Substituent and Secondary α-Deuterium Isotope Effects on Rates of Elimination of HBr from 1-Aryl-1-bromopropanes with Tetra-*n*-butylammonium Bromide in Acetone

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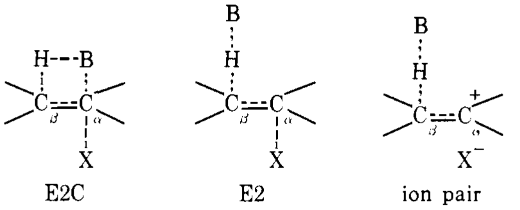
Abstract: Rate constants for tetra-*n*-butylammonium bromide catalyzed elimination of HBr from seven 1-aryl-1-bromopropanes have been determined in acetone at 74.63°. A Hammett plot of the rate data *vs.* σ^+ is curved. Electron-providing substituents cause slightly faster reaction, but the rate difference between p-CH_3 and m-NO_2 compounds is only a factor of 4. Rate constants of the competing uncatalyzed E1 eliminations were determined with four 1-aryl-1-bromopropanes. A Hammett plot of the uncatalyzed rates *vs.* σ^+ gives $\rho = -4.76$. The E1 reaction of 1-bromo-1-(4-methoxyphenyl)propane is so fast that 0.094 M Bu_4NBr fails to promote the elimination rate. Secondary α-deuterium isotope effects on the Bu_4NBr-catalyzed reactions of 1-bromo-1-phenylpropane and 1-bromo-1-(4-tolyl)propane are $k_H/k_D = 1.128$ and 1.146, respectively. The substituent effects rule out a carbonium ion intermediate for the Bu_4NBr-catalyzed eliminations. The isotope effects point to nearly sp^2-hybridized carbon and rule out extensive bonding between base and C_α in the elimination transition state. A concerted E2 mechanism in which the double bond is substantially formed in the transition state is most compatible with the results.

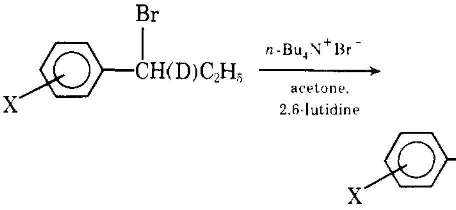
In a recent review,[1] three possible mechanisms were considered for eliminations catalyzed by weak bases such as halide and thioalkoxide ions: (1) E2C, in which the base interacts with C_α in the elimination transition state; (2) E2, in which there is no base-C_α interaction; (3) a tight ion-pair intermediate with rate-limiting attack of base on the ion pair (see Scheme I). Much experimental evidence is compatible with each mechanism. Most contributors to the elimination-mechanism field agree there is a wide spectrum of E2 mechanisms for strong base-catalyzed eliminations ranging from E1cb like to E1 like.[2-6] To this spectrum, Parker[7] adds another ranging from E2C to E2H (identical with the E2 in Scheme I) in which base strength and substrate structure are responsible for a reaction's position in the spectrum. Others[4,8] contend that the E2C mechanism is unnecessary, and that weak base-catalyzed eliminations fit nicely into the conventional E1cb-like to E1-like spectrum. The tight ion-pair mechanism places them at the E1-like end of the transition-state spectrum.

Scheme I. Hypothetical Transition States of Three Weak Base-Catalyzed Elimination Mechanisms



We[1] and others[9,10] have suggested that ion-pair-elimination mechanisms deserve more careful consideration. This paper reports tests of the ion-pair mechanism by substituent effects and secondary α-deuterium isotope effects. The substrates and solvent-base system chosen for the investigation, 1-aryl-1-bromopropanes and tetra-*n*-butylammonium bromide in acetone, are archetypical examples of the conditions which Parker says favor the E2C mechanism.

Lloyd and Parker[11] previously found that the elimination rates of three compounds in this series did not fit a Hammett correlation. They concluded that the substituent effects supported the E2C mechanism and ruled out an ion-pair mechanism. We felt that a more systematic study of substituent effects at C_α in halide ion-catalyzed eliminations was needed to test the possibility of an E1-like transition state. Parker[12] also recently revived this possibility after discounting it for years.



