Aromatic Reactivity. Part LI.[1] Nitrosodesilylation as a Route to Nitrodesilylation Products from Aryltrimethylsilanes and Nitric Acid in Acetic Anhydride

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A detailed study of the reaction between *p*-tolyltrimethylsilane and nitric acid in acetic anhydride has shown that the formation of the nitrodesilylation product, *p*-nitrotoluene, takes place predominantly, and possibly exclusively, *via* nitrosodesilylation. Thus, (i) when the mixture of nitric acid and acetic anhydride was heated briefly to 100° then used at 15°, the ratio of nitrodesilylation to nitration product (2-nitro-4-trimethylsilyltoluene) was 90, (ii) when the mixture was made up and used at 15° the ratio was 0·64, (iii) when the mixture was made up and used at 15° but with urea present, the ratio was 0·14, and (iv) when the mixture was made up at 15° and nitrous fumes were dissolved in it before use at 15° the ratio was 4·8. With a solution of nitrous fumes in acetic acid–acetic anhydride, only the nitrodesilylation product was formed. The *p*-nitrotoluene formed in the reaction with solutions of acetyl nitrate or dinitrogen pentoxide also seems to be produced predominantly and exclusively through nitrosodesilylation.

The reactions between nitric acid and phenyltrimethylsilane, *m*-methyl-, *m*-chloro-, or *p*-chloro-phenyltrimethylsilane in acetic anhydride have been more briefly studied, but the results are again consistent with the assumption that the formation of nitrodesilylation products involves initial nitrosodesilylation. In the reaction with a solution of nitrous fumes in acetic acid–acetic anhydride, *p*-tolyl- is *ca.* 50 times as reactive as phenyl-trimethylsilane.

MANY electrophilic reagents cleave aryl–$SiMe_3$ bonds, and in general such cleavages are faster than those of the corresponding aryl–H bonds.[2,3] It is known that certain nitrating agents can bring about predominantly nitration of aryltrimethylsilanes, to give nitroaryltrimethylsilanes, while others favour formation of nitrodesilylation products, *i.e.* cleavage of the aryl–$SiMe_3$ bond.[2] Thus phenyltrimethylsilane with nitric acid or copper nitrate in acetic anhydride gives mainly *o*-, *m*-, and *p*-nitrophenyltrimethylsilane,[4,5] though some nitrobenzene is produced by desilylation.[6] On the other hand, addition of nitric acid to a solution of phenyltrimethylsilane in acetic anhydride without cooling, followed by refluxing, has been found to give nitrobenzene in 71% yield.[7] Again, *p*-nitrophenyltrimethylsilane has been obtained in 80% yield by treatment of *p*-bis(trimethylsilyl)benzene

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[1] Part L, R. Baker, C. Eaborn, and R. Taylor, *J.C.S. Perkin II*, 1972, 97.

[2] C. Eaborn and R. W. Bott, in ' Organometallic Compounds of the Group IV Elements,' ed. A. G. MacDiarmid, Dekker, New York, 1969, vol. 1, part 1, pp. 407—431.

[3] C. Eaborn, *Pure and Applied Chem.*, 1969, **19**, 375.

[4] R. A. Benkeser and P. E. Brumfield, *J. Amer. Chem. Soc.*, 1951, **73**, 4770.

[5] J. L. Speier, *J. Amer. Chem. Soc.*, 1953, **75**, 2930.

[6] T. Hashimoto, *Yakugaku Zasshi*, 1965, **85**, 524.

[7] V. Chvalovský and V. Bažant, *Coll. Czech. Chem. Comm.*, 1951, **16**, 580.

with fuming nitric acid in acetic anhydride at the reflux temperature.[8] *

One of us (C. E.) was involved some years ago with Dr. K. Leyshon in a study of the nature of nitrodesilylation by nitric acid in acetic anhydride in which *p*-tolyltrimethylsilane was used as the substrate.[11] [The advantage of this compound is that nitrodesilylation can be distinguished readily from acid cleavage (protodesilylation) of the aryl–silicon bond followed by nitration, since nitrodesilylation gives only *p*-nitrotoluene while nitration of toluene gives a mixture of *o*-, *m*-, and *p*-isomers, and the presence of the *o*-isomer indicates that simple nitrodesilylation is not being observed.] A detailed account of that study was not published, but the results were summarized in a review,[10] in which it was tentatively suggested that dinitrogen pentoxide might be responsible for the nitrodesilylation. Although the experimental results obtained in the earlier study were mainly valid, we have now found that the nitrodesilylation products are, in fact, produced mainly, and possibly exclusively, by nitrosodesilylation followed by oxidation.

