Solvolysis of 2-substituted-9-(*ortho*-substituted phenylmethyl)fluoren-9-yltrimethylammonium ions in various solvents. The effect of steric crowding on alkene formation

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This paper is dedicated to Professor Arthur N. Bourns

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The solvolytic reaction of several 9-(*ortho*-substituted phenylmethyl)fluoren-9-yltrimethylammonium salts has been investigated in several different solvents. Substitution and elimination products were found for the reactions in all the solvents studied, with the exceptions that reaction in both *tert*-butyl alcohol and chloroform led exclusively to the alkene product. The observed rate constants for alkene formation and the percent alkene were measured and it was found that the di-*ortho* compounds reacted at a faster rate but produced less alkene than the reaction of the corresponding mono-*ortho* salts. Hydrogen–deuterium isotope effects were also determined for the various reactions. The results are discussed in terms of the reaction proceeding by way of the E1 mechanism, where steric acceleration promotes the loss of the bulky ammonium leaving group to give the carbocation intermediate.

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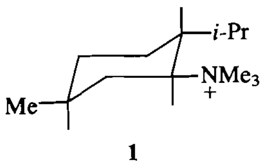
Opérant dans plusieurs solvants, on a étudié la réaction solvolytique de plusieurs sels triméthylammonium des ⟨phénylméthyles substitués en *ortho*⟩-9 fluorène-9 yles. À l'exception des réactions dans l'alcool *tert*-butylique ou dans le chloroforme, toutes les réactions étudiées dans les autres solvants ont conduit à la formation de produits de substitution ainsi que d'élimination. On a mesuré les constantes de vitesse pour la formation des alcènes ainsi que les pourcentages d'alcènes formés; on a trouvé que les composés doublement substitués en *ortho* réagissent plus rapidement mais qu'ils produisent moins d'alcènes que les réactions des sels correspondants qui ne portent qu'un substituant en *ortho*. On a déterminé les effets cinétiques hydrogène–deutérium pour diverses réactions. On discute des résultats en fonction d'une réaction qui se produirait par le biais d'un mécanisme E1 et dans lequel l'accélération stérique favoriserait le perte du nucléofuge ammonium encombrant au profit de la formation d'un carbocation intermédiaire.

[Traduit par la revue]

Introduction

Studies on the base-promoted 1,2 elimination reaction of quaternary ammonium salts have received considerable attention both from the experimental (1–6) and theoretical approaches (7, 8). Such substrates generally react with alkoxide bases by way of the one-step concerted E2 mechanism (9, 10) although reaction proceeding by the ylide mechanism (α′, β) has been demonstrated by Cope and Mehta (11) for a substrate where approach of base to the β-hydrogen is unfavourable for steric reasons.

Generally, quaternary ammonium salts do not undergo elimination via a carbocation intermediate under solvolytic conditions and, hence, amines have been classified as "poor leaving groups" (poor nucleofuges (2, 12)). However, in a study on the degradation of ax-7-cholestanyltrimethylammonium iodide in boiling ethanol it was reported (13) that the reaction undoubtedly proceeded via an E1 process. Similarly, Hughes and Wilby (14) proposed that menthyltrimethyl- and neomenthyltrimethylammonium hydroxides, **1** and **2**, underwent reaction in water by the unimolecular E1 pathway. Since the neomenthyltrimethylammonium ion, where the —$\overset{+}{N}(CH_3)_3$ group is *cis* to the isopropyl substituent, showed a much larger propensity for reaction via the E1 mechanism than the menthyl substrate, the authors considered that carbocation formation is made favourable due to a relief in steric strain in the molecule.



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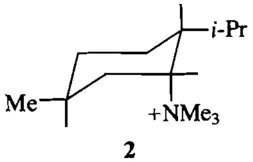

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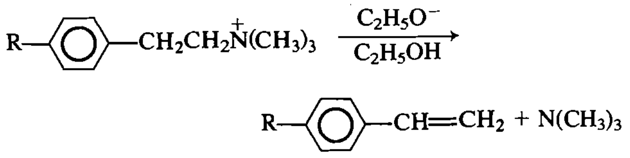
The effect of *para* substituents on the aryl ring on the nature of the E2 transition state was examined (2) for the reaction of 2-arylethyltrimethylammonium salts with ethoxide ion in ethanol, eq. [1]. It was found that when the *para* substituent was made more electron withdrawing the reaction rate *increased*. Also, measurements (2) and calculations (8) of both the primary hydrogen–deuterium and nitrogen (leaving group) isotope effects indicated that an increase in the electron-withdrawing power of the ring substituent leads to a corresponding transition state with *both decreased* C—H and C—$\overset{+}{N}$ bond weakening. This substituent effect on transition state geometry (a Hammond effect) was considered to be consistent with the theories of Thornton (15, 16), More O'Ferrall (17) and Jencks (18).

[1]


In an investigation (19) on the E2 reaction of 9-(4-substituted phenylmethyl)fluoren-9-yltrimethylammonium bromides, **3**, with ethoxide in ethanol, however, it was found that the

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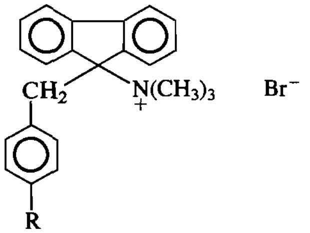
variation of both the primary hydrogen–deuterium and nitrogen isotope effects with changes of the 4-substituent (R) on the phenyl ring were the *opposite* to those found in the earlier studies on the 2-arylethyl system. As well, the Hammett ρ value of +1.33 found for the reaction of **3** was very much less than the value of +3.77 found for the reaction of the 2-arylethyl salts with ethoxide (2), in spite of the fact that in both cases a benzylic hydrogen was being removed with ethoxide ion. It was concluded (19) that for reaction of **3** where the 4-substituent (R) is an electron withdrawer, which leads to an *increase* in the rate of reaction, the extent of both the β-carbon–hydrogen and the α-carbon–nitrogen bond rupture at the transition state is *more* advanced.[3] This apparent variance with the conclusions reached in the earlier studies (2) was discussed in the light of possible steric effects between the *ortho* hydrogens on the phenyl ring and the 1,8 hydrogens on the fluorene nucleus in the reactant and in the transition state.

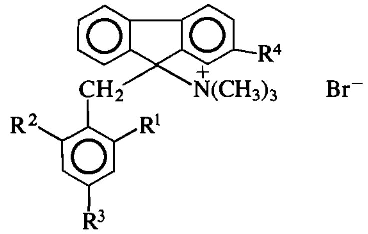


The effect of the nature of the leaving group has been extensively studied (20–30) for several elimination reactions in terms of mechanism as well as in transition-state structure. In all cases, nucleofugality was considered essentially as being entirely due to "electronic factors" (basicity, polarizability, etc). In order to test the proposal (19) that steric interactions might affect leaving group ability and, hence, are responsible for the unexpected results obtained from the study of the reaction of **3** in terms of transition-state geometry, several 9-(*ortho*-substituted phenylmethyl)fluoren-9-yltrimethylammonium salts have been prepared in order to investigate the possible effect of the *ortho* substituents on the phenyl ring in terms of mechanism and (or) transition-state structure. An examination of Dreiding models of the *para*-substituted salts, **3**, suggests that there is a possible steric interaction between the *ortho* hydrogens on the phenyl ring and the fluorenyl 1,8 hydrogens. Consequently, replacing the *ortho* hydrogens with bulkier groups should enhance the "steric effect".

In the present study,[4] the rate of reaction of a series of 2-substituted-9-(*ortho*-substituted phenylmethyl)fluoren-9-yltrimethylammonium salts, and their β-d_2 analogues, have been measured in a variety of protic solvents as well as in the aprotic solvent chloroform, and the product composition determined. Also, the effect of externally added trimethylamine and, as well, the effect of the addition of the strong base, sodium ethoxide, on both the rate of reaction and the product ratios have been examined for reaction of the *ortho*-substituted compounds in ethanol. Secondary β-hydrogen–deuterium isotope effects on carbocation formation have been measured and, as well, an estimate of the primary β-hydrogen–deuterium isotope effect for proton loss from the carbocation has been made by determining the product ratios. Activation parameters for the reaction of several 9-(*ortho*-substituted) salts in both absolute ethanol and 2-propanol were also determined.

