584. *Substituent Effects in Fluorene Compounds. Part III.*[1] *Hydrolysis of 9-Chloro-9-phenylfluorenes.*

By C. EABORN, R. C. GOLESWORTHY, and M. N. LILLY.

We have measured the rates of hydrolysis in 90% or 95% acetone (mainly in presence of an excess of lithium chloride) of 9-chloro-9-phenylfluorene and its derivatives having a methyl, methoxy-, or chloro-substituent in the *meta*- or *para*-position of the phenyl group or in the 2- or 3-position of the fluorenyl group. The effects of 2-substituents on the rate are close to those of *meta*-substituents, but the 2-methyl and 2-methoxy-compounds are slightly less reactive than their *meta*-analogues. The tautomeric release of electrons by the 2-methoxy-group is not significantly transmitted towards the 9-position through the unsubstituted ring.

The reactivities of 3-chloro- and 3-methyl-derivatives are not significantly different from those of their respective *para*-substituted analogues. The 3-methoxy-derivative is more reactive than the *p*-methoxy-derivative, but the difference is small relative to the overall effect of the substituent concerned.

THE aim of this series of investigations is to compare the electrical effects of substituents in the fluorene nucleus with those of substituents in the benzene ring. As far as effects at the 9-carbon atom are concerned, the simplest way of treating 2- and 3-substituents in fluorene is to assume that they are equivalent to *meta*- and *para*-substituents in toluene or its derivatives, but this may be incorrect for two reasons. First, the aromatic rings in fluorene are distorted from regular hexagons,[2] and the nature of the C–C bonds must

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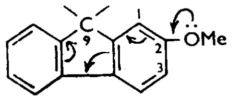
[1] Part II, Dickinson and Eaborn, *J.*, 1959, 3641.

[2] Brown and Bortner, *Acta Cryst.*, 1954, **7**, 139; Burns and Iball, *Nature*, 1954, **173**, 635.

be somewhat different from that of the bonds in benzene. Secondly, and at first sight possibly more importantly, tautomeric effects might be transmitted from the 2-position towards the 9-carbon atom through the unsubstituted ring, as in (I); such an effect was invoked by Arcus and Coombs[3] to explain the influence of substituents on the rearrangement of 9-fluorenyl azides to phenanthridines (see below). In the reaction of 9-bromofluorenes with potassium iodide in acetone,[4] and in oxime formation from 9-fluorenones,[1] 2-substituents were shown to have effects consistent with their being regarded as simple *meta*-substituents, but for the former reaction the possibility of some transmission of the $+T$ effect of the 2-methoxy-group by process (I) could not be excluded.



(I)

We have now measured the rates of hydrolysis in 90% aqueous acetone of a series of 9-chloro-9-phenylfluorenes having methyl, methoxy-, or chloro-groups in the 2- or 3-position of the fluorene nucleus or in the *meta*- or *para*-position of the phenyl group. This system has two considerable advantages: (i) the reaction is of the S_N1 type, and the presence in the transition state of an incipient carbonium ion adjacent to the rings can call forth the electromeric effects of substituents, and (ii) the influence of a group attached to the fluorene nucleus can be compared in absolute terms with the influence of the same group in the analogous position of the phenyl nucleus. In comparing effects of substituents in the fluorene system and in, say, the diphenylmethyl system, one can at best only hope to show that the effects on one system are *proportional*, on a free-energy of activation basis, to those in the other; no absolute comparison is possible because different reaction centres are involved in the two cases.

