N-Salicylidene derivatives were prepared from the respective amines[4–7] by the usual procedure.[25] Yields and physical properties are given in Table III.

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Heterogeneous Catalysis by Solid Superacids. 3.[1a] Alkylation of Benzene and Transalkylation of Alkylbenzenes over Graphite-Intercalated Lewis Acid Halide and Perfluorinated Resin-Sulfonic Acid (Nafion-H) Catalysts

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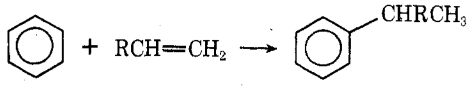
The use of superacidic solid catalysts in heterogeneous gas-phase alkylation reactions, such as the ethylation of benzene by ethene and the transethylation of benzene with diethylbenzene, was studied. Such catalysts enable us to conduct the reactions under relatively mild conditions and to obtain clean reaction products. Reactions were carried out in a flow system, in the gas phase, in the temperature range of 125–210 °C at atmospheric pressure. Intercalated $AlCl_3$ and $AlBr_3$ gave good initial yields of alkylated products. The lifetime of the catalyst was, however, limited as the active Lewis acid is leached out from the catalyst, causing a sharp decline in the catalytic activity with onstream time. Other possible reasons of the deactivation of the catalyst are also discussed. A perfluorinated sulfonic acid resin catalyst (Nafion-H) was found to have a much better stability, while showing good catalytic activity. Alcohols were also found to dehydrate in the gas phase efficiently over this catalyst and could be used as alkylating agents for benzene.

Friedel–Crafts alkylation and transalkylation reactions are traditionally carried out in the liquid phase. Catalysts are generally based on aluminum chloride and related Lewis acid halides. The ethylation of benzene with ethylene to form ethylbenzene using aluminum chloride as catalyst is one of the largest chemical processes carried out in industry. Application of solid supported catalysts in heterogeneous vapor phase ethylation started to gain importance only recently. One of the major difficulties is the sluggishness of the ethylation reaction. Ethene is far less readily protonated than, for example, the more polar propene, and its equilibrium with the ethyl cation is rather unfavorable. Few (if any) of the known solid acid catalysts are able to catalyze efficiently the ethylation of benzene or the transethylating benzene with polyethylbenzenes (which are inevitably formed as by-products in the ethylation of benzene). This is not the case with the isopropylation of benzene to cumene. Cumene has been industrially produced for decades over supported acid catalysts such as supported phosphoric acid. Obviously, the more polar propene is protonated much more readily than ethene and polyisopropylbenzenes also transalkylate benzene with greater ease.

In continuation of our studies of Friedel–Crafts and superacid chemistry, our interest was directed to the possibility of applying solid superacidic catalysts to heterogeneous reactions.[1–3] These catalysts can be based either on Lewis acid halides bound or intercalated to suitable supports or solid (polymeric) protic acid, such as perfluorinated resin sulfonic acids.

Results and Discussion

The alkylation of benzene with ethene and propene (eq 1)



(1)

$R = H, CH_3$

and the transethylation of benzene with diethylbenzenes (eq 2) was studied over several solid superacidic catalysts. Reac-

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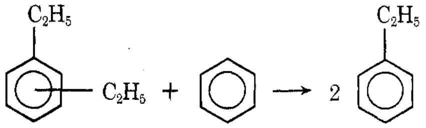
Table I. Ethylation of Benzene with Ethene over Graphite-Intercalated Metal Halides

Metal halide	$AlCl_3$	$AlCl_3$	$AlCl_3$	$AlCl_3$	$AlBr_3$	SbF_5	$FeCl_3$
% intercalated	16.6	16.6	16.6	28.4	4.5	26.1	50.5
Temp, °C	125	160	200	160	160	160	185
$[C_6H_6]/[C_2H_4]$ ratio	3.3	3.4	3.2	3.5	3.3	3.6	3.2
Onstream time, h	% conversion (based on ethene)						
1	61.7	41.7	15.1	60.4	31.7	4.8	
2	10.3	12.0	5.7	62.9	15.1		
3	5.4	7.3	2.4	43.8			
4	4.3	5.3	1.7	33.7			
5	2.9	5.7	1.9	26.5			
6	1.9	1.4	0.7	6.8			
7				2.6			
8				2.2			
9				1.7			
10				1.5			



(2)

tions were carried out in the gas phase in the temperature range of 125–210 °C.