Results

The compounds investigated in the present study are shown below:



4, $R^1 = R^2 = CH_3$; $R^3 = R^4 = H$
5, $R^1 = R^2 = Cl$; $R^3 = R^4 = H$
6, $R^1 = CH_3$; $R^2 = R^3 = R^4 = H$
7, $R^1 = R^3 = CH_3$; $R^2 = R^4 = H$
8, $R^1 = R^2 = R^3 = CH_3$; $R^4 = H$
9, $R^1 = R^2 = CH_3$; $R^3 = H$; $R^4 = Br$

The observed rate constants for alkene formation, k_1, for reaction of the *ortho*-substituted salts, **4**–**9**, and their β-dideuterated analogues in absolute ethanol at 57.3°C are shown in Table 1. The secondary β-hydrogen–deuterium isotope effects, k_1^H/k_1^D, as well as the primary β-hydrogen–deuterium isotope effects,[5] k_E^H/k_E^D, determined from the product ratio data, are also given in this table. A comparison of the observed rate constant for alkene formation, k_1, for reaction of the bromine-substituted fluorenyl ring salt, **9**, with that for reaction of **4** at 68.4°C in absolute ethanol, $120 \pm 3.0 \times 10^{-5}$ (s^{-1}) and $109 \pm 0.5 \times 10^{-4}$ (s^{-1}), gives a Hammett ρ value of −2.5 for reaction of the 2,6-diMe substrate in ethanol.

The effect of externally added trimethylamine on the observed rate of alkene formation, k_1, and, as well, on the percent alkene product, was determined for the reaction of the 2-Me, **6**, and 2,4,6-triMe, **8**, salts in ethanol at approximately[6] 57°C, Table 2. The effect of the addition of a strong abstracting base, sodium ethoxide, on the observed rate constant for alkene formation, k_1, and on the percent alkene formed, was investigated for the reaction of the 2,4,6-triMe salt, **8**, in ethanol at the same temperature as used for the trimethylamine experiments, Table 2.

The effect of a change in solvent on the observed rate constant for alkene formation, k_1, the percent alkene, the secondary β-deuterium isotope effect, k_1^H/k_1^D, and the primary β-deuterium isotope effect, k_E^H/k_E^D, for the reaction of the 2-Me, 2,6-diMe, and 2,4,6-triMe salts, **6**, **4**, and **8**, respectively, were examined for reaction in a series of alcohol solvents as well as in two alcohol–water mixtures at 57.3°C, and the results are given in Table 3. The thermodynamic activation parameters were determined for the reaction of the 2-Me (**6**), 2,6-diMe (**4**), and 2,6-diCl (**5**) substrates in absolute ethanol and also for the reaction of the 2,6-diMe salt in 2-propanol. The observed rate constants for alkene formation, k_1, together with the per-

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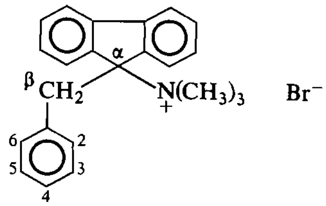
[3] This apparent "anti-Hammond" behavior on E2 transition state geometry can be accounted for by the More O'Ferrall theory (17) and will be discussed in a manuscript currently under preparation.

[4] A preliminary account of some of the studies has been published (31, 32).

[5] The method used for the determination of this effect will be given in the discussion section.

[6] The temperature was not exactly 57.3°C as used in the previous experiments and, hence, the rate constants differ slightly from those shown in Table 1.

TABLE 1. Hydrogen–deuterium isotope effects for reaction of a series of 9-(*ortho*-substituted phenylmethyl)fluoren-9-yltrimethylammonium bromides in absolute ethanol at 57.3°C



Substrate	$k_1 \times 10^5$ (s^{-1})	% alkene	k_1^H/k_1^D	$(k_E^H/k_E^D)^a$
2-Me (**6**)	2.35±0.09[b]	55±1.0[c]	1.22±0.05[d]	1.6±0.2[c]
6-d_2	1.92±0.04	43±1.0		
2,4-diMe (**7**)	2.85±0.03	57±1.0	1.16±0.01	2.0±0.2
7-d_2	2.46±0.02	40±1.0		
2,6-diCl (**5**)	9.59±0.20	29±1.0	1.45±0.04	2.5±0.6
5-d_2	6.60±0.12	14±2.0		
2,6-diMe (**4**)	295±4	28±1.0	1.62±0.03	3.1±1.0
4-d_2	182±2	11±2.0		
2,4,6-triMe (**8**)	297±16	30±1.0	1.39±0.10	4.9±2.0
8-d_2	214±10	8.0±2.0		

[a] Calculated from the product ratios: $k_E^H/k_E^D = \frac{(\%\text{alkene}/\%\text{ether})_H}{(\%\text{alkene}/\%\text{ether})_D}$, assuming $k_S^H = k_S^D$.
[b] Standard deviation.
[c] Estimated uncertainty.
[d] Ratios of observed rate constants for alkene formation: deviation = $\pm k^H/k^D[(r^H/k^H)^2 + (r^D/k^D)^2]^{1/2}$ where r is the standard deviation in k.

TABLE 2. First-order rate constants, k_1, and the percent alkene obtained for the reaction of the 2-Me, **6**, and 2,4,6-triMe, **8**, salts in the presence and absence of both externally added trimethylamine and sodium ethoxide in absolute ethanol at 57°C[a]

Substrate	[Substrate] × 10^4 (M)	[Trimethylamine] (M)	[Sodium ethoxide] (M)	$k_1 \times 10^5$ (s^{-1})	% alkene
2-Me (**6**)	1.856	—	—	2.56±0.04[b]	55±1.0[c]
	1.856	3.5 × 10^{-3}	—	2.46±0.04	55±1.0
2,4,6-triMe (**8**)	1.570	—	—	330±14	31±1.0
	1.570	3.5 × 10^{-3}	—	345±8	31±1.0
	1.542	—	3.08 × 10^{-4}	312±8	31±1.0
	1.542	—	3.08 × 10^{-3}	340±9	31±1.0

[a] The temperature was slightly different for these experiments than that used to acquire the data shown in Table. 1.
[b] Standard deviation.
[c] Estimated uncertainty.

cent alkene values determined at three diferent temperatures for reaction of the three substrates, **4**, **5**, and **6**, are given in Table 4 alone with the values for E_A, $\Delta H^{\ddagger}$ (60°C), and $\Delta S^{\ddagger}$ (60°C).

The effect of an aprotic solvent, chloroform, on the observed rate constant for alkene formation, k_1, for reaction of the 2,6-diMe (**4**), 2,4,6-triMe (**8**), and 2-Me (**6**) salts and their β-dideuterated analogues was determined by both the uv (ultraviolet) spectroscopic method, used in all the preceding studies, and a nuclear magnetic resonance procedure (see the experimental section for details). The results are shown in Table 5 along with the secondary β-hydrogen–deuterium isotope effects, k_1^H/k_1^D. In all cases, the alkene was formed in 100 ± 5% yield. The rate constant for the bromine-substituted fluorene ring substituted salt, **9**, of 16.6 ± 0.2 × 10^{-5} (s^{-1}) can be compared with that of 128 ± 3 × 10^{-5} (s^{-1}) for reaction of **4** to give a ρ value for reaction of the 2,6-diMe salt in chloroform of −2.3 at 50°C.

Discussion

*Reaction of 2-substituted-9-(*ortho*-substituted phenylmethyl)-fluorene-9-yltrimethylammonium ions in absolute ethanol at 57.3°C*

In order to investigate the elimination reaction of the *ortho*-substituted quaternary ammonium salts **4–9** with ethoxide they were first dissolved in dry absolute ethanol and a uv spectrum was obtained for each solution. Surprisingly, it was found that the uv spectra of all the substrate solutions changed with time, indicating that reaction was taking place in the *absence* of base. It must be noted that the *para*-substituted analogues **3** (with hydrogens at the *ortho* positions) were completely stable in ethanol in the absence of ethoxide ion.

