

AROMATIC REACTIVITY

LII*. ACID CLEAVAGE OF SOME TRIMETHYLSILYL DERIVATIVES OF DIPHENYLMETHANE, PHENANTHRENE, DIHYDROPHENANTHRENE, AND PYRENE, AND A GENERAL COMPARISON OF SUBSTITUENT EFFECTS IN DESILYLATION AND DETRITIATION

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SUMMARY

Rates of cleavage by aqueous methanolic perchloric acid have been measured for 4-(trimethylsilyl)diphenylmethane, 2-, 3-, and 9-(trimethylsilyl)phenanthrene, 2-(trimethylsilyl)-9,10-dihydrophenanthrene, and 1-(trimethylsilyl)pyrene. The values of the rates, k_{rel} , relative to those for trimethylsilylbenzene at 50° are 7.9, 1.76, 2.1, 4.5, 12.8, and 223, respectively. In a plot of $\log k_{rel}$ against $\log f$, where f is the corresponding rate factor for detritiation in trifluoroacetic acid at 70°, the points for single-ring systems (mono-substituted benzenes and thiophene) mainly fall about a straight line through the origin, but those for polycyclic systems (including heterocycles) lie, with a large scatter, about a different line which lies well away from the origin. It is suggested that in these systems resonance effects are unusually large, and that a measure of these resonance effects $\sigma_{Res} [= (\sigma^+ - \sigma)]$ is given by the equation $-1.85 \sigma_{Res} = 0.6 \log f - \log k_{rel}$.

INTRODUCTION

Some previous parts of this series have described studies of acid cleavage (protodesilylation) of trimethylsilyl derivatives of a large range of substituted benzenes and heterocyclic compounds¹⁻⁸. Apart from the naphthalene system⁴, however, no polynuclear hydrocarbons containing fused aromatic rings were included in the desilylation studies, and we now present results for some positions of phenanthrene, 9,10-dihydrophenanthrene, and pyrene. The 4-position of diphenylmethane, a useful reference system, has also been examined. This work was carried out some years ago⁹ and in the meantime the results have been used by others^{10**}. Publication was delayed in unfulfilled hope of extending the study to other positions of the polynuclear systems examined and to additional polynuclear systems.

* For Part LI see ref. 33.

** In ref. 10 the value of k_{rel} for the 1-position of pyrene is erroneously shown as 2.23.

RESULTS AND DISCUSSION

First-order rate constants for cleavage of 4-(trimethylsilyl)diphenylmethane, 2-, 3-, and 9-(trimethylsilyl)phenanthrene, 2-(trimethylsilyl)-9,10-dihydrophenanthrene, and 1-(trimethylsilyl)pyrene by aqueous methanolic perchloric acid at 50°

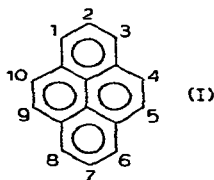
TABLE 1

CLEAVAGE OF ArSiMe_3 COMPOUNDS BY AQUEOUS METHANOLIC PERCHLORIC ACID AT 50.0°

ArSiMe_3	$[\text{HClO}_4]^a$ (M)	λ^b (Å)	$10^3 k$ (min^{-1})	k_{rel}
(Trimethylsilyl)benzene	9.45	2700	1.92	1.00
	12.07	2700	7.86	1.00
4-(Trimethylsilyl)diphenylmethane	12.07	2540	62	7.9
2-(Trimethylsilyl)phenanthrene	12.07	2600	13.8	1.76
3-(Trimethylsilyl)phenanthrene	12.07	3045	16.4	2.1
9-(Trimethylsilyl)phenanthrene	9.45	3020	8.6	4.5
	12.07	3020	35.0	4.45
1-(Trimethylsilyl)pyrene	6.05	3450	70	223
2-(Trimethylsilyl)-9,10-dihydrophenanthrene	12.07	3152	101	12.8
1-(Trimethylsilyl)benzothiophene ^{b,c}	9.45	3060	76	39.6 ^d
	6.05	3060	12.5	

^a Concn. of the aqueous acid, 2 vol. of which were mixed with 5 vol. of a methanolic solution of the organosilane. ^b Wave-length used in following the reaction. ^c Included to provide an "overlap" with the pyrene compound. ^d Ref. 5.

are shown in Table 1, along with values of the rates, k_{rel} , relative to those for (trimethylsilyl)benzene. The numbering used for the pyrene ring is illustrated in (I) since a different numbering has been used in connection with these results^{9,10}.



