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Comparison of the Addition of Bromine Chloride to 1-Hexene and 1-Hexyne in Carbon Tetrachloride and Methanol

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Addition of bromine chloride (BrCl) to 1-hexene in CCl_4 gives a 61:39 ratio of Markownikoff to anti-Markownikoff products (1-bromo-2-chlorohexane to 1-chloro-2-bromohexane), suggesting a symmetrically bridged bromonium ion intermediate in this reaction. 1-Hexyne reacts with BrCl to give Markownikoff and anti-Markownikoff products in the ratio of 90:10 (*trans*-1-bromo-2-chloro-1-hexene/*trans*-1-chloro-2-bromo-1-hexene). These data, together with the fact that the alkene products have trans stereochemistry, implicate a weakly bridged bromonium in the addition of BrCl to 1-hexyne. The bromochlorohexanes were analyzed by mass specrometry, and ^{13}C NMR analyses distinguished between the bromochlorohexenes. In CH_3OH, 1-hexyne and BrCl give only Markownikoff bromochloride (trans isomer) and 1,1-dibromo-2-hexanone. (The result of two additions of Br, OCH_3, followed by hydrolysis of the intermediate ketal.) Markownikoff and trans additions suggest that a weakly bridged bromonium ion, rather than a vinyl cation, is involved. Addition of BrCl to 1-hexene in CH_3OH gives the following ratios of Markownikoff to anti-Markownikoff bromochlorides and methoxy bromides: 25:24 and 34:17.

A few years ago, Pincock and Yates[1] suggested that the intermediate involved in the bromination of some alkylacetylenes in acetic acid is a bridged bromonium ion (**1a**) and not an open vinyl cation (**1b**). They based their conclusion on the assumption that an unbridged vinyl cation should give some *cis*-1,2-dibromide; only *trans*-1,2-dibromide was reported.[2] More recently, Olah and Hochswender[3] drew the same conclusion from their studies of the bromination of 1-hexyne in 1,1,2-trichlorotrifluoroethane. Neither study, however, permitted a conclusion to be drawn concerning the symmetry of the bridging in the bromonium ion. Conceivably a weakly bridged ion such as **1c** is involved, but with sufficient bridging to prevent syn addition.
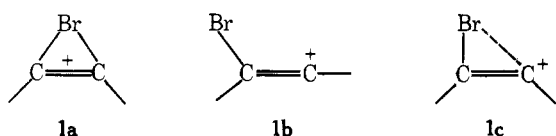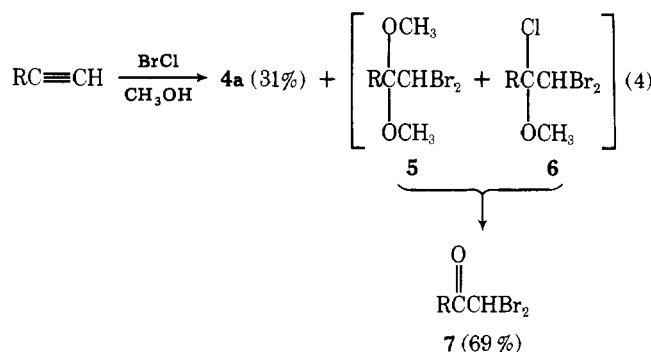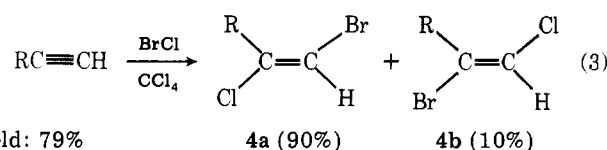

We proposed to study the addition of bromine chloride (BrCl) to both 1-hexene and 1-hexyne in a nonpolar solvent (CCl_4) and a polar solvent (CH_3OH). Our initial assumption was that the extent of anti-Markownikoff ring opening of either the saturated bromonium ion from 1-hexene or the unsaturated ion from 1-hexyne should be significant if the bridging is symmetrical and decrease to zero with a carbocation. Although Pincock and Yates[1] did not observe solvent incorporation when 1-hexyne was brominated in acetic acid, we suspected that ring opening of the intermediate bromonium ions would occur in the more nucleophilic solvent methanol. Solvent incorporation is a predominant reaction in the bromination of 1-hexene in methanol.[4,5]