The products of the reaction of the *ortho*-substituted salts **4–9** in dry ethanol were found to be the corresponding alkene **10** as well as the ethyl ether, 9-ethoxy-9-(*ortho*-substituted phenylmethyl)fluorene, **11**, eq. [2]. The rate of reaction of the

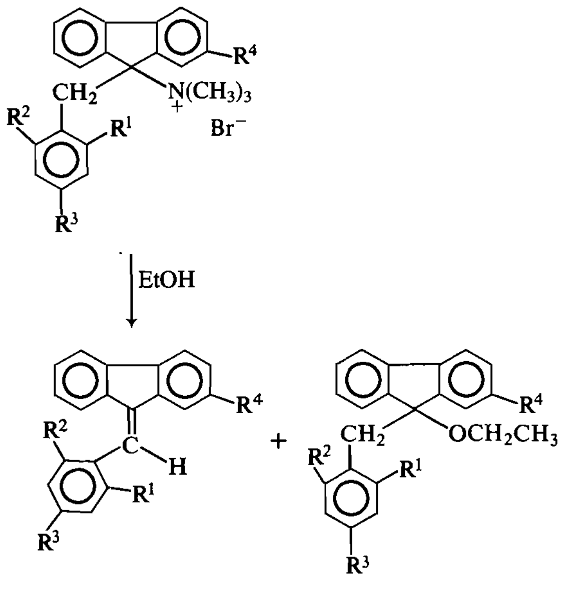
TABLE 3. Hydrogen–deuterium isotope effects for reaction of the 2-Me, 2,6-diMe, and 2,4,6-triMe salts and their β-dideuterated analogues in various alcohol solvents at 57.3°C

Substrate	Solvent	$k_1 \times 10^5$ (s^{-1})	% alkene	k_1^H/k_1^D	$(k_E^H/k_E^D)^a$
2-Me (**6**)	MeOH	2.18±0.0^b	43±1.0^c	1.56±0.04^d	1.3±0.1^c
6-d_2	MeOH	1.40±0.02	37±1.0		
6	EtOH	2.35±0.09	55±1.0	1.22±0.05	1.6±0.2
6-d_2	EtOH	1.92±0.04	43±1.0		
6	95% EtOH	1.58±0.03	58±1.0	1.66±0.04	1.2±0.2
6-d_2	95% EtOH	0.95±0.01	53±1.0		
6	70% EtOH	0.93±0.02	54±1.0	—	—
6	*t*-BuOH	0.63±0.02	100±1.0	1.24±0.06	—
6-d_2	*t*-BuOH	0.51±0.02	100±1.0		
2,6-diMe (**4**)	EtOH	294±4	28±1.0	1.62±0.03	3.1±1.0
4-d_2	EtOH	182±2	11±2.0		
4	95% EtOH	212±3	30±1.0	1.32±0.02	3.1±1.0
4-d_2	95% EtOH	161±1	12±2.0		
4	2-PrOH	337±9	52±1.0	1.43±0.03	3.8±1.0
4-d_2	2-PrOH	236±3	22±1.0		
4	*t*-BuOH	195±11	100±1.0	1.57±0.09	—
4-d_2	*t*-BuOH	124±2	100±1.0		
2,4,6-triMe (**8**)	MeOH	245±6	21±1.0	1.10±0.06	5.1±2.0
8-d_2	MeOh	222±10	5±2.0		
8	EtOH	297±16	30±1.0	1.39±0.10	4.9±2.0
8-d_2	EtOH	214±10	8±2.0		

[a] Calculated from the product ratios assuming $k_S^H = k_S^D$.
[b] Standard deviation.

ortho-substituted salts in ethanol was determined by measuring the formation of the alkene product at 320 nm since the uv spectrum of the ether does not show any absorption at this wavelength. The percent alkene formed in the reaction was calculated from the absorbance reading at infinite time (see the experimental section for details).

[2]



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A consideration of the data in Table 1 indicates that the mono-*ortho*-substituted substrates react in ethanol to give a greater amount of alkene product, as compared with the reaction of the di-*ortho*-substituted salts; i.e., reaction of the undeuterated 2-Me and 2,4-diMe compounds give 55 and 57% alkene, respectively, while reaction of the 2,6-diMe salt gives approximately 28% alkene.

It can also be seen that the rate of reaction of the mono-*ortho*-substituted compounds is considerably slower than the rate of reaction of the di-*ortho*-substituted substrates. The observed rate constants for alkene formation, k_1, for reaction of the undeuterated 2-Me and 2,4-diMe salts in ethanol at 57.3°C are 2.35 and 2.85 × 10^{-5} (s^{-1}), respectively, while the corresponding rate constants for reaction of the 2,6-diCl, 2,6-diMe, and 2,4,6-triMe compounds are 9.59, 294, and 297 × 10^{-5} (s^{-1}), respectively. The compounds with only one *ortho* substituent react at a slower rate but give a greater yield of alkene product.

It is noteworthy that a 4-methyl substituent does not change significantly the observed rate constant for alkene formation, k_1, or the percent alkene, as compared to the reaction of compounds with only *ortho* substituents. The observed rate constants for alkene formation, k_1, together with the percent alkene for reaction of the undeuterated 2-Me and 2,4-diMe substrates are 2.35 × 10^{-5} (s^{-1}) (55%) and 2.85 × 10^{-5} (s^{-1}) (57%), respectively, while the corresponding values for reaction of the 2,6-diMe and 2,4,6-triMe compounds are 294 × 10^{-5} (s^{-1}) (28%) and 297 × 10^{-5} (s^{-1}) (30%), respectively.

The only mechanism that is consistent with the above results for reaction of the *ortho*-substituted salts in ethanol in the absence of a strong abstracting base is the E1 process involving carbocation formation. In principle, the formation of this carbocation can be a reversible process, eq. [3], and conse-

$$[3]\quad \begin{tikzcd} \textit{ortho}\text{-Substituted salts} \arrow[r, shift left, "k_1"] & \text{carbocation + trimethylamine} \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_2"] \\ & \text{products} \end{tikzcd}$$

TABLE 4. First-order rate constants k_1, E_A, $\Delta H^{\neq}$, $\Delta S^{\neq}$ values, and percent alkene formation for the reaction of the 2-Me, 2,6-diMe, and 2,6-diCl salts in absolute ethanol and 2-propanol at various temperatures

Substrate	Solvent	Temperature (°C)[a] (±0.01°C)	$k_1 \times 10^5$ (s^{-1})	% alkene	E_A (kcal mol^{-1})	$\Delta H^{\neq}$(60°C) (kcal mol^{-1})	$\Delta S^{\neq}$(60°C) (cal K^{-1} mol^{-1})
2-Me (**6**)	EtOH	47.2	0.458±0.025[b]	57±1[c]	36.9±0.5[b]	36.2±0.5[b]	29.9±1.6[b]
		57.3	2.35±0.09	55±1			
		67.3	13.1±0.3	53±1			
2,6-diCl (**5**)	EtOH	47.2	1.93±0.04	31±1	34.8±0.6	34.1±0.4	26.2±1.2
		57.3	9.59±0.20	29±1			
		69.1	63.7±0.8	27±1			
2,6-diMe (**4**)	EtOH	47.2	77.2±0.3	28±1	30.2±0.4	29.6±0.4	19.4±1.2
		57.3	294±4	28±1			
		67.3	1200±60	26±1			
	2-PrOH	48.3	93.4±2.7	52±1	28.4±1.8	27.7±1.8	13.7±5.5
		57.3	377±9	52±1			
		68.4	1230±40	52±1			

[a] The temperatures were determined using a platinum resistance thermometer.
[b] Standard deviation.
[c] Estimated uncertainty.

TABLE 5. Hydrogen–deuterium isotope effects for reaction of the 2-Me and 2,4,6-triMe salts and their β-dideuterated analogues in chloroform

Substrate	Temperature (°C)	$k_1 \times 10^5$ (s^{-1})	k_1^H/k_1^D
2,6-diMe (**4**)	50.6	128±3[a,b]	1.47±0.04[c]
4-d_2	50.6	87.2±1.3[a]	
4	50[d]	88.9±3.4[b,e]	1.88±0.12
4-d_2	50[d]	47.2±2.2[e]	
2,4,6-triMe (**8**)	50[d]	108±2[e]	1.55±0.03
8-d_2	50[d]	68.6±1.3[e]	
2-Me (**6**)	50[d]	0.760[e]	

[a] Determined using the uv method.
[b] Standard deviation.
[c] Deviation = $\pm k^H/k^D\,[(r^H/k^H)^2 + (r^D/k^D)^2]^{1/2}$ where r is the standard deviation in k.
[d] The approximate temperature in the probe of the nmr spectrometer.
[e] Determined using the nmr method.

quently the rate of alkene formation and the percent alkene were determined for reaction of both the 2-Me and 2,4,6-triMe substrates in absolute ethanol, both in the absence and presence of added trimethylamine, Table 2.