TABLE 1

Yields of *p*-$NO_2 \cdot C_6H_4Me$ (I) and 2-NO_2-4-$Me_3Si \cdot C_6H_3Me$ (II) in the reaction between *p*-$MeC_6H_4 \cdot SiMe_3$ (III) and nitric acid in acetic anhydride [a]

Expt. No.	Special conditions	Temp. and time	(I) (%)	(II) (%)	(III) [b] (%)	*R* [c]
(*a*) Nitric acid mixed with Ac_2O at 0°, then added to arylsilane in acetic anhydride at reaction temp. Medium: HNO_3 (0·20 mol) in Ac_2O (20 wt-%) and AcOH (80 wt-%)						
(1)		5°; 5 h	24	55	0	0·44
(2)		25°; 5 h	35	46	0	0·76
(3)		50°; 5 h	60	28	0	2·1
(4)		100°; 5 h	62	18	13	3·5
(5)	H_2SO_4 (2 mmol) added to nitrating mixture immediately before use	5°; 8 h	70	28	0	2·5
(6)	As in (5)	25°; 8 h	34	7	0	4·9 [d]
(7)	As in (5)	50°; 5 h	88	7	0	12·3
(8)	$NaNO_3$ (2 mmol) added to nitric acid	5°; 10 h	33	55	0	0·60
(*b*) Nitric acid mixed with Ac_2O at 20°, then taken to −20° and solution of arylsilane in Ac_2O added. Medium: HNO_3 (0·20 mol) in Ac_2O (75 wt-%) and AcOH (25 wt-%)						
(9)		−20°; 0·75 h	8·6	52	39	0·16
(10)		−20°; 0·25 h	5·0	39	35	0·13
(11)	H_2SO_4 (2 mmol) added to nitrating mixture before use	−20°; 0·25 h	11	71	0	0·15
(12)	$NaNO_3$ (2 mmol) added to nitrating mixture	−20°; 0·75 h	6·5	28	45	0·23
(*c*) The nitric acid was added to the Ac_2O maintained at 15°, and mixture added to arylsilane in acetic acid maintained at 15°. Medium: HNO_3 (0·25 mol) in Ac_2O (20 wt-%) and AcOH (80 wt-%)						
(13)		15°; 6 h	37·5	59	0	0·64
(14)	Nitrating mixture heated for 1 min at 100°, then cooled quickly before use	15°; 6 h	81	0·9	11	90
(15)	Nitrous fumes dissolved in nitrating mixture	15°; 6 h	82	17	0	4·8
(16)	$NaNO_2$ (20 mmol) added to nitrating mixture	15°; 6 h	57	39	0	1·4
(17)	HNO_3 heated briefly with urea before use, and urea added to arylsilane solution	15°; 6 h	11	79	2	0·14
(18)	H_2SO_4 (2 mmol) added to nitrating mixture, which was heated to 100° for 1 min then quickly cooled	15°; 6 h	48	0	14	>100 [d]
(19)	$NaNO_3$ (50 mmol) added to the HNO_3	15°; 6 h	38	49	0	0·77
(*d*) HNO_3 added to the arylsilane in Ac_2O without cooling. Temp. rose to 110° and was maintained there.						
(20)		110°; 5 h	55	14	0 [e]	3·9

[a] For additional details see the Experimental section. [b] Recovered starting material. [c] Ratio (I)/(II). [d] Low total recovery. [e] Toluene was formed in 21% yield.

RESULTS AND DISCUSSION

Tables 1 and 2 show the results of the reaction between *p*-trimethylsilyltoluene and nitrating mixtures under a variety of conditions, the yields of nitrosodesilylation product, *p*-$NO_2 \cdot C_6H_4Me$, nitration product, 2-NO_2-4-$Me_3Si \cdot C_6H_3Me$, and recovered starting material being listed, along with the ratio, *R*, of nitrodesilylation to nitration product. It will be seen from Table 1, experiments (1)—(4), that elevation of the reaction temperature raises the value of *R*, as previously noted,[10,11] but experiments (13) and (14) show that a dramatic increase in *R* occurs when the mixture is first heated under reflux for 1 min and then cooled to 15° before the addition of the arylsilane; under these conditions nitrodesilylation products greatly predominate. It is thus clear that in reactions at high temperatures it is not the temperature as such which favours nitrodesilylation products but the formation of a new reagent which selectively attacks the aryl–silicon bond. It is known that nitrosating species are developed in nitric acid–acetic anhydride mixtures at room temperature, and that they readily bring about nitration *via* nitrosation in

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* Mixtures of nitric acid and acetic anhydride can be explosive.[9] However, we know of no example of explosion under conditions used for nitrodesilylation; a statement in ref. 10 implying the contrary resulted from a misunderstanding in the publisher's office.

[8] F. B. Deans and C. Eaborn, *J. Chem. Soc.*, 1957, 498.

[9] T. A. Brown and J. A. C. Watt, *Chem. in Britain*, 1967, **3**, 504.

[10] Ref. 2, pp. 422—423.

[11] K. Leyshon, Ph.D. Thesis, University of Leicester, 1962.

the case of reactive aromatic compounds.[12] Furthermore, brown fumes are evolved when the nitrating mixture is taken to reflux, and it thus seemed likely that lower nitrogen oxides were responsible for the selective attack on the aryl–silicon bond and this was shown to be the case. Thus experiments (13) and (17) of Table 1 show that urea, which destroys nitrous acid and other nitrosating species, suppresses the formation of nitrodesilylation products at 15°, while sodium nitrite favours the formation of these products [experiments (13) and (16)].