Results

Products from the addition of BrCl to 1-hexene in CCl_4 and CH_3OH under ionic conditions are shown in eq 1 and 2.
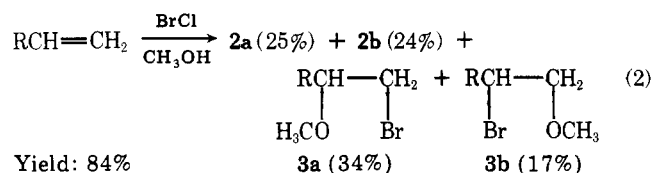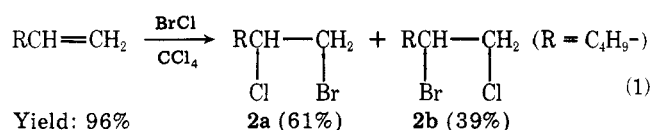
1-Hexyne and BrCl under ionic conditions gave the products shown in eq 3 and 4. We postulate that **5** and **6** are in-

volved and that they result from addition to **8**, because **8** is more reactive than the starting 1-hexyne (eq 5). 2,2-Dibromohexanal (**9**) was not detected, indicating that anti-Markownikoff addition of Br, OCH_3 did not occur (eq 6).

$$RC{\equiv}CH \xrightarrow[\text{CH}_3\text{OH}]{\text{Br}_2} \mathbf{7}\ (60\%) + \underset{\mathbf{10}\ (40\%)}{\overset{\displaystyle R}{\underset{\displaystyle Br}{C}}{=}\overset{\displaystyle Br}{\underset{\displaystyle H}{C}}} \quad (7)$$
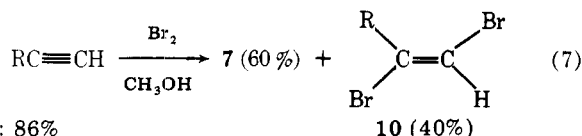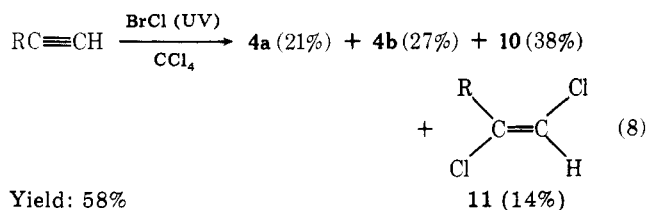
(5)

(6)
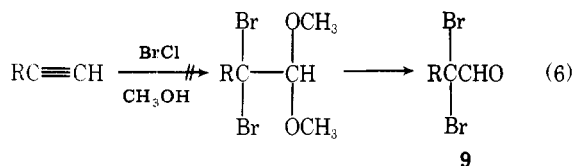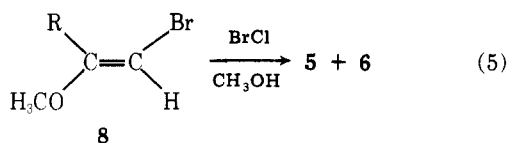
We also examined the bromination of 1-hexyne in methanol (eq 7).

Yield: 86%

Radical addition (ultraviolet irradiation) of BrCl to 1-hexyne in CCl₄ gave a much different product composition than ionic addition (eq 8).

$$RC{\equiv}CH \xrightarrow[\text{CCl}_4]{\text{BrCl (UV)}} \mathbf{4a}\,(21\%) + \mathbf{4b}\,(27\%) + \mathbf{10}\,(38\%)$$

$$+\ \underset{\mathbf{11}\ (14\%)}{\overset{\displaystyle R}{\underset{\displaystyle Cl}{C}}{=}\overset{\displaystyle Cl}{\underset{\displaystyle H}{C}}} \quad (8)$$

Yield: 58%

The structures of bromochlorides **2a,b** from 1-hexene were established by their mass spectra. Both isomers (**2a,b**) have the same isotope cluster at *m/e* 169, 171, and 173, which corresponds to five-membered halonium ions **12a,b** (see Scheme I).[6] Loss of halogen Y and hydrogen halide HY gives isotope clusters which we assigned structures **13a** and **14a** or **13b**, and **14b**. Apparently, mass spectral analysis is a general diagnostic procedure for the structural determination of vicinal dihalides.[7]