A. Reactions over Graphite-Intercalated Metal Halides. Many metal halides when heated with graphite are capable of inserting themselves between the graphite layers thus forming intercalates.[4] As a result the distance between the graphite layers is increased from 3.35 to 9–10 Å depending on the intercalated halides. Some chlorides such as aluminum chloride are intercalated only in the presence of chlorine gas and it was shown[5] that the intercalated $AlCl_3$ contains more than 3 Cl atoms per Al atom. Lately,[6] intercalation of $AlCl_3$ and other halides was also achieved by treating graphite with solutions of the metal halides. Higher valency metal fluorides such as SbF_5[7] and AsF_5[8] were also shown to intercalate easily into graphite. Wide-line NMR studies showed that intercalated SbF_5 behaves as a liquid well below the freezing point of SbF_5.[9]

The possibility of intercalating metal halides into graphite suggested their use as Friedel–Crafts catalysts.[10] Lalancette[11] reported the catalytic activity of intercalated $AlCl_3$ for aromatic alkylations of liquid hydrocarbons with alkyl halides or alkenes as alkylating agents. In his experiments the intercalate was stirred in the solution as a heterogeneous catalyst. It was found that intercalated $AlCl_3$ is a milder catalyst than neat $AlCl_3$. The rate of the reaction was somewhat lower but the tendency to form polyalkylbenzenes was reduced. It was, however, observed that under these conditions $AlCl_3$ is leached out from the intercalate into the reaction medium and reactions thus may be to a significant degree catalyzed in the conventional fashion with the intercalate serving only as a reservoir for the $AlCl_3$ catalyst.

We have studied graphite intercalated aluminum chloride and bromide, as well as antimony pentafluoride and ferric chloride, as solid heterogeneous catalysts for the gas-phase ethylation of benzene with ethene. A flow system with a fixed bed catalyst was used in our experiments. Products were collected, periodically sampled, and analyzed by gas–liquid chromatography. Results obtained are summarized in Table I.

As seen from data in Table I intercalated $AlCl_3$ and $AlBr_3$ are efficient ethylation catalysts. High initial conversions were observed at temperatures as low as 125 °C. Of the two additional acidic haldies investigated SbF_5 gave lower initial conversions and rapidly lost activity, indicating the extreme sensitivity of this catalyst to hydrolysis and other impurities. The weaker Lewis acid $FeCl_3$ was, on the other hand, inactive. However, both the $AlCl_3$ and $AlBr_3$ intercalates were efficient only for 3 to 6 h under the continuous experimental conditions. Reactivity declined with onstream time and the catalyst became deactivated after 6 to 8 h.

Transethylation of benzene with diethylbenzenes was also studied over the same catalysts at 180 °C. Results are shown in Table II. Good initial catalytic reactivity was again observed which decreased sharply with onstream time.

Several factors can contribute to the loss of the catalytic activity. Upon following the course of the $AlCl_3$-graphite-catalyzed reaction aluminum chloride was found (analyzed as hydrolyzed chloride) in the liquid products and HCl was found in the effluent gases. The amount of the eluted chloride in each fraction was measured. Figure 1 shows the amount of the eluted chloride against the conversions obtained in the ethylation of benzene.[12] As seen from the figure the elution of $AlCl_3$ and the loss of catalytic reactivity are related to each other. In the ethylation reaction loss of 30% of the overall aluminum chloride content caused complete deactivation of the catalyst. Similar results were also obtained in the transethylation reaction of benzene with diethylbenzenes.

There may be two reasons for the loss of the catalytic halides. The first is the possible hydrolysis of $AlCl_3$ by small amounts of moisture in the feed. It is known[4b] that intercalated $FeCl_3$ which is more stable to hydrolysis by aqueous HCl[4b] also showed loss of chloride ion during attempted transethylation reaction. This is in accord with the desorption of metal halide from the catalyst. Intercalation into graphite is a reversible process and there is always a certain vapor pressure of the free metal halide at the reaction temperatures studied. The conditions in a fixed bed flow reactor favor desorption because the desorbed aluminum halide is readily complexed by the organic reagents and thus can be continuously carried away by the fresh feed. This is also sustained by the observation that the completely deactivated catalyst kept further loss of $AlCl_3$ at approximately the same rate (Figure 1). These observations are in accord with Lalancette's observations concerning intercalation of metal halides from their solutions in CCl_4.[6] Intercalation took place only for halides which are slightly soluble in CCl_4. Those which showed better solubility stayed in the solution and did not intercalate (or were desorbed to the extend that no intercalation was observed).