Hydrolytic S_N1 reactions of organic chlorides are frequently,[5] but not always,[6] retarded by common-ion salts, by added lithium chloride, for example, or by the hydrochloric acid formed in the hydrolysis. Such common-ion retardation is marked with 9-chloro-9-phenylfluorene (initially 0·01M) in 90% acetone; the calculated first-order constant falls by about 12% during the first 50% of reaction, while addition of 0·1M-lithium chloride lowers the rate by a factor of *ca.* 2·8. The initial rate is increased by a factor of 2·2 by the presence of 0·100M-lithium perchlorate which also causes the fall-off in rate constant during the first 50% of reaction to increase to *ca.* 22%. (The latter effect is explicable in terms of swamping-out of the ionic-strength effect of formed hydrochloric acid, which brings the common-ion effect into greater prominence.) The fall-off in first-order rate constant in absence of added salts is more marked the more reactive the chloride involved; the fall-off during the first 50% of reaction for some of the compounds is as follows: 3-Cl, 4%; *m*-MeO, 9%; 2-MeO, 8%; 2-Me, 14%; *p*-Me, 19%. No fall-off was observed for the *m*-chloro- and the 2-chloro-compound. (This effect can be understood in terms of increasing stability of the carbonium ion, which permits it to discriminate more effectively between the weakly nucleophilic water, present in high concentration, and the more strongly nucleophilic chloride ion present in low concentration. For a quantitative interpretation, of course, salt effects on the various reaction steps must be assessed.)

For reactions in absence of added salt, approximate rate constants at zero ionic strength can be obtained by extrapolation of a plot of the rate constant against the extent of reaction, and the results are shown as k_1° in Table 1 (and also as rates, k°_{rel}, relative to that of the unsubstituted compound). But the uncertainty in such extrapolation was too great for our purposes,* and so we measured the rates in presence of lithium chloride

* In fact the pattern of substituent effects is much the same whether values or k°_{rel} of k_{rel} (Table 1) are considered. A plot of log k°_{rel} against log k_{rel} is a good straight line.

[3] Arcus and Coombs, *J.*, 1954, 4319.

[4] Dickinson and Eaborn, *J.*, 1959, 3574.

[5] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, Ltd., London, 1953, pp. 360—370.

[6] Bunton and Nayak, *J.*, 1959, 3854.

(0·101M), which swamps the effect of chloride ion formed (0·01M for complete reaction) so that the first-order rate coefficients are constant throughout a run. (The added lithium chloride depresses the rate by a factor which increases with the reactivity of the organic chloride concerned, and thus there is a smaller spread of rates over the range of substituents.) The observed average first-order constants k_1 are shown in Table 1, along with the rates, k_{rel}, relative to that of 9-chloro-9-phenylfluorene. The reaction of the 3-methoxy-derivative was too fast in 90% acetone containing 0·101M-lithium chloride to be studied by our method, and so rates for 3-methyl, 3-methoxy-, and *p*-methoxy-derivatives were measured in 95% acetone containing 0·050M-lithium chloride, and the rate for the 3-methoxy-derivative in the former medium was calculated by assuming a linear free-energy relation between the rates in the two media. Any error introduced in this calculation is unimportant for our purposes.

TALBE 1. *Hydrolysis of* 9-*chloro*-9-*phenylfluorenes in* 90% *acetone at* 25·0°.

			In presence of 0·101M-LiCl					In presence of 0·101M-LiCl	
Substituent	$10^5k_1^\circ$ (sec.$^{-1}$)	k°_{rel}	10^5k_1 (sec.$^{-1}$)	k_{rel}	Substituent	$10^5k_1^\circ$ (sec.$^{-1}$)	k°_{rel}	10^5k_1 (sec.$^{-1}$)	k_{rel}
m-Gl	0·50	0·045	0·297	0·074	*m*-Me	19	1·7	5·91	1·47
2-Cl	0·49	0·045	0·289	0·072	2-Me	17	1·5	4·56	1·14
p-Cl	3·9	0·35	1·61	0·401	*p*-Me	78	7·1	19·4	4·83
3-Cl	4·5	0·41	1·64	0·409	3-Me	—	—	20·1	5·01
m-MeO	9·1	0·82	3·33	0·83	*p*-OMe	1250	110	260	64·5
2-MeO	6·2	0·56	2·67	0·67	3-OMe	—	—	(410) [a]	(102) [a]
None	11·1	1·00	4·01	1·00					

[a] Calculated (see text) from the following values of 10^5k_1 in 95% acetone containing 0·050M-LiCl: *p*-Me, 0·595; *p*-MeO, 25·8; 3-MeO, 48·4 sec.$^{-1}$.