The structures of the dihaloalkenes (**4a,b**) from 1-hexyne were determined by carbon-13 magnetic resonance. Chemical shifts of the vinyl carbons are reported in Table I. When bromine is on carbon-2, resonance is ca. 127 ppm, whereas the chemical shift is ca. 137 ppm when chlorine is on the same carbon. Resonances with bromine and chlorine on carbon-1 are about 102 and 114 ppm, respectively.[8] The coupling constant between carbon-1 and the vinyl hydrogen of carbon-1 was determined to be 244 Hz for **4a**.
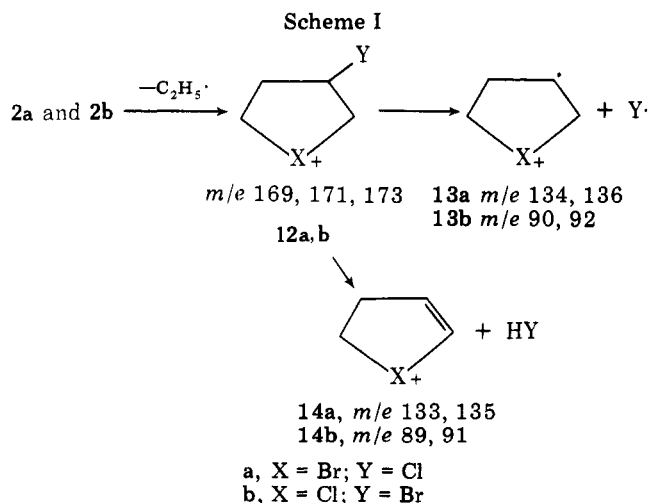
Scheme I

m/e 169, 171, 173
12a, b

13a m/e 134, 136
13b m/e 90, 92

14a, m/e 133, 135
14b, m/e 89, 91

a, X = Br; Y = Cl
b, X = Cl; Y = Br

Table I. ¹³C Chemical Shifts for *trans*-1,2-Dihalohexenes in CDCl₃

| haloalkene	registry no.	X	Y	C_2	C_1
4a	66538-70-3	Br	Cl	137.8	101.6
4b	66538-71-4	Cl	Br	127.2	115.6
10	49677-13-6	Br	Br	127.8	102.7
11	59697-51-7	Cl	Cl	137.5	114.3

Discussion

The results show that anti-Markownikoff attack by chloride ion on bromonium ion **15** from 1-hexene to give **2b** is a significant pathway in CCl₄ and CH₃OH, indicating a symmetrically bridged intermediate in this reaction.[9] Attack by CH₃OH on the terminal carbon of **15** to give **3b** is also im-

15
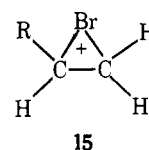
portant. On the other hand, formation of only minor amounts of anti-Markownikoff product **4b** for BrCl and 1-hexyne in CCl₄ implicates an intermediate bromonium ion with very weak bridging (**16**).

16
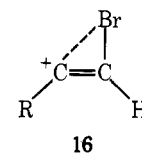
Although no *anti*-Markownikoff addition (**4b** or **9**) occurs in CH₃OH, we believe that a weakly bridged ion (like **16**), rather than an open vinyl cation, also is involved in this solvent, since an open ion should lead to some cis product.[10]
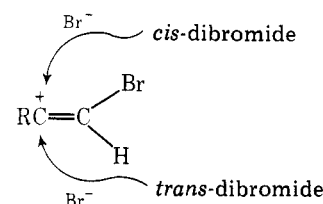
Suppose that a symmetrically bridged bromonium ion (**17**) were involved in the additions to 1-hexyne: How should it be opened? Since the bromonium ion from 1-hexene is opened to a significant extent at carbon-1, we can see no reason why attack should not occur just as readily at carbon-1 in **17**.

17
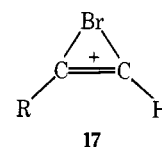
Furthermore, Schmid and co-workers[11] have shown that anti-Markownikoff addition is the main pathway in the reaction of 4-chlorobenzenesulfenyl chloride with 1-hexyne. These authors point out that an alkyl group should cause greater steric hindrance toward Markownikoff ring opening in a particular alkyne than in the corresponding alkene. Therefore, we conclude that the intermediate bromonium ion in the addition of BrCl to 1-hexyne is weakly bridged.