TABLE 2

Formation of *p*-$NO_2{\cdot}C_6H_4Me$ (I) and 2-(NO_2)-4-$Me_3Si{\cdot}C_6H_3Me$ (II) in the reaction between *p*-$Me_3Si{\cdot}C_6H_4Me$ (III) and various nitrating media [a]

Expt. No.	Nitrating medium and conditions	(I)	(II)	(III) [b]	*R* [c]
(21)	$AcO{\cdot}NO_2$ from $AgNO_3$ and AcCl; MeCN as solvent; 0; 9 h	10	16	60	0·62
(22)	$AcO{\cdot}NO_2$ from $AgNO_3$ and AcCl; MeCN–Ac_2O–AcOH solvent; 15°; 6 h	80	19	0	4·2
(23)	As in (22) but brown fumes added	89	5·6	0	16
(24)	As in (23) but urea added	3	27	57	0·11
(25)	HNO_3 in Ac_2O–AcOH (20 : 80 w/w); 15°; 6 h	37·5	59	0	0·63
(26)	HNO_3 in Ac_2O–AcOH (51·5 : 48·5 w/w); 15°; 6 h	37	50	0	0·74
(27)	HNO_3 in Ac_2O–AcOH (96 : 4 w/w); 15°; 6 h	29	55	0	0·53
(28)	N_2O_5 in Ac_2O–AcOH; −20°; 0·25 h	11	51	20	0·22
(29)	N_2O_5 in Ac_2O–AcOH; −20°; 9 h	14	70	0	0·22
(30)	N_2O_5 in Ac_2O–AcOH; −25°; 5 h	12	65	6	0·19
(31)	N_2O_5 in Ac_2O–AcOH; 0°; 5 h	38	52	0	0·74
(32)	N_2O_5 in Ac_2O–AcOH; 25°; 5 h	70	29	0	2·4
(33)	N_2O_5 in CCl_4 added to silane in CCl_4; 0°; 8 h	56	25	3	2·2
(34)	Silane in CCl_4 added to N_2O_5 in CCl_4; 0°; 8 h	14	50	22	0·29
(35)	$Cu(NO_3)_2$ in Ac_2O; 15°; 6 h	48	24	21	2·0
(36)	Brown fumes from $Pb(NO_3)_2$ dissolved in Ac_2O–AcOH; 15°; 6 h	19	0	58	>50
(37)	As in (36) but brown fumes from decompn. of HNO_3–Ac_2O; 15°; 6 h	57	0	30	>100

[a] For additional details see Experimental section. [b] Recovered starting material. [c] Ratio (I)/(II).

Again, a solution in acetic acid–acetic anhydride of brown nitrous fumes (mainly nitrogen dioxide) generated by decomposition either of lead nitrate or of nitric acid in acetic anhydride under reflux, gave only nitrodesilylation products, along with unchanged *p*-trimethylsilyltoluene [experiments (36) and (37)]. On the other hand, solutions of dinitrogen pentoxide gave predominantly nitration products at low temperatures but predominantly nitrodesilylation products at 25° [experiments (28)—(32)], at which, presumably, there is significant decomposition of the pentoxide to lower oxides of nitrogen. The high value of *R* previously reported for dinitrogen pentoxide solutions [10,11] can be reasonably attributed to the formation of nitrosating species. With dinitrogen pentoxide in carbon tetrachloride, a low value of *R* was obtained when the arylsilane was added to the cooled solution of pentoxide, but a high value when the reverse addition was used [experiments (33) and (34)]. We attribute this latter result to decomposition of the uncooled pentoxide solution in the dropping funnel.

In a separate experiment it was shown that *p*-nitrosotoluene is rapidly converted into *p*-nitrotoluene by nitric acid in acetic anhydride, no doubt with regeneration of nitrosating species. We conclude that the nitrodesilylation products obtained with nitric acid in acetic anhydride arise mainly, and perhaps exclusively, from nitrosodesilylation followed by oxidation. The formation of small amounts of *p*-nitrotoluene in presence of urea may possibly result from direct nitrodesilylation.

Solutions of acetyl nitrate prepared from silver nitrate and acetyl chloride in acetonitrile gave mainly nitration products [experiment (21)], though when such a solution was mixed with acetic anhydride–acetic acid before use a high value of *R*, *viz.* 4·2, was obtained [experiment (22)]. However, an even higher value, *viz.* 16, was obtained when brown fumes were dissolved in the latter mixture [experiment (23)], and when urea was present [experiment (24)] the value of *R* was much lower, *viz.* 0·11, indicating that once again nitrosating species are predominantly or exclusively responsible for the formation of *p*-nitrotoluene. These results also reveal that the presence of substantial quantities of strong acid is not necessary either for the nitration or the nitrosodesilylation.

We confirmed the previous report [10,11] that addition of sulphuric acid to the nitric acid in acetic anhydride solutions increases the rate of formation of both nitration and nitrodesilylation products [experiments (9)—(11)] but favours the latter [experiments (1) and (5)]. This can be reasonably attributed to the well known acid-catalysis of nitration accompanied by an even more effective acid-catalysis of the decomposition which produces nitrosating species.