Results

A summary of rate constants for Bu_4NBr-catalyzed elimination of HBr from 1-aryl-1-bromopropanes is in Table I. All rates were measured at the same Bu_4NBr concentration under pseudo-first-order conditions to ensure constant base activity. Undoubtedly, both dissociated Br^- and Bu_4NBr ion pairs were present in the 0.093 M solutions, and Br^- and Bu_4NBr have different kinetic activities.[13-16] With the p-F compound, k_2 was 11% greater at 0.0462 M than at 0.0922 M Bu_4NBr. This indicates qualitatively that dissociated Br^- is more reactive than the Bu_4NBr ion pair. All rates were measured in the presence of excess 2,6-lutidine, which traps the liberated HBr as kinetically inactive lutidinium bromide.[17] In every case, the only products of the reaction derived from the 1-aryl-1-bromopropane and detectable by pmr were 1-arylpropenes, whose isomeric compositions were not determined.

To assess the importance of the competing uncatalyzed first-order reaction, we obtained rate constants in the absence of added salt and in the presence of tetra-*n*-butylammonium tetrafluoroborate and perchlorate as shown in Table II. The most notable result in Table II is that the p-CH_3O compound reacts so fast by an E1 process that 0.094 M Bu_4NBr does not increase its elimination rate!

When the Bu_4NClO_4 rates in Table II are compared with the Bu_4NBr rates in Table I, the contribution of the uncatalyzed first-order elimination to k_2^{obsd} is small for all compounds except p-CH_3. Corrected values of k_2 appear in the last column of Table I. The corrections assume that Bu_4NBr exerts the same "salt effect" as Bu_4NClO_4 on the uncatalyzed elimination. Two kinds of experiments in Table II may serve as tests of this assumption. First, the equal

Table I. Second-Order Rate Constants for Reaction of 1-Aryl-1-bromopropanes with *n*-Bu_4NBr in Acetone at 74.63°[a]

X	No. of runs	$10^4 \times k_2^{obsd}$, M^{-1} sec^{-1} [b]	$10^4 \times k_2^{corr}$, M^{-1} sec^{-1} [c]
p-CH_3	5	16.91 ± 0.52	14.36
p-CH_3, α-D	3	14.75 ± 0.08	
p-F	2	9.59	9.36
p-Cl	2	7.04	
m-CH_3	2	6.45	
H	6	5.784 ± 0.105	5.53
H, α-D	4	5.130 ± 0.114	
m-Cl	2	3.62	
m-NO_2	2	3.54	

[a] ±0.10°. [b] Error limits are two standard deviations. When no error limit is given, k_2^{obsd} is the average of two runs which differed by less than 4%. [c] Second-order rate constants after correction for competing uncatalyzed elimination (see text).

Table II. First-Order Rate Constants for Loss of HBr from 1-Aryl-1-bromopropanes in Acetone with 2,6-Lutidine at 74.63°[a]

X	Salt[b]	k_1, sec^{-1}
p-CH_3O	0	0.55×10^{-2} [c]
	Bu_4NClO_4	1.15×10^{-2}
	Bu_4NBr	1.14×10^{-2} [c]
p-CH_3	0	1.00×10^{-5}
	Bu_4NBF_4	1.94×10^{-5}
	Bu_4NClO_4	2.24×10^{-5}
p-F	0	0.09×10^{-6}
	Bu_4NBF_4	1.89×10^{-6}
	Bu_4NClO_4	2.14×10^{-6}
H	0	0.04×10^{-6}
	Bu_4NBF_4	1.25×10^{-6}
	Bu_4NClO_4	1.11×10^{-6}

[a] ±0.10°. [b] Concentrations were 0.092–0.094 *M*. [c] Average of two runs. All other data are for one run only.