Another interesting aspect of this research concerns the

change in regiospecificity of ring opening of the intermediate bromonium ion (15) from 1-hexene by chloride in CCl_4 and CH_3OH. The results show that the ratio of Markownikoff to anti-Markownikoff attack (2a/2b) by chloride ion on 15 is ~60:40 in CCl_4 and ~50:50 in CH_3OH. Since the bridging in 15 should be weaker in the polar solvent CH_3OH, we anticipated an increase in Markownikoff addition (2a). An explanation of this unexpected result is that the chloride ion in CCl_4 is "naked" and experiences little steric hindrance from the alkyl group during ring opening at carbon-2. In CH_3OH, however, the chloride ion is solvated, $Cl(CH_3OH)_n^-$, and much larger, and prefers to attack the less hindered position (carbon-2) in bromonium ion 15.

The greater ratio (2:1) of Markownikoff to anti-Markownikoff methoxy bromides (3a/3b) compared to the ratio (1:1) of bromo chlorides (2a/2b) for 1-hexene in CH_3OH probably results from the fact that methanol is less nucleophilic and prefers to react at carbon-2 which has greater carbocation character.

Under radical conditions, 4a,b could result from photoaddition of either BrCl or a mixture of Br_2 and Cl_2 to 1-hexyne, since BrCl solution is known to contain a mixture of Br_2 and Cl_2.

Experimental Section

Materials. All solvents were obtained commercially in high purity and were used without further purification. 1-Hexene and 1-hexyne were distilled prior to use.

General Reaction Conditions. All ionic reactions of 1-hexene and 1-hexyne in CCl_4 and CH_3OH with BrCl were carried out in the dark to approximately 20% completion at room temperature; the concentration of the solutions was 0.04 mol fraction in alkene or alkyne.

Reaction of Bromine Chloride with 1-Hexene in Carbon Tetrachloride. To 1.00 g (0.012 mol) of 1-hexene in 27.5 mL of CCl_4 was added 1.9 mL of a 1.26 M bromine chloride–CCl_4 solution. The reaction mixture was stirred in the dark for 5 min and the solvent was then removed at reduced pressure. The yield of 2a,b was obtained by NMR analysis of the crude mixture with benzene as an internal standard. The relative amounts of 2a,b were determined by VPC analysis on a 10% DEGS column (19 ft × 0.25 in.) at 70 °C; retention times (min) are: 2b, 16.3; 2a, 17.2; 1,2-dichlorohexane, 11.2; and 1,2-dibromohexane, 23.4. The accuracy of the VPC analyses probably does not exceed ±(percentage of compound) × 0.025.

Compounds 2a,b were separated by preparative VPC, and the following NMR data (CCl_4) were obtained: 2a δ 0.97 (t, J = 5.0 Hz, 3 H), 1.1–2.5 (m, 6 H), 3.60 (d, J = 4.0 Hz, superimposed on multiplet), 3.2–4.3 (3 H). 2b δ 0.97 (t, J = 5.0 Hz, 3 H), 1.1–2.5 (m, 6 H), 3.83 (d, J = 4.0 Hz, superimposed on multiplet) 3.3–4.3 (3 H).

The structures of 2a,b were deduced from their mass spectra (70 eV). 2a gave an isotope cluster at m/e 169, 171, and 173, which was assigned to the five-membered cyclic halonium ion 12a (Scheme I). Loss of chlorine and hydrogen chloride from 12a gave two sets of isotope clusters at m/e 134 and 136 and m/e 133 and 135 for 13a and 14a, respectively. Mass spectral analysis of 2b gave isotope clusters at m/e 169, 171, and 173 for the cyclic halonium ion 12b. Loss of bromine and hydrogen bromine from 12b gave two sets of isotope clusters at m/e 90 and 92 and m/e 89 and 91, for 13b and 14b, respectively.