The relation between the catalytic activity and the overall amount of intercalated $AlCl_3$ is not a simple one. The actual catalytic sites of intercalated metal halides are not well known. Considering the layer structure and steric requirements of the intercalate it is reasonable to assume that catalysis can take

Table II. Transethylation of Benzene with Diethylbenzene over Graphite-Intercalated Metal Halides

Metal halide	$AlCl_3$	$AlBr_3$	SbF_5
% intercalated	28.4	4.5	26.1
Temp, °C	180	180	180
$[C_6H_6]/[C_6H_4Et_2]$ ratio	4	4	4
Onstream time, h	% conversion (based on diethylbenzene)		
1	45.0	66.2	2.4
2	70.4	51.8	
3	66.9	41.4	
4	70.3	3.1	
5	56.9		
6	16.2		
7	13.8		
8	15.2		
9	12.7		
10	10.4		

place only on the exposed surface areas or edges but not in the deeper layers of the catalyst. For steric reasons alone the reactants cannot be expected to penetrate well into the deeper layers containing metal halides. Diminished reactivity thus may involve desorption of the metal halide from the catalytically active exposed areas which, however, account only for a fraction of the overall amount of intercalated halide. One must further consider the probable migration of halide intercalated into the deeper inside layers of the surface areas. Comparative elementary analysis of fresh catalyst and samples of the same catalyst taken from the reactor after prolonged reaction time showed that 56% of the chlorine and 34% of the aluminum were lost in the spent catalyst. ESCA spectral study, which is detecting the upper 30 Å of the catalyst's surface, showed at the same time chlorine loss of 66 and 32% loss of aluminum. These results indicate that the bulk of the graphite-intercalated catalyst loses $AlCl_3$ at a different rate than the catalytically active exposed surface areas. In a typical ethylation reaction it was observed that complete deactivation of the catalyst took place after ca. 30% of the chloride was lost (Figure 1). Such an amount of $AlCl_3$ is much too large to be present on the surface alone. Furthermore, even after the catalytic activity is completely lost, chlorine continues to be eluted at about the same rate. This shows that at the reaction temperature (160 °C) there is some equilibration between the $AlCl_3$ in the deeper lattice areas and that of the surface.

We had already mentioned the possible hydrolysis of the metal halide by traces of moisture in the feed. Analytical data of the deactivated catalysts indeed clearly show that more chloride than aluminum is lost from the catalyst, i.e., the ratio Cl/Al in the spent caltalyst decreases, in good agreement with partial hydrolysis of exposed $AlCl_3$. As the result of hydrolysis chloride is lost as HCl, while the aluminum remains as a nonvolatile hydroxide (or oxide).

Finally, there must be considered another source of catalyst deactivation, not connected with loss of the metal halide. Ethene and other alkenes are well-known poisons for many solid acidic catalysts as they have the tendency to polymerize on the catalyst surface. Higher pressure reactions and high dilution of ethene by the alkylated compound give partial relief from this problem. The transalkylation reaction which does not involve ethene shows much lesser tendency for deactivation.

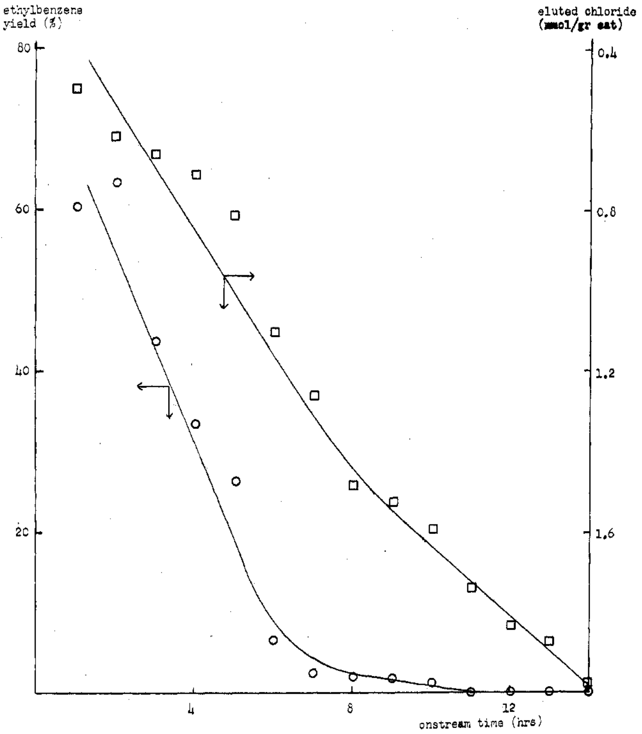


Figure 1. Yield of ethylbenzene and loss of chloride from intercalated $AlCl_3$ against onstream time in the ethylation of benzene by ethene.