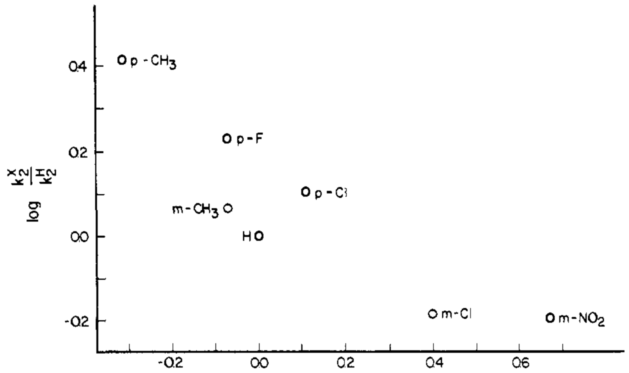


Figure 1. Hammett plot for rates of reaction of 1-aryl-1-bromopropanes with 0.093 *M* Bu_4NBr in acetone at 74.63°.

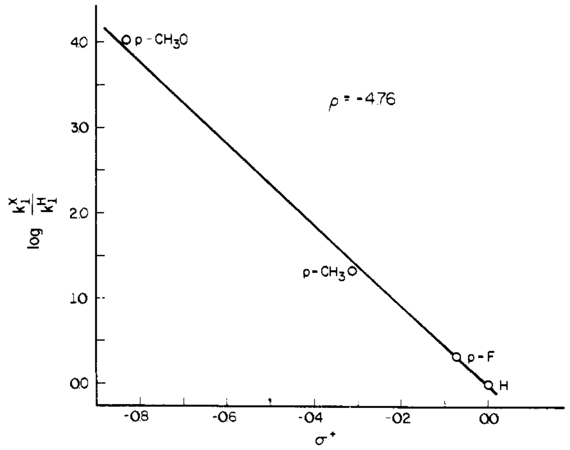


Figure 2. Hammett plot for rates of reaction of 1-aryl-1-bromopropanes in acetone at 74.63° with 0.094 *M* Bu_4NClO_4.

first-order elimination rates of the *p*-CH_3O compound with added Bu_4NBr and with added Bu_4NClO_4 require either that both salts exert the same salt effect, or that Bu_4NBr exerts a lesser salt effect and also a second-order contribution to the rate. Since the degree of dissociation of Bu_4NClO_4 is greater than that of Bu_4NBr in acetone at 25°,[14] it is reasonable that Bu_4NBr may exert the lesser salt effect. Second, another salt, Bu_4NBF_4, has a smaller effect on the uncatalyzed rates than Bu_4NClO_4. Even if the salt effect of Bu_4NBr were assumed to be equal to that of Bu_4NBF_4, the corrected rate constant for the *p*-CH_3 compound would be 14.70×10^{-4} M^{-1} sec^{-1}, only 2.4% larger than that reported in Table I.

Secondary kinetic isotope effects for Bu_4NBr-catalyzed elimination from the *p*-CH_3 and H compounds are k_H/k_D = 1.146 ± 0.048 and 1.128 ± 0.045, respectively. (The error limits are two standard deviations from averages of three to six kinetic runs.) The 1-bromo-1-phenylpropane-*1-d* and 1-bromo-1-(4-tolyl)propane-*1-d* employed contained ≥0.96 atom excess D. The k_H/k_D values are not corrected for either the uncatalyzed elimination or elimination from the small amounts of undeuterated material present in each deuterated sample, but these factors are negligible within the reported error limits.

Discussion

Figure 1 shows a Hammett plot of the substituent effects on Bu_4NBr-catalyzed eliminations from Table I using σ^+ substituent constants and rate constants corrected for uncatalyzed elimination. We use σ^+ to test the hypothetical ion-pair mechamism. The correlation clearly is poor. A similar plot using σ instead of σ^+ deviates still farther from linearity. All reasonable curves drawn through the points in Figure 1 lead to values of ρ (tangents to the curves) which lie in the range −1.3 to 0.0. Our substituent effects on Bu_4NBr-catalyzed elimination rates agree qualitatively with the earlier limited results of Lloyd and Parker,[11] who found that the *p*-CH_3, H, and *p*-NO_2 compounds did not form a linear Hammett plot.

