377. *Organosilicon Compounds. Part XXVIII.*[1] *Cleavage of Trimethyl-(ω-trimethylsilylalkylphenyl)silanes by Aqueous-methanolic Perchloric Acid.*

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We have measured the rates of cleavage by aqueous-methanolic perchloric acid of the aryl–silicon bonds of the compounds *o*-, *m*-, and *p*-$Me_3Si{\cdot}[CH_2]_n{\cdot}C_6H_4{\cdot}SiMe_3$, where $n = 1$—4. The results can be interpreted in terms of a fairly large inductive release of electrons by the trimethylsilyl group.

The trimethylsilylmethyl group activates the *ortho*-position only one-ninth as effectively as the *para*-position, in marked contrast to the effects in nitration.

A STUDY by Chernyshev, Dolgaya, and Petrov [2] of the nitration in acetic anhydride of some ω-trimethylsilylalkylbenzenes, $Me_3Si{\cdot}[CH_2]_n{\cdot}Ph$ ($n = 1$—4), revealed interesting variations in the effects of the trimethylsilyl groups with different values of n. Table 1 shows the partial rate factors they reported, and also lists the partial rate factors which we, having failed to find justification for those they quote, derived from their rate ratios, K_{rel} (measured by the competition method), and isomer distributions. The outstanding features of the results are (i) the high reactivity of the *ortho*- compared with the *para*-position in the compound with $n = 1$, (ii) the sharp fall in reactivity from the compound with $n = 1$ to that with $n = 2$, and (iii) the small rise in reactivity from the compound with $n = 3$ to that with $n = 4$.

TABLE 1.

Reactivity of $Me_3Si{\cdot}[CH_2]_n{\cdot}Ph$ compounds in nitration in acetic anhydride at −10° (see ref. 2).

n	K_{rel}	*o*- (%)	*p*- (%)	f_o *	f_p *	f_o †	f_p †
1	77·2	85·0	15	182	48	197	69·5
2	8·87	45·8	54·2	8·85	21·7	12	29
3	10·62	49·2	50·8	7·7	16·0	16	32
4	18·96	64·9	35·1	26·4	25·6	37	40

* Values given in ref. 2. † Values recalculated from values of K_{rel} and isomer proportions (as listed) from ref. 2.

TABLE 2.

Cleavage of $X{\cdot}C_6H_4{\cdot}SiMe_3$ compounds by aqueous-methanolic perchloric acid at 50·15°.

X	$[HClO_4]$ * (M)	10^3k_1 (min.$^{-1}$)	k_{rel}	X	$[HClO_4]$ * (M)	10^3k_1 (min.$^{-1}$)	k_{rel}
H	12·05	7·29	1·00	*m*-$Me_3Si{\cdot}[CH_2]_3$	12·05	28·1	3·8
H	9·09	1·56	1·00	*m*-$Me_3Si{\cdot}[CH_2]_4$	12·05	25·7	3·6
o-Me	9·09	26·5	17	*p*-Me	9·09	32·5	21
o-$Me_3Si{\cdot}CH_2$	9·09	48·5	31	*p*-Me	4·54	2·70	(21)
o-$Me_3Si{\cdot}[CH_2]_2$	9·09	27·2	17	*p*-$Me_3Si{\cdot}CH_2$	4·54	35·5	270
o-$Me_3Si{\cdot}[CH_2]_3$	9·09	18·7	12	*p*-$Me_3Si{\cdot}[CH_2]_2$	9·09	44	28
o-$Me_3Si{\cdot}[CH_2]_4$	9·09	21·0	13	*p*-$Me_3Si{\cdot}[CH_2]_3$	9·09	34	22
m-Me	12·05	18·5	2·5	*p*-$Me_3Si{\cdot}[CH_2]_4$	9·09	37	24
m-$Me_3Si{\cdot}CH_2$	12·05	48	6·6	*m*-$Me_3Si{\cdot}(Pr^n)CH$	12·05	59·5	8·2
m-$Me_3Si{\cdot}[CH_2]_2$	12·05	26·5	3·6	*p*-$Me_3Si{\cdot}(Pr^n)CH$	4·54	34	260

* Concn. of aqueous acid, 2 vol. of which were mixed with 5 vol. of a methanolic solution of the organosilane.