Reaction of Bromine Chloride with 1-Hexyne in Carbon Tetrachloride. Ionic Conditions. To 1.00 g (0.012 mol) of 1-hexyne in 28.3 mL of carbon tetrachloride was added 1.9 mL of a 1.26 M bromine chloride–CCl_4 solution. The reaction mixture was stirred in the dark for ca. 12 h, and the solvent was removed at reduced pressure. Crude reaction mixtures of 4a,b were analyzed by NMR using benzene as an internal standard. All attempts to separate 4a,b by VPC failed.

A mixture of 4a,b was isolated by preparative VPC: 2.5% SE-30 column (8 ft × 0.15 in.) at 60 °C; retention times (min): 4a,b, 4.8; 10, 8.1; and 11, 2.8. NMR spectra were made of the collected material: ^1H NMR (CCl_4) δ 0.97 (t, J = 6.2 Hz, 3 H), 1.1–1.9 (m, 4 H), 2.53 and 2.60 (2t, J = 6.0 Hz, 2 H), 6.16 and 6.23 (for 4a and 4b, respectively, s, 1 H). ^{13}C NMR ($CHCl_3$) 4a δ 101.6 and 137.8 for the vinyl carbons C_1 and C_2, respectively; 4b δ 115.6 and 127.2 for the vinyl carbons C_1 and C_2, respectively.

NMR data for *trans*-1,2-dibromo-1-hexene (10):[1] ^1H NMR (CCl_4) δ 0.98 (t, J = 6.8 Hz, 3 H), 1.1–1.9 (m, 4 H), 2.63 (t, J = 6.8 Hz, 2 H),

6.38 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 102.7 and 127.8 for the vinyl carbons C_1 and C_2, respectively.

NMR data for *trans*-1,2-dichloro-1-hexene (11): ^1H NMR (CCl_4) δ 1.00 (t, J = 6.5 Hz, 3 H), 1.50 (m, 4 H), 2.5 (t, J = 6.8 Hz, 2 H), 6.10 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 114.3 and 137.5 for the vinyl carbons C_1 and C_2, respectively.

Reaction of Bromine Chloride with 1-Hexene in Methanol. To 1.00 g (0.012 mol) of 1-hexene in 11.5 mL of CH_3OH was added 2 mL of a 1.26 M bromine chloride–CCl_4 solution. The reaction mixture was stirred for 5 min and added to water. The organic products were extracted into CCl_4.

The bromo chlorides and methoxy bromides[12] were analyzed by VPC using chlorobenzene as an internal standard: 2–5% FFAP column (14 ft × 0.125 in.) at 70 °C; retention times (min) are: 2b, 17.9; 2a, 19.3; 3b, 14.0; and 3a, 16.3.

Reaction of Bromine Chloride with 1-Hexyne in Methanol. To 1.0 g (0.012 mol) of 1-hexyne in 12.1 mL of CH_3OH was added 1.7 mL of a 1.45 M bromine chloride–CCl_4 solution. The reaction mixture was stirred for a short time and then was added to water containing a few drops of concentrated HBr to assure hydrolysis of the ketal. The organic products were extracted into CCl_4. After removal of the solvent, the crude mixture was analyzed by NMR using benzene as an internal standard.

1,1-Dibromo-2-hexanone (7) was isolated from the reaction mixture by preparative VPC: 2.5% SE-30 column (11 ft × 0.125 in.) at 100 °C; retention times (min): 7, 12.8; 4a,b, 4.9; and 10, 7.6. The ketone was identified by its IR spectrum (CCl_4, C=O, 1725 cm^{-1}) and NMR spectrum (CCl_4): δ 0.97 (t, J = 6.2 Hz, 3 H), 1.2–1.8 (m, 4 H), 2.93 (t, J = 6.6 Hz, 2 H), 5.67 (s, 1 H).

Attempts were made to detect the aldehyde proton of 2,2-dibromohexanal (9) by NMR, but without success. A trace (ca. 2%) would have been detected had it been present. The oxidation product of the aldehyde, the carboxylic acid, was not observed by NMR.

Reaction of Bromine with 1-Hexyne in Methanol. To 1.0 g (0.012 mol) of 1-hexyne in 12.1 mL of CH_3OH was added 0.39 g of Br_2 dissolved in 2.73 mL of CCl_4. The reaction mixture, composed of dibromo ketone (7) and *trans*-dibromide (10), was isolated and analyzed by NMR as reported for the product from BrCl addition. Both 10 and 7 were isolated by preparative VPC (the SE-30 column). NMR and IR analyses established that the dibromo ketones from Br_2 and BrCl additions were identical. The NMR spectra of the dibromide and authentic 10 from bromination of 1-hexyne were identical.