To assess how substituents affect an elimination reaction which does proceed *via* a carbonium ion-like transition state, the uncatalyzed elimination rate data with Bu_4NClO_4 in Table II are plotted against σ^+ in Figure 2. Its ρ = −4.76 is consistent with an E1 mechanism. A similar plot of elimination rates in the absence of added salt (Table II) *vs.* σ^+ gives ρ = −6.6. Similar solvolyses of 1-aryl-1-bromopropanes[11] and of α-phenylethyl chlorides[18] in aqueous acetone also correlate with σ^+ and give ρ values of −5.3 and −5.7, respectively.

An inescapable conclusion is that the Bu_4NBr-catalyzed elimination transition states have little if any carbonium ion character. Earlier observations, that tertiary alkyl halides react with weak bases in acetone only moderately faster than secondary alkyl halides,[19] and that even alkyl halides located α to a carbonyl group[20] undergo halide ion-catalyzed eliminations readily, also suggest that weak base-catalyzed eliminations have little carbonium ion character.

Why is the Hammett plot of Figure 1 not linear? Rates of Bu_4NBr-catalyzed elimination of HBr from 1-aryl-1-bromopropanes do not respond to substituents in the same way as rates of solvolysis of cumyl chlorides, the reaction on which σ^+ values are based. Curved Hammett plots have been reported before for SN2 reactions and solvolyses of benzylic halides and tosylates.[21-25] The solvolysis examples, however, are most likely SN2 reactions with solvent. Reactions of benzyl bromides with pyridine in acetone even give a Hammett plot in which the meta and para substituents appear to lie on two different curves just as the points in Figure 1 do.[21] The most reasonable explanation available for curved Hammett plots of SN2 reactions is that the degrees of bonding of nucleophile and leaving group to the substituted carbon in the transition state vary with substituents: the more electron providing the substituent, the greater the SN1 character of reaction.

Advocates of the E2C mechanism for bromide ion-catalyzed eliminations will likely cite Figure 1 as support for bonding between base and C_α in the elimination transition states. However, curved Hammett plots also are found for strong base-catalyzed eliminations, such as the reactions of substituted α-phenylethyl bromides with potassium *tert*-butoxide in dimethyl sulfoxide and *tert*-butyl alcohol and with sodium ethoxide in ethanol.[26] These strongly basic media favor the E2H end of Parker's E2C-E2H spectrum of transition states. Although our substituent effects rule out substantial carbonium ion character in Bu_4NBr-catalyzed eliminations, they do not permit evaluation of whether the base interacts with C_α in the transition state.

Secondary α-deuterium isotope effects provide a different probe into the nature of bonding at C_α in elimination transition states. They have been used often to determine the degree of carbonium ion character of solvolysis transition states.[27-30] The known isotope effects on substitution reactions may be used to determine hybridization changes at C_α in elimination reactions. For SN2 reactions, k_H/k_D is 1.01 ± 0.01 (per D) for benzyl chlorides[27] and brosylates.[28] An alkyl group at benzyl carbon should raise k_H/k_D for SN2 reactions to about 1.05.[29] With increasing SN1 character in solvolyses, k_H/k_D rises to limiting values which depend on the leaving group.[29,30] The limiting value for leaving bromide is 1.125 on quasi-theoretical grounds[31] and also experimentally for solvolyses of substituted α-phenylethyl bromides in aqueous acetone and aqueous ethanol.[32] Positive k_H/k_D is attributed to a reduction in bending force constants of C-H bonds as hybridization at carbon changes from sp^3 to sp^2. The meager data available on secondary α-deuterium isotope effects on E2 eliminations, k_H/k_D = 1.017-1.047 for reactions of 2-arylethyl tosylates with potassium *tert*-butoxide in *tert*-butyl alcohol and k_H/k_D = 1.14-1.15 for reactions of cyclohexyl tosylate with lyate ions in ethanol and *tert*-butyl alcohol,[6,33] suggest that in those E2 transition states, hybridization at C_α lies between sp^3 and sp^2 with the exact hybridization depending on substrate, base, and solvent. (The limiting solvolytic k_H/k_D for tosylates is ~1.22.)[30]