To obtain further, more precise, information on the activating effects of $Me_3Si{\cdot}[CH_2]_n$ groups in electrophilic aromatic substitution, we have measured the rates of cleavage of

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[1] Part XXVII, Bott, Eaborn, and Leyshon, *J.*, 1964, 1548.

[2] Chernyshev, Dolgaya, and Petrov, *Bull. Acad. Sci. U.S.S.R.*, 1960, 1323.

o-, *m*-, and *p*-$Me_3Si{\cdot}[CH_2]_n{\cdot}C_6H_4{\cdot}SiMe_3$ compounds by a mixture of methanol (5 vol.) and aqueous perchloric acid (2 vol.) at 50·15°. Table 2 lists the reactivities, k_{rel}, of the compounds, relative to that of phenyltrimethylsilane, along with those for *o*-, *m*-, and *p*-$Me{\cdot}C_6H_4{\cdot}SiMe_3$, and *m*- and *p*-$(Pr^n)(Me_3Si)CH{\cdot}C_6H_4{\cdot}SiMe_3$. The main features of the results, and some comments, are as follows.

(*a*) The *p*-$Me_3Si{\cdot}CH_2$ group has a large activating effect, markedly greater than that of the *p*-Me group, as has been previously noted.[3] [The value of k_{rel} for the *para*-position of benzyltrimethylsilane, 270, differs from previously reported values,[3,4] 315 and 300, by an amount which somewhat exceeds the estimated experimental uncertainty thought usually to apply to k_{rel} values in this reaction. Some variation in medium from worker to worker, leading to a somewhat different spread of rates (or ρ-factor) may account for part of the discrepancy; the reaction mixture is made up usually by mixing small volumes of methanol and aqueous perchloric acid for each run (frequently 5 ml. of methanol and 2 ml. of acid), and there is more chance of such variation than when a mixed solvent is made in bulk.] The other *p*-$Me_3Si{\cdot}[CH_2]_n$ groups have markedly smaller activating effects, which are not much larger than that of the *p*-Me group, and which do not vary much from compound to compound. This is as expected, for the strong $+I$ effect of the trimethylsilyl group will fall off sharply with increase in the number of methylene groups between it and the ring; replacement of a hydrogen atom of a *p*-methyl group by the trimethylsilyl group results in a 13-fold increase in activation, but similar replacement of a β-hydrogen atom of a *p*-ethyl group (which activates rather less than the *p*-methyl group in this reaction [3]) results in only a 1·4-fold increase.

(*b*) The *m*-trimethylsilylmethyl group activates about 2·5 times as effectively as the *m*-methyl group, which is again consistent with the operation of a substantial $+I$ effect from the trimethylsilyl group. [One of us previously drew attention to the fact that the ratio of rate factors $f_p(Me_3Si{\cdot}CH_2)/f_m(Me_3Si{\cdot}CH_2)$ was considerably larger than that of the ratio $f_p(Me)/f_m(Me)$, and suggested that this might indicate a conjugative as well as an inductive release of electrons by the *p*-trimethylsilyl group,[3] but we note that the ratio, $\log f_p(Me_3Si{\cdot}CH_2)/\log f_m(Me_3Si{\cdot}CH_2)$ (*viz.*, 3·0), which is more significant, is smaller than the ratio $\log f_p(Me)/\log f_m(Me)$ (*viz.*, 3·3). We thus see no evidence for a conjugative mechanism for release of electrons by the carbon–silicon bond, though we cannot rule it out.]

The activating effects of the groups *m*-$Me_3Si{\cdot}[CH_2]_n$ with $n = 2$—4 are similar to one another, and about 1·5 times as great as that of the *m*-Me group.

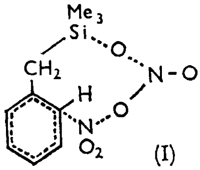
(*c*) The additional alkyl substitution at the α-carbon atom on going from the $Me_3Si{\cdot}CH_2$ to the $Me_3Si{\cdot}(Pr^n)CH$ group, causes little or no change in activation at the *para*-position (possibly lowering it) but a relatively large change in activation at the *meta*-position. Such additional α-substitution is known [3,5] to lower the activation at the *para*-position slightly, *e.g.*, $f_p(Me) > f_p(Bu^t)$, but to raise it at the *meta*-position, $f_m(Bu^t) > f_m(Me)$.