The most important feature of the results is the relatively small difference between the effects of 2- as compared with *meta*-substituents and 3- as compared with *para*-substituents. However, some of the differences warrant discussion.

The 2-methyl and 2-methoxy-derivatives react slightly more slowly than the corresponding *meta*-substituted analogues (the difference between the 2- and *m*-chloro-compounds is within experimental error); clearly there is no significant transmission of the $+T$ effect of the 2-methoxy-group by process (I). If differences in the ease of transmission of inductive effects from *meta*- and 2-positions were important, the relative reactivity of 2- and *meta*-substituted compounds would be in one direction for methyl substituents (with $+I$ effects), and in the other for methoxy- and chloro-substituents (with $-I$ effects), and it seems that the lower reactivities of the 2-substituted compounds arises from a slightly poorer transmission of $+T$ effects towards the 9-position by secondary relay from positions conjugated with 2-substituents than from those conjugated with *meta*-substituents.

There is no significant difference between the reactivities of 3- and *para*-derivatives for chloro- and methyl substituents. The 3-methoxy-derivative is clearly more reactive than its *para*-analogue, but the difference is small relative to the overall effect of the substituent concerned. Since only the methoxy-group has a different effect from 3- and *para*-positions, it is likely that there is more effective transmission of the $+T$ effect towards the 9-position from the 3- than from the *para*-position. There is no obvious reason why this should be so, since there is no question of transmission of the $+T$ effect of a 3-methoxy-group towards the 9-position *via* the unsubstituted ring. Before speculating further on the nature of the effect of 3-substituents in fluorene we await results for other types of reactions and for additional substituents, particularly those having strong $-T$ effects.

The effects of substituents could be expected to correlate well with the σ^+ constants, since these are derived from an analogous reaction, the hydrolysis of αα-dimethylbenzyl chlorides in 90% acetone.[7] For the *meta*- and *para*-substituted compounds a plot of

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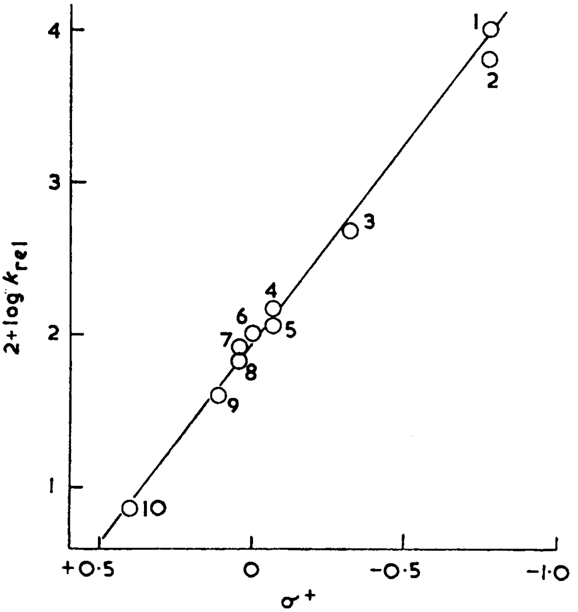
[7] H. C. Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

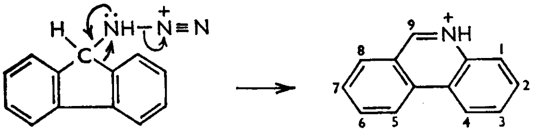
log k_{rel} against σ^+ approximates to a straight line (see Figure); activation by the *p*-methoxy-group is somewhat less than expected from its σ^+ constant, and this may be a result of the small electron demand (as measured, for example, by the effect of a *p*-methyl group) in the hydrolysis of 9-chloro-9-phenylfluorenes when compared with the hydrolysis of αα-dimethylbenzyl chlorides. The log k_{rel}–σ^+ plot for the 2- and 3-derivatives (σ^+ constants for *meta*- and *para*-substituents, respectively, being used) is a slightly better straight line. This illustrates that the observed differences between the effects of 2- and *meta*- or 3- and *para*-substituents are small compared with the variation in the effect of *meta*- and *para*-substitution even from one reaction to an analogous reaction. It also emphasises the value of comparing effects in phenyl and fluorenyl systems directly within one structure, as we have done; had we measured only the effects of 2- and 3-substituents, and analysed these by use of σ^+ constants (or by direct comparison on a free-energy basis with other carbonium-ion-forming reactions of diphenylmethyl and other substituted-tolyl systems) we should have concluded that, relative to one another, the groups behaved exactly as though they were simple *meta*- and *para*-substituents in a benzene system, and should have missed the small but significant differences discussed above.