We also partly confirmed the previous report that the presence of nitrate ion decreased the overall rate of reaction without significant effect on the value of *R*.[10,11] As experiments (1) and (8), and (13) and (19) show, we found that addition of sodium nitrate had little effect on *R*, but under the conditions used no reduction in rate was apparent.

Contrary to the earlier report, we found that variation in the proportions of acetic acid and acetic anhydride in the medium had little effect on the value of *R* [experiments (25)—(27)]. In the earlier work,[10,11] when the importance of nitrosating species had not been recognized, less care was taken to produce the reaction mixtures under standardized conditions, and amounts of such species present no doubt varied markedly. The earlier observation that the value of *R* rose as the

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[12] J. G. Hoggett, R. B. Moodie, and K. Schofield, *Chem. Comm.*, 1969, 605.

reaction progressed [10,11] can now be readily understood in terms of increasing formation of nitrosating species by decomposition of the medium.

TABLE 3

Formation of the nitrodesilylation product, (I), and the nitration product(s), (II), in the reaction of $YC_6H_4{\cdot}SiMe_3$ (III), with nitric acid in acetic anhydride.

Expt. No.	Y	Conditions [a]	(I) (%)	(II) (%)	(III) [b] (%)
(38)	*m*-Me	Nitrating mixture allowed to warm to 100° and cooled slowly before use; 15°; 6 h	12	0	69 [c]
(39)		120°; 5 h	25	13	35 [c]
(40)		Nitrous fumes added; 100°; 6 h	76	12	0
(41)		HNO_3 added to silane in Ac_2O at 110°; 6 h	51	29 [d]	0
(42)	*p*-Cl	Nitrous fumes added, and escape prevented; 100°; 6 h	56	0	40
(43)		Nitrous fumes added and escape prevented; 110°; 6 h	81	0	7
(44)		HNO_3 added without cooling to solution of silane in Ac_2O; then kept at 90° for 6 h	57	0 [e]	24
(45)	*m*-Cl	Nitrous fumes added, and escape prevented; 110°; 6 h	30	0	60

[a] For further details see the Experimental section. [b] Recovered starting material. [c] Much decomposition of the nitrating mixture has occurred. [d] An additional product (*ca.* 8%) was formed, having a retention time similar to that of the nitro(trimethylsilyl)toluenes. [e] Chlorobenzene was formed in 20% yield.

Results with Other Aryltrimethylsilanes.—Results obtained with *m*-trimethylsilyltoluene in nitric acid–acetic anhydride mixtures are shown in Table 3. With this compound the rate of cleavage of the aryl–Si bond should be substantially lower than with the *p*-isomer, and the reactive *para*-position is available for nitration, so the probability of producing nitration rather than nitrodesilylation products should be increased. Even so, when reaction was carried out at 100° in presence of lower nitrogen oxides, 76% of the nitrodesilylation product, *m*-nitrotoluene, was obtained along with a total of 12% of mixed mononitro-*m*-trimethylsilyltoluenes. Only the nitrodesilylation product was obtained, along with much unchanged *m*-trimethylsilyltoluene, when the nitrating mixture was heated before use without precautions to retain the nitrogen oxides [experiment (38)], indicating that the nitrating species had substantially decomposed.

TABLE 4

Formation of $PhNO_2$ (I) and *o*- (II), *m*- (III), and *p*-$NO_2{\cdot}C_6H_4{\cdot}SiMe_3$ (IV), in the reaction between phenyltrimethylsilane, (V), and nitrating agents in acetic anhydride [a]

Expt. No.	Conditions	(I) (%)	(II) (%)	(III) (%)	(IV) (%)	(I) + (II) + (III) (%)	(V) [b] (%)	*R* [c]
(46)	15°; 6 h	7	21	32	24	77	11	0·1
(47)	Nitrous fumes added; 15°; 6 h	47	10·5	16	14	40·5	9	1·2
(48)	Urea present; 15°; 6 h	4·5	11	18	14	43	46	0·1
(49)	HNO_3/Ac_2O heated at 110° for 1 min then used at 15°; 6 h	5·4	1·1	1·7	2·5	5·3	73	1·0
(50)	120°; 6 h	71				3·7	21	19
(51)	HNO_3 added to silane in Ac_2O at 90°; 6 h	50	2·0	3·1	2·0	7·1	15	7
(52)	Nitrous fumes dissolved in Ac_2O at 20°; 24 h	46	0	0	0	0	49	>100
(53)	$Cu(NO_3)_2$ in Ac_2O, no HNO_3; 15°; 6 h	5·3	16	25	16	57	31	0·1

[a] For additional details see the Experimental section. [b] Recovered starting material. [c] Ratio of nitrodesilylation to nitration.