The α-deuterium isotope effects of 1.128 and 1.146 for reactions of 1-bromo-1-phenylpropane and 1-bromo-1-(4-tolyl)propane with Bu_4NBr in acetone point to elimination transition states in which C_α is nearly sp^2 hybridized. Yet the substituent effects on elimination rates of 1-aryl-1-bromopropanes rule out extensive carbonium ion character. Therefore the developing double bond must be well formed at C_α. The large values of k_H/k_D are strong evidence that the transition states of these weak base-catalyzed eliminations differ markedly from the transition states of comparable SN2 reactions, which should have an α-deuterium isotope effect of about 1.05. Parker and coworkers[34] recently reported α-dueterium isotope effects of 1.13 ± 0.04 for elimination and 1.02 ± 0.05 for substitution with cyclohexyl tosylate and n-Bu_4NOAc in acetone. Parker[34] attributes the large elimination isotope effect to a "loose" E2C transition state but admits "the discrepancy between loose SN2 and E2C-like reactions is . . . a little surprising." The discrepancy is easily explained if base does not participate at C_α in the E2 transition states. Because α-deuterium isotope effects are large, and severe steric hindrance adjacent to C_α does not retard appreciably rates of elimination,[8] the E2C mechanism appears to us to be an unnecessary complication to elimination mechanisms.

The long-standing theory of variable E2 transition states can describe adequately Bu_4NBr-promoted eliminations from 1-aryl-1-bromopropanes. Their transition states have considerable double-bond character, substantially broken C_α-X bonds, and may have slight carbonium ion character when electron-providing substituents such as p-CH_3 are available for stabilization. Halide ions are most effective elimination catalysts when the substrate readily forms carbonium ions in solvolyses, although even DDT derivatives, which favor a more Elcb-like transition state, undergo chloride ion-catalyzed elimination readily in dipolar aprotic solvents.[35] Structural factors which stabilize carbonium ions and carbanions also stabilize transition states of concerted bimolecular eliminations.[5] Electron-withdrawing substituents at C_β favor E1cb character and positive ρ values. Strong proton bases also favor E1cb character. Electron-providing substituents at C_α favor E1 chraracter and negative ρ values. Good leaving groups such as tosylate favor E1 character. The reactions called E2C fit into the variable E2 transition state spectrum near the E1-like end.

The substrates, solvent, and base employed here are prototypes for the E2C mechanism, yet the α-deuterium isotope effects deny significant bonding of bromide ion to C_α in Bu_4NBr-catalyzed eliminations from 1-aryl-1-bromopropanes. Extensive stereochemical and kinetic isotope-effect evidence conclusively proves that competing E2 and SN2 reactions have different transition states.[36] Since the prototypes fail to support SN2 character, we support Bunnett's[8] recommendation that the E2C concept be abandoned and that weak base-catalyzed eliminations be described in terms of the theory of variable E2 transition states.

Experimental Section[37]

1-Aryl-1-propanols. m-Nitropropiophenone was obtained in 62% yield by treatment of 1 mol of propiophenone with fuming red nitric acid at ≤−15° and recrystallized from ethanol-ethyl acetate: mp 100-101° (lit.[38] mp 99-100°). All other propiophenones and benzaldehydes were purchased from Aldrich Chemical Co. or Eastman Organic Chemicals. 1-(4-Chlorophenyl)-1-propanol, 1-(4-tolyl)-1-propanol, 1-(3-chlorophenyl)-1-propanol, and 1-(3-tolyl)-1-propanol were prepared by addition of the appropriate benzaldehydes to ethylmagnesium bromide in diethyl ether. 1-Phenyl-1-propanol, 1-(3-nitrophenyl)-1-propanol, and 1-(4-fluorophenyl)-1-propanol were prepared by reduction of the appropriate propiophenones with sodium borohydride in basic aqueous methanol. All the 1-aryl-1-propanols were distilled at reduced pressure through a 10-cm vacuum-jacketed Vigreux column. Their yields and boiling points are listed in Table III. They all had ir and pmr spectra consistent with those of the assigned structures.