The change from the *p*-Me to the *p*-PhCH₂ substituent results in an approximately 3-fold reduction in the activation. The order of reactivity for the positions of phenanthrene studied in the desilylation is 9 > 3 > 2, which agrees with the order in detritiation¹¹ and nitration¹², but the spread of rates is very much smaller in the desilylation than in the other reactions. As in detritiation¹¹, the reactivity of the 2-position of 9,10-dihydrophenanthrene in desilylation is substantially greater than that of the corresponding 4-position of biphenyl and substantially less than that of the 2-position in fluorene. The relatively high reactivity of the 1-position of pyrene, which is almost 30 times as reactive as the 1-position of naphthalene, is also reflected in the detritiation¹¹ and nitration results¹⁴, though again, of course, the spread of reactivities is greater in those reactions.

TABLE 2

VALUES OF $\log k_{rel}$ FOR DESILYLATION IN AQUEOUS METHANOLIC PERCHLORIC ACID^a AT 50° AND OF $\log f$ FOR DETRITIATION IN TRIFLUOROACETIC ACID AT 70°

No.	Aromatic system and position of reaction	$\log k_{rel}$	Ref.	$\log f$	Ref.
1	Benzene-1	0.00		0.00	
2	Toluene-3	0.36	1	0.78	17
3	Toluene-4	1.32	1	2.65	18
4	[(Trimethylsilyl)methyl] benzene-4	2.43	1	ca. 5.15	19
5	Diphenylmethane-4	0.90	Table 1	2.08	17
6	Anisole-4	3.18	1	ca. 6.85 ^b	20
7	Thioanisole-4	1.88	8	4.84	20
8	Diphenyl sulphide-4	1.03	5	3.99	21
9	Biphenyl-4	0.45	3	2.21	21
10	Fluorene-2	1.66	6	4.23	6
11	9,10-Dihydrophenanthrene-2	1.11	Table 1	3.44	11
12	Thiophene-3	ca. 1.98 ^c	2	4.28	20
13	Thiophene-2	3.68	2	7.38	20
14	Naphthalene-1	0.91	4	3.06	23
15	Naphthalene-2	0.34	4	2.18	23
16	Biphenylene-1	-0.28	16	2.02	22
17	Biphenylene-2	1.44	16	4.15	22
18	Phenanthrene-2	0.24	Table 1	2.24	16
19	Phenanthrene-3	0.32	Table 1	2.60	16
20	Phenanthrene-9	0.65	Table 1	3.22	16
21	Pyrene-1	2.35	Table 1	5.91	13
22	Benzothiophene-2	1.60	5	5.34	19
23	Benzothiophene-3	1.61	5	5.49	19
24	Dibenzofuran-1	-0.19	5	2.13	21
25	Dibenzofuran-2	1.28	5	3.56	21
26	Dibenzofuran-3	0.38	5	2.50	21
27	Dibenzofuran-4	-0.04	5	2.20	21
28	Dibenzothiophene-1	0.74	5	2.43	21
29	Dibenzothiophene-2	0.80	5	3.26	21
30	Dibenzothiophene-3	0.30	5	2.63	21
31	Dibenzothiophene-4	0.06	5	2.56	21

^a Aqueous acid (2 vol.) mixed with a solution of the silane in methanol (5 vol.). ^b Corrected for the interaction between the methoxy group and the trifluoroacetic acid²⁰. ^c Derived from the value in $\text{CH}_3\text{CO}_2\text{H}/\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ ².