Table III. Alkylation of Benzene over Nafion-H Catalyst

Alkene	Temp, °C	$[C_6H_6]/[alkene]$	Contact time, s	Alkene conversion, %
Ethene	110	4	7	10
	150	4	6	24
	180	4	6	36
	190	3.4	3.5	44
Propene	110	1.5	7	9
	150	1.5	6	16
	180	1.5	6	19
	180	3	4	21
	180	6	4	29

B. Reactions over Perfluorinated Resin-Sulfonic Acid (Nafion-H). Sulfonated ion exchange resins, of the cross-linked polystyrene type (Dowex, Amberlyst) in which the sulfonic acid group is bound to the polymeric framework, are frequently used as acid catalysts of moderate strength. The use of such sulfonic acid resins in acid catalysis was reviewed.[13] The acidity of these catalysts can be enhanced by complexing with Lewis acid halides such as $AlCl_3$,[14] SbF_5, or TaF_5 and the like. However, by increasing the acidity to the superacidic range, protolytic cleavage (degradation) of the hydrocarbon polymer backbone can take place. We therefore searched for strong resin sulfonic acids which at the same time are stable under highly acidic conditions. The commercially available copolymer of a perfluorinated ether and perfluoroalkanesulfonic acid, Du Pont's Nafion resin,[15] used as its K salt in dielectric membranes material, in its activated free acid form (Nafion-H) was found to fulfill best these requirements.

(1) Alkylation with Alkenes and Transalkylation with Dialkylbenzenes. When ethene or propene were reacted with benzene over Nafion-H at temperatures between 125 and 190 °C, alkylated benzenes were obtained with yields significantly increasing at higher temperatures. The results are summarized in Table III. Transalkylation of benzene with diethylbenzene (as well as diisopropylbenzene) was also found to be efficiently catalyzed by Nafion-H. Using a typical ratio of benzene:diethylbenzene of 4.5:1 the yield of ethylbenzene (based on diethylbenzene) was 45% at 130 °C and 76% at 190 °C. At 130 °C there was no decline in the reactivity of the catalyst after

Table IV. Dehydration of Alcohols over Nafion-H Catalyst

Alcohol	Temp, °C	Contact time, s	% dehydration	Product	
				% alkene	% ether
i-PrOH	100	10	9		100
	130	9	28	45	55
	160	8	>97	100	
n-PrOH	130	4.5	8	47	53
	160	8	96	100	
t-BuOH	120	5	100	100	

15 h onstream time (the longest experiments carried out) and at 190 °C after 8 h. This contrasts sharply with the rapid deactivation of intercalated metal halides. However, the thermal stability of Nafion-H rapidly decreases at the region of 220 °C. Extended exposure to such temperatures results in loss of sulfonic groups and of activity which is substantiated by observed loss of sulfur as found by ESCA spectroscopy in the thermally deactivated catalyst.