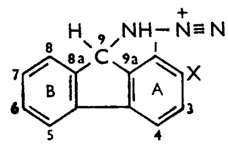
Plot of (2 + log k_{rel}) *for hydrolyses of chlorides against* σ^+. *Substituent in* 9-*chloro*-9-*phenylfluorene*: 1, 3-OMe; 2, *p*-OMe; 3, 3-Me and *p*-Me; 4, *m*-Me; 5, 2-Me; 6, H (unsubst.); 7, *m*-OMe; 8, 2-OMe; 9, 3-Cl and *p*-Cl; 10, 2-Cl and *m*-Cl.

Since we conclude that electron-release by the 2-methoxy-group is not significantly transmitted towards the 9-position through the unsubstituted ring, it is important to consider Arcus and Coombs's evidence for such a process. They analysed the phenanthridine isomers formed from fluoren-9-ols on treatment with hydrazoic acid and sulphuric acid.[3] The rearrangement involved can be represented as (II) ⟶ (III). Electron supply towards the C–C bond to be broken assists the migration. Thus in a 2-substituted compound (IV), if the electron supply to the 8a–9 carbon bond is greater than that to the 9–9a bond, then the former bond migrates preferentially and 7-X-phenanthridine predominates over 2-X-phenanthridine in the product. From a 3-substituted fluorenol the 6- and 3-X-phenanthridines are correspondingly formed.

The experimental observations which need to be considered here are shown in Table 2. Arcus and Coombs concluded from the results that transmission of the $+I$ effect of the 2-methyl group to the 9–9a bond was approximately as effective as transmission of its $+T$ (hyperconjugation) effect to the 8a–9 bond by a process analogous to (I). The predominant migration of the B-ring in 2-methoxyfluorenol was taken to accord with inductive electron-withdrawal from 9–9a coupled with tautomeric electron-supply to 8a–9 by process (I). But it can equally satisfactorily be assumed that the substituents have no effect on the 8a–9 bond; the 2-methyl group would then have to activate the 9–9a bond by a factor of 1·13, and the 2-methoxy-, 2-nitro-, and 3-nitro-groups would have to deactivate the bond by factors of 2, 32, and 16, respectively. Within the limits of accuracy of the isomer proportions reported, these factors are quite consistent with the 2-substituents' acting as simple *meta*-substituents towards the 9–9a bond. It is true that the 3-nitro-group would then be expected to deactivate rather more than the 2-nitro-group (compare the σ^+ constants,[7] which should indicate the effects of *meta*- and *para*-groups in this type of rearrangement), but the experimental results do not, in fact, contradict this expectation because of the uncertainties in the isomeric compositions of the products.



(II) (III)



(IV)

TABLE 2.

Fluorenyl derivative	Total yield (%) of phenanthridine	Phenanthridine formed	Percentage of total yield (%)
2-NO_2	92	2-NO_2	3
		7-NO_2	97
3-NO_2	88	3-NO_2	6
		6-NO_2	94
2-MeO	32	2-MeO	32
		7-MeO	68
2-Me	81	2-Me	53
		7-Me	47

(For example, the phenanthridines from 2-nitrofluorenol were partly separated into 2- and 7-isomers by fractional crystallization, but 19% of the nitrophenanthridines was not recovered, and if allowance is made for this the proportion of 2-nitro-product is 2·5—21·5% and of 7-NO_2 product is 78·5—97·5%. If the proportion of 2-nitro-compound were 7%, this would mean that the 9–9a bond was deactivated only by a factor of 13.) In any case, the isomeric compositions quoted in Table 2 are even less in agreement with Arcus and Coombs's interpretations, for the 2-nitro-group, in addition to deactivating the 9–9a bond less effectively than the 3-nitro-group, should also deactivate the 8a–9 bond in a process analogous to (I), so that the proportion of migration of the B-ring should be markedly smaller for the 2-nitro- than for the 3-nitro-fluorenol. But the uncertainty in the isomer proportions reported by Arcus and Coombes renders further speculation unfruitful, and we can merely conclude that their inference of electron transmission of type (I) was unjustified.