Stability of Bromo Chlorides 4a,b in Methanol, Water, and Acid. A known amount of bromo chlorides 4a,b with an internal standard was stirred in CH_3OH for a short time and then added to water and several drops of concentrated HBr to simulate reaction conditions. NMR and VPC analyses established that no dibromo ketone 7 was formed, nor did the amount of 4a,b decrease.

Radical Reaction of Bromine Chloride with 1-Hexyne. To 1.0 g (0.012 mol) of 1-hexyne in 28.8 mL of CCl_4 was added 1.9 mL of a 1.28 M bromine chloride–CCl_4 solution. The solution was irradiated with a sunlamp, and the reaction was completed in approximately 2 min. The solvent was removed under pressure, and the mixture was analyzed by NMR using benzene as an internal standard.

Proof that Bromine Chloride Adds to 1-Hexyne by an Ionic Mechanism in the Dark. The reaction of BrCl with 1-hexyne in the dark was carried out using isoamyl nitrite as a radical inhibitor. Lower concentrations of isoamyl nitrite (4 equiv with respect to Br_2) appeared to induce a radical reaction, since the ratio of 4a/4b increased from 90:10 (no inhibitor) to 70:30. Larger amounts of inhibitor (up to 8 equiv) reduced the ratio of 4a/4b to a constant level of 90:10.

Registry No.—2a, 66538-72-5; 2b, 66538-73-6; 3a, 24618-32-4; 3b, 24618-33-5; 7, 54899-26-2; 12a, 66538-74-7; 12b, 66538-75-8; 13a, 66538-76-9; 13b, 66538-77-0; 14a, 66538-78-1; 14b, 66538-79-2; 1-hexene, 592-41-6; bromine chloride, 13863-41-7; 1-hexyne, 693-02-7.

References and Notes

(1) J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 3332 (1970).
(2) Although Pincock and Yates state in the Results and Discussion section of their paper (ref 1) that only *trans*-dibromide is formed, the Experimental Section indicates that a mixture of *trans*- and *cis*-1,2-dibromide (72:28%) is formed when bromine in acetic acid is added to 1-hexyne in acetic acid. Therefore, we reinvestigated the bromination of 1-hexyne in acetic acid and found that *cis* dibromide is formed in concentrated solutions (13:87% cis to trans at a mole fraction of 0.8 in 1-hexyne), but that only *trans*-dibromide is formed in dilute solutions. We interpret these data as suggesting that *cis*-dibromide is a product of a molecule-induced radical reaction at higher concentrations, whereas ionic addition occurs in dilute solution.
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(6) The formation and stability of five-membered cyclic halonium ions in the

mass spectrometer is well established. See H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds", Holden-Day, San Francisco, Calif., 1964, chapter 7.
(7) We found analogous isotope cluster patterns for the 1,2-dichloro- and 1,2-dibromohexanes.
(8) The ^{13}C chemical shifts for *trans*-dibromoethylene and *trans*-dichloroethylene are 109 and 119.4 ppm, respectively. See G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, p 64.
(9) P. B. D. De La Mare and S. Galandauer, *J. Chem. Soc.*, 36 (1958), obtained a Markownikoff to anti-Markownikoff ratio of 54:46 in the addition of BrCl to 1-propene in the polar solvent water.
(10) Two alkynes which apparently involve open vinyl cations give both *trans*- and *cis*-dibromides: phenylacetylene[1] and cyclopropylacetylene (D. F. Shellhamer and M. L. Oakes, *J. Org. Chem.*, in press).
(11) G. J. Schmid, A. Modro, F. Lenz, D. G. Garratt, and K. Yates, *J. Org. Chem.*, **41**, 2331 (1976).
(12) A mixture of the methoxy bromides (**3a,b**) was prepared unambiguously by addition of *N*-bromosuccinimide to 1-hexene in methanol. The structures of **3a,b** have been established previously.[4,5]

Heterogeneous Catalysis by Solid Superacids. 4.[1] Methylation of Phenols with Methyl Alcohol and the Rearrangement of Anisole and Methylanisoles over a Perfluorinated Resinsulfonic Acid (Nafion-H) Catalyst