A plot of $\log k_{rel}$ for desilylation against the corresponding values of $\log f$ for detritiation (f =rate factor compared with a position of benzene) for a large range of aromatic systems (see Table 2), shown in Fig. 1, is informative*. In this plot, the points for the 2- and 3-positions of thiophene and for the mono-substituted benzenes, with the revealing exceptions of those for *p*-SMe, *p*-SPh, and *p*-Ph which are discussed below, lie close to a straight line through the origin of slope 0.48, while those for polycyclic systems containing non-fused and fused rings (including heterocyclic rings) lie well away from this line, and fall with a rather large scatter about a different line of

* Points for *tert*-butylbenzene are omitted because of evidence that this compound behaves anomalously in trifluoroacetic acid¹⁵.

slope 0.6, which intercepts the $\log f$ axis at about 2.0. While the order of reactivity for these systems in desilylation is mainly similar to that in detritiation, it is clear that for such systems the rates of desilylation offer a very poor direct quantitative guide to relative reactivities in detritiation, and thus in other familiar aromatic substitutions such as nitration and halogenation.

The clue to the reasons for this can be found in the positions on the graph of the points for the *p*-SMe, *p*-SPh, and *p*-Ph substituents. It is known that for the detritiation the relationship $\log f = \rho \cdot \sigma^+$ applies²⁰. For the desilylation this relationship applies approximately to a range of substituents^{2,27}, but much more satisfactory is the relationship^{8,28} $\log k_{\text{rel}} = \rho \cdot [\sigma + 0.65(\sigma^+ - \sigma)]$, indicating that resonance effects are substantially less effective in the desilylation than in the detritiation. The point for the *p*-SMe group, for which the value of the quantity $(\sigma^+ - \sigma)$ (which is a measure of the resonance effect) is especially large, and the point for the *p*-Ph group lie badly off the simple $\log k_{\text{rel}}$ versus σ^+ plots, but fall on the plots of $\log k_{\text{rel}}$ versus $[\sigma + 0.65(\sigma^+ - \sigma)]$ ^{8,*}. It is thus reasonable to assume that for the polycyclic systems which lie around the lower line in Fig. 1, the contributions from resonance effects to the activation towards electrophilic substitution are likewise large, and that the influence of these substituents in desilylation would be fairly normal in terms of the relationship $\log k_{\text{rel}} = \rho \cdot [\sigma + 0.65(\sigma^+ - \sigma)]$, although the relevant σ and σ^+ constants are not available to test this.

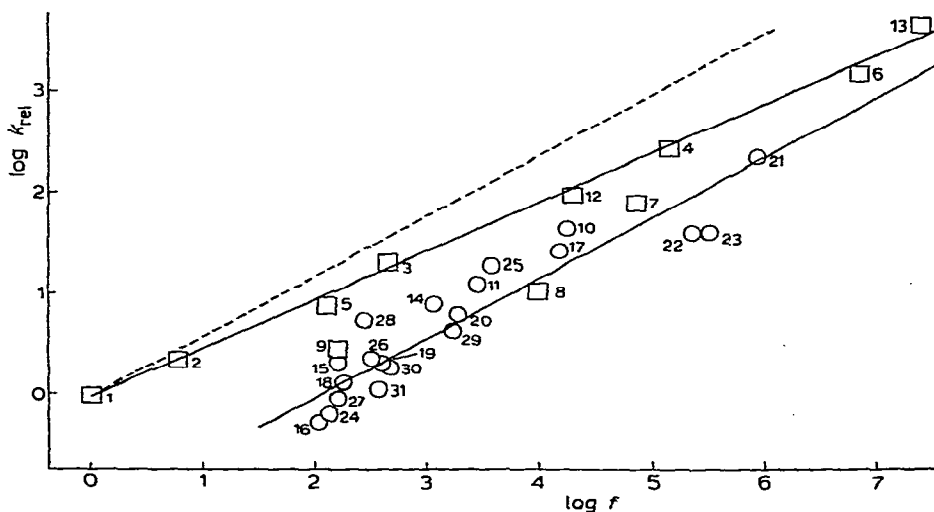


Fig. 1. Plot of $\log k_{\text{rel}}$ (protodesilylation) against $\log f$ (detritiation). The numbers on the points are shown in Table 2. Circles denote systems containing fused aromatic rings.

