Effect of Alkene Structure on the Course of Reactions with XeF$_2$ and CsSO$_4$F [1]

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XeF$_2$ reacted at room temperature in dichloromethane in the presence of HF with triphenylethene, 9-benzylidenefluorene and tetraphenylethene to form vicinal difluorides in high yield, the relative reactivities being in the following order: 1,1-diphenylethene:triphenylethene:tetraphenylethene:9-benzylidenefluorene = 0.4:1:1.1:0.2. CsSO$_4$F did not react at 35 °C with phenyl substituted alkenes in dichloromethane, while vicinal fluoro-methoxy adducts were formed in the presence of methanol. The methoxy group entered according to the Markovnikov rule for regioselectivity in the case of triphenylethene and 9-benzylidenefluorene, with the relative reactivities: 1,1-diphenylethene:triphenylethene:tetraphenylethene:9-benzylidenefluorene =1.2:1:0.2:0.3.

The reactivity of fluorinating agents [2-4] strongly depends on the structure of the reagent, the structure of the organic molecule and the reaction conditions, where solvent, catalyst and temperature are the most important factors. Prediction of the course of fluorine atom introduction into organic molecules is still only a partly solved problem, but in order to improve our knowledge about the role of the reagent structure in the course of fluorination, as much information as possible is needed on several target organic molecules. Phenyl substituted alkenes represent excellent target [5] molecules for fluorination and, of these, 1,1-diphenylethene is that most widely used, because the products usually formed are stable enough for conclusions to be drawn from the product distribution. The following main processes have already been observed: addition, addition–elimination, rearrangement and dimerisation. Low-temperature elemental fluorination of 1,1-diphenylethene [6] resulted mainly in an addition–elimination process, 2-fluoro-1,1-diphenylethene being observed as the main product. Low-temperature reaction with CF$_3$OF was more complex and up to five products were formed,[7] while the reaction with OF$_2$ gave α-fluoroacetophenone [8] as the main product; the low temperature reaction with Pb(OAc)$_4$–HF resulted in rearranged 1,2-difluoro-1,2-diphenylethane.[9] In contrast, room temperature reactions with XeF$_2$ in the presence of HF gave vicinal difluorides in high yield,[10] rearranged 1,1-difluoro-1,2-diphenylethane was formed by various aryl substituted iodo(III) difluorides,[11] while reactions with CsSO$_4$F depended on the reaction conditions: in dichloromethane the addition–elimination process occurred but in the presence of HF and other nucleophiles (acetic acid, methanol, *etc.*), the ratio of the addition *versus* the addition–elimination process varied according to the medium.[12] It has already been demonstrated that the reactions of organic molecules with XeF$_2$ depends on the catalyst used, so that the fluorination of a less reactive substrate could be achieved with BF$_3$ as catalyst,[13] while BF$_3$–diethyl ether [14] and BF$_3$ immobilised on a polymer matrix [15] were much milder. Moreover, the course of the reaction could also be modulated by the type and the amount of catalyst.[16] For reactions of XeF$_2$ with olefins in the presence of CF$_3$CO$_2$H [17] or alcohols,[18] only a small variation in the structure of the olefin or catalyst can completely change the course of the reaction. Similar sensitivity to the reaction conditions has also been pointed out by Zefirov *et al.,*[19] who found that CsSO$_4$F reacted with an excess of olefin so that vicinal fluoro sulfates were formed with predominately anti-Markovnikov type regioselectivity, while we found that fluorination in methanol followed the Markovnikov type of regioselectivity.[20] In order to further our understanding of

the role of the olefin and fluorinating reagent structure and to clarify the literature,[18,19] we now report further studies on the reactions of various phenyl substituted olefins [5] with XeF$_2$ and CsSO$_4$F.

