Isobutane: column A; 80° (12 psi); *tert*-butyl chloride (331), isobutyl chloride (371), 1-chlorobutane (395, standard).

Neopentane: column A; 80° (20 psi); neopentyl chloride (265), 1,1-dichloro-2,2-dimethylpropane (650), norbornane (380, standard).

Cyclohexane: (B) stainless steel open tubular column, 150 ft × .01 in.; stationary phase, *m*-bis(*m*-phenoxyphenoxy)benzene + Apiezon L; column temperature 80°; helium pressure 30 psi; cyclohexyl chloride (357), cyclohexyl bromide (610, standard).

Norbornane: (C) stainless steel open tubular column, 150 ft × 0.01 in.; stationary phase, Carbowax 1540; column temperature 60°; helium pressure 30 psi; 7-chloronorbornane (552), *exo*-2-chloronorbornane (571), *endo*-2-chloronorbornane (593), norbornane (167, used as standard).

Adamantane: (D) stainless steel open tubular column, 150 ft × .01 in.; stationary phase, butanediolsuccinate; column temperature 80°; helium pressure 20 psi; 1-chloroadamantane (175), 2-chloroadamantane (190), adamantane (30, used as standard).

General Procedure for Chlorination of Alkylaromatics without Solvent. The individual arylaromatics (100 mmol) and (10 PCl_5 (10 mmol) were placed into the reaction flask. A slow stream of finely dispersed chlorine gas (dried by H_2SO_4) was passed through the reaction mixture for 30 min in the dark (by external cooling the temperature was kept at 25°). Excess chlorine was removed by passing nitrogen through the reaction mixture, which was then several times washed with water and dried, and the reaction products were analyzed by glc or nmr spectroscopy.

In Nitromethane as Solvent. The same amount of aromatics and PCl_5 was dissolved in a 20-fold excess of nitromethane and for 30 min a slow stream of finely dispersed chlorine gas was passed through the cooled (25°) solution in the dark. The washed and dried nitromethane solutions were analyzed by glc (after addition of a known amount of internal standard).

Gas-Liquid Chromatographic Analysis. Side-Chain Chlorinated Aromatics: (G) stainless steel packed column, 12 ft × 1/8 in.; stationary phase, 5% Benton and 5% silicon oil DC 200 on acid washed Chromosorb W, 60–80 mesh; column temperature 130°; helium pressure 25 psi; benzyl chloride (348), α-chloroethylbenzene (396), β-chloroethylbenzene (510), α-chlorocumene (decomposition product α-methylstyrene 300), β-chlorocumene (552). Column E; 100° (30 psi); α-chlorocumene (decomposition product, α-methylstyrene 505), β-chlorocumene (1163).

Ring-Chlorinated Aromatics: (E) stainless steel open tubular column, 150 ft × .01 in.; stationary phase, *m*-bis(*m*-phenoxyphenoxy)benzene + Apiezon L; column temperature 100°; helium pressure 30 psi; chlorotoluenes,[28] o (321), m (331), p (331); chloroethylbenzenes, o (430), m (479), p (479); chlorocumenes, o (591), m (681), p (733); chloro-*tert*-butyl-benzenes, o (830), m (883), p (923); chloro-o-xylenes (80° (30 psi)), 3 (1188), 4 (1230); chloro-*m*-xylenes (80° (30 psi)), 2 (921), 4 (961); 2-chloro-*p*-xylene (100° (30 psi), 535); 2-chloromesitylene (100° (30 psi), 1302).

Determination of Relative Substrate Selectivity. In a typical experiment 8.4 g (0.1 mol) of cyclohexane, 9.2 g (0.1 mol) of toluene, 4.06 g (0.02 mol) of PCl_5, and 1.4 g (20 mmol) of chlorine were reacted in the dark for 10 hr at 25°. Glc analysis of the reaction products on column G: 100° (40 psi); benzyl chloride (345), cyclohexyl chloride (900). Ethylbenzene–toluene (1:1) and cumene–toluene (1:1) were reacted in the same way. The reaction products were analyzed by glc on column G (130° (25 psi)).

Determination of Substrate and Positional Selectivity of Ring Chlorination in Nitromethane. Mixtures (1:1) of benzene and alkylbenzenes were dissolved in a 20-fold amount of nitromethane, 20 mol % of PCl_5 (based on the amount of the aromatics) was added and then chlorine gas (10 mol %) was introduced into the well stirred solution at 25°. The work-up and glc analysis was performed as described (column E).

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Registry No.—PCl_5, 10026-13-8; PCl_3, 7719-12-2.