In principle, knowledge of the relative rates for any compound in both the desilylation and the detritiation enables the quantity $(\sigma^+ - \sigma)$, which we denote σ_{Res} and which provides a measure of the resonance effect for the aromatic position

* There is no reason to doubt that the point for the *p*-SPh group would also lie on this plot, but the relevant σ and σ^+ constants are not available.

concerned²⁴, to be calculated. Thus since $\log k_{\text{rel}} = -5.3 (\sigma + 0.65 \sigma_{\text{Res}})$ and $\log f = -8.8 (\sigma + \sigma_{\text{Res}})^{8,20}$, elimination of σ gives eqn. (1). Application of eqn. (1) to the

$$-1.85 \sigma_{\text{Res}} = 0.60 \log f - \log k_{\text{rel}} \quad (1)$$

substituents *p*-SMe, *p*-OMe, and *p*-CH₂SiMe₃ then gives calculated σ_{Res} values of -0.60 , -0.50 , and -0.35 , respectively, compared with actual values of -0.60^{25} , -0.51^{25} , and -0.25^{26} . This agreement is partly, of course, an artifact, since the points for *p*-OMe and *p*-SMe groups influenced the original choice of the ρ and r values for desilylation and detritiation, and in any case such good agreement will only be obtained when the points for the substituents concerned themselves lie satisfactorily close to the separate plots of $\log k_{\text{rel}}$ versus $-5.3 (\sigma + 0.65 \sigma_{\text{Res}})$ and $\log f$ versus $-8.8 \sigma^+$. Thus for the *p*-Ph group, which deviates quite markedly from the latter plot, the calculated value of σ_{Res} is -0.47 , compared with the actual value²⁴ of -0.17 , and for the 2-position of naphthalene the calculated value of σ_{Res} is -0.52 , while the actual value is -0.18 or -0.24 , depending on which value^{27,29} is taken for σ^+ .

It follows from the above analysis that the fact that the points for the *m*-Me, *p*-Me, *p*-CH₂SiMe₃ and *p*-OMe groups and the 2- and 3-positions of thiophene lie near a straight line in Fig. 1 is mainly fortuitous. The existence of this linear relationship nevertheless justifies the use of desilylation as an approximate guide to the reactivity of such systems in electrophilic substitution generally. A better reference line, however, is not the one through these points, but that, shown broken, with the calculated slope of 0.60 (which should apply to systems for which $\sigma_{\text{Res}} = 0$), and it is the deviation from this line which should strictly be used as an indication of the resonance effects in the system concerned. The line shown through the points for the polycyclic systems (the bottom line in Fig. 1) has somewhat arbitrarily been drawn parallel to this reference line, and the distance between the lines implies that the magnitudes of the resonance effects in these systems lie roughly around that indicated by $\sigma_{\text{Res}} = -0.65$.