Results and Discussion
The substitution of the alkyl group by a phenyl ring usually increases the reactivity of the alkene and this effect usually strongly depends on the reagent and the reaction conditions. Styrene is twice as reactive towards bromination in methanol than propene, and the introduction of a further phenyl ring in the case of 1,1-diphenylethene [21] increases the reactivity 25 times; however 1,1-diphenylethene is 13 times more reactive than styrene to oxidation with chromyl chloride and only 4 times more reactive in the epoxidation with peracetic acid. Further introduction of a phenyl ring, *e.g.* triphenylethene, decreases the reactivity in comparison with diphenylethene 8.3 times in the reaction with peracid and 32 times in the oxidation with chromyl chloride. A fourth phenyl group diminishes the reactivity of tetraphenylethene by 37 times in comparison with triphenylethene and 1150 times in comparison with 1,1-diphenylethene in the oxidation with chromyl chloride.[21] Phenyl substituted alkenes are usually more convenient model substances for the investigation of the role of the reagent structure in halogenations than their aliphatic analogues, especially for fluorination, because fluorides or vicinal fluorides are more stable (the decomposition of the primary products, which are very sensitive to even small amounts of HF, can be prevented by the addition of a small amount of tributylamine immediately after the reaction is completed, while the polymerisation process during the reaction can be decreased or even prevented in some cases by higher dilution). The course of the reaction with phenyl substituted alkenes depends on the structure of the alkene, and comparison of the product distribution with model olefins enabled us to gain further information about the role of reagent structure and the reaction conditions on the course of the reaction. There are two main possibilities in the reactions of phenyl substituted alkenes: addition or the addition–elimination process (presented in Scheme 1). We know that the degree of the addition–elimination process strongly depends on the nature of the L-part of the halogenating agent L–X (in the case of fluorine the addition–elimination process is predominant, while in the fluorination of 1,1-diphenylethene with XeF$_2$ the addition process was observed exclusively). Further, we can gain a better understanding of the role of the L-part of the reagent, and especially the solvent in the processes before the
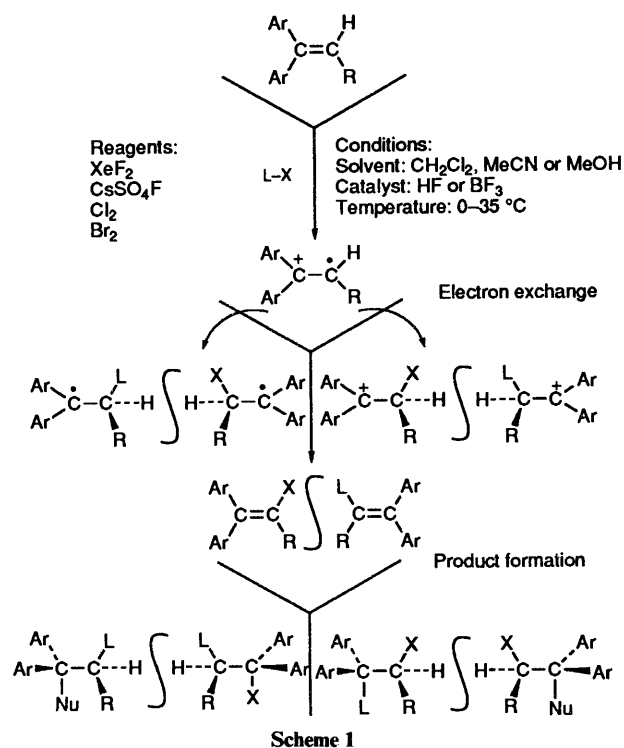
Reagents:
XeF$_2$
CsSO$_4$F
Cl$_2$
Br$_2$

Conditions:
Solvent: CH$_2$Cl$_2$, MeCN or MeOH
Catalyst: HF or BF$_3$
Temperature: 0–35 °C

Electron exchange

Product formation

Scheme 1

Table 1 The effect of alkene and reagent structure on relative rates of reactions (relative to triphenylethene)

	Alkene		
Reagent	1a	1c	1d
XeF$_2$–HF	0.4	1.1	0.2
CsSO$_4$F–MeOH	1.3	0.2	0.3
CrO$_2$Cl$_2$[21]	31.9	0.03	
PhCOOOH[21]	8.3		

formation of a β-halogenium ion or some other species, by the careful analysis of product composition regioselectivity and the degree of solvent or other competitive nucleophile incorporation.