EXPERIMENTAL

Materials.—Acetone was purified and dried by Conant and Kirner's method.[8] One volume of water was made up to 10 or 20 volumes with acetone to give 90% or 95% acetone, respectively.

9-Phenylfluoren-9-ols containing substituents in the phenyl group were prepared from fluoren-9-one and the appropriate arylmagnesium bromide in ether.[9,10] The insoluble complex formed was separated and washed with ether before being hydrolysed with dilute hydrochloric acid.[9] The fluorenols were extracted with benzene, the extract was concentrated and diluted

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[8] Conant and Kirner, *J. Amer. Chem. Soc.*, 1924, **46**, 245.

[9] Ullman and von Wurstemberger, *Ber.*, 1904, **37**, 73.

[10] Williamson, Anderson, and Watt, *J. Amer. Chem. Soc.*, 1943, **65**, 49.

with a little light petroleum, and the resulting precipitate was recrystallized from light petroleum (b. p. 60—80°). The properties of the 9-($X\cdot C_6H_4$)$\cdot C_{13}H_8\cdot$OH-9 compounds were as follows: (X=) H, m. p. 85° (but 109° when examined several months later; cf. refs. 9 and 11); *m*-Cl, m. p. 81—82° (Found: C, 78·9; H, 4·4. $C_{19}H_{13}OCl$ requires C, 78·2; H, 4·5%); *p*-Cl, m. p. 91—92° (Found: C, 78·3; H, 4·6%); *m*-Me, m. p. 81·5—82·5° (Found: C, 88·5; H, 6·1. $C_{20}H_{16}O$ requires C, 88·2; H, 5·9%); *p*-Me, m. p. 85·5—86·5° (Found: C, 87·8; H, 5·9%); *m*-MeO, m. p. 89—90° (Found: C, 83·5; H, 5·5. $C_{20}H_{16}O_2$ requires C, 83·3; H, 5·6%); *p*-MeO, m. p. 130—132° (Found: C, 83·9; H, 6·2%). A m. p. of 87—88° has been recorded [12] for the last compound. Our sample gave poor analysis figures, but yielded the 9-chloro-compound on the usual treatment described below.

The above fluorenols were treated with hydrogen chloride in benzene in presence of calcium chloride,[13] and the resulting solution was filtered and concentrated at reduced pressure in a stream of hydrogen chloride. Addition of light petroleum gave 9-aryl-9-chlorofluorenes which, after recrystallization from light petroleum (b. p. 60—80°) with exclusion of moisture, had the following properties: (X=) H, m. p. 79° (lit.,[10,13,14] 79·5°); *m*-Cl, m. p. 72·5—73° (Found: hydrolysable Cl, 11·3. $C_{19}H_{12}Cl_2$ requires 1Cl, 11·4%); *p*-Cl, m. p. 79·5—80·5° (Found: hydrolysable Cl, 11·4%); *m*-Me, m. p. 83·5—84·5° (Found: hydrolysable Cl, 12·1. $C_{20}H_{15}Cl$ requires Cl, 12·2%); *p*-Me, m. p. 97° (lit.,[15] 96—97°) (Found: hydrolysable Cl, 12·1%); *m*-MeO, 108·5—109° (Found: hydrolysable Cl, 11·5. $C_{20}H_{15}ClO$ requires Cl, 11·55%); *p*-MeO, m. p. 151·5—152·5° (lit.,[12,16] 149—151°) (hydrolysable Cl, 11·4%).