Results with phenyltrimethylsilane (Table 4) parallel closely those with *p*-tolyltrimethylsilane, though substantial amounts of unchanged arylsilane remain under the conditions used, in line with the markedly lower reactivity of this compound compared with that of the *p*- and *m*-tolyl compounds. Since no significant protodesilylation occurred with either *m*- or *p*-tolyltrimethylsilane, we think it unlikely that any significant quantity of the nitrobenzene was produced *via* protodesilylation to benzene followed by nitration (*cf.* refs. 6 and 7). A value of 19 was obtained for the nitrodesilylation/nitration ratio in the reaction at 120°. In contrast with the results obtained for *p*-tolyltrimethylsilane, when the nitrating mixture was preheated to 100° but then used at 15° the value of *R* was not especially high, but much significance cannot be attached to this result in view of the fairly small overall extent of reaction. Speier obtained nitrobenzene in 7 and 3% yield ($R = ca.$ 0·15 and 0·08) from the reaction with nitric acid in acetic anhydride [5] at 25—70° and 0—10°, respectively, while Benkeser and Brumfield obtained it in 25% yield ($R = ca.$ 0·3) from the reaction with copper nitrate in acetic anhydride.[4]

p-Chlorophenyltrimethylsilane was too unreactive to react with nitric acid in acetic anhydride at the reflux temperature unless precautions were taken to prevent escape of nitrogen oxides from the system, decomposition of the nitrating species presumably occurring before appreciable substitution. When lower nitrogen oxides were added, however, and a cold finger used to prevent escape of these oxides, *p*-nitrochlorobenzene was obtained in up to 81% yield, but no nitration products were produced (Table 3). The nitrodesilylation product was also formed when the nitric acid was added to *p*-chlorophenyltrimethylsilane in acetic anhydride without cooling, so that the temperature rose to *ca.* 90°, but in this case a substantial amount of the protodesilylation product, chlorobenzene, was also formed.

With *m*-chlorophenyltrimethylsilane reaction was, as expected, even slower, but up to 36% of the nitrodesilylation product, *m*-chloronitrobenzene, was produced when the nitric acid was added to the heated solution of the arylsilane in acetic anhydride with precautions to retain the nitrogen oxides. Much unchanged *m*-chlorophenyltrimethylsilane was also recovered, but no nitration product, although Hashimoto has obtained 2-nitro-5-chlorophenyltrimethylsilane in 80% yield from the reaction with acetyl nitrate.[13]

Preparative Aspects.—Our results indicate that the yields of nitrodesilylation products should generally be maximized by use of mixtures prepared from acetic anhydride and nitric acid and containing added lower nitrogen oxides, or, in the case of more reactive compounds, even more effectively, by use of solutions of lower nitrogen oxides alone. However, Chvalovský and Bažant obtained very high yields of nitrodesilylation products by addition of 71% nitric acid without cooling to solutions of aryltrimethylsilanes in acetic anhydride, followed by 6 h under reflux.[7] We have been unable to reproduce their high yields; for example, with *m*-tolyltrimethylsilane under their conditions, we obtained only 51% of *m*-nitrotoluene, compared with their 77%, whereas we were able to obtain a 76% yield by using pre-prepared nitric acid–acetic anhydride mixtures containing added nitrogen oxides. Again, compared with their 93% yield, we could obtain only a 57% yield of *p*-nitrochlorobenzene from *p*-chlorophenyltrimethylsilane under their conditions, along with 20% of chlorobenzene produced by protodesilylation (Table 3). This does not, of course, imply that Chvalovský and Bažant's results are in error, because there could fortuitously have been substantial quantities of lower nitrogen oxides present in their reactions, but the possibility of protodesilylation may make their method less attractive generally than use of lower nitrogen oxides in acetic acid–acetic anhydride or of pre-prepared nitric acid–acetic anhydride mixtures containing added nitrosating species, with precautions to minimize the escape of nitrogen oxides.

Relative Reactivities of Phenyl- and p-*Tolyl-trimethylsilane.*—*p*-Tolyl- and phenyl-trimethylsilane were allowed to compete for a deficiency of the reagent produced by dissolving nitrous fumes in acetic anhydride–acetic acid, conditions under which no nitration products are formed. The results reveal that the *p*-tolyl- is *ca.* 50 times as reactive as the phenyl-compound. The corresponding factor is 21 in protodesilylation by aqueous methanolic perchloric acid,[14] and 49 in bromodesilylation in acetic acid,[15] indicating that the reagent responsible for the nitrosodesilylation is as selective as molecular bromine, both being less selective than oxonium ion in reactions at aryl–$SiMe_3$ bonds.