First, we studied the HF-catalysed reaction of XeF$_2$ in dichloromethane at room temperature with triphenylethene **1b** and found that 1,2-difluoro-1,1,2-triphenylethane was formed in high yield; similar reactions with tetraphenylethene **1c** and 9-benzylidenefluorene **1d** also gave vicinal difluorides in high yield. We also studied the effect of substrate structure on the fluorination and found that introduction of a phenyl group into the diphenylethene did not decrease the reactivity as observed in the case of oxidation, and that tetraphenylethene was slightly more reactive than triphenylethene, while 9-benzylidenefluorene **1d** was five times less reactive than triphenylethene (Scheme 2), Table 1. Shellhamer and co-workers demonstrated[18] that XeF$_2$ reacted with alcohols and the formation of F–XeOR species was suggested; however, the reactivity of the new reagent depended on the catalyst HF or BF$_3$. In the presence of HF, fluorine was suggested to be an 'electrophilic species', while in the case of the BF$_3$-catalysed reaction a 'positive oxygen' electrophile explained the formation of vicinal alkoxy fluorides and their regioselectivity in the reactions with (Z)- and (E)-1-phenylpropene and indene. To verify these suggestions we carried out the following experiments: triphenylethene (0.5 mmol) was dissolved in dry

1a R^1 = R^2 = Ph, R^3 = R^4 = H   1c R^1 = R^2 = R^3 = R^4 = Ph
1b R^1 = R^2 = R^4 = Ph, R^3 = H

1d

Scheme 2
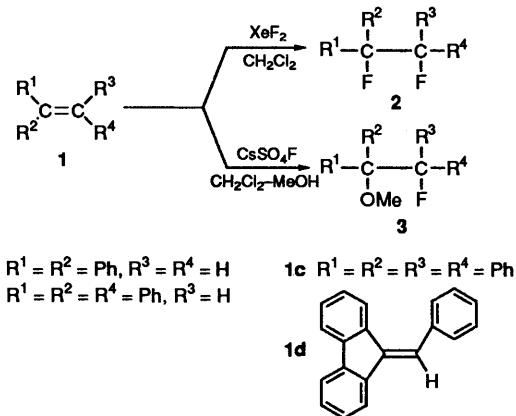
methanol (5 cm^3) [in the second experiment we added dichloromethane (0.2 cm^3) because of the low solubility of the alkene in methanol], to which XeF$_2$ (0.5 mmol) was added with stirring at 0 °C and finally HF gas or BF$_3$ gas (or BF$_3$–diethyl ether or BF$_3$ complex with methanol); only a small change in colour from light yellow to orange and slow Xe gas evolution were observed. After 4 h, when no further Xe gas evolution was observed, the mixture was poured into water and extracted with diethyl ether. The extract was dried and evaporated under reduced pressure and the crude reaction mixture was analysed by ^{1}H and ^{19}F NMR spectroscopy. No fluorination had occurred only the starting olefin being present.