(*d*) After the expected fall in the activating effect of the *o*- and *p*-$Me_3Si{\cdot}[CH_2]_n$ groups as n varies from 1—3, there is a small, but real, rise to that of the groups with $n = 4$. In nitration [2] also, the groups with $n = 4$ activate more than those with $n = 3$, the differences apparently being greater in this case. (In nitration the groups with $n = 3$ may activate more than those with $n = 2$, but the figures are not sufficiently accurate to say whether this is so.) It is noteworthy that, in bromination of primary alkylbenzenes,[6] $Ph{\cdot}[CH_2]_n{\cdot}H$, in acetic acid, the rate falls as n is raised from 1 to 3, but rises again to the compound with $n = 4$.

(*e*) The very large activating effect of the *o*-trimethylsilylmethyl group in nitration is not reflected in the rates of protodesilylation; the group activates only one-ninth as

[3] Eaborn, *J.*, 1956, 4858.
[4] Bott, Eaborn, Pande, and Swaddle, *J.*, 1962, 1217.
[5] Eaborn and Greasley, unpublished work.
[6] Berliner and Berliner, *J. Amer. Chem. Soc.*, 1949, **71**, 1195.

effectively as the *p*-trimethylsilylmethyl group, and less than twice as effectively as the *o*-methyl group. It is possible that there is some steric hindrance by the *o*-trimethylsilylmethyl group to protodesilylation, for although when *o*-methyl or *o*-phenyl substituents are present there seems to be release of strain as the leaving trimethylsilyl group moves out of the plane of the ring (as the central carbon tends towards a tetrahedral configuration);[7] the opposite could be true with branched *ortho*-substituents. Even more hindrance would then be expected, however, for nitration at the *ortho*-position of trimethylsilylmethylbenzene, and a special explanation has to be sought for the much greater reactivity at this than at the *para*-position in nitration. The explanation advanced by Chernyshev, Dolgaya, and Petrov was that a nitronium ion initially co-ordinates to the silicon atom and then migrates to the *ortho*-position,[2] but this is not attractive; even bases do not co-ordinate easily to the silicon atom in tetraorganosilanes, and it seems most unlikely that a co-ordinate bond between silicon and the positively-charged nitronium ion would be strong enough to cause significant lowering of the activation energy of the nitration. There is evidence, however, that the nitronium ion is not the only nitrating entity present in nitric acid–acetic anhydride mixtures,[8,9] and interaction of the silicon atom with incipient nitrate ion from dinitrogen pentoxide, in a transition state such as (I), seems a reasonable postulate.



(I)

There are other puzzling features in the results for nitration of $Me_3Si\cdot[CH_2]_n\cdot Ph$ compounds at −10° obtained by Chernyshev and his colleagues. In particular, it is surprising that activation of the *para*-position by the groups $Me_3Si\cdot[CH_2]_n$, where $n = 2$—4, is markedly lower than that for activation by the *p*-methyl $[f_p(\mathrm{Me}) = 60]$ [9] or *p*-ethyl group $[f_p(\mathrm{Et}) = 69{\cdot}5]$,[9] since the opposite would be expected from the $+I$ effect of the trimethylsilyl group, as is found in desilylation. The rate ratios, K_{rel}, for rates of nitration of the substituted benzenes relative to that of benzene (and thus the partial rate factors) may be inaccurate, because there were serious losses of material during the experiments. For example, in the competitive nitration of 1 mole each of benzene and benzyltrimethylsilane, the amount of recovered benzene plus nitrobenzene obtained was only 0·983 mole, and of recovered benzyltrimethylsilane plus nitrobenzyltrimethylsilane only 0·921 mole. Different assumptions about the origin of these losses lead to different values of K_{rel} and thus of partial rate factors. (Chernyshev *et al.* do not say what assumptions they made in calculating K_{rel} values.) The uncertainty is, in our opinion, sufficient to cast doubt on the reality of the apparent increase in reactivity on going from the compound $Me_3Si\cdot[CH_2]_3\cdot Ph$ to the compound $Me_3Si\cdot[CH_2]_4\cdot Ph$, but not to explain away the observation that the reactivity of the *para*-position of each of the compounds $Me_3Si\cdot[CH_2]_n\cdot Ph$ with $n = 2$—4 is less than that of the *para*-position of toluene.