1-Aryl-1-bromopropanes. All the bromides in Table III were prepared by this general method. A solution of about 20 ml of the alcohol, 20 ml of benzene, and 7 ml of toluene in a 100-ml three-necked flask equipped with low-temperature thermometer and gas-dispersion tube was cooled to 0° in an ice-salt bath with rapid magnetic stirring. Dry HBr was introduced through the gas-dispersion tube until the reaction mixture foamed because of saturation with HBr. Additional small amounts of HBr were introduced periodically until the reaction mixture appeared cloudy because of separation of an aqueous phase. At this time, the reaction was about 90% complete according to pmr spectra. Further small amounts of HBr were added until no more alcohol could be detected by pmr. The mixture was extracted twice with ice-water, dried over $MgSO_4$, and distilled at reduced pressure through a 25-cm vacuum-jacketed Vigreux column. Yields and boiling points are listed in Table III. The procedure differed somewhat for 1-(3-nitrophenyl)-1-propanol: the reaction mixture was saturated with HBr and stored at −10° for 12 hr before work-up. Solid 1-bromo-1-(3-nitrophenyl)propane crystallized in the distillation receiver and

Table III. Yields and Boiling Points of 1-Aryl-1-propanols and 1-Aryl-1-bromopropanes

Compd	Yield, %[a]	Bp, °C (pressure in Torr) Obsd	Lit.	Ref
1-(4-Tolyl)-1-propanol	58	73 (0.6)	118–125 (18)	38
1-(4-Fluorophenyl)-1-propanol	85	55 (0.3)		
1-(4-Chlorophenyl)-1-propanol	68	91 (0.95)	128–132 (17)	38
1-(3-Tolyl)-1-propanol	30	66 (0.4)	113–118 (15)	38
1-Phenyl-1-propanol	82	61 (0.3)		
1-(3-Chlorophenyl)-1-propanol	30	72.5 (0.4)	129–132 (17)	38
1-(3-Nitrophenyl)-1-propanol	48	104 (0.15)	136–137 (1.7)	38
1-Bromo-1-(4-tolyl)propane	92	56.5 (0.35)		
1-Bromo-1-(4-fluorophenyl)propane	93	43 (0.34)		
1-Bromo-1-(4-chlorophenyl)propane	88	70–71 (0.34)		
1-Bromo-1-(3-tolyl)propane	23	56 (0.3)		
1-Bromo-1-phenylpropane	96	46–50 (0.2)	59–63 (0.04)	*b*
1-Bromo-1-(3-chlorophenyl)propane	18	56.5 (0.3)		
1-Bromo-1-(3-nitrophenyl)propane	65			

[a] Reported yields are of distilled material. Crude yields of alcohols were all at least 68%, and crude yields of bromides were all at least 88%. [b] P. A. Levine and L. A. Mikesa, *J. Biol. Chem.*, **70**, 362 (1926).

was recrystallized from hexane: mp 37–38°. All the 1-aryl-1-bromopropanes had ir and nmr spectra consistent with those of the assigned structures.

1-Bromo-1-phenylpropane-*1-d* and 1-Bromo-1-(4-tolyl)propane-*1-d*. To a vigorously stirred mixture of 10 mmol of lithium aluminum deuteride (Merck, A.G., 99% D) and 50 ml of dry tetrahydrofuran (freshly distilled from benzophenone ketyl) in a nitrogen atmosphere was added a solution of 20 mmol of propiophenone in 10 ml of tetrahydrofuran. The mixture was refluxed 8 hr, hydrolyzed with water, and extracted three times with diethyl ether. The ether solution was dried and evaporated *in vacuo* to 1-phenyl-1-propanol-*1-d*, which was converted without purification by the method of the preceding paragraph to 1-bromo-1-phenylpropane-*1-d* which contained 0.986 atom excess D by low-electronvolt mass spectrometry, 0.960 atom excess D by combustion–falling-drop analysis,[39] and no detectable 1-H by pmr. 1-Bromo-1-(4-tolyl)propane-*1-d*, prepared by the same method except for an 18-hr reflux period, contained 0.984 atom excess D by low-electronvolt mass spectrometry, 0.962 atom excess D by combustion–falling-drop analysis,[39] and no detectable 1-H by pmr.