Mechanistic Considerations.—It is to be expected that nitrosating species, which are known to be relatively unreactive and highly selective towards benzene derivatives (and much less reactive than common nitrating species),[16] should selectively cleave Ar–$SiMe_3$ rather than Ar–H bonds. Thus molecular bromine in acetic acid, which is possibly a reagent of comparable selectivity as noted above, cleaves the Ph–$SiMe_3$ bond some 10^8 times as readily as the Ph–H bond,[15] while a factor of 10^4 applies even with the more reactive oxonium ion in aqueous sulphuric acid.[17] The high reactivity of the Ph–$SiMe_3$ bond towards electrophiles can be mainly attributed to stabilization of the Wheland intermediate by the strong electron release from the C–$SiMe_3$ bond [18] (mainly hyperconjugative [19]), but it is possible that an additional effect operates in nitrosodeprotonations and nitrosodesilylations. It is known that in nitrosation, at least in aqueous sulphuric acid, the loss of the proton from the Wheland intermediate is rate-determining; [20] in other words, the nitrosonium ion is lost from the intermediate much more often than the proton. Since in hydroxylic media a trimethylsilyl group is normally much more readily lost than a proton (C–$SiMe_3$ bonds normally being much more readily cleaved than the C–H bonds by nucleophilic reagents in such media [21]),* it would be expected that even if the Wheland intermediate were formed from phenyltrimethylsilane no more readily than from benzene (which is unlikely), the greater ease of loss of the trimethylsilyl group would cause the nitrosodesilylation to occur markedly more rapidly than the nitrosation.

The difficulty which remains is to explain why the nitrating species present should selectively attack the C–H rather than C–$SiMe_3$ bond. This problem is complicated by the fact that it is not even known with certainty what the dominant nitrating entity is in nitric acid–acetic anhydride mixtures.[12,23,24] Whatever it is, this entity (assuming, for simplicity, that only one is effective) discriminates markedly less effectively between toluene and benzene [24] than does the oxonium ion of aqueous sulphuric acid, and very much less effectively than bromine in acetic acid, and so a relatively low selectivity between corresponding Ar–$SiMe_3$ and Ar–H bonds would also be expected, but not to the virtual exclusion of nitrodesilylation. Possibly steric effects are

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* For a discussion of the relative leaving abilities of various groups in electrophilic aromatic substitution see ref. 22.

[13] T. Hashimoto, *Yakugaku Zasshi*, 1967, **87**, 291.

[14] C. Eaborn, *J. Chem. Soc.*, 1956, 4858.

[15] C. Eaborn and D. E. Webster, *J. Chem. Soc.*, 1957, 4449; 1960, 179.

[16] R. O. C. Norman and R. Taylor, ' Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965, pp. 91—92.

[17] C. Eaborn and K. C. Pande, *J. Chem. Soc.*, 1960, 1566.

[18] R. W. Bott, C. Eaborn, and P. M. Greasley, *J. Chem. Soc.*, 1964, 4804.

[19] M. A. Cook, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1970, **24**, 293; A. R. Bassindale, C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Organometallic Chem.*, 1969, **20**, 49; C. G. Pitt, *J. Organometallic Chem.*, 1970, **23**, C35.

[20] B. C. Challis, R. J. Higgins, and A. J. Lawson, *Chem. Comm.*, 1970, 1223.

[21] Ref. 2, p. 359.

[22] C. L. Perrin, *J. Org. Chem.*, 1971, **36**, 420.

[23] S. R. Hartshorn, R. B. Moodie, K. Schofield, *J. Chem. Soc.* (*B*), 1970, 1256.

[24] J. H. Ridd, ' Studies on Chemical Structure and Reactivity,' Methuen, London, 1966, pp. 133—153.

of unusual importance in the nitrodesilylation, even though nitration in acetic anhydride is not associated with large steric requirements as judged by the effects of substituents on reaction at the *ortho*-positions. For example if the nitrating (and nitrodesilylating) entity were protonated acetyl nitrate (see refs. 25 and 26),* encumbered with molecules of solvation, there might be serious interaction between this entity and the Me_3Si group in the transition state on the way to the Wheland intermediate, and also marked hindrance to solvation to both sides of the ring in the forming intermediate.

EXPERIMENTAL

Aryltrimethylsilanes.—The $XC_6H_4{\cdot}SiMe_3$ compounds, all previously known, were prepared by established procedures, and had the following physical properties: (X =) H, b.p. 170°, n_D^{25} 1·4870; *m*-Me, b.p. 190°, n_D^{25} 1·4901; *p*-Me, b.p. 191°, n_D^{25} 1·4890; *m*-Cl, b.p. 206°, n_D^{25} 1·5092; *p*-Cl, b.p. 206°, n_D^{25} 1·5068.

4-*Methyl*-3-*nitrophenyltrimethylsilane*.—The ethereal extract from a reaction identical with that described from experiment (3) below (50° for 5 h), was fractionally distilled to give, in addition to *p*-nitrotoluene, 4-*methyl*-3-*nitrophenyltrimethylsilane*, b.p. 136°/10 mm, n_D^{25} 1·5218 (Found: C, 57·6; H, 7·4; N, 6·3. $C_{10}H_{15}NO_2Si$ requires C, 57·4; H, 7·2; N, 6·7%). The ^1H n.m.r. spectrum of a solution in deuteriochloroform (with tetramethylsilane as internal standard) had the expected pattern, with τ values as follows: Me_3Si, 9·71(s), 4-Me, 7·45(s), 4-H and 5-H, 2·51(q), and 2-H, 1·94(s). G.l.c. analysis revealed no impurities.