9-Phenylfluoren-9-ols with substituents in the fluorene nucleus were prepared from the corresponding fluoren-9-ones [17] and phenylmagnesium bromide in ether, but were usually not isolated. The precipitated complex formed in the coupling was filtered off, washed with ether, and then hydrolysed in the usual way in presence of ether. The ether was replaced by benzene, and water was removed by azeotropic distillation. The benzene solution was then treated with hydrogen chloride in presence of calcium chloride to give substituted 9-*chloro*-9-*phenylfluorenes*, which, after recrystallization from light petroleum (b. p. 60—80°) had the following properties: 2-Cl, m. p. 106·5—107° (Found: C, 73·5; H, 4·0; hydrolysable Cl, 11·3. $C_{19}H_{12}Cl_2$ requires C, 73·5; H, 3·9; 1Cl, 11·4%); 3-Cl, m. p. 112—113° (Found: C, 73·4; H, 3·9; hydrolysable Cl. 11·4%); 2-Me, m. p. 100·5—101·5° (Found: C, 82·6; H, 5·3; hydrolysable Cl, 11·8. $C_{20}H_{15}Cl$ requires C, 82·6; H, 5·2; 1Cl, 12·2%); 2-MeO, m. p. 88·5—89° (Found: C, 78·3; H, 5·0; Cl, 11·8; 1Cl, 11·3. $C_{20}H_{15}ClO$ requires: C, 78·3; H, 4·9; 1Cl, 11·55%).

3-Methoxy-9-phenylfluoren-9-ol was isolated in 75% yield and recrystallized from light petroleum to a m. p. of 83—84° (lit.,[12] m. p. 84°). It was converted into the 9-chloro-compound in the usual way, but recrystallization gave a solid of m. p. 225°, containing no hydrolysable chlorine. However, recrystallization of the freshly prepared chloride from light petroleum containing acetyl chloride gave 9-chloro-3-methoxy-9-phenylfluorene, m. p. 118° (lit.,[12] m. p. 119°) (Found: C, 78·5; H, 5·0; hydrolysable Cl, 11·5. Calc. for $C_{20}H_{15}ClO$: C, 78·3; H, 4·9; 1Cl, 11·55%).

9-Chloro-3-methyl-9-phenylfluorene was not obtained pure in spite of several attempts, and the sample used for rate measurements was obtained by removal of the benzene in a stream of hydrogen chloride from a solution obtained by treating the alcohol with hydrogen chloride in the usual way; the sample contained only 82% of the calculated amount of hydrolysable chlorine, but its hydrolysis showed satisfactory first-order kinetics. Attempts to purify this and other samples by recrystallization gave material containing no hydrolysable chlorine; for example, recrystallization from light petroleum containing acetyl chloride gave a hydrocarbon of m. p. 110·5—111·5° (Found: C, 93·55; H, 6·55%).

Hydrolysis Products.—For a few typical 9-chloro-9-(X-phenyl)-fluorenes, hydrolysis was shown to give the corresponding alcohols substantially pure. A solution of the chloride in 90% acetone was set aside for an appropriate time and then added to excess of water. The mixture was kept in a refrigerator until the precipitated oil had crystallized, and the crystals were removed and dried and their m. p.s were found, with the following results: phenyl, m. p.

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[11] Bachmann, *J. Amer. Chem. Soc.*, 1930, **52**, 3287; Arcus and Coombs, *J.*, 1954, 3977.

[12] Gomberg and Buchler, *J. Amer. Chem. Soc.*, 1923, **45**, 207.

[13] Gomberg and Cone, *Ber.*, 1906, **39**, 2957.

[14] Kliegl, *Ber.*, 1905, **38**, 284.

[15] Schniepp and Marvel, *J. Amer. Chem. Soc.*, 1935, **57**, 1635.

[16] Schlenk and Mair, *Annalen*, 1912, **394**, 198.

[17] Dickinson and Eaborn, *J.*, 1959, 2337.

108°; *m*-chlorophenyl, m. p. 80·0°; *p*-methylphenyl, 86·0°; *m*-methoxyphenyl, 88·5°. From 9-chloro-3-methoxy-9-phenylfluorene a solid of m. p. 83·5° was similarly obtained.