The selectivity of Nafion-H in effecting polyalkylation is relatively low. About 20% of the alkylated products at 190 °C are diethylbenzenes. The isomeric composition of the diethylbenzenes is 9% ortho, 75% meta, and 34% para. Venuto[16] studied the ethylation of benzene over a rare earth exchanged Zeolite X catalyst. He found that with a feed composition of benzene/ethene of 5:1 the ratio of diethylbenzene/ethylbenzene was 1:4.65. Similar results were obtained with a silica–alumina catalyst.[17] Ten percent diethylated products were obtained using a feed ratio benzene/ethene of 10:1. The large amount of *m*-diethylbenzene formed shows significant thermodynamically influenced isomerization (probably in the arenium ion intermediates). Electrophilic attack on ethylbenzene is prone to occur initially at the ortho and para positions. Isomerization is, however, incomplete as higher amounts of *m*-diethylbenzene were obtained in the isomerization of diethylbenzenes using $AlCl_3$,[17,18] Nafion-H,[19] or Zeolite Y type[20] catalysts. Formation of substantial amounts of *m*-diethylbenzene is common for all acidic catalysts. The strong complexing ability of $AlCl_3$ (or its conjugate acid) helps to form increased amounts of the meta isomer, whereas silica–alumina gives amounts similar to those obtained with Nafion-H. The less acidic zeolite Y is reported to give mostly the ortho and para isomers.[20] Formation of *sec*-butylbenzene, expected by possible ipso attack of ethene on ethylbenzene, was detected with some catalysts such as supported phosphoric acid,[17] ferric phosphate,[17] or $AlCl_3$–NiO–SiO_2.[21] In some cases *sec*-butylbenzene is indeed an important alkylation product. No *sec*-butylbenzene was found, however, with $AlCl_3$ (maybe due to the ready dealkylation of *sec*-butylbenzene with such a strong catalyst). Similarly there was no evidence for the formation of *sec*-butylbenzene using Nafion-H catalyst.

(2) Alkylation with Alcohols. Perfluoro resin sulfonic acids of the Nafion-H type also allow the use of alcohols as the alkylating agents. Water formed as by-product in the reactions does not affect the acidic groups of the catalyst by hydrolysis. The use of alcohols instead of alkenes indeed improves the lifetime of the catalyst. With alcohols no ready polymerization side reactions take place whereas alkenes, such as ethene, can poison the catalyst by polymer formation on its surface. To avoid polymer formation it was recommended to use higher pressures and to introduce first the benzene into the reactor followed by the ethene–benzene mixture. The use of alcohols which form water as a by-product thus inhibits polymerization and helps to minimize poisoning of the catalyst.

The behavior of several neat alcohols over Nafion-H catalyst in the gas phase was studied. The results, summarized in Table IV, show that the alcohols are efficiently dehydrated under these conditions. There is no evidence for other side reactions such as dehydrogenation[22a] or decomposition[22b] often found over other solid acid catalysts. The ease of dehydration is in the order tertiary > secondary > primary alcohols. At higher temperatures the alcohols are dehydrated in nearly quantitative yield and the appropriate alkenes are formed. At lower temperatures ether formation predominates. The ease of the dehydration of alcohols over Nafion-H prompted us to study their alkylating ability of benzene under similar conditions.

Table V. Alkylation of Benzene with Alcohols over Nafion-H Catalyst

Alcohol	$[C_6H_6]$/[ROH]	Temp, °C	Contact time, s	% alcohol conversion
EtOH	2.6	180	9	3.5
	2.6	210	8	6
n-PrOH	0.85	110	10	0
	0.85	175	9	5
	2	175	9	17
i-PrOH	2	170	9	11
	2	210	8	16

The alkylation of benzene was studied with ethanol, 1-propanol, and 2-propanol. The results of these alkylations are summarized in Table V. 1-Proponal gave only cumene as the alkylation product. Propylbenzene could not be detected. This indicates the intermediacy of the 2-propyl cation in the alkylation process. The initial formation of *O*-protonated 1-propanol is assumed as the first step of the reaction. This species was indeed shown to be formed from 1-propanol in FSO_3H–SbF_5 at low temperatures[23a] and to cleave to water and propyl cation above 0 °C.[23b] But the sole formation of cumene as the reaction product rules out the possibility of alkylation by it through an S_N2 type process. Hydration of the 2-propyl cation to give 2-propanol is not a favored reaction under the reaction conditions. The only alcohol recovered from an incomplete conversion of the feed was 1-propanol. The 2-propyl cation either alkylates benzene or reforms (via proton elimination) propene. In control experiments under the same conditions propene was found to hardly react with water over Nafion-H to give 2-propanol. Alkylation of benzene by alcohols gave lower yields than with alkenes. Possible reasons may be the difference in the catalytic activity as a consequence of water formed[24] or the shorter contact time for the alkylation reaction as dehydration clearly precedes alkylation and thus decreases the de facto contact time for the alkylation step.