Especially interesting are the systems, such as the 1-positions of biphenylene and dibenzofuran and the 4-position of dibenzofuran, at which there is deactivation in desilylation but substantial activation in detritiation^{5,21}, since the deactivation in desilylation, at first sight surprising, is effectively normal in the context of the relationships revealed by Fig. 1. For a hypothetical system giving a point lying on the bottom line of Fig. 1 at the point of intersection with the $\log f$ axis, ($\log k_{\text{rel}} = 0.0$, $\log f = 2.0$), a value of -0.23 for σ^+ would be needed to put the corresponding point on the plot of $\log f$ versus σ^+ , and a value for σ of 0.41 would then be needed to put the relevant point on the plot of $\log k_{\text{rel}}$ versus $(\sigma + 0.65 \sigma_{\text{Res}})$. Again, for the 1-position of pyrene, a value for σ of -0.67 is needed to put the relevant point on the plot of $\log f$ versus σ^+ , and the implied value of σ is -0.02 . It is likely, as is implied by the calculated σ_{Res} values, that many of the polycyclic hydrocarbons do have positive values of σ (σ for the 2-position of naphthalene is $+0.04$), and even larger positive values might be expected for some of the polynuclear systems containing electronegative heteroelements. While it seems a little unlikely that the value of σ for the 1-position of biphenylene is as high as $+0.53$ (with $\sigma^+ = -0.23$ and $\sigma_{\text{Res}} = -0.76$), as required to correlate the desilylation and detritiation rates (see also ref. 16), a fairly large positive value would be consistent with the relatively high acidity of the 1-H atom and with

postulated marked electron-withdrawing influence of a carbon atom at a strained bridgehead³⁰. As measured by the application of eqn. (1), the largest resonance effects in the system listed in Table 2 are those for the 2- and 3-positions of benzothiophene, for which the calculated values of σ_{Res} are -0.86 and -0.91 , respectively, implying σ values of $+0.46$ and $+0.37$ based on σ^+ values derived from a side-chain reaction³¹, and σ values of $+0.25$ and $+0.29$, respectively, based on σ^+ values derived from detritiation²⁰.

It seems possible that use of eqn. (1), or of the deviations from the broken line of Fig. 1, as above, lead to values of σ_{Res} which are too large. It could be, for example, that if a wider range of accurate σ and σ^+ constants were available, a value of r of, say, 1.1 in the relation $\log f = \rho \cdot [\sigma + r \cdot \sigma_{Res}]$ might be found to apply to detritiation more accurately than the value of 1.0 assumed above, and this (even allowing for a compensatory decrease in ρ) would have the effect of reducing the calculated σ_{Res} values, though the new values would be proportional to those deduced by use of eqn. (1).

While the relationships and generalizations developed above are unlikely to be exact, it does seem that joint study of detritiation and desilylation of an aromatic system can give information not only about the inherent reactivity of the system in electrophilic substitutions, but also an indication of the extent to which that reactivity arises from resonance effects.

EXPERIMENTAL

Preparation of aryltrimethylsilanes

(i). 4-(Trimethylsilyl)diphenylmethane. *p*-Bromobenzophenone was converted, by means of the Huang–Minlon modification of the Wolff–Kishner reduction, into 4-bromodiphenylmethane, b.p. 143–145°/3 mm, n_D^{20} 1.6053. The latter (35 g, 0.14 mole) was converted into the Grignard reagent by ethylene dibromide entrainment in ether, and chlorotrimethylsilane (19.5 g, 0.18 mole) was added. The mixture was refluxed for 4 h, then aqueous ammonium chloride was cautiously added. The ether layer was separated, washed, dried (Na_2SO_4), and fractionated to give 4-(trimethylsilyl)diphenylmethane (nc), (14 g, 41%), b.p. 132–135°/2 mm, n_D^{20} 1.5528. (Found: C, 80.3; H, 8.5. $\text{C}_{16}\text{H}_{20}\text{Si}$ calcd.: C, 79.9; H, 8.4%.)

(ii). 9-(Trimethylsilyl)phenanthrene. 9-Bromophenanthrene in light petroleum was treated with *n*-butyllithium in ether and the mixture was refluxed for 30 min. Addition of chlorotrimethylsilane and subsequent refluxing for 2 h was followed by the usual working-up, culminating in fraction distillation at reduced pressure and recrystallization from ethanol, to give 9-(trimethylsilyl)phenanthrene (30%), m.p. 62° (cf. ref. 32).