Analysis of Products.—After reaction between the nitrating agent and the aryltrimethylsilane had occurred, the mixture was cooled and added to an excess of concentrated solution of sodium hydroxide in water. Internal standards (see below) were then added, and organic materials were extracted several times with ether. The ethereal extracts were combined, and washed with water, the aqueous washings being re-extracted with ether; samples of the combined extracts were used for g.l.c. analysis. In some cases the ether extraction was carried out without addition of internal standards; the extracts were dried (Na_2SO_4), the ether was taken off by slow distillation through a precision-made Vigreux column (20 plates), and the internal standards were added.

The internal standards used were: n-octane for phenyltrimethylsilane, and *m*- and *p*-tolyltrimethylsilane; n-tridecane for *m*- and *p*-nitrotoluene, 4-nitro-3-methyltrimethylsilane, nitrobenzene, and nitrophenyltrimethylsilanes; n-undecane for *m*- and *p*-chlorotrimethylsilane and nitrochlorobenzenes.

G.l.c. analysis were carried out on a Pye series 104 model 64 instrument, fitted with a flame-ionization detector. Columns (9 ft) of 5% S.E. 30 on silanized Chromasorb G were used with nitrogen (50 ml/min) as carrier gas. Calibration curves based on peak-area ratios were drawn-up for internal standards and authentic samples of starting materials and products. For analysis of ethereal solutions the column was maintained at 180°, but in cases in which the ether was removed before the analysis, temperature programming in the range 60—230° was used. Checks on several mixtures showed that effectively identical results were obtained by the two methods.

Reactions.—The experiment nos. below refer to Tables 1—4. In all cases the reactions were carried out in a vessel fitted with a reflux water condenser, and sometimes (as indicated below) a cold finger cooled with solid carbon dioxide was attached to the top of the condenser. The nitric acid was 70% w/w unless otherwise indicated.

Experiments (1)—(8). Nitric acid (18·0 g) was added dropwise to acetic anhydride (55·6 g, 0·545 mol) pre-cooled in an ice–salt mixture, the temperature being maintained at about 0°. The solution was then added dropwise with vigorous stirring to a solution of *p*-tolyltrimethylsilane (16·4 g, 0·10 mol) in acetic acid (64·0 g, 1·07 mol) which was pre-cooled or pre-heated to the required temperature, this temperature (±5°) being maintained throughout the addition. After the time stated in Table 1 the solution was cooled, where necessary, and added to a solution of sodium hydroxide (95 g) in water (400 ml) with strong cooling. Organic material was extracted with ether (100 ml, then 6 × 50 ml), the combined extracts were washed with water (2 × 50 ml) the aqueous washings were extracted with ether (2 × 50 ml), and the combined ethereal solutions were then analysed, either immediately or in some cases after removal of the ether.

On the assumption that all the water was taken up by hydrolysis of acetic anhydride, the medium consisted of 12·6 g (0·20 mol) of nitric acid in a mixture of 25 g (20 wt-%) of acetic anhydride and 100 g (80 wt-%) of acetic acid.

Experiments (9)—(12). Nitric acid (18·0 g) was added dropwise to acetic anhydride (130 g, 1·27 mol) maintained at 20—25°. The mixture was cooled to −20 ± 5°, and a solution of *p*-tolyltrimethylsilane (16·4 g, 0·10 mol) in acetic anhydride (10·0 g, 0·098 mol) was added dropwise, with strong cooling to maintain the temperature at −20 ± 5°. The mixture was kept at this temperature for the time stated in Table 1, and was then added to aqueous sodium hydroxide as described above. The medium was nitric acid (12·8 g, 0·20 mol) in 109 g (75·2 wt-%) acetic anhydride and 36 g (24·8 wt-%) acetic acid.

p-Tolyltrimethylsilane was recovered almost quantitatively when the nitric acid–acetic anhydride was made up at −20° before a 4 h reaction period with the arylsilane at −20°.

Experiments (13)—(19). Nitric acid (22·5 g) was added dropwise to acetic anhydride (63·3 g, 0·62 mol) with cooling to maintain the temperature at 15 ± 5°. The mixture was then normally added to *p*-tolyltrimethylsilane (16·4 g, 0·10 mol) in acetic acid (55·0 g, 0·92 mol) maintained at 15°, and the mixture was kept at this temperature for 6 h before being added to aqueous sodium hydroxide. The medium was nitric acid (15·75 g, 0·31 mol) in 25·0 g (20 wt-%) acetic anhydride and 100 g (80 wt-%) acetic acid.

In experiment (15), fumes from the decomposition of solid lead nitrate were bubbled through the nitric acid–acetic anhydride mixture for 5 min at 15°.

Experiment (20). Nitric acid (5 ml) was added during 5 min to *p*-tolyltrimethylsilane (8·2 g, 0·050 mol) in acetic anhydride (8·3 ml) at room temperature without cooling.

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* *p*-Tolyltrimethylsilane did not react with a nitric acid–acetic anhydride mixture made up and used at −20°, at which no acetyl nitrate would be formed (see ref. 26).

[25] A. Fischer, J. Packer, J. Vaughan, and G. J. Wright, *J. Chem. Soc.*, 1964, 3687.

[26] F. G. Bordwell and E. W. Garbisch, jun., *J. Amer. Chem. Soc.*, 1960, **82**, 3588.