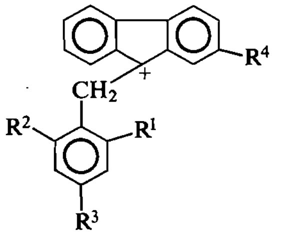
The results in Table 2 indicate that the rate of alkene formation, k_1, and the amount of alkene formed do not change for reaction of either the 2-Me or the 2,4,6-triMe compounds in ethanol when trimethylamine is added. Hence the formation of the carbocation in the system under study is irreversible, i.e. $k_2 >> k_1$ eq. [3].

The proton removal step to give the alkene product, k_E in eq. [4], was investigated for the reaction of the 2,4,6-triMe salt

$$[4]\quad \textit{ortho}\text{-Substituted salts} \xrightarrow{k_1\ (\text{slow})} \text{carbocation} \begin{array}{l} \nearrow^{k_E}\ \text{alkene} \\ \searrow_{k_S}\ \text{ether} \end{array}$$

when the strong base, sodium ethoxide, was added to the reaction solution, Table 2. It is seen that the observed rate constant for alkene formation, k_1, and the percent alkene were essentially unaffected when the concentration of the added ethoxide ion was either a factor of two or ten times as great as the substrate concentration. The loss of the proton from the carbocation must, therefore, not be rate determining, i.e. $k_1 \ll (k_E + k_S)$. Furthermore, the failure of the addition of ethoxide to change the alkene : ether ratio suggests that the solvent ethanol, and not ethoxide, is involved in the removal of the proton to give the alkene in the k_E step, as it is unlikely that ethoxide ion would affect the rate of alkene and ether formation in an identical fashion. The failure of ethoxide to affect the reaction can possibly be due to electrostatic control of the approach of $^-$OEt to a non-reacting site of the substrate, which leaves the β-proton and α-carbon open to attack by solvent.

The rate-determining formation of the 9-fluorenyl carbocation **12** is consistent with the observation of a Hammett ρ of −2.5, calculated from the k_1 values determined for the reaction of the 2,6-diMe salt **4** and the 2,6-diMe salt with a 2-bromo substituent on the 9-fluorenyl ring, **9**. Several groups of workers have prepared the 9-substituted 9-fluorenyl carbocations by reaction of the corresponding alcohol in acid media for spectroscopic (33, 34) and kinetic studies (35). As well, in spite of their "antiaromaticity", the 9-fluorenyl and the 9-methyl-9-fluorenyl carbocations have been proposed as intermediates in the solvolytic reaction of the 9-chloro (36) and 9-(3,5-dinitrobenzoate) (37) derivatives, respectively.



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Reaction proceeding via the E1 mechanism where formation of the carbocation is rate determining, eq. [4], should give rise mainly to a secondary β-deuterium kinetic isotope effect (38) since rupture of the β-hydrogen bond occurs in a subsequent fast step. Applying the steady-state treatment to the reaction scheme shown in eq. [4] leads to the expression for the rate of formation of the alkene product,

$$\frac{\mathrm{d[alkene]}}{\mathrm{d}t} = \left(\frac{k_1 k_\mathrm{E}}{k_\mathrm{E} + k_\mathrm{S}}\right) A$$

where A represents the substrate concentration.

Setting E and S as the concentration of the alkene and ether products, respectively, it follows that the quaternary ammonium salt concentration, A, at a time T is given by

$$A_T = E_\infty - E_T + S_\infty - S_T$$

and since $k_\mathrm{E}/k_\mathrm{S} = E/S$ then

$$A_T = E_\infty - E_T + E_\infty\left(\frac{k_\mathrm{S}}{k_\mathrm{E}}\right) - E_T\left(\frac{k_\mathrm{S}}{k_\mathrm{E}}\right)$$

which becomes

$$A_T = (E_\infty - E_T)\left(\frac{k_\mathrm{E} + k_\mathrm{S}}{k_\mathrm{E}}\right)$$

therefore

$$\frac{\mathrm{d}E}{\mathrm{d}T} = \frac{k_1 k_\mathrm{E}}{(k_\mathrm{E} + k_\mathrm{S})}\left(\frac{k_\mathrm{E} + k_\mathrm{S}}{k_\mathrm{E}}\right)(E_\infty - E_T)$$

which reduces to

$$\frac{\mathrm{d}E}{E_\infty - E_T} = k_1 \mathrm{d}T$$

which integrates to $-\ln(E_\infty - E_T) = k_1 T +$ constant. Since the alkene is the only absorbing species, then $\mathrm{OD}_\infty = \epsilon_\mathrm{E} El$ (OD is optical density), and the equation can be rewritten as

$$-\ln(\mathrm{OD}_\infty - \mathrm{OD}_E) = k_1 T + \text{constant}$$

Consequently the observed rate constant for alkene formation is, in fact, k_1 and the secondary β-deuterium isotope effect for carbocation formation is given by $k_1^\mathrm{H}/k_1^\mathrm{D}$.

The primary β-hydrogen–deuterium isotope effect for proton loss from the carbocation to give the alkene, $k_\mathrm{E}^\mathrm{H}/k_\mathrm{E}^\mathrm{D}$, can be determined from the product ratios. since

$$\frac{k_\mathrm{E}^\mathrm{H}}{k_\mathrm{S}^\mathrm{H}} = \frac{E^\mathrm{H}}{S^\mathrm{H}}$$

and

$$\frac{k_\mathrm{E}^\mathrm{D}}{k_\mathrm{S}^\mathrm{D}} = \frac{E^\mathrm{D}}{S^\mathrm{D}}$$

then

$$\frac{k_\mathrm{E}^\mathrm{H}}{k_\mathrm{E}^\mathrm{D}} = \frac{(\%E/\%S)_\mathrm{H}}{(\%E/\%S)_\mathrm{D}}$$

if the valid assumption is made that $k_\mathrm{S}^\mathrm{H} = k_\mathrm{S}^\mathrm{D}$.

It is seen that $k_1^\mathrm{H}/k_1^\mathrm{D}$ varies between 1.16 ± 0.01 and 1.62 ± 0.03, while values for $k_\mathrm{E}^\mathrm{H}/k_\mathrm{E}^\mathrm{D}$ vary between 1.6 ± 0.2 and 4.9 ± 2.0. In all cases the amount of alkene formed was decreased as a result of deuterium substitution at C_β; i.e. percent alkene was 55 ± 1.0 and 43 ± 1.0 for reaction of the 2-Me salt and its 2,2-d_2 analogue, respectively, while reaction of the 2,6-diMe compound and its 2,2-d_2 analogue led to values of percent alkene of 28 ± 1.0 and 11 ± 2.0, respectively. It is apparent, therefore, that a primary hydrogen–deuterium isotope effect is operative in the fast proton removal step. The values for the secondary β-deuterium isotope effects are consistent with literature values (38) for reactions proceeding by way of a slow rate-determining step involving carbocation formation, while the primary effects are reasonable in terms of the proposed mechanism where proton loss occurs in a fast step.

It appears from the data in Table 1 that the $k_1^\mathrm{H}/k_1^\mathrm{D}$ values are significantly lower when the substrate has only one *ortho* substituent as compared to two, i.e. $k_1^\mathrm{H}/k_1^\mathrm{D}$ = 1.22 ± 0.05 and 1.62 ± 0.03 found for reaction of the 2-Me and 2,6-diMe salts, respectively. As well, the magnitude of the primary β-hydrogen–deuterium isotope effect also is lower when the reactant has only one *ortho* substituent as compared to two, i.e. $k_\mathrm{E}^\mathrm{H}/k_\mathrm{E}^\mathrm{D}$ = 1.6 ± 0.2 and 3.1 ± 1.0 found for reaction of the 2-Me and 2,6-diMe substrates, respectively. Although a comparison of the primary isotope effects, which are similar within experimental error, is difficult due to the error involved in the determination of the % alkene when elimination is a minor process, it may be concluded that the increase in the magnitude of the secondary β-deuterium effect is due to an increase in carbocation character at the transition state.