This compound was also made (in 35% yield) from 9-bromophenanthrene by treatment with chlorotrimethylsilane and sodium in refluxing toluene, and after fractional distillation (b.p. 220–222°/17–20 mm) and recrystallization from methanol had m.p. 62°. (Found: C, 81.4; H, 7.1. $\text{C}_{17}\text{H}_{18}\text{Si}$ calcd.: C, 81.5; H, 7.5%.)

(iii). 2-(Trimethylsilyl)phenanthrene. A solution of 2-chlorophenanthrene (3.0 g), m.p. 85–86°, and chlorotrimethylsilane (2.0 g) in toluene (15 ml) was added during 1 h to a stirred refluxing mixture of sodium (1.0 g), chlorotrimethylsilane (1.0 g) and toluene (7 ml). Stirring and refluxing were continued for 2 h, then the solution was

cooled and filtered. The filtrate was treated carefully with water, and the organic layer was washed with aqueous sodium bicarbonate and finally several times with water, then dried (Na_2SO_4). The toluene was distilled off, and the residue fractionated. The fraction of b.p. 200–210°/22 mm was recrystallized from ethanol to give 2-(trimethylsilyl)phenanthrene (nc) (52%), m.p. 118.5°. (Found: C, 81.2; H, 7.2. $\text{C}_{17}\text{H}_{18}\text{Si}$ calcd.: C, 81.5; H, 7.5%.)

This product, m.p. 118°, was also obtained in 51% yield from chlorotrimethylsilane and the Grignard reagent prepared from 2-bromophenanthrene, m.p. 95°, by ethylene dibromide entrainment in ether.

(iv). 3-(Trimethylsilyl)phenanthrene. 3-Chlorophenanthrene, m.p. 80–81°, was used in a Wurtz–Fittig procedure, as described above for the 2-isomer, to give 3-(trimethylsilyl)phenanthrene (nc), m.p. 72° (from methanol), in 72% yield. (Found: C, 81.3; H, 7.1%.)

(v). 2-(Trimethylsilyl)-9,10-dihydrophenanthrene. 2-Bromo-9,10-dihydrophenanthrene, b.p. 174°/2–3 mm (obtained, along with 2-bromophenanthrene and 2,7-dibromo-9,10-dihydrophenanthrene by treatment of 9,10-dihydrophenanthrene with bromine in chloroform), was converted into a Grignard reagent by ethylene dibromide entrainment in ether. Treatment with chlorotrimethylsilane, followed by the usual working-up, culminating in fractional distillation, gave 2-(trimethylsilyl)-9,10-dihydrophenanthrene (nc), b.p. 138–140°/2–3 mm, n_D^{20} 1.6062, in 10% yield. (Found: C, 81.1; H, 7.6. $\text{C}_{17}\text{H}_{20}\text{Si}$ calcd.: C, 80.9; H, 8.0%.)

(vi). 1-(Trimethylsilyl)pyrene. Phenyllithium (0.16 mole) in ether was added to 1-bromopyrene (43 g, 0.15 mole), m.p. 95°, in benzene (200 ml) with stirring and ice-cooling. The mixture was stirred at room temperature for 6 h then treated with chlorotrimethylsilane (22 g, 0.20 mole), and the mixture was kept at room temperature for 1 h then refluxed for 1 h. Working-up as usual, culminating in fractional distillation (b.p. 170–173°/ca. 0.3 mm) and recrystallization from ethanol, gave 1-(trimethylsilyl)pyrene (35 g, 82%), m.p. 111° (cf. ref. 32). (Found: C, 83.2; H, 6.4. $\text{C}_{19}\text{H}_{18}\text{Si}$ calcd.: C, 83.15; H, 6.6%.)

When *n*-butyllithium was used in a similar experiment, but with 4 h of reflux after the addition of the *n*-butyllithium, the only product isolated was 1-*n*-butylpyrene, m.p. 65°. (Found: C, 92.9; H, 6.9. $\text{C}_{20}\text{H}_{18}$ calcd.: C, 93.0; H, 7.0%.)

Rate studies

Rates were measured as previously described¹⁸. Good first-order kinetics were obtained in every case.

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