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Anisole and methylanisoles are rearranged when passed in the gas phase over highly acidic solid perfluorinated resinsulfonic acid (Nafion-H) catalyst at 205 °C and atmospheric pressure. A mixture of anisole, mono- and dimethylanisoles, phenol, cresols, and xylenols was obtained. Methyl alcohol and phenol (for cresols) reacted under the same conditions to give a mixture of O- and C-methylated products. The latter reaction was shown to proceed via fast initial O-methylation of the phenol followed by an intermolecular rearrangement of the aryl methyl ether to methylphenols. Rearrangement of anisole and methylation of phenol gave *o*- and *p*-cresol. Methylanisoles or a mixture of cresol and methyl alcohol yielded mixtures of mono- and dimethylated ring products. When the directing effects of the methyl, methoxyl, or hydroxyl groups oppose each other, as is the case with *o*- and *p*-methylanisoles or cresols, 6–14% of products methylated meta to the methoxyl or hydroxyl group was obtained. Isomerization and ring transmethylation were negligible under the experimental conditions. Nafion-H was also compared to other solid catalysts. Its lack of selectivity toward ortho methylation is attributed to the absence of basic sites on the catalyst.

Alkylation of phenols by alcohols is well known.[3] Gasphase methylation of phenol by methyl alcohol was reported by Ipatieff as early as 1925.[4] Liquid phase, acid catalyzed methylation gave ortho and para substitution with low selectivity. Meta alkylation was reported in some cases,[5] but forcing conditions were required and the meta isomer was obtained via secondary isomerization. Lately, solid catalysts of the mixed oxides type containing basic sites, or acidic and basic sites, were found to catalyze efficiently the methylation of phenols with methyl alcohol with high selectivity for ortho methylation.

Recently we reported the use of highly acidic perfluorinated resin sulfonic acid catalysts, such as Nafion-H,[6] for the alkylation of benzene and alkylbenzenes.[7] In continuation of our studies we felt it of particular interest to study the methylation of phenols with methyl alcohol using mild reaction conditions (ca. 200 °C and atmospheric pressure) and to compare the activity of Nafion-H with other solid catalysts. The behavior of anisoles and methylanisoles was also studied under the same conditions.

Experimental Section

Materials. Methyl alcohol, phenols, and anisoles used were of highest commercially available purity, higher than 99%. Dimethylanisoles and xylenols used for comparison in identifying products in

the GLC analyses were also commercially available. The activation of the Nafion-H catalyst was as mentioned.[7]

Experimental Procedure. The catalytic flow reactor and the general procedures used were described previously.[8] All the reactions were carried out at 205 °C in a N_2 flow of 5 mL/min, using 2 g of the catalyst. Phenols, anisoles, or their mixtures with methyl alcohol (1:1 molar ratio) were introduced at a liquid rate of 0.02 mL/min. The contact time of the reagents over the catalyst under these conditions is 6–7 s.

Analysis. Product compositions were determined by gas liquid chromatography using a Perkin-Elmer Model 226 gas chromatograph equipped with a flame ionization detector. A capillary column of 150 ft × 0.01 in. coated with *m*-bis(*m*-phenoxyphenoxy)benzene + Apiezon L was used to separate the products. Anisoles were separated as such. Phenols were first silylated by hexamethyldisilazane or trimethylchlorosilane and identified as the trimethylsilyl ethers. Some of the dimethylanisole peaks overlapped with those of aryl trimethylsilyl ethers. Therefore, each fraction was analyzed twice. One portion was dissolved in ether and extracted with aqueous NaOH and the ethereal solution was analyzed for anisoles. Another portion was silylated and analyzed for phenols and anisoles. In cases where peak overlap occurred, corrections were made on the basis of the known composition of the anisoles. *m*- and *p*-methylanisole were not separated under these conditions. They were, however, separated by using a 20 ft × 0.125 in. column packed with 15% *p*-azoxyanisole on Chromosorb W at 125 °C (a liquid crystal column[9]), using a Perkin-Elmer Model 900 gas chromatograph. Peak areas were measured by an electronic integrator, using corrections for differences in detector sensitivities. The accuracy of the determination of the product com-