1-Bromo-1-(4-methoxyphenyl)propane. In a 100-ml flask equipped with gas-dispersion tube and thermometer, 50 ml of butane was condensed at −5°. With rapid magnetic stirring, 20 g of 1-(4-methoxyphenyl)propene was added, and it crystallized immediately. Dry HBr was added at a moderate rate with rapid stirring until the solid went into solution. The temperature of the mixture was lowered to −30°, and further small amounts of HBr were added until no 1-(4-methoxyphenyl)propene remained in its pmr spectrum. The solution was decanted away from some polymeric solid into a flask containing calcium hydride and decolorizing carbon and stored at −15°. Just before use, the mixture was filtered through a fine sintered glass frit, and the volatile components were removed *in vacuo* for 30 min at 0°. The remaining colorless 1-bromo-1-(4-methoxyphenyl)propane had pmr δ 0.98 (t, J = 7 Hz, 3 H), 2.17 (m, 2 H), 3.68 (s, 3 H), 4.87 (t, J = 7 Hz, 1 H), 6.60–7.40 (m, 4 H), consistent with the assigned structure, and was contaminated, according to its pmr spectrum, with only <5% of 1-(4-methoxyphenyl)propene. It was too unstable for distillation, and attempts to crystallize it at low temperature from butane failed.

Kinetics. Materials. Reagent-grade acetone was agitated for 24 hr with 4A molecular sieves and distilled under dry nitrogen. 2,6-Lutidine (Eastman) was refluxed over barium oxide for 2 hr and distilled under dry nitrogen. Tetra-*n*-butylammonium bromide (Eastman) was recrystallized from chloroform–diethyl ether to a constant mp of 119–120° and dried at 100° (0.2 Torr) for 24 hr. *Anal.* Calcd Br, 24.79. Found Br, 24.76. Tetra-*n*-butylammonium tetrafluoroborate and tetra-*n*-butylammonium perchlorate were prepared from Bu_4NBr and recrystallized to constant melting point as described elsewhere.[40] Analyses for bromide showed 0.4 wt % Br^- in the Bu_4NBF_4 and no detectable (<0.2%) Br^- in the Bu_4NClO_4.

Procedure. All glassware was acid washed, rinsed thoroughly with distilled water, and dried for 24 hr at 130° before use. Into a 50-ml volumetric flask were weighed 1.25 mmol of 2,6-lutidine and 5.00 mmol of Bu_4NBr. Then 30 ml of acetone was added, 1.00 mmol of the 1-aryl-1-bromopropane was weighed into the flask, and more acetone was added to the 50-ml mark. The mixture was shaken for 5 min, and 3.00-ml aliquots were transferred to each of 12 test tubes and sealed under vacuum. The tubes were placed in a bath at 74.63 ± 0.10° and quenched at appropriate intervals by cooling to −78°. Their contents were titrated at 25° under nitrogen with standardized 0.01 M sodium methoxide in methanol to the Thymol Blue endpoint. Each run consisted of ten data points collected over 2–4 half-lives and duplicate infinity points, taken after at least 8 half-lives, whose titers accounted for 100 ± 3% production of HBr from the 1-aryl-1-bromopropane. Corrected for volume expansion to 75°, the concentration ranges of materials used were: 1-aryl-1-bromopropanes, 0.0179–0.0201 M; 2,6-lutidine, 0.0222–0.0274 M; and Bu_4NBr, 0.0917–0.0955 M. Runs which employed Bu_4NBF_4, Bu_4NClO_4, or no salt at all were carried out by the same method.

Rates with 1-bromo-1-(4-methoxyphenyl)propane required minor modifications of the procedure. Solutions were prepared at room temperature, but at the time of immersion of the sealed tubes in the constant temperature bath one tube was quenched to determine the extent of reaction before the actual kinetic run began. Titrations were performed at −30° to prevent fading of the endpoint due to solvolysis of the substrate.