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Radical Reactions. II.[1] Lewis Base Catalyzed Anti-Markovnikov Addition of Hydrogen Bromide to Alkenes

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Lewis base catalysts such as PBr_3 and $POCl_3$ promote anti-Markovnikov addition of hydrogen bromide to alkenes. Inhibitor effects, as well as observed isomerization of *cis*-stilbene, further illustrate the homolytic nature of the reactions. An initiation mechanism is proposed involving initial interaction of hydrogen bromide with the Lewis base type catalysts leading subsequently to homolytic cleavage of the weakened hydrogen–bromine bond.

The mechanism of the free-radical addition of hydrogen bromide to alkenes was first clarified by Kharasch and Mayo.[2] Following the development of the chain reaction concept in additions of hydrogen bromide,[3,4] numerous investigations have shown that the type of reaction (ionic or radical) taking place depends largely on the experimental conditions. In general, heterolytic reactions are favored in polar solvents in the presence of radical inhibitors, while homolytic processes are promoted in nonpolar solvents by the presence of air, light, peroxides, or other initiators.

The strict requirements needed in performing reactions under the specified conditions were not realized by earlier workers, so that frequently products of both reaction types were observed. The review of Mayo and Walling[5] illustrates the dramatic effect of experimental conditions on the orientation of the addition and thereby on the mechanism of the reaction.

The generally accepted role of Lewis acid catalysts in addition reactions in the past has been as promoters of electrophilic reactions[6] presumably *via* polarization of the adding reagent as to provide a more electrophilic species. Though this type of catalysis is of primary importance for reactions of aromatic systems, its application to nonconjugated unsaturated systems has been limited, due to extensive secondary reactions caused by such catalysts in aliphatic systems.

Olah, Schilling, Renner, and Kerekes have reported that phosphorus chlorides are effective catalysts for the free-radical side-chain chlorination of alkylbenzenes and chlorination of alkanes.[1] They suggested that the formation of the involved free radicals ($PCl_4\cdot$ and $Cl\cdot$) was a consequence of coordination of the weak Lewis acid phosphorus chlorides (PCl_5 or PCl_3) with chlorine, followed by homolysis of the weakened Cl–Cl bond. These results encouraged us to study the effect of related coordination catalysts on addition reactions to alkenes.

We have investigated and report now our results on catalytic effects in the addition reaction of hydrogen bromide to alkenes. We chose to study this system as the dual ionic and radical pathways are well understood in reactions of hydrogen bromide.[7] Of some relevance is also a recent patent in which it was reported that phosgene promotes anti-Markovnikov addition of hydrogen bromide to alkenes, although because of lack of purification of alkenes used it is difficult to exclude peroxide-initiated addition reactions.[8] It should be pointed out that whereas molecule-induced homolyses due to solvent association or coordination effects are well recognized in free-radical reactions,[9] catalytic homolysis by Lewis acids and bases seems to be a novel approach.

Results and Discussion

The addition of hydrogen bromide to a number of representative alkenes was investigated generally in 1,1,2-trichlorotrifluoroethane solution at 25°.[10] The effect of added catalyst on the formation of anti-Markovnikov addition products is summarized in Table I. In control experiments, in the same solvent, carefully purified alkenes gave no detectible anti-Markovnikov addition. All experiments were performed under identical, carefully controlled, conditions. The appropriate alkene (purified, as described in the experimental part, to eliminate peroxide impurities), solvent, and catalyst were placed in a predried Teflon reaction vessel under anhydrous conditions. Hydrogen bromide in the same solvent was slowly added with magnetic stirring in the dark. After quenching, the product composition was determined by gas chromatography and nmr spectroscopy. The data summarized in Table I clearly illustrate that the catalysts employed, particularly phosphorus tribromide, promote anti-Markovnikov addition of hydrogen bromide.

Phosgene as catalyst for the addition to styrene also gave some anti-Markovnikov product. However, the results obtained were erratic, most likely due to loss of the volatile catalyst from the system.

Table I
Product Compositions in the Lewis Base Catalyzed[a] Addition of Hydrogen Bromide to Alkenes in 1,1,2-Trichlorotrifluoroethane at 25°

		Per cent anti-Markovnikov addition of total addition product		
Alkene	Registry no.	PCl_5[b]	$POCl_3$[b]	PBr_3
1-Methylcyclohexene	591-49-1	10.0[c]	2.0[c]	18.0 (23.0[d])
1-Methylcyclopentene	693-89-0			5.0
Octene	111-66-0			13.0
Hexene	592-41-6	25.0	2.0	26.5
Styrene	100-42-5	9.0	6.1	20.0
2-Methyl-2-butene	513-35-9	1.0	10.0	40.0 (54.0[e]) (62.5[e,f])

[a] Catalyst concentration was 10% by weight, relative to alkene unless otherwise noted. [b] Exclusive of chlorinated by-products formed. [c] Solvent, pentane. [d] Catalyst was 15 wt %. [e] Reaction performed in a glass flask. [f] Catalyst was 20 wt %.

