature and below; and (3) that a Friedel–Crafts reaction takes place when gaseous benzene and carbon tetrachloride are mixed over an aluminum chloride surface.[2]

The present paper gives the results of experiments on the ethylation of gaseous benzene with gaseous ethyl chloride catalyzed by aluminum chloride.

Experimental[4]

Procedure.—Aluminum chloride synthesized[1,2] *in situ* on a vacuum system from aluminum and silver chloride was sublimed onto the walls of a one-liter flask which served as the reaction vessel. Metered quantities of gaseous ethyl chloride and benzene were condensed together in a trap and then rapidly vaporized together and allowed to pass into the reaction vessel. Following the desired time of contact the products and unconsumed reactants were removed by condensing them in cold traps.

One experiment (No. IV of Table I) was carried out on a flow system in which the reaction vessel was a glass tube 3.7 cm. in diameter and 30 cm. long with large projections, similar to those of a Vigreux column, pushed into the walls. The interior surfaces were coated with aluminum chloride as above. In order to carry out a reaction, benzene and ethyl chloride vapors were continuously bled into the reaction region through 0.05-mm. capillary tubes and pumped out through a 0.75-mm. capillary tube into a product collecting trap. The pressure was measured with a mercury-oil multiplying manometer. The amount of each reactant used was determined by weighing its reservoir before and after the experiment.

Methods of Analysis.—Three methods of analysis were used to determine the extent of the reaction $C_6H_6 + C_2H_5Cl \rightarrow C_6H_{6-x}(C_2H_5)_x + xHCl$.

In those experiments where the information desired was the gross amount of reaction, the quantity of hydrogen chloride produced was measured. This was done by condensing it in a liquid air trap, dissolving in water, adding excess potassium iodide and potassium iodate and titrating the liberated iodine with standard thiosulfate.

A quantitative measure of the fraction of the initial benzene which was converted to ethylbenzene as compared to that converted to more highly ethylated benzenes was obtained by using benzene labeled with C^{14}. The unreacted radioactive benzene and radioactive ethylated products (0.1 to 0.2 cc.) were condensed in a Dry Ice trap and diluted with measured amounts of inactive benzene, ethylbenzene and diethylbenzenes. This mixture was fractionated in a Piros–Glover micro-still operating at an efficiency of 20 theoretical plates, and small cuts of pure benzene and ethylbenzene were isolated. The residue in the still-pot was used for estimation of higher-boiling activity. A sample of each cut was oxidized to carbon dioxide, precipitated as barium carbonate and counted as an "infinitely thick" sample in a windowless proportional counter. From the relative counting rates the amounts of benzene converted to ethylbenzene and higher boiling products were calculated.

Infrared absorption analysis was used in experiments designed to identify the ethylation products more rapidly

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[1] C. H. Wallace and J. E. Willard, THIS JOURNAL, **72**, 5275 (1950).

[2] M. Blau and J. E. Willard, *ibid.*, **73**, 442 (1951).

[3] M. Blau, W. T. Carnall and J. E. Willard, *ibid.*, **74**, 5762 (1952).

[4] Further details are given in the Ph.D. thesis of Monte Blau, University of Wisconsin (1952).

and in more detail than could be done by the radiocarbon analysis. Samples of the reaction products were run against benzene in a Baird Associates double beam recording spectrophotometer. An NaCl cell with a path length of 0.1 mm. was used and the region from 2 to 16 microns was scanned. The spectra obtained were compared to standard spectra run in the same cell using samples of ethylbenzene and the three diethylbenzenes obtained from the National Bureau of Standards. Because of the presence of additional peaks of unknown compounds in the reaction products the infrared data allowed only an estimate rather than a quantitative evaluation of the absolute amount of reaction.

Materials.—Thiophene-free benzene was purified by several fractional recrystallizations and fractional distillation through a Vigreux column. It was dried on a vacuum line by distillation through P_2O_5 on glass wool. Eastman white label ethyl chloride was purified by passing it, in the vapor phase, through a sintered glass disk into a 20″ scrubbing column of concentrated sulfuric acid. After two passes through the column it no longer discolored a small quantity of sulfuric acid on shaking. The ethyl chloride was condensed, washed with cold water, dried over P_2O_5, and distilled through a Vigreux column equipped with a cooling jacket. Final drying was accomplished by passing the vapor through P_2O_5 on glass wool *in vacuo*.