Pseudo-first-order rate constants were calculated with an unweighted least-squares program and divided by Bu_4NBr concentration to give the rate constants in Table I. Our rate constants at 74.63° for 1-bromo-1-phenylpropane and 1-bromo-1-(4-tolyl)propane are 1.34 and 1.39 times larger, respectively, than those previously reported at "75°" by Lloyd and Parker.[11]

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Substituent Effects. XII.[1] Substituent Effects by ^{19}F NMR

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Abstract: FMMF calculations for ^{19}F SCS in the 10-substituted 9-fluoroanthracenes and 4-substituted 3,5-dimethylfluorobenzenes are reported. The analysis strongly supports the idea that polar effects on ^{19}F chemical shifts are enhanced when the fluorine atom is attached to a carbon atom which is part of a π system. Further, a comparison of FMMF calculations for increasingly rigid para-substituted aryl fluorides suggests that σ skeletal deformation can make a significant contribution to the ^{19}F chemical shift, when the substituent and fluorine are in the same ring. ^{19}F chemical shift data for a number of new substituted aryl fluorides are presented which appear to partially support the latter conclusion. In addition, the new data help to throw further light on the factors determining ^{19}F chemical shifts.

In this series of papers, a general theory of substituent effects has been developed on the assumption that only three factors are important, i.e., the field effect (F), the mesomeric effect (M), and the π inductive effect which is usually indistinguishable from the mesomeric effect. In its latest form (FMMF method), allowance is also made for the mesomeric field effect (MF), due to electrostatic interactions with charges set up in a π system through mesomeric interactions with substituents.

Although this improved empirical treatment accounts very well for chemical reactions of side chains, it was found that an analysis of aryl ^{19}F chemical shifts leads to deviations of the hydrogen substituent from the least-squares lines for most of the systems investigated.[3] Since the deviations as well as the scatter of points from the line were greater when the substituent and fluorine are attached to the same ring, it was suggested that ^{19}F chemical shifts in aryl fluorides are sensitive to substituent-induced structural distortions that alter the environment of the fluorine atom, i.e., insertion of any substituent into a fluorinated aromatic produces a chemical shift merely by its presence, independent of any specific electronic effect.

Because this proposal has serious consequences regarding the continued and widespread use of the aryl fluorine atom as a probe for investigating substituent effects,[4] we have extended the analysis (FMMF method) to other available systems, in particular, the 4-substituted 3,5-dimethylfluorobenzenes[6] and the 10-substituted 9-fluoroanthracenes.[7] These two systems are of interest since nonlinear substituent groups must be rotated out of the plane of the ring because of steric interactions with the o-methyl groups or the peri-hydrogen atoms, respectively. Such a rotation destroys π overlaps with the ring so such groups can exhibit only polar effects (electric field and π-inductive effects).

In this paper, we report the results of that study together with the synthesis and ^{19}F spectra of a number of new aryl fluorides, as well as five new fluoromethylnaphthalenes, which shed further light upon the factors determining ^{19}F chemical shifts. Moreover, the new ^{19}F NMR data allow interesting deductions to be made concerning the electronic behavior of alkyl groups in the neutral ground state.

Theory

The FMMF method uses a simplified model in which the dipole moment of the bond CX between a substituent and an adjacent carbon i is represented by equal and opposite point charges on carbon and at a point (j) one standard bond length (1.40 Å) from carbon along the CX bond. The interaction with a fluorine atom attached at atom m is given by the general equation[3]

$$\sigma_{im}{}^{\mathrm{SF}} = F^{\mathrm{S}}R_{im}{}^2 + M^{\mathrm{S}}q_{im} + M_F{}^{\mathrm{S}}\sum_{k \neq m}\frac{q_{ik}\cos\theta_{kn}}{r_{kn}{}^2} \quad (1)$$

where

$$R_{im}{}^2 = \frac{\cos\theta_{in}}{r_{in}{}^2} - \frac{\cos\theta_{jn}}{r_{jn}{}^2} \quad (2)$$

θ_{in} being the angle between the CF bond vector and a line of length r_{im} drawn from atom i to the midpoint (n) of the CF bond. q_{im} is the charge produced at atom m by an amino