Secondary β-deuterium isotope effects of approximately 1.3 (for two hydrogens (deuteriums)) found in the present study are in accord with literature values found for other solvolytic reactions leading to carbocation formation (38–41). It is generally considered (38) that secondary β-deuterium isotope effects arise due to hyperconjugative assistance by the β-hydrogens to the formation of the carbocation. The magnitude of this isotope effect, in the absence of competing reactions, participation, ion-pairing, etc., depends on the ability of the β-CH(D) bond to overlap with the developing vacant orbital of an incipient carbocation at C_α. When they are orthogonal, a kinetic isotope effect of unity is expected (42, 43). Consequently, for the reaction under study where a normal secondary β-deuterium isotope effect is found, it appears that rotation is sufficiently free about the C_α—C_β bond to allow the required overlap.

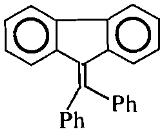
As indicated earlier in the discussion section, the salts with only one *ortho* substituent react at a slower rate in ethanol but give a greater yield of elimination product, as compared to the reaction of the *ortho*-disubstituted compounds. As well, it was noted that a *para* substituent had a negligible effect on the solvolytic process, indicating the absence of a significant polar effect due to the alkyl groups. It appears, therefore, that the reaction of the ammonium salts in ethanol in the present investigation is promoted by "steric acceleration" due to the bulky trimethylammonium group (14, 44), leading to the favourable conversion of a tetrahedral carbon to a less crowded trigonal carbon. Dreiding stereomodels indicate considerable interaction between the *ortho* substituents and the 1,8 hydrogens on the fluorene ring as well as with the onium group. This supports the observation, Table 1, that the 2,6-diCl salt is less reactive than the 2,6-diMe compound but more reactive than the 2,4-diMe substrate since chlorine is "smaller" than methyl (Taft E_S steric substituent scale).

The accelerating effect of the relief of steric strain has been investigated by a series of workers for a variety of reactions (45–49). To our knowledge, however, the accelerating effect observed in the present study is only the second example (14) where a trialkylammonium salt (poor leaving group) undergoes solvolysis to give an alkene in an E1 process.

The observed variation of the alkene:ether ratio (% alkene) with the number of *ortho* substituents indicates that the alkene forming step (k_E) becomes less favourable relative to the competing ether forming step (k_S) for reaction of the di-*ortho*-

substituted compounds as compared to the reaction of the mono-*ortho*-substituted substrates. It is generally considered that, for reactions proceeding by way of a carbocation intermediate, the most important factor that determines the relative amount of elimination and substitution products is the stability of the alkene. The more stable the alkene the greater the amount of alkene product relative to the substitution product.

Extensive studies have been carried out on both the static and dynamic stereochemistry of "crowded" ethylenes (50–55) and it is now clear that bulky groups attached to the ethylenic carbons can lead to a twisting about the ethylene bond. Furthermore, it has been concluded (56, 57) that both 1,1-diphenylethylene and 9-diphenylmethylenefluorene **13**, which is related to the alkenes formed in the present study, have a phenyl group twisted out of the plane of the molecule due to steric interactions between the groups attached to the double bond. This is illustrated in **14** for the alkenes formed in the present study where the *ortho* methyl group "interacts" with the 1,8 hydrogens of the fluorene nucleus. The addition of a second *ortho* group to **14** (R^1 = CH_3) will lead to a further decrease in the planarity of the alkene, leading to decreased stability and hence a decrease in the percent alkene formed as observed.



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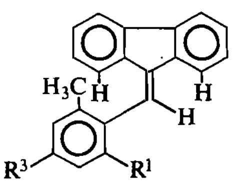

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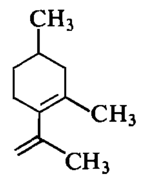
The proposal that the interaction between the *ortho* methyl groups with the 1,8 hydrogens on the fluorene nucleus leads to a decrease in the stability of the alkene receives support from uv spectroscopic data (see the experimental section). The λ_{max} values for the solutions of the *ortho*-substituted alkenes (obtained from compounds **4–9**) are the same within experimental error but are significantly lower[7] than those of the corresponding *para*-substituted alkenes where the *ortho* groups are hydrogens. The twisting of the aryl groups out of the plane of the double bond and the fluorenyl ring will lead to a decrease in the extent of conjugation and hence to higher energy electronic transitions. Such steric inhibition to effective conjugation has been observed in other systems (59, 60), where it was found that the conjugated 1,3 diene **15** did not have a uv maximum down to 200 nm whereas the structurally related conjugated diene **16** exhibited a more normal uv maximum at 232 nm.



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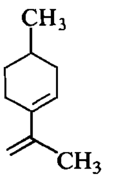

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An alternative explanation for the changes in alkene:ether ratios effected by *ortho* substitution can be considered since it has been proposed that reaction to give the carbocation is induced by significant steric interactions in the substrate. The solvated carbocation can be neutralized by either proton loss from C_β with solvent acting as the base or by direct substitution of solvent to give the ether. Steric access of solvent to the carbocationic centre and the β-hydrogen could play a role in determining the relative amounts of the two products. This possibility will be discussed in the following section where the effect of solvent changes on both the rate of alkene formation and on product ratios is considered.

*Reaction of 9-(*ortho*-substituted phenylmethyl)fluoren-9-yltrimethylammonium ions in various solvents at 57.3°C*

A test for the carbocation mechanism proposed for the reaction of the *ortho*-substituted salts in ethanol, eq. [4], is determination of the effect of a change in the reaction medium on both reaction rate and product composition. Accordingly, the k_1 values for alkene formation as well as the percent alkene were determined for the reaction of three representative compounds, 2-Me, 2,6-diMe, and 2,4,6-triMe salts, in a variety of solvents, Table 3. The hydrogen–deuterium isotope effects, k_1^H/k_1^D and k_E^H/k_E^D, are also included.

It is seen that for reaction of all three substrates the amount of elimination product, % alkene, varies significantly when the alcohol solvent is changed; i.e. the percent alkene formed for reaction of the 2,6-diMe salt in ethanol, 2-propanol, and *tert*-butyl alcohol was 28, 52, and 100, respectively, while reaction of the 2-Me compound gave 43, 55, and 100% alkene for reaction in methanol, ethanol and *tert*-butyl alcohol, respectively. For reaction in all of the solvents studied, with the exception of the *tert*-butyl alcohol solvent where all the compounds gave exclusively the alkene product, the mono-*ortho* salt gave a greater percentage of alkene than the di-*ortho*-substituted compounds, in agreement with the results obtained for reactions in ethanol.

The increase in the amount of alkene formed when the solvent is varied from methanol to ethanol, 2-propanol, and *tert*-butyl alcohol can be attributed to an increase in the rate of proton abstraction as compared to the direct attack of solvent at the carbocationic centre. As the "size" of the alcohol molecule increases (primary < secondary < tertiary), the transition state for reaction proceeding to the ether products becomes more sterically crowded and, hence, of higher energy. This leads to a decrease in the amount of substitution relative to elimination.

Brown and Fletcher (61) were the first to suggest that steric effects are mainly responsible for the increase in olefin yields in reactions proceeding by way of a carbocation intermediate. They considered that since the trigonal carbocation is less strained than both the tetrahedral reactant and substitution product, an increase in the size of the groups attached to the reaction centre carbon would lower the rate of the substitution reaction relative to the elimination process.