The silver chloride used in the synthesis of the aluminum chloride was prepared from reagent grade silver nitrate and hydrochloric acid. It was dried in air for several hours at 120°, and finally fused *in vacuo* to remove the last traces of water. For the synthesis it was heated to about 450° with an excess of Baker and Adamson 30-mesh aluminum pellets (cleaned just before use by washing with hydrochloric acid).

The benzene labeled with C^{14} was obtained from a commercial supplier. When an aliquot was fractionated on the Piros–Glover still with added benzene, ethylbenzene and diethylbenzenes as carriers 2.2% of the radioactivity appeared in the ethylbenzene fraction and 1.1% in the still-pot fraction. All results on the fractionation of products from the ethylation experiments were corrected for this apparent contamination.

The gaseous ethylene was Ohio Chemical Co. U.S.P. grade and the hydrogen chloride was Matheson Co. Anhydrous grade. These gases were used directly from the original tanks after passing through a phosphorus pentoxide train.

Results

Products of Reaction.—Both infrared analyses and analyses by the C^{14} method indicated that appreciable amounts of both monoethylbenzene and more highly ethylated products were formed when low pressures of ethyl chloride and benzene were exposed to aluminum chloride for times of the order of a minute. Typical results are given in Table I. The infrared spectra showed absorption bands corresponding to monoethylbenzene and to each of the three diethylbenzenes, and other peaks.

All of the experiments of Table I except IV were made by the static method where the reproducibility of results must be dependent on the success achieved in reproducible mixing of the reagents and the maintaining of constant conditions with respect to diffusion and convection near the surface. Considerations of this nature may account for the difference in ratio of monoethyl to higher alkylation products in experiments such as IIa and b compared to IIc and I.

Experiment III was made to test the effect of long exposure of the reactants to the surface. After standing overnight most of the solid aluminum chloride had disappeared in a yellow brown colored non-volatile liquid deposit which formed. This material, which proved to be insoluble in benzene, was decomposed with water, following which it was extracted with benzene for product analysis.

In order to obtain some indication of the durability of the catalytic surface through successive exposures, ten reaction mixtures were admitted in turn to surface VII of Table I. The contact time for each was one minute and each was removed by opening the reaction vessel to a liquid air trap for three minutes. The magnitude of the infrared absorption peaks corresponding to individual products in the successive product mixtures varied considerably from run to run in an irregular way but the total fraction of the benzene reacted remained at about 15% per exposure throughout the series. At the end of the series the surface had developed a light brown color.

TABLE I

PRODUCT YIELDS FROM FRIEDEL–CRAFTS REACTIONS BETWEEN GASEOUS ETHYL CHLORIDE AND BENZENE IN CONTACT WITH SOLID ALUMINUM CHLORIDE

Exp.[a]	Time, min.	Pressure, cm. C_6H_6	Pressure, cm. EtCl	Anal. method	Ethylated benzenes formed, % of C_6H_6 used: Mono ethyl	Higher	Total
Ia	2.0	3.0	3.0	C^{14}	3.6	2.0	5.6
Ib	3.0	3.0	3.0	C^{14}	5.3	2.7	8.0
IIa	2.0	3.0	3.0	C^{14}	0.8	2.7	3.5
IIb	2.0	3.0	3.0	C^{14}	1.4	2.3	3.7
IIc	2.0	3.0	3.0	C^{14}	4.3	2.0	6.3
III	1000	3.5	3.5	C^{14}	12.2	88.0	100
IV[b]	0.6	0.02	0.38	C^{14}	8.5	21.4	29.9
V[c]	.5	3.0	3.0	IR[d]	10	20	30
VI[c]	.5	3.0	3.0	IR[d]	10	15	25
VIIa-j	1.0	3.0	3.0	IR[d]	..	..	15

[a] Roman numerals indicate new surfaces. It is not possible to reproduce accurately the surface area from one preparation to another. Therefore quantitative comparisons of the yields from different surfaces are not valid. All experiments except IV were made at 25° in a 1-liter reaction flask with 100–125 mg. of aluminum chloride. [b] Exp. IV was carried out on the flow system, all others were made with the static system. [c] Experiments V and VI were made on "red" $AlCl_3$ surfaces. [d] All IR (infrared analysis) results are estimates which are only semi-quantitative.