The activating effect of the *p*-trimethylsilylmethyl group in nitration, only a little greater than that of the *p*-methyl group, is very much lower than would be expected from its influence in protodesilylation. In protodesilylation the ratio log $f_p(Me_3Si\cdot CH_2)$/log $f_p(\mathrm{Me})$ has a value of 1·85; if this ratio applied to nitration in acetic anhydride the value of $f_p(Me_3Si\cdot CH_2)$ would be 1950, in marked contrast with the experimental value of about 69.

EXPERIMENTAL

Materials.—The preparations of the organosilanes have been previously described.[1]

Rate Studies.—Rates were measured spectrophotometrically by the methods described

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[7] Benkeser and Krysiak, *J. Amer. Chem. Soc.*, 1954, **76**, 6353; Benkeser, Hickner, Hoke, and Thomas, *ibid.*, 1958, **80**, 5289; Eaborn and Moore, *J.*, 1959, 3640; Deans, Eaborn, and Webster, *J.*, 1959, 3031.

[8] Vandoni and Viala, *Mém. Services chim. État.*, 1945, **32**, 80 (*Chem. Abs.*, 1948, **42**, 4812); Chédin and Fénéant, *Compt. rend.*, 1949, **229**, 115; Marcus and Fresco., *J. Chem. Phys.*, 1957, **27**, 564; Malkova, *Zhur. obshchei Khim.*, 1954, **24**, 1157; Bonner, *J.*, 1959, 3908; Bordwell and Garbisch, *J. Amer. Chem. Soc.*, 1960, **82**, 3588; Norman and Radda, *J.*, 1961, 3030; Knowles and Norman, *J.*, 1961, 2938, 3888; Billing and Norman, *J.*, 1961, 3885.

[9] Knowles, Norman, and Radda, *J.*, 1960, 4885; Ingold, Lapworth, Rothstein, and Ward, *J.*, 1931, 1959.

TABLE 3.

Wavelengths (λ), and concentrations (*C*) of the methanolic solutions of compounds $X\cdot C_6H_4\cdot SiMe_3$.

X	λ (Å)	10^3C (M)	X	λ (Å)	10^3C (M)
H	2700	12	*o*-$Me_3Si\cdot[CH_2]_3$	2750	4
o-Me	2750	4	*m*-$Me_3Si\cdot[CH_2]_3$	2745	4
m-Me	2755	4	*p*-$Me_3Si\cdot[CH_2]_3$	2370	5
p-Me	2730	10	*p*-$Me_3Si\cdot[CH_2]_3$	2725	5
o-$Me_3Si\cdot CH_2$	2815	2	*o*-$Me_3Si\cdot[CH_2]_4$	2750	4
m-$Me_3Si\cdot CH_2$	2810	3	*m*-$Me_3Si\cdot[CH_2]_4$	2745	4
p-$Me_3Si\cdot CH_2$	2490	2	*p*-$Me_3Si\cdot[CH_2]_4$	2370	5
o-$Me_3Si\cdot[CH_2]_2$	2750	4	*p*-$Me_3Si\cdot[CH_2]_4$	2725	5
m-$Me_3Si\cdot[CH_2]_2$	2745	4	*m*-$Me_3Si\cdot(Pr^n)CH$	2810	4
p-$Me_3Si\cdot[CH_2]_2$	2385	6	*p*-$Me_3Si\cdot(Pr^n)CH$	2530	2
p-$Me_3Si\cdot[CH_2]_2$	2725	6			

previously.[3,10] For runs of half-life <1 hr., aqueous perchloric acid (2 ml.) was mixed with a methanolic solution of the silane (5 ml.), but for slower runs 10 ml. of acid was mixed with 25 ml. of the methanolic solution so that several samples could be kept in sealed tubes at 50° for 10 half-lives to give the " infinity " value of the optical density. The wave-lengths employed and the concentrations of the methanolic solutions are shown in Table 3.

Rate constants measured at a given wavelength were reproducible to within ±1%. For the three compounds studied at two wavelengths, rate constants at the separate wavelengths differed from the mean by less than 2%.

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[10] Deans and Eaborn, *J.*, 1959, 2299.