Similarly, triphenylethene failed to react with CsSO$_4$F (molar ratio of 1:1.3) in dichloromethane or acetonitrile at 35 °C. We have already demonstrated[12] that 1,1-diphenylethene reacted in dichloromethane with CsSO$_4$F only when a larger excess of reagent was added stepwise at 35 °C to yield 2-fluoro-1,1-diphenylethene. Also, Zefirov et al.[19] observed the formation of two vicinal fluoro sulfates with styrene in acetonitrile with a preference for anti-Markovnikov type of regioselectivity. However, the reaction conditions were different (excess of olefin) from ours (excess of reagent). We then carried out the following experiment with 1,1-diphenylethene–CsSO$_4$F (0.5 mmol) was suspended in dry dichloromethane or acetonitrile (1.25 cm^3) and stirred for 30 min at 0 °C, after which 1,1-diphenylethene (1.3 mmol) dissolved in dichloromethane or acetonitrile (0.3 cm^3) was added and the reaction mixture stirred at room temperature for 96 h when the reagent still exhibited oxidative properties (KJ-starch indicator). Dry diethyl ether (5 cm^3) was then added to give a white solid which was filtered off. The organic layer was evaporated under reduced pressure and both the solid part (dissolved in dimethyl sulfoxide) and organic residue (dissolved in CCl$_4$) were analysed by ^{1}H and ^{19}F NMR spectroscopy. Only 5% of 2-fluoro-1,1-diphenylethene was present in the organic layer while the solid residue showed only the presence of small amounts of diphenylethene. We have already demonstrated that reactions with olefins proceeded very well in dichloromethane in the presence of alcohols or in alcohols themselves and the alkoxy group entered the molecule following Markovnikov-type regioselectivity. Triphenylethene (1 mmol) was dissolved in dichloromethane (1 cm^3), and methanol (5 cm^3) was added with stirring at 35 °C; CsSO$_4$F (1.3 mmol) was then added. After 2 h the insoluble residue was filtered off and after work-up the crude reaction mixture was analysed by ^{1}H and ^{19}F NMR spectroscopy. Complete conversion of alkene into 2-fluoro-1-methoxy-1,1,2-triphenylethane was established. Similar regioselectivity as observed before was also found by fluorination of 9-benzylidenefluorene. CsSO$_4$F did not react with triphenylethene in acetonitrile at 35 °C when a 30% excess of reagent was used; however, the formation of 2-fluoro-1-methoxytetra-

phenylethane was observed in a dichloromethane–methanol mixture in the reaction with tetraphenylethene. Further, we studied the effect of substrate structure on fluorination and found that the introduction of a phenyl group into diphenylethene, in contrast to the results observed with XeF_2, decreased the reactivity of the alkene. Thus, 1,1-diphenylethene was 1.3 times more reactive than triphenylethene and additional introduction of a phenyl group decreased the reactivity of tetraphenylethene five times, while 9-benzylidenefluorene is less reactive than triphenylethene, as in the case of XeF_2 (Scheme 2). Finally, we studied the effect of reagent structure X–L and solvent incorporation into the substrate (Scheme 1). For this purpose we treated triphenylethene in dichloromethane with chlorine and found that only the addition process occurred to form 1,2-dichloro-1,1,2-triphenylethane. The addition process was also observed exclusively in a 1:2 mixture of CH_2Cl_2–MeOH, while incorporation of methoxy group was less complete than in the case of $CsSO_4F$ reaction and 2-chloro-1-methoxy and 1,2-dichloro-1,1,2-triphenylethane were formed in the ratio of 2:1. Reaction with bromine in a 1:5 mixture of CH_2Cl_2–MeOH resulted only in the formation of 2-bromo-1-methoxy-1,1,2-triphenylethane which was transformed to known bromotriphenylethene.[22] However bromination of 9-benzylidenefluorene in the same mixture resulted in the formation of the vicinal dibromide (30%) and 9-(α-bromobenzyl)-9-methoxyfluorene (70%), while no addition–elimination process was detected in the bromination in dichloromethane, where only 9-bromo-9-(α(bromobenzyl)fluorene was formed.

The present study again demonstrates that fluorinating agents are very sensitive and only small variations in the structure of the organic molecule and reaction conditions can completely change the course of the reaction.

Experimental

IR spectra were recorded with a Perkin-Elmer 277 B spectrometer, ^1H and ^{19}F NMR spectra with a Varian EM-360L spectrometer at 60 and 56.45 MHz, respectively. Chemical shifts are expressed in ppm from Me_4Si or CCl_3F as internal standards. J Values are given in Hz. Mass spectra and high resolution measurements were taken on a VG Auto spec Q spectrometer. TLC was carried out on Merck PCS-Fertigplatten Silica gel F-254, elemental analysis on a Parkin-Elmer 2400 CHN and melting points with a Buchi 535. $CsSO_4F$ was prepared according to the literature,[23] XeF_2 was prepared by a photosynthetic method[24] and its purity was better than 99%. Diphenylethene and tetraphenylethene were commercially available and purified before use, but triphenylethene[25] and 9-benzylidenefluorene[26] were prepared by known procedures, HF and BF_3-Fluka were used without further purification, while solvents were purified before use.[27]