Pressure Dependence.—Figure 1 is a plot of the amount of hydrogen chloride formed against the

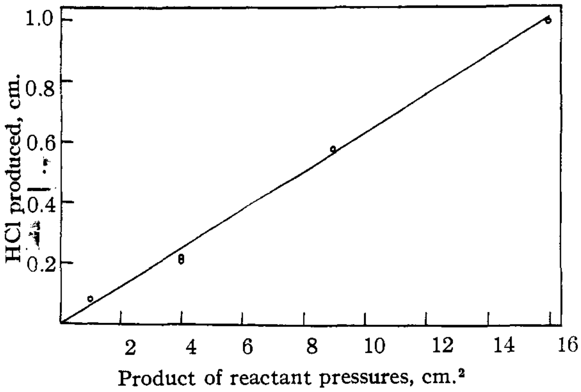

Fig. 1.—Effect of pressure of ethyl chloride and of benzene on the rate of ethylation. Points on the graph show the pressure of hydrogen chloride developed in 2-min. exposures of separate mixtures of gaseous ethyl chloride and benzene to about 250 mg. of aluminum chloride in a 1-liter flask. In each run the ethyl chloride pressure equalled the benzene pressure and the sequence of individual reactant pressures in the five runs was 1, 2, 3, 4 and 2 cm.

product of the pressures of benzene and ethyl chloride for a series of experiments on a single aluminum chloride surface. The results of this experiment, together with similar experiments on other aluminum chloride surfaces in which the pressure of each reactant was varied independently while the other was held constant, indicate that the reaction rate is proportional to the pressure of benzene and to the pressure of ethyl chloride. That is, $d[HCl]/dt = k[C_6H_6][C_2H_5Cl]$, where the magnitude of k varies with the surface used. It was possible to obtain nearly equal rates for identical pressures on the same surface even though several runs at different pressures intervened before the check runs. This indicates that the catalytic activity of the surface did not change rapidly with use. Since the first power pressure dependence seems to hold for reactions in which appreciable polyethylation occurs, it seems likely that the reaction rate constants do not differ radically between benzene and the various ethylbenzenes, at least within the limits of these fairly crude experiments.

Temperature Dependence.—The temperature dependence of the over-all ethylation reaction was determined by measuring the rate of hydrogen chloride production by reaction mixtures of identical molar concentrations in contact with the same aluminum chloride surface alternately at 25 and 0°. The reactants were mixed in a metering flask at a pressure such that when this flask was opened to the evacuated reaction flask held at the reaction temperature the reaction flask would fill to the desired concentration. The reactants passed through a glass coil immersed in the thermostating liquid before entering the reaction vessel. Transfer of the reactants was complete in a few seconds or less. Measurements were made on each of two surfaces with concentrations of ethyl chloride and benzene of 1.6×10^{-3} mole/l. and 1.1×10^{-3} mole/l., respectively.

In the first experiment the exposure temperatures and concentrations of hydrogen chloride produced in successive three minute exposures were as follows, using concentration units of mole/l. $\times 10^4$: 0°, 1.74; 0°, 1.66; 25°, 3.29; 25°, 3.40; 0°, 1.40; 25°, 3.11. In the second experiment two minute exposures gave the following results: 25°, 2.38; 25°, 2.56; 0°, 1.41; 0°, 1.55; 25°, 2.28; 0°, 1.34. The corresponding over-all Arrhenius activation energies are 3.3 and 4.6 kcal./mole.