The alkenes employed in this study have generally been subjected to free-radical additions previously, so that ready comparison of the data is possible. The reaction of 1-methylcyclohexene with hydrogen bromide was reported to produce 33% anti-Markovnikov product when initiated with benzoyl peroxide at 35°.[11] An attempt to reproduce these results in our study, however, gave only 27% anti-Markovnikov product, possibly because the previous work was performed in glass equipment rather than Teflon employed in our work. The last two entries of Table I illustrate the effect of glass instead of Teflon on the product composition of the addition reaction.

Hydrogen bromide addition to both styrene and 2-methyl-2-butene has been investigated previously under free-radical conditions[12] and was found to give varying amounts of anti-Markovnikov product. Ionic addition was found to be competitive under most conditions studied so that the Markovnikov product was at least 20 or 40% for styrene and 2-methyl-2-butene, respectively. Data of Table I show that the most effective phosphorus tribromide–hydrogen bromide system is still apparently not as effective as peroxide or ultraviolet light initiated reactions. However, the effect of catalyst concentration and of glass instead of Teflon reaction vessels must be taken into consideration when attempting comparisons.

The purity of the systems studied is essential to establish the real catalytic nature of the anti-Markovnikov addition reactions. If the alkenes employed were not carefully purified, particularly of small peroxide impurities, varying amounts (~10%) of anti-Markovnikov addition products were obtained even in the absence of added catalyst. The case of 1-octene further amplifies this point. 1-Octene (Phillips Petroleum Corp >99 mol % purity), which was not purified, gave a positive peroxide test and its addition reaction with hydrogen bromide gave 73% anti-Markovnikov addition without added catalyst. Upon adding 10 wt % phosphorus tribromide as catalyst, the yield increased to 94%! For other alkenes, the combination of PBr_3 with impure alkene did not uniformly lead to high anti-Markovnikov addition products due presumably to the variability of peroxide content and possible catalyst–peroxide reaction. The combination of peroxide and catalyst effect is being further studied in our continuing work.

The lower yields of anti-Markovnikov HBr addition products observed in the case of phosphorus chloride catalysts than with the phosphorus tribromide are at least in part due to chlorinated side-product formation.

One of the simplest methods for determining the free-radical nature of a reaction is through the effect of inhibitors such as oxygen or hydroquinone. Both showed marked effects inhibiting the catalytic anti-Markovnikov addition reaction. However, only in the case of 1-hexene (in the HBr–PBr_3 system) was oxygen completely effective in eliminating the radical pathway. When the solution of 2-methyl-2-butene prior to addition of hydrogen bromide was saturated with oxygen or if hydroquinone (5 wt %) was added, some of the anti-Markovnikov product (2-bromo-3-methylbutane) was still formed, though in an amount decreased by 50–60% compared with runs in which no inhibitor was employed. Since the effect of oxygen is dependent on the effectiveness of initiators present in the system,[13] and hydroquinone is scarcely soluble in the solvents used, the fact that smaller amounts of anti-Markovnikov, *i.e.*, radical derived, product was still observed is not unreasonable. The use of other inhibitors such as phenols, thiols, sulfides, etc., was precluded by the reactivity of phosphorus tribromide with these and related compounds.[14]

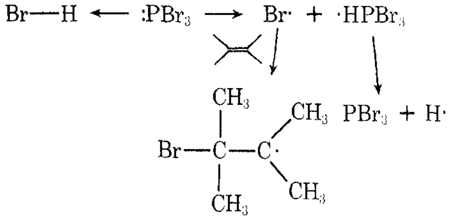
A decrease in the reaction temperature to 0° for the PBr_3-catalyzed reaction of the corresponding alkenes resulted in the formation of only 19% 2-bromo-3-methylbutane and 5% 1-bromohexane. This decrease in anti-Markovnikov oriented addition product is qualitatively in accord with typical radical behavior.[15,16]

Further evidence for the radical nature of the studied system was obtained from the behavior of *cis*-stilbene. It is known that *cis*-stilbene could be isomerized by light,[17] mineral acids[18,19] (though not by Lewis acids),[20] and certain radical sources.[21] This last study demonstrated that hydrogen bromide alone was insufficient to cause isomerization, which occurred only upon the addition of effective radical initiators, such as peroxides. These results were confirmed in the present investigation in which a solution of *cis*-stilbene in 1,1,2-trichlorotrifluoroethane showed with hydrogen bromide no isomerization even after a period of 20 hr, while the hydrogen bromide–phosphorus tribromide mixture isomerized 72% of the *cis*-stilbene (as determined by nmr).