Fluorination of Phenyl-substituted Alkenes with XeF_2.—XeF_2 (1.1 mmol) was added at 20 °C to a stirred solution of the alkene (1 mmol) in dichloromethane (6 cm^3) followed by anhydrous HF (0.5–1 mmol). After a few seconds the colourless solution turned blue and Xe gas was evolved. After 1 h, the reaction mixture was diluted with dichloromethane, washed with aqueous $NaHCO_3$ (10 cm^3) and water, dried (Na_2SO_4) and evaporated under reduced pressure. The crude reaction mixture was analysed by ^1H and ^{19}F NMR spectroscopy and the amount of fluoro substituted products were determined by the addition of a known amount of octafluoronaphthalene as internal standard.

1,2-Difluorotriphenylethane **2b**. A portion (130 mg) of the crude reaction mixture (222 mg) was separated by TLC [SiO$_2$, light petroleum (40–70 °C)–dichloromethane, 3:1] to give a white solid. This was twice recrystallised from light petroleum

(40–70 °C) to give 1,2-difluorotriphenylethane (75 mg, 44% yield, calculated on starting material); m.p. 120 °C (Found: C, 81.1; H, 5.3. Calc. for $C_{20}H_{16}F_2$: C, 81.60; H, 5.49%); $\delta_H(CCl_4)$ 6.25 (dd, 1 H, $^2J_{F-H}$ 45, $^3J_{F-H}$ 15) and 6.9–7.8 (m, 15 H); δ_F −161.5 (dd, 1 F, $^3J_{F-H}$ = $^3J_{F-F}$ = 15) and −184.5 (dd, 1 F, $^3J_{F-H}$ 45, $^3J_{F-F}$ 15).

1,2-Difluorotetraphenylethane **2c**. A portion (138 mg) of the crude reaction mixture (300 mg) was recrystallised from light petroleum to give a white solid (113 mg, 66%); this was twice recrystallised from light petroleum to give an analysis sample (53.2 mg, 31% yield, calculated on starting material) of 1,2-difluorotetraphenylethane was isolated; m.p. 240–241 °C (Found: C, 84.0; H, 5.5. Calc. for $C_{26}H_{20}F_2$: C, 84.29; H, 5.45%); $\delta_H(CCl_4)$ 7.1–7.5 (m); δ_F −150.3 (s).

9-Fluoro-9-(α-fluorobenzyl)fluorene **2d**. A portion (130 mg) of the crude reaction mixture (244 mg) was separated by TLC (SiO$_2$, hexane–dichloromethane, 3:1) to give a white solid (116 mg, 75%); this was twice recrystallised from hexane to give an analysis sample (45 mg, 29% yield, calculated on starting material) of 9-fluoro-9-(α-fluorobenzyl)fluorene was isolated; m.p. 86–88 °C (Found: C, 82.2; H, 4.7. Calc. for $C_{21}H_{14}F_2$: C, 82.17; H, 4.84%); $\delta_H(CCl_4)$ 5.73 (dd, 1 H, $^2J_{F-H}$ 46, $^3J_{F-H}$ 15) and 6.8–7.7 (m, 13 H); δ_F −186.4 (dd, 1 F, $^2J_{F-H}$ 46, $^3J_{F-F}$ 15) and −171.6 (dd, 1 F, $^3J_{F-F}$ 15, $^3J_{F-H}$ 15).

Fluorination of Phenyl Substituted Alkenes with $CsSO_4F$.— The alkene (1 mmol) was dissolved in a mixture of dichloromethane (1 cm^3) and dry methanol (5 cm^3) and, with stirring, $CsSO_4F$ (1.3 mmol) was added. The mixture was stirred at 35 °C for 2 h, after which it was diluted with dichloromethane (40 cm^3). The precipitate was filtered off, and the filtrate washed with water, dried (Na_2SO_4) and evaporated under reduced pressure. The crude reaction mixture was analysed by ^1H and ^{19}F NMR spectroscopy and the amount of fluoro substituted products was determined by the addition of a known amount of octafluoronaphthalene as internal standard.