With the *exception* of the results obtained for reaction in *tert*-butyl alcohol, the k_1 values for the reaction of the three compounds (**4**, **6**, and **8**) increased when the polarity of the alcohol solvent (as given by both *Y* and *Z* values) decreased. The k_1 values for reaction of the 2,6-diMe salt in 95% ethanol, ethanol, and 2-propanol were 212×10^{-5}, 294×10^{-5}, and 337×10^{-5} (s^{-1}), respectively. Similarly, the 2,4,6-triMe compound produced the alkene with rate constants of 245×10^{-5} and 297×10^{-5} (s^{-1}) for reaction in methanol and ethanol,

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[7] P. J. Smith, D. S. K. Tsui, and G. S. Dyson. Unpublished results.

respectively. A study of the reaction of the 2-Me salt in 70% ethanol, 95% ethanol, methanol, and ethanol gave rate constants of 0.93×10^{-5}, 1.58×10^{-5}, 2.18×10^{-5}, and 2.35×10^{-5} (s^{-1}), respectively.

The observed trends in rate constants when the solvent is changed from methanol to the aqueous ethanol solutions, ethanol, and 2-propanol are predictable since the charged substrates, which will be solvated in the polar media, react via a transition state where there is charge dispersal. Consequently, reaction of a charged substrate proceeding via the rate-determining formation of a carbocation will proceed at a faster rate in a less polar solvent.

It was anticipated that the reaction of both the 2-Me and 2,6-diMe salts would proceed at the greatest rate in *t*-BuOH, the least polar solvent studied. However, the k_1 values were found to be the lowest in this solvent for reaction of both the 2-Me and 2,6-diMe compounds, Table 3. This unexpected effect of *tert*-butyl alcohol on the rate of reaction can perhaps be attributed to solvation effects. It has been suggested (8) that direct solvation of the positive nitrogen of the trimethylammonium group is unlikely, and that the interactions occur between solvent and the C—H dipoles induced by the positive nitogen. While *t*-BuOH and the other alcohol solvents can participate in this solvation, perhaps *t*-BuOH is less able to solvate the carbocationic intermediate for steric reasons.

In order to gain additional information concerning the reaction of the *ortho*-substituted salts, the thermodynamic activation parameters were determined for the reaction of the 2-Me, 2,6-diCl, and 2,6-diMe compounds in ethanol and also for the reaction of the 2,6-diMe substrate in 2-propanol. The appropriate rate constants and the percent alkene determined for reaction at three different temperatures along with values for E_A, $\Delta H^{\neq}$(60°C), and $\Delta S^{\neq}$(60°C) are given in Table 4. The Arrhenius plots all gave correlation coefficients better than 0.99.

The data in Table 4 indicate that the magnitude of $\Delta H^{\neq}$ decreases when a second *ortho* substituent is placed on the phenyl ring; $\Delta H^{\neq}(60°C) = 36.2$ and 29.6 kcal mol^{-1} for reaction of the 2-Me and 2,6-diMe substrates, respectively. As well, it is seen that the reaction of the 2,6-diMe salt (a charged substrate) has a lower enthalpy of activation when carried out in a solvent of decreased polarity; $\Delta H^{\neq}(60°C) = 29.6$ and 27.7 kcal mol^{-1} for reaction in absolute ethanol and 2-propanol, respectively. These results are consistent with the suggestion of steric acceleration promoting the ionization process via a charge-dispersed transition state.

The positive values for $\Delta S^{\neq}$ found for the reactions is consistent with reduced solvation at the transition state as compared with the initial state. A trend in $\Delta S^{\neq}$ is noted when the substrate is changed from 2-Me to 2,6-diCl to the 2,6-diMe compound for reaction in ethanol; $\Delta S^{\neq}(60°C) = 29.9$, 26.2, and 19.4 cal K^{-1} mol^{-1}, respectively. It may be concluded that reaction of the di-*ortho*-substituted compounds in ethanol are less entropically favoured due to decreased solvation of the ammonium ion for steric reasons. The change in the value $\Delta S^{\neq}$ when the solvent for the reaction of the 2,6-diMe compound is changed from ethanol to 2-propanol can be rationalized similarly, since 2-propanol will solvate the onium group to a lesser extent ($\Delta S^{\neq}(60°C) = 13.7$ and 19.4 cal K^{-1} mol^{-1} for the reaction of the 2,6-diMe salt in 2-propanol and ethanol, respectively).

The observed isotope effects, k_1^H/k_1^D, for reaction of the 2-Me, 2,6-diMe, and 2,4,6-triMe salts in the various solvents fall in the range between 1.1 and 1.7, Table 3. These values are consistent with the expected values for a secondary β-deuterium isotope effect associated with rate-determining carbocation formation. There does not appear to be a trend in the magnitude of these isotope effects for reaction of the three salts when the solvent is varied. The values for k_E^H/k_E^D lie in the range between 1.2 and 5.1. The error involved in the determination of these values does not allow a detailed discussion on the observed variations when the three substrates are reacted in the different solvents. It has been pointed out (62) that α- and β-deuterium effects in solvolytic reactions generally do not strongly depend on solvent changes.

As noted earlier, reaction of both the 2-Me and 2,6-diMe compounds in *tert*-butyl alcohol gave the alkene product in 100% yield. Consequently the values of k_1^H/k_1^D (the secondary β-deuterium isotope effect for slow rate-determining carbocation formation) of 1.24 and 1.57, for reaction of the 2-Me and 2,6-diMe compounds, appear to be significantly different. The difference between these two values indicates that the respective transition states for carbocation formation differ in the extent of positive charge developed at the 9-fluorenyl carbon and (or) that the extent to which the β-hydrogens can stabilize the developing charge by hyperconjugation is different (presumably for steric reasons).

*Reaction of 2-substituted-9-(*ortho*-substituted phenylmethyl)-fluoren-9-yltrimethylammonium ions in the aprotic solvent chloroform*

In order to further investigate the solvolytic reaction of the *ortho*-substituted compounds, it was decided to measure the rate of alkene formation for reaction of several substrates in the nonpolar aprotic solvent chlorform. It was reasoned that reaction in this nonpolar solvent would be favourable due to charge dispersal at the transition state for carbocation formation. Furthermore, reaction cannot proceed with solvent acting as either the base or nucleophile, and only the counterion, bromide, is capable of abstracting the β-hydrogen.

The rate of alkene formation, k_1, for reaction of the 2-Me, 2,6-diMe, and 2,4,6-triMe compounds was determined at 50°C in chloroform, Table 5, as well as the secondary β-deuterium isotope effects, k_1^H/k_1^D. In all cases the alkene was formed in 100 ± 5% yield. The present results are in contrast to earlier studies (63)[8] on the reaction of quaternary ammonium salts in chloroform, where substitution products were formed exclusively.

Reaction of the three salts in chloroform appears also, as in the other solvents, to proceed via the E1 mechanism. The observed ρ value of −2.3 and values of $k_1^H/k_1^D = 1.47–1.88$, which are unlikely to be primary effects, are consistent with reaction proceeding via a carbocation intermediate.

The variation in the k_1 values with changes in the *ortho* substituents follows the same trend for reactions of the salts in chloroform as in the other solvents. The observed rate constants for reaction of the di-*ortho*-substituted salts, 2,6-diMe and 2,4,6-triMe, at 50°C are 88.9×10^{-5} and 108×10^{-5} (s^{-1}), respectively, while the rate constant for reaction of the mono-*ortho*-substituted compound, 2-Me, is 0.76×10^{-5} (s^{-1}). Presumably, reaction in chloroform, as in the other solvents, is promoted by steric relief.