Attempting to determine the optimum conditions for formation of anti-Markovnikov products we also studied the effect of catalyst concentration on the product compositions. In the case of both 2-methyl-2-butene and styrene it was found that increasing the amount of catalyst (all other variable being kept constant) initially increased the amount of radical addition products. However, further increase of phosphorus tribromide decreased both the total amount of bromoalkane as well as the percentage of anti-Markovnikov product in the bromoalkane mixture, with simultaneous formation of the corresponging dibromoalkanes (1,2-dibromo-1-phenylethane and 2,3-dibromo-2-methylbutane, respectively). Their formation by an ionic route is not likely since no bromoalkenes, the ionic precursors, were found and addition to such bromoalkenes would be very slow. Thus a radical route is indicated for their formation utilizing PBr_3, in line with the conclusion that dibromoalkane formation is the cause of decreased anti-Markovnikov addition.

As in the absence of catalysts no anti-Markovnikov product was observed in the HBr addition reaction to alkenes, the combination of hydrogen bromide with such catalysts is evidently essential to the course of the reaction.

Phosphorus trihalides are amphoteric in nature, having both Lewis acid and Lewis base character. Accordingly, phosphorus tribromide can form, as a Lewis acid, complexes with amines,[22] but also can form complexes as a Lewis base (through its nonbonded electron pair on phosphorus) with acids.[23] Consequently a possible path for the initiation of the catalytic anti-Markovnikov HBr addition is the following.



The interaction of hydrogen bromide with the nonbonded electron pair of phosphorus weakens the hydrogen–bromide bond. This is equivalent to a decrease in the dipolar character of the molecular bond with a consequently decreased tendency to undergo ionic cleavage. Homolytic cleavage is thus facilitated. Addition of the formed bromine atom to alkene gives the corresponding bromoalkyl radical. This radical then would react further *via* the well known radical chain pathway[24] leading to the anti-Markovnikov product. PBr_3 would be regenerated allowing further complexation–initiation reactions to occur.[25]

The suggested mechanism also can explain the effect of other Lewis base type catalysts ($POCl_3$, $COCl_2$, PCl_3) in that these also contain nonbonded, lone-pair electrons capable of interacting with hydrogen bromide, as depicted above for phosphorus tribromide.

Experimental Section

Materials. 1,1,2-Trichlorotrifluoroethane used as solvent was Union Carbide Ucon Solvent 113-LR1 (with less than 1 ppm residue) which was dried over $MgSO_4$ then P_2O_5 and distilled in a stream of dry nitrogen from Linde 4A molecular sieves in an all glass apparatus protected from moisture. The solvent was distilled directly into storage bottles containing additional molecular sieves. The other solvents employed were spectroqualtiy grade and dried with molecular sieves except for chloroform which was first washed to remove ethanol, dried, then distilled immediately before use.

The catalysts employed were reagent grade and used as received except for phosphorus tribromide which was distilled in an all glass apparatus before use.

All alkenes studied were commercially available materials (Aldrich, Phillips, Chemical Samples Co.) of highest available purity (99% min) and were further purified by drying with $MgSO_4$ followed by distillation from lithium aluminum hydride and storage in the cold. Styrene was purified by first washing with 5% NaOH,[26] drying with $MgSO_4$, and distilling from LAH, and it was stored at −90°.

Alkyl bromides, chlorides, and dibromides used for comparison were commercially available and purified by conventional techniques (distillation, recrystallization).

The general procedure of Lane and Brown[27] was used to prepare 2-bromo-3-methylbutane and 1-bromo-2-methylcyclopentane from the related alkenes. Due to their tendency to decompose, storage as dilute solutions in 1,1,2-trichlorotrifluoroethane at 0° was found to be essential. 2-Bromohexane and 1-bromo-1-methylcyclohexane were prepared by the reaction of the corresponding alcohol with phosphorus tribromide at 0°.[28] This latter compound was also obtained from the reaction of methylcyclohexane with *N*-bromosuccinimide in the presence of benzoyl peroxide and as a mixture with 1-bromo-2-methylcyclohexane from the benzoyl peroxide promoted addition of hydrogen bromide to 1-methylcyclohexene.[11] This mixture served to characterize the products obtained in the present investigation and was also stored dilute at 0°. 1-Bromo- and 1-chloroethylbenzene were prepared in good yield by the method of Olah, Kuhn, and Barnes.[29] 1-Bromo-1-penylethene was obtained from laboratory stock and distilled before analysis. 2,3-Dibromo-2-methylbutane, 2,3-dichloro-2-methylbutane, and 2-bromo-3-chloro-3-methylbutane were each prepared by the method of Baird.[30]