2-Fluoro-1-methoxy-1,1,2-triphenylethane **3b**. The crude reaction mixture (262 mg), was purified by column chromatography [SiO$_2$, light petroleum (b.p. 40–70 °C)], gave a white solid (180 mg, 58%). For elemental analysis the latter was recrystallised from ethanol to give 2-fluoro-1-methoxy-1,1,2-triphenylethane (90 mg, 29%), m.p. 61–62 °C (Found: C, 82.8; H, 6.1. Calc. for $C_{21}H_{19}FO$: C, 82.31; H, 6.26%); $\delta_H(CCl_4)$ 3.26 (s, 3 H), 6.3 (d, 1 H, $^2J_{F-H}$ 46) and 6.4–7.5 (m, 15 H); δ_F −181.5 (d, 1 F, $^2J_{F-H}$ 46).

2-Fluoro-1-methoxy-1,1,2,2-tetraphenylethane **3c**. The crude reaction mixture (290 mg) purified by column chromatography (SiO$_2$, hexane), gave a white solid (212 mg, 61%). For elemental analysis the latter was recrystallised from ethanol to give 2-fluoro-1-methoxytetraphenylethane (160 mg, 46%), m.p. 152.9–153.5 °C (Found: C, 84.6; H, 6.0. Calc. for $C_{27}H_{23}FO$: C, 84.77; H, 6.07%); $\delta_H(CCl_4)$ 3.2 (s, 3 H) and 6.93–7.7 (m, 20 H); δ_F −153.7 (s, 1 F).

(α-Fluorobenzyl)-9-methoxyfluorene **3d**. The crude reaction mixture (220 mg), separated by TLC (SiO$_2$, hexane–dichloromethane, 2:5) gave a white solid (168 mg, 55%). For elemental analysis the latter was twice recrystallised from hexane to give 9-(α-fluorobenzyl)-9-methoxyfluorene (95 mg, 31%), m.p. 95.9–96.9 °C (Found: C, 82.8; H, 5.5. Calc. for $C_{21}H_{17}FO$: C, 82.86; H, 5.64%); $\delta_H(CDCl_3)$ 2.9 (s, 3 H), 5.63 (d, 1 H, $^2J_{F-H}$ 46) and 5.72–8.82 (m, 13 H); δ_F −185 (d, 1 F, $^2J_{F-H}$ 46).

Determination of Relative Rate Factors for the Reaction of Phenyl Substituted Alkenes with: (A) XeF_2.—XeF_2 (1 mmol) was introduced to a stirred solution of triphenylethene (1 mmol) and phenyl substituted alkene (1 mmol) (1,1-diphenylethene, 9-benzylidenefluorene or tetraphenylethene) in dichloromethane (6 cm^3), at 20 °C, followed by anhydrous HF (0.1–0.5 mmol).

After 30 min a known amount of octafluoronaphthalene and dichloromethane (20 cm³) were added to the mixture which was then washed with aqueous $NaHCO_3$ (20 cm³) and water (20 cm³), dried (Na_2SO_4) and evaporated under reduced pressure. The amounts of fluoro substituted products were calculated from ^{19}F NMR spectra with octafluoronaphthalene as standard. Applying this known competitive technique, relative reactivities expressed by relative rate factors (k_{rel}) were calculated from the equation derived from the Ingold–Shaw relation:[28,29] $k_{rel} = k_A/k_B = \log[(A - X)/A]/\log[(B-Y)/B]$ where A and B are the amounts (in mmol) of starting material and X and Y are the amounts of products derived from them: the following rate factors were established: 1a:1b = 0.4; 1c:1b = 1.1; 1d:1b = 0.2.

(B) $CsSO_4F$. Triphenylethene (1 mmol) and the phenyl substituted alkene (1 mmol) (1,1-diphenylethene, 9-benzylidene-fluorene or tetraphenylethene) was dissolved in dichloromethane (1 cm³) and dry methanol (5 cm³) and $CsSO_4F$ (1 mmol) was added to the solution at 30 °C. The mixture was stirred for 1 h at 30 °C after which a known amount of octafluoronaphthalene and dichloromethane (20 cm³) were added to give a precipitate. This was filtered off and the filtrate was washed with water, dried (Na_2SO_4) and evaporated under reduced pressure. The amounts of fluoro substituted products were calculated from the ^{19}F NMR spectra with octafluoro-naphthalene as standard. The following relative rate factors were calculated: 1a:1b = 1.3; 1c:1b = 0.2; 1d:1b = 0.3.