Reaction of the *ortho*-substituted salts in chloroform appears to be similar to that in the poorly solvating *tert*-butyl alcohol

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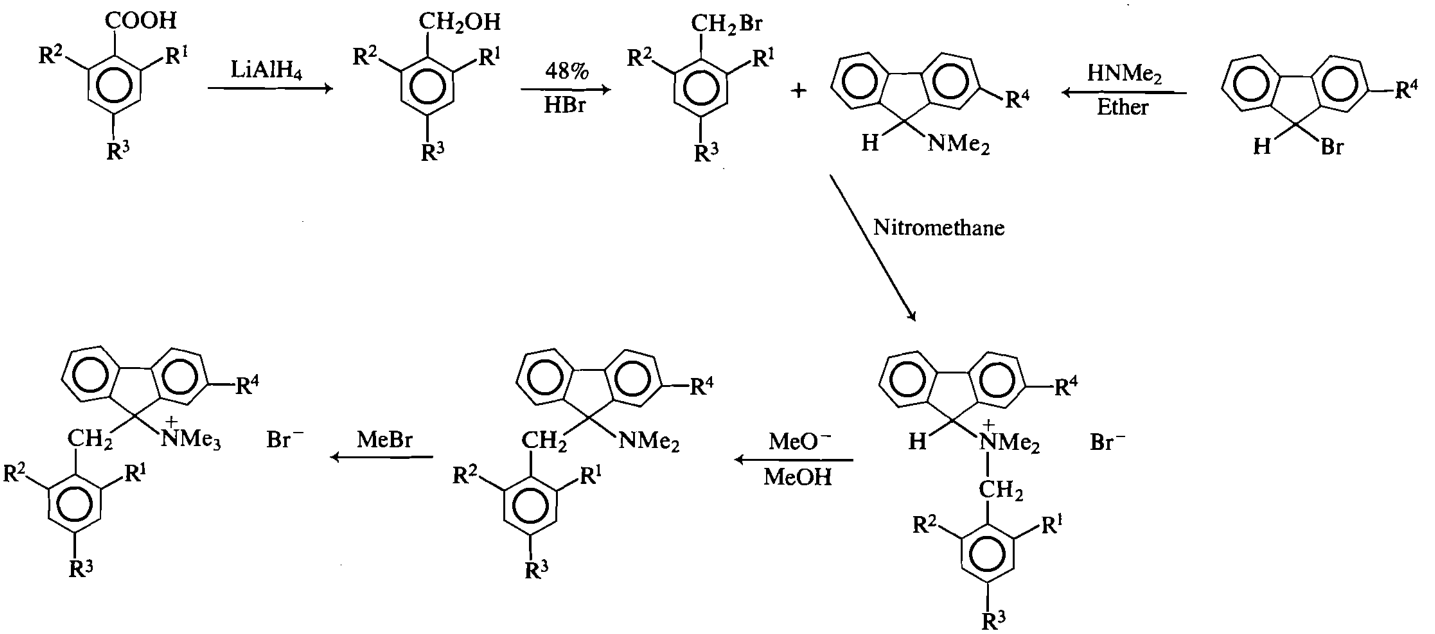
[8] K. C. Westaway and H. Joly. Private communication.



SCHEME 1. Synthetic route to 9-(*ortho*-substituted phenylmethyl)fluoren-9-yltrimethylammonium bromides.

solvent. This is reasonable since the onium group of the reactant and the developing carbocationic centre will be very poorly solvated in both solvents. Perhaps in chloroform the quaternary ammonium halides exist to a significant extent as ion pairs.

Experimental

Melting points are uncorrected. The ^1H nmr spectra were determined on a Varian T60 spectrometer. Mass spectra were obtained on an AEI M-12 mass spectrometer. Elemental analyses were carried out by the Guelph Chemical Laboratories, Guelph, Ontario, Canada. All reagents and solvents were reagent grade and were dried and purified by the usual procedures.

The synthetic pathways for most of the compounds in this study were similar and are outlined in Scheme 1. The deuterated substrates were all better than 95% deuterated since nmr and mass spectrometric analyses indicate complete deuteration.

Benzyl alcohols which were not commercially available and the α,α-dideuterated analogues of the benzyl alcohols were prepared by reduction of the corresponding benzoic acid or the methyl ester (65, 66).

2,6-Dimethylbenzyl alcohol

A solution of 2,6-dimethylbenzoic acid (80 g, 0.53 mol) in 500 mL of anhydrous diethyl ether was added to a slurry of $LiAlH_4$ (30 g, 0.79 mol) in 350 mL ether. After refluxing for 108 h the excess lithium aluminum hydride was destroyed using 30 mL water and 150 mL 10% sulphuric acid. The organic layer was separated and the aqueous layer washed three times with ether. The combined organic extracts were dried and evaporated to give 2,6-dimethylbenzyl alcohol, which was recrystallized from absolute ethanol; 77% yield, mp 80.5–81°C (lit. (67) mp 81–82°C).

2,6-Dimethylbenzyl bromide

2,6-Dimethylbenzyl alcohol (27.2 g, 0.2 mol) was refluxed with 48% HBr (105 g, 1.3 mol) for 5 h (58). After work-up, 35.9 g (0.18 mol) of 2,6-dimethylbenzyl bromide was obtained (90% yield). Since the nmr mass spectra showed no impurities and because of the extreme lachrymatory nature of the compound, it was used without further purification.

9-Fluorenyldimethylamine

Anhydrous dimethylamine gas was passed into an ice-cold solution of 49.4 g (0.2 mol) of 9-bromofluorene dissolved in 500 mL of anhydrous diethyl ether for 0.5 h. This mixture was stirred for a further 2 h and the resulting white precipitate was filtered off. The solvent was removed from the yellow filtrate using a rotary evaporator to give a solid, which on crystallization from *n*-hexane afforded pale yellow crystals (35.3 g, 0.17 mol) in 84% yield; mp 47.5–48°C; nmr and mass spectra confirmed the structure.

2,6-Dimethylphenylmethyl-9-fluorenyldimethylammonium bromide

A 10-mL solution of 18.5 g (0.093 mol) of 2,6-dimethylbenzyl bromide in nitromethane was added to a solution of 21 g (0.01 mol) of *N*,*N*-dimethylfluoren-9-ylamine in 20 mL of nitromethane. This mixture was stirred for 15 h and 200 mL of anhydrous diethyl ether was added to precipitate the salt. The white precipitate was filtered and dried and then recrystallized from ethanol–ether to give 29.3 g (0.072 mol) of pure compound in 78% yield, mp 169–170°C. The melting points of the various analogues of this compound are given in Table 6.

N,N-Dimethyl-9-(2,6-dimethylphenylmethyl)fluoren-9-ylamine

2,6-Dimethylphenylmethyl-9-fluorenyldimethylammonium bromide, 22.6 g (0.055 mol), was dissolved in 40 mL of methanol. Freshly cut metallic sodium, 4.6 g (0.2 mol), dissolved in 40 mL of methanol was added to the ammonium salt solution. This reaction mixture was stirred for 10 h at room temperature and then poured into 100 mL of water. This was extracted four times with 50-mL portions of chloroform. The combined organic extracts were dried over anhydrous $MgSO_4$ and rotary evaporated to give the crude amine, 17.2 g (0.053 mol) in 96% yield, mp 105–105.5°C. Repeated crystallization from 95% ethanol gave a pure white compound with satisfactory C, H, N analysis. The nmr and mass spectra confirmed the structure. The other *ortho*-substituted amines were similarly prepared by the Steven's rearrangement and the pertinent data is given in Table 7.

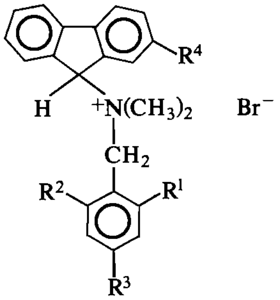
9,(2,6-Dimethylphenylmethyl)fluoren-9-yltrimethylammonium bromide

Pure *N*,*N*-dimethyl-9-(2,6-dimethylphenylmethyl)fluoren-9-ylamine, 2 g (0.0061 mol), was dissolved in 10 mL of sodium-dried benzene. This was refluxed with 20 mL of bromomethane at 0°C till turbidity was observed. The mixture was maintained at 5°C for a few days and the pure white solid was filtered off using a sintered glass funnel and washed three times with sodium-dried benzene (16% yield). Mass spectra and elemental analysis, Table 8, confirmed the structure.

2,6-Dimethylphenyldibenzofulvene

2,4-Dimethylbenzyltriphenylphosphonium bromide, 9.5 g (0.021 mol), prepared by Wittig's method (64), in 20 mL of dry benzene was

TABLE 6. The melting points of 2-substituted-9-fluorenyl-(*ortho*-substituted)-phenylmethyldimethylammonium bromides



Compound		Melting point (°C)
$R^4 = H$	$R^1 = Me; R^2 = R^3 = H$	140–141
$R^4 = H$	$R^1 = R^3 = Me; R^2 = H$	120–121
$R^4 = H$	$R^1 = R^2 = Me; R^3 = H$	134–134.5
$R^4 = H$	$R^1 = R^2 = Cl; R^3 = H$	138–139
$R^4 = H$	$R^1 = R^2 = R^3 = Me$	116–119
$R^4 = Br$	$R^1 = R^2 = Me; R^3 = H$	220–222

stirred under nitrogen for 2 h with 3 g of sodium *tert*-butoxide. After the addition of 4 g (0.022 mol) of fluorenone in 50 mL of dry benzene the solution was stirred for another 2 h. The crude alkene obtained after work-up was separated on an alumina column (2 cm × 40 cm) using hexane as a solvent. The product was further purified by recrystallization from 95% ethanol, mp 165–165.5°C. The elemental analysis data for the above alkene and the related dibenzofulvenes are given in Table 9.