Rate Measurements.—Sufficient of the 9-chloro-9-phenylfluorene to give a *ca.* 0·01M-solution was weighed into a 50-ml. graduated flask, which was then placed in a thermostat at 25·0° ± 0·04°. Solvent, with or without dissolved lithium chloride, pre-heated to 25·0°, was added to the mark, the flask being shaken vigorously, still immersed in the thermostat, during and immediately after the addition. The solid normally dissolved within a few seconds. Aliquot parts (usually 5 ml.) were withdrawn at suitable times (usually measured from completion of the addition of the solvent to the chloride, but sometimes from the time of removal of the first sample) and added to 50 ml. of acetone which had been cooled in ethanol–solid carbon dioxide, the time of half-addition being noted. The cold solution was quickly titrated against standard aqueous sodium hydroxide with lacmoid as indicator. For the fastest runs, involving the *p*-methoxy-derivative in 90% acetone in absence of lithium chloride, the moments of removal of samples were noted verbally on a tape-recorder and the times subsequently derived on play-back. The quenched samples were stored at −78° until the end of the reaction, and then titrated.

First-order rate constants, k_1, were obtained from plots of t against $\log (T_\infty - T_t)$, but in the typical runs below have been calculated directly from the equation $k_1t = 2{\cdot}303 \log [(T_\infty - T_0)/(T_\infty - T_t)]$ where T_0 is the titre at " zero " time (see above), T_t the titre at time t, and T_∞ that at complete reaction. The value of T_∞ was obtained either from a reaction mixture left at 25·0° for at least 10 half-lives, or, in the case of slower reactions by adding water (insufficient to cause precipitation but sufficient to speed-up hydrolysis considerably) to a 5 ml. sample and keeping the mixture at 25° for a short time before adding it to acetone for titration.

The following runs are typical. (*a*) 9-Chloro-9-*m*-tolylfluorene (0·137 g.) in 50 ml. of 90% acetone.

t (min.)	0	12	26	43	58	104	137	185	∞
Ml. of 0·00520M-NaOH	0·260	1·345	2·330	3·340	4·05	5·710	6·550	7·390	9·225
10^5k_1 (sec.$^{-1}$)	—	17·9	16·8	16·3	15·8	15·0	14·7	14·3	—

Times were measured from that for the first sample. Extrapolation to zero titre gave a value for $k_1°$ of 19×10^{-5} sec.$^{-1}$.

(*b*) 9-Chloro-9-*m*-tolylfluorene (0·160 g.) in 50 ml. of 90% acetone containing 0·101M-LiCl; times measured from mixing of reactants.

t (min.)	30	66	150	250	400	∞
Ml. of 0·00520M-NaOH	0·545	1·090	2·130	3·055	3·965	5·205
10^5k_1 (sec.$^{-1}$)	6·01	5·93	5·83	5·84	5·98	—

(*c*) 9-Chloro-9-*p*-methoxyphenylfluorene (0·125 g.) in 50 ml. of 95% acetone containing 0·0500M-LiCl; times measured from mixing of reactants.

t (min.)	15	30	67	98	161	∞
Ml. of 0·0106M-NaOH	0·80	1·41	2·41	2·85	3·46	3·77
10^5k_1 (sec.$^{-1}$)	26·4	26·0	25·4	26·3	25·7	—

The rate constants quoted in Table 1 are in most cases the mean of values obtained graphically from three independent runs on each compound. Rate constants could normally be duplicated to within ±1·5% for runs in 90% or 95% acetone containing lithium chloride. Rate constants for these media are believed to be accurate to within ±3% except possibly for (i) the *p*-methoxy-derivative in 90% acetone containing 0·101M-LiCl, since reaction was so fast that the error in k_1 could be as large as ±10%, and (ii) the 3-methyl derivative, which was impure, but which gave good first-order kinetics.

Values of $k°$ determined in 90% acetone in absence of lithium chloride cannot be regarded generally as accurate to better than ±10% because of the extrapolation involved, but the error is probably smaller with less reactive chlorides for which the rate constant did not fall much during a run.

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