Reaction of Triphenylethene with Chlorine.—To a solution of alkene (0.5 mmol) in solvent (2 cm³) (CCl_4, CH_2Cl_2, MeCN or a 1:2 mixture of CH_2Cl_2–MeOH) solvent (1 cm³), containing chlorine (0.5 mmol), was added at room temperature and the crude reaction mixture analysed by ^1H NMR spectroscopy. The products were isolated by TLC. Structures were determined on the basis of the spectroscopic data.

1,2-Dichlorotriphenylethane. Recrystallisation from hexane, gave a solid product (96 mg, 63%), m.p. 111 °C (lit.,[30] 110.5–111.5 °C); $\delta_H(CCl_4)$ (s, 1 H) and 6.8–7.9 (m, 15 H).

1-Chloro-1-methoxy-1,1,2-triphenylethane. Column chromatography on silica gel with light petroleum, gave 1,2-dichloro-1,1,2-triphenylethane (21 mg, 13%) and 2-chloro-1-meth-oxy-1,1,2-triphenylethane (98 g, 59%), m.p. 118 °C (lit.,[30] 117.5–118 °C); $\delta_H(CCl_4)$ 3.0 (s, 3 H), 5.9 (s, 1 H) and 6.6–7.7 (m, 15 H).

Reaction of 9-Benzylidenefluorene with Bromine.—9-Benzyli-denefluorene (1 mmol) was dissolved in CH_2Cl_2 (1 cm³) and a solution of bromine in CH_2Cl_2 or methanol (1.1 mmol; 5 cm³) was added at 20 °C. The reaction mixture was left for 1 h and then CH_2Cl_2 (20 cm³) was added to it. The resulting mixture was washed with aqueous $NaHSO_3$ and water, dried (Na_2SO_4), and evaporated under reduced pressure. The crude reaction mixture was analysed by ^1H NMR spectroscopy and TLC. 9-Bromo-9-(α-bromobenzyl)fluorene was isolated as a solid (250 mg, 61%) by column chromatography (SiO_2, light petroleum); m.p. 117–117.7 °C and recrystallised for elemental analysis from hexane (180 mg, 44%) (Found: C, 58.3; H, 3.6. Calc. for $C_{20}H_{14}Br_2$: C, 58.00; H, 3.41%); $\delta_H(CCl_4)$ 5.85 (s, 1 H) and 6.95–8.4 (m, 13 H). It was converted with KOH in MeOH at room temp. into α-bromobenzylidenefluorene; m.p. 128–128.4 °C, (lit.,[31] 128 °C); $\delta_H(CCl_4)$ 6.1–9.2 (m).

9-(α-Bromobenzyl)-9-methoxyfluorene. The mixture (365 mg), obtained from a reaction in CH_2Cl_2–MeOH (1:5), containing 30% 9-bromo-9-(α-bromobenzyl)fluorene and 70% 9-(α-bromo-benzyl)-9-methoxyfluorene gave 9-bromo-9-(α-bromobenzyl)-fluorene (106 mg, 26%) and 9-(bromobenzyl)-9-methoxy-fluorene (155 mg, 43%) by preparative TLC (SiO_2, CH_2Cl_2–hexane, 1:1). 9-(α-Bromobenzyl)-9-methoxyfluorene was

further purified for elemental analysis by recrystallisation from hexane and to give a white solid (34 mg, 10%); m.p. 104–104.5 °C (Found: C, 68.9; H, 4.5. Calc. for $C_{21}H_{17}BrO$: C, 69.05; H, 4.70%); $\delta_H(CCl_4)$ 3.0 (s, 3 H), 5.4 (s, 1 H) and 6.5–8.2 (m, 13 H).

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