Kinetic measurements

The reactions were carried out in cuvettes with gas-tight covers inside a Bausch and Lomb Spectronic 710 instrument. The cuvette holder was linked to an external Haake FS circulator. The temperature of the water in the circulator was maintained at ±0.02°C. The temperature at which kinetic measurements were made was the actual temperature inside the cuvette, measured using a thermocouple attached to a digital thermometer. The fluctuations in the temperature in the cuvette were less than ±0.05°C.

Since the absorbance of the sample under study had to be directly measurable, the concentrations of the quaternary ammonium salt solution had to be appropriately adjusted. A stock solution of the compound under study was made using the dry ethanol (or the other solvents) at room temperature. These solutions were stored in the refrigerator and it was found that, except for the very reactive 2,6-diMe and the 2,4,6-triMe substrates, the storage did not affect the initial absorbance readings over a period of months.

Just before a kinetic run was initiated, the solution of the quaternary salt was brought to room temperature. A small amount was poured into a uv cell that had been rinsed with the solution. The tightly stoppered cuvette was fitted into the cuvette holder of the uv spectrometer and the timer started. A matched reference cell containing only the solvent was used to zero the absorbance before a reading was noted. In most cases the first reading was taken after at least 3 min so that the reaction mixture was in thermal equilibrium with the surroundings. The absorbance values were then taken at the appropriate time intervals. The reactions were generally followed up to 40–80% completion and at least three runs were made for each compound. Since it was not possible to measure more than one kinetic run at a time, the rates of reaction of the hydrogen and the deuterium substrates had to be measured consecutively within the least possible time.

The wavelength of the uv light used was fixed at 320 nm. It was determined that at this wavelength the product of the substitution reaction, the ether, did not have any significant absorption. Therefore, the change in the optical density that was monitored was due only to the increasing concentration of the alkene products.

The infinity readings were obtained by taking 5-mL aliquots of the initial salt solution in 10-mL volumetric flasks and filling to the mark. This was done in triplicate. These flasks were then lowered into an oil bath, which was maintained at the temperature of the reaction, and allowed to stand for at least 8–10 half-lives. These flasks were then withdrawn at different times and allowed to reach room temperature. If any solvent loss had occurred it was made up by addition of the pure solvent to the volumetric flask. A sample of this solution was used to measure the absorbance, which was the value at infinite time. This was repeated with the other two flasks. The infinity reading was taken as the average of the three readings. Using this average value of absorbance at infinite time, $\ln (A_\infty - A_t)$ was plotted versus time to obtain good linear first-order plots. At least three such plots for each compound were obtained. The experimentally obtained data were treated by least-squares analysis to determine the first-order rate constants using a HP 200A computer.

The *ortho*-substituted phenyldibenzofulvene solutions in the various solvents were used to determine values of the extinction coefficients at various wavelengths, Table 10. These extinction coefficients and the absorbance at infinite time were used to calculate the percent alkene formed in the reaction.

TABLE 7. The melting points and elemental analysis of the 9-(*ortho*-substituted phenylmethyl)fluoren-9-yldimethylamines

			Elemental analysis		
Compound		Melting point (°C)	C	H	N
$R^4 = H$	$R^1 = Me; R^2 = R^3 = H$	87–87.5	88.38 (88.14)	7.35 (7.40)	4.37[a] (4.47)[b]
$R^4 = H$	$R^1 = R^3 = Me; R^2 = H$	74.5–75	87.72 (88.03)	7.91 (7.70)	4.17 (4.28)
$R^4 = H$	$R^1 = R^2 = Me; R^3 = H$	105–105.5	87.96 (88.03)	7.58 (7.70)	4.11 (4.28)
$R^4 = H$	$R^1 = R^2 = Cl; R^3 = H$	135–135.5	71.62 (71.75)	5.14 (5.20)	3.72 (3.80)
$R^4 = H$	$R^1 = R^2 = R^3 = Me$	112–112.5	87.88 (87.93)	8.10 (7.97)	4.08 (4.10)
$R^4 = Br$	$R^1 = R^2 = Me; R^3 = H$	128.5–129	71.09 (70.94)	5.77 (5.95)	3.61 (3.45)

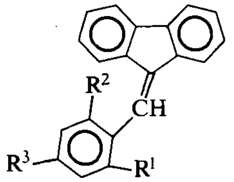
[a] Experimentally observed values.
[b] Theoretical values.

TABLE 8. Elemental analysis of the 9-(*ortho*-substituted phenylmethyl)-fluoren-9-yltrimethylammonium bromides

Compound number	C, H, N analysis C	 H	 N
4	70.21 (71.09)	6.60 (6.68)	3.21[a] (3.32)[b]
4-d_2	69.94 (70.75)	6.60 (7.12)	3.38 (3.30)
5	59.63 (59.95)	4.79 (4.97)	3.02 (2.93)
5-d_2	59.54 (59.38)	5.23 (5.20)	3.11 (3.01)
6	70.40 (70.59)	6.38 (6.42)	3.37 (3.43)
6-d_2	69.12 (70.24)	6.71 (6.88)	3.37 (3.41)
7	70.80 (71.09)	6.71 (6.88)	3.23 (3.32)
7-d_2	70.30 (70.75)	7.00 (7.12)	3.35 (3.30)
8	70.92 (71.55)	7.11 (6.93)	3.28 (3.21)
8-d_2	68.69 (71.23)	7.00 (7.36)	3.66 (3.20)
9	71.09 (70.94)	5.77 (5.95)	3.61 (3.45)

[a] The top row numbers refer to the experimental value.
[b] These figures refer to theoretical values.

TABLE 9. The melting points and elemental analysis of the *ortho*-substituted phenyldibenzofulvenes



Substituent	Melting point (°C)	Elemental analysis
2-Me	110.5–111.5	C 93.84, H 5.94[a] (C 93.99, H 6.01)[b]
2,4-diMe	88–88.5	C 92.51, H 6.42 (C 93.62, H 6.38)
2,6-diMe	165–165.5	C 93.27, H 6.39 (C 93.62, H 6.38)
2,6-diCl	123–125.5	C 74.55, H 3.78 (C 74.32, H 3.74)
2,4,6-triMe	115.5–116	C 93.53, H 6.49 (C 93.20, H 6.80)

[a] Experimentally observed values.
[b] Theoretical values.

TABLE 10. The ultraviolet absorption data for the *ortho*-substituted phenyldibenzofulvenes in ethanol

Substituent	λ_{max} (nm)	Molar extinction coefficient at λ_{max} ($\times 10^{-4}$)	Molar extinction coefficient at 320 nm ($\times 10^{-4}$)
2-Me	311	1.36	1.20
2,6-diMe	310	1.16	0.753
2,4-diMe	311	1.37	1.36
2,4,6-triMe	309	1.52	1.08
2,6-diCl	310	1.39	0.868

Kinetic measurements by nuclear magnetic resonance method

The rates of reaction of the 2-Me, 2,6-diMe, and the 2,4,6-triMe substrates and the β-d_2 analogues of the 2,6-diMe and the 2,4,6-triMe compounds in chloroform at 50°C were determined by following the disappearance of appropriate hydrogen signals using a nmr spectrometer.

A dilute solution of the ammonium salt in $CDCl_3$ was prepared at room temperature and immediately placed in the probe of a Brüker WP-80 spectrometer maintained at 50°C. Several peaks in the spectrum (usually the peaks due to the hydrogen of the $—N^+(CH_3)_3$ and the ring methyl groups) were integrated at suitable times using chloroform as an internal standard. The slope of the plot of log (integral of the appropriate peak) against time was determined by least squares. The rate constants determined by monitoring the disappearance of several different hydrogen signals agreed to within 5% in all cases.

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