Conclusions

The alkylation of benzene and the transalkylation of alkylbenzenes were studied in the gas phase over highly acidic solid catalysts. The high activity of these catalysts permitted the use of relatively low temperatures and atmospheric pressure, instead of the higher temperatures and pressures usually employed in such reactions, without significantly affecting the yields. The major difficulties encountered with these catalysts are their relatively short lifetime and ease of deactivation. Perflorinated resin-sulfonic acids such as Nafion-H were found to give significant improvement in this regard. They offer the possibility to extend the application of acid-catalyzed Friedel–Crafts reactions to "clean" heterogeneous gas-phase reactions without complex formation and many of the side reactions observed in solution chemistry.

Experimental Section

Materials. Ethene and propene were at least 99.5% pure. Aromatics used were highest purity commercial products (>99%). Diethylben-

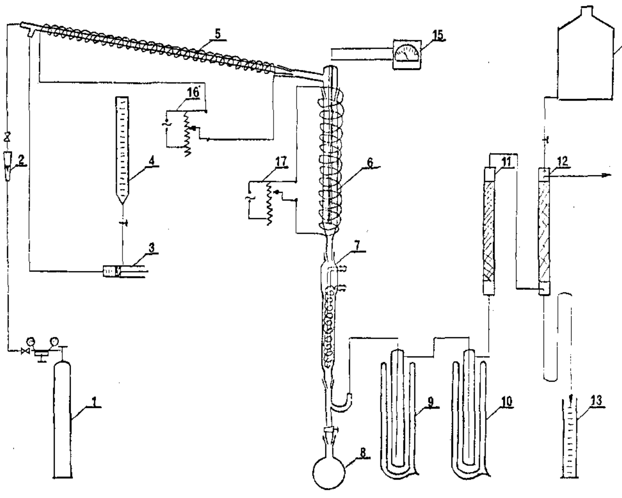


Figure 2. Scheme of the catalytic reactor: (1) alkene supply; (2) flow controller; (3) syringe pump; (4) reservoir for liquid feed; (5) evaporator; (6) reactor; (7) condenser; (8) liquid product receiver; (9, 10) traps; (11) $CaCl_2$ drying tube; (12) water absorber; (13) receiver for water; (14) water reservoir; (15) pyrometer; (16, 17) heater powerstat.

zenes used were a commercial mixture containing 8% ortho, 66% meta, and 26% para isomer.

Catalytic Reactor. We used a single pass, fixed bed flow reactor which is schematically depicted in Figure 2. When Nafion-H was used as a catalyst the HCl absorption system (No. 11–14 in Figure 2) could be omitted.

Catalysts. Graphite intercalated metal halides were either prepared according to known procedures[7,25] or were commercially available (Alfa Products). Nafion 501 as the potassium salt was obtained from the Du Pont Co. The acidic form (Nafion-H) was prepared by treatment with 20% aqueous nitric acid followed by that with fluorosulfuric acid.

Procedure for Catalytic Alkylations. Reactions were carried out in a 170 × 12 mm glass tube reactor in which the catalyst was supported by a sintered glass disk. The reactor was charged with 1 g of the activated dry catalyst, while dry N_2 was passed through generally at the rate of 5 mL/min. The reactor was electrically heated. The reactions were introduced with a syringe pump at a constant liquid rate of 0.02 mL/min. Products emerging from the catalytic reactor were condensed and analyzed at time intervals by gas–liquid chromatography. During individual experiments the reactor temperature did not deviate by more than ±1 °C. The maximal variation of the temperature in all the experiments was less than 4 °C. Under the used experimental conditions the space velocity was in the range of 1.6–2.2 $\times 10^{-6}$ mol/s·g catalyst and the contact time over the catalyst (if otherwise not indicated) was 4–5 s. Variations are mainly due to the different molecular weights and densities of the liquid reactants, as they were introduced on a fixed volume basis.

Analysis of Products. Products were analyzed by gas–liquid chromatography using a Perkin-Elmer Model 226 gas chromatograph equipped with flame ionization detector. A 150 ft × 0.1 in. capillary column coated with *m*-bis(*m*-phenoxyphenoxy)benzene + Apiezon L at 120 °C separated the products very efficiently.

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Registry No.—Benzene, 71-43-2; ethene, 74-85-1; graphite aluminum chloride, 39383-90-9; graphite aluminum bromido, 11129-35-4; graphite antimony floride, 56093-42-6; graphite iron chloride, 11115-86-9; diethylbenzene, 25340-17-4; Nafion-H, 63937-00-8; propene, 115-07-1; 2-propanol, 67-63-0; 1-propanol, 71-23-8; 1-butanol, 71-36-3; ethanol, 64-17-5.

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