Reaction with Ethylene.—As part of this exploratory investigation of reactions of gases in contact with solid aluminum chloride the rates of ethylation of benzene by ethyl chloride, by ethylene, and by mixtures of ethylene and hydrogen chloride were compared, the products being determined by infrared analysis. All exposures were for three minutes. The pressures were: (1) 4 cm. ethyl chloride and 4 cm. benzene; (2) 4 cm. ethylene and 4 cm. benzene; (3) 3 cm. ethylene, 3 cm. hydrogen chloride and 3 cm. benzene; (4) 20 cm. ethylene, 20 cm. hydrogen chloride and 3 cm. benzene. The first two runs were made on one aluminum chloride surface and the last two on another. Approximately 6% of the benzene reacted in the case where ethyl chloride was used, none (less than 0.1%) reacted when ethylene was used, and 3% and 5% of the benzene was found as ethyl benzenes in the tests with hydrogen chloride present. In the second test with hydrogen chloride, where the pressures were relatively high, it is probable that much more reaction occurred than indicated by the condensable gaseous products since the surface turned brown and some liquid formed which presumably contained highly ethylated benzenes which were too low in volatility to be collected in the product trap.

These results and subsequent tests of much longer duration made by Mr. Marshall Peterson in our laboratory indicate that in the absence of hydrogen chloride ethylene does not react with benzene vapor over aluminum chloride. In the presence of an equivalent amount of hydrogen chloride the rate of reaction of ethylene is, however, similar to that of ethyl chloride. The possibility exists that in the latter case ethyl chloride is formed as an intermediate.

Abnormally Active Surfaces.—During the course of this work it occasionally was observed that when aluminum chloride was sublimed from the vessel where it was synthesized to the reaction vessel, which was cooled in liquid air, there were red areas on the fresh surface. When the surface was allowed to warm to room temperature these disappeared and did not reappear when the surface was again surrounded with liquid air. Such surfaces showed abnormal reactivity as evidenced by the rate of benzene ethylation (exps. V and VI, Table I) and by the fact that as soon as the reactants were admitted at room temperature the areas which had been red at liquid air temperature immediately turned brown and after half a minute liquid reaction products began to condense out on them. The cause of the red color and the increased reactivity is not clear. A test was made to determine whether hydrogen chloride present during the synthesis or sublimation could have been responsible for the effect. Aluminum chloride was synthesized, sublimed and frozen down with liquid air in the presence of hydrogen chloride but no red color was formed.

Discussion

The results described above allow certain conclusions pertinent to the mechanism of the reaction.

(1) Since the rate of reaction is dependent on the pressures of both benzene and ethyl chloride each of these reactants must be only weakly adsorbed on the surface rather than saturating it.

(2) The fact that a significant fraction of the ethylation products is polyethylated even when the total conversion of benzene is less than 10% indicates either that ethylbenzene is more easily ethylated than is benzene or that under the conditions of these experiments its average local concentration in the vapor film near the aluminum chloride surface is much higher than its average concentration in the reaction vessel.

(3) The over-all activation energy of the ethylation reaction under the conditions tested is about 4 kcal./mole.

(4) Solid aluminum chloride can form liquid complexes with the polyethylation products which are formed during prolonged contact of the reactants with the surface (exp. III, Table I). Since hydrogen chloride also is produced it may be a necessary part of the complex, as Brown and coworkers[5] have demonstrated to be the case for aluminum chloride complexes with toluene. Because of their low vapor pressure it is quite possible that the polyethylated compounds condensed as liquids on the surface before complex formation occurred in the present work. It has been demonstrated by Mr. James Reavis in our laboratory that neither gaseous mixtures of hydrogen chloride with benzene or with ethyl chloride show appreciable reaction with solid aluminum chloride.

It would be premature to attempt to state a detailed mechanism depicting the manner in which the reacting molecules become attached to the aluminum chloride surface, and undergo reaction. It may be that the localized centers of coulombic attraction on the surface of the ionic lattice play an important role.[2] Alternatively it may be that the initial step involves adsorption of the ethyl chloride and benzene by the aluminum atom acting as an acid.[6]

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[5] (a) H. C. Brown, H. W. Pearsall and L. P. Eddy, THIS JOURNAL, **72**, 5347 (1950); (b) H. C. Brown and H. W. Pearsall, *ibid.*, **74**, 191 (1952).