Gas chromatographic analysis was performed on a Perkin-Elmer Model F-11 gas chromatograph equipped with a flame ionization detector, temperature programmer, and flow controller. Peak areas were measured with a Disc integrator. The columns employed were all stainless steel since serious decomposition was noted otherwise. The columns were either 0.125 ft × 6 or 12 ft 15% SF-96 on 60–80 Chromosorb P, 0.125 in. × 6 ft 15% DEGS on 60–80 Chromosorb W, or (for analysis of products from 2-methyl-2-butene) a 150 ft × 0.01 in. Golay column coated with Ucon LB-550-X. Proton magnetic magnetic resonance spectra were obtained on a Varian Associates Model A56/60 spectrometer.

Experimental Procedures. Unless stated in the text, all experimental runs were preformed in an inert Teflon vessel bored out of a Teflon rod. This vessel was thoroughly washed prior to each use, dried in an oven, then cooled in either a stream of dry nitrogen or a desiccator. The appropriate amounts of reagents were added by the indicated methods and the reaction was performed under an aluminum foil cover in a darkened hood. Hydrogen bromide solutions were prepared by dissolving the gas in the appropriate solvent, contained in a previously baked-out bottle, avoiding contact with the atmosphere *via* a suitable venting arrangement. The solution thus obtained was found to be sensitive to trace inpurities, as indicated by slight discoloration, so that any such solution was discarded. The concentration of acid in the solution was determined by titration in a mixed solvent system to a phenolphthalein end point. More accurate determination, when required, was obtained by mixing an aliquot amount of acid solution with an excess of triphenylphosphine in the same solvent, cooling to precipitate the stable triphenylphosphonium bromide salt,[31] filtering, and weighing the dried salt.

The general procedure for HBr addition to alkenes summarized in Table I was to add a solution of hydrogen bromide (15 ml of *ca.* 0.075 *M*) to a solution of 2.0 ml of alkene in 1,1,2-trichlorotrifluoroethane containing the catalyst. The mixture was then stirred 2–6 hr depending on the alkene reactivity. All runs were carried out to less than 10% total conversion to ensure pseudo-first-order behavior in alkene. In addition, an appropriate internal standard was added to determine a material balance. Quantitative conversions (HBr limiting) were generally obtained if allowances for side reactions (as mentioned previously) were made.

Appropriate control experiments in the absence of catalysts were performed under identical conditions free from moisture, light, or surface catalysis. No radical-derived product was observed.

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Registry No.—*cis*-Stilbene, 645-49-8; PCl_5, 10026-13-8; $POCl_3$, 10025-87-3; PBr_3, 7789-60-8.

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Kinetics of Bromination of Some Substituted Pyridinium Ions by Hypobromous Acid in Aqueous Perchloric Acid

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The rates of bromination in the 3 and 5 positions of 2-methyl-, 4-methyl-, and 2,4-dimethylpyridine with hypobromous acid have been measured in aqueous perchloric acid at 25.0 ± 0.1°. Reaction occurs through the corresponding pyridinium cations. The rates of bromination of 1,2-dimethyl-, 1,4-dimethyl-, 1,2,6-trimethyl-, 1,2,4-trimethyl-, 1,2,4,6-tetramethyl-, 1-methyl-2-methoxy-, and 1-methyl-2,6-dimethoxypyridinium perchlorates have also been studied. Bromination of the unsubstituted pyridinium cation was not observed; however, the partial rate factor for the bromination of this cation at the 3 position is estimated to be approximately 6×10^{-13}.

The strong deactivation of the pyridinium cation to electrophilic substitution has prevented a detailed kinetic study of these reactions. High temperatures and long reaction times are characteristic of electrophilic halogenation, nitration, and tritiation of the pyridinium cations.[2,3] den Hertog, van der Does, and Landheer[4] have brominated pyridine at 130° with bromine in fuming sulfuric acid, obtaining a good yield of 3-bromopyridine. 2-Methyl-, 3-methyl-, and 4-methylpyridine have also been brominated in fuming sulfuric acid at 80° and 2,6-dimethylpyridine at