[6] For discussions of such interactions in solution and references, see for example: (a) H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952); (b) M. Tamres, *ibid.*, **74**, 3375 (1952).

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, NEW MEXICO HIGHLANDS UNIVERSITY, AND FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MISSOURI]

Condensations of Aromatic Aldehydes and Aryl Carbinols with Aluminum Chloride and Aromatic Systems

BY HERBERT E. UNGNADE,[1] EDWARD F. KLINE[2] AND ELBERT W. CRANDALL[3]

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The reaction of aryl carbinols and aromatic aldehydes with aromatic hydrocarbons and excess aluminum chloride has been extended to include substituted benzyl alcohols as donors and mesitylene, biphenyl and diphenyl ether as acceptor molecules. An unexpected reaction occurred with diphenyl ether. The implications of the experimental results are discussed.

Various aromatic aldehydes, benzyl alcohol and benzhydrol can be cleaved with excess aluminum chloride at 60° to give carbon monoxide. When the reaction is carried out in benzene the carbon monoxide is not evolved but reacts with the solvent to give anthracene and triphenylcarbinol. With toluene and diphenylmethane a condensation occurs which yields dimethyl- and dibenzylanthracenes as end-products.[4] In these reactions the oxygenated carbon of the donor molecule furnishes only the *meso* carbons of the anthracenes and the carbinol carbon of triphenylcarbinol. The aryl portion of the donor molecule is generally isolated as ArH.[4-6]

The reaction with biphenyl, benzaldehyde and excess (2 moles) aluminum chloride furnishes a diphenylanthracene, m.p. 202–203° (diphenylanthraquinone, m.p. 270–271°), which differs from the substance obtained previously under somewhat different conditions,[7] but is doubtless formed in the same fashion.[8]

The three xylenes were shown to react with benzaldehyde and excess aluminum chloride to give different tetramethylanthracenes,[7] evidently without appreciable rearrangement of the methyl groups. A reaction of this sort is not possible with mesitylene. The product of the reaction was identical with the tetramethylanthracene prepared from *m*-xylene.[7,9] The volatile fraction from the reaction contained xylenes as well as tetramethylbenzenes, further establishing the cleavage of a methyl group in mesitylene.

When the reaction takes place in diphenyl ether the same solid product (I) is formed from benzaldehyde, benzyl alcohol or benzhydrol. This substance is not an anthracene but has been identified as 9-phenylxanthydrol by degradation and synthesis. Its formation in these reactions is unique since the oxygenated compounds apparently

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[1] Chemistry Department, Purdue University, Lafayette, Ind.

[2] From the master's thesis of E. F. Kline, N. M. Highlands University, 1952.

[3] In part from the Ph.D. thesis of E. W. Crandall, University of Missouri, 1950.

[4] H. E. Ungnade and E. W. Crandall, THIS JOURNAL, **71**, 2209, 3009 (1949).

[5] D. H. Hey, *J. Chem. Soc.*, 72 (1935).

[6] For an understanding of the reaction it is necessary to point out that the reaction mixtures are decomposed with ice and hydrochloric acid and separated by steam distillation. Under these conditions tertiary halides analogous to triphenylchloromethane will be rapidly hydrolyzed to carbinols (W. Hemilian, *Ber.*, **7**, 1208 (1874)). The non-volatile products usually contain tar and oily by-products without characteristic absorption spectra in the ultraviolet or visible region. These may represent hydrogen acceptors.

[7] H. Ellison and D. H. Hey, *J. Chem. Soc.*, 1847 (1938).

[8] The absorption spectrum of this substance indicates that the phenyl substituents will be in beta positions.

[9] A precedent for this reaction is the formation of hexamethylanthracene from isodurene and pivalyl chloride (D. Nightingale, R. L. Sublett, R. A. Carpenter and H. D. Radford, *J. Org. Chem.*, **16**, 658 (1951)).