The temperature rose rapidly to 110°, and was maintained there for 5 h.

Experiment (21). *p*-Tolyltrimethylsilane (16·4 g, 0·10 mol) was added to a solution of silver nitrate (34·0 g, 0·20 mol) in acetonitrile (100 g) at 0°. A solution of acetyl chloride (15·7 g, 0·20 mol) in acetonitrile (25 g) was added dropwise. The temperature was maintained at 0—5° during the addition and for a total of 9 h. The mixture was then added to sodium hydroxide (100 g) in water (500 ml) and the resulting mixture was set aside overnight and then filtered. Internal standards were added to the filtrate, which was then extracted with ether in the usual way.

Experiments (22)—(24). In experiment (22), silver nitrate (34·0 g, 0·20 mol) was dissolved in acetonitrile (30 ml), and acetic anhydride (53·3 g) and acetic acid (25 g) were added to it. A solution of acetyl chloride (15·7 g, 0·20 mol) in acetic anhydride (10 g) was added dropwise with shaking, the mixture being maintained at 0—5°. Silver chloride was filtered off under nitrogen, and the filtrate was added dropwise with vigorous stirring to a solution of *p*-tolyltrimethylsilane (16·4 g, 0·10 mol) in acetic acid (30 g) at 15°. The mixture was kept at 15° for 6 h and then addition to the aqueous sodium hydroxide was followed by work-up.

In experiment (23), brown fumes from the decomposition of the refluxing nitric acid–acetic anhydride mixture were bubbled into the acetyl nitrate solution for 5 min before use. In experiment (24), urea (1·0 g) was added to the acetyl nitrate solution 5 min before use.

Experiments (25)—(27). The conditions for experiment (25) were identical with those for experiments (1)—(4) except for the reaction temperature.

In experiment (26), nitric acid (22·5 g) was added dropwise to acetic anhydride (63·3 g, 0·62 mol) maintained at 15°, and the mixture was then added to *p*-tolyltrimethylsilane (0·10 mol) in acetic anhydride (23 g, 0·22 mol) at 15°. The medium was thus: nitric acid (15·7 g, 0·25 mol) in 47·8 g (51·3 wt-%) of acetic anhydride and 45·3 g (48·7 wt-%) of acetic acid.

In experiment (27), nitric acid (16·3 g, of 96·6 wt-% acid) was added to acetic anhydride (57·9 g) at 15°, and the mixture was added to *p*-tolyltrimethylsilane (0·10 mol) in acetic anhydride (34·8 g) at 15°. The medium was thus: nitric acid (15·7 g, 0·25 mol) in 89·3 g (95·7%) of acetic anhydride and 4·0 g (4·3%) of acetic acid.

Experiments (28)—(32). Dinitrogen pentoxide (4·90 g, 0·045 mol) was dissolved in a mixture of acetic anhydride (35·8 g) and acetic acid (6·0 g) at the temperature subsequently used for reaction, except that in experiment (32) the mixture was made up at −20° and then allowed to warm to 25° and kept at this temperature for 30 min before use.

Experiments (33) *and* (34). In experiment (33), dinitrogen pentoxide (5·00 g, 0·046 mol) was dissolved at 0—5° in anhydrous carbon tetrachloride (50 ml) containing sodium fluoride (4·0 g). A solution of *p*-tolyltrimethylsilane (4·10 g, 0·025 mol) in carbon tetrachloride (10 ml) was added dropwise with vigorous stirring, the temperature being maintained at 0—5° during the mixing and for a total of 8 h. The mixture was added to sodium hydroxide (15 g) in water (100 ml) at 0°, and after filtration the carbon tetrachloride layer was separated, washed until neutral, and combined with ether extracts (6 × 1·5 ml) of the acqueous layers. The extracts were dried (Na_2SO_4) and solvent was removed by fractional distillation.

In experiment (34), a solution of dinitrogen pentoxide (11 g, 0·102 mol) in carbon tetrachloride (150 ml) was added from a dropping funnel at room temperature to a mixture of *p*-tolyltrimethylsilane (16·4 g, 0·10 mol), carbon tetrachloride (250 ml), and sodium fluoride (15·0 g) held at 0—5°.

Experiment (35). A mixture of finely divided copper nitrate trihydrate (120 g, 0·050 mol) and acetic anhydride (60 ml) was shaken at room temperature for 5 min, and was then warmed to 50° for 2 min, and cooled to room temperature. Solid was removed by filtration under nitrogen, and washed with acetic anhydride; the combined acetic anhydride solutions were added dropwise to *p*-tolyltrimethylsilane (0·10 mol) in acetic anhydride (100 ml) at 15°, and the mixture was kept at 15° for 6 h. Work-up was as usual.

Experiments (36) *and* (37). Brown fumes, from the decomposition of lead nitrate in experiment (36), and from the decomposition of a refluxing solution of nitric acid in acetic anhydride in experiment (37), were dissolved in acetic anhydride at 15°. This solution was added to *p*-tolyltrimethylsilane (0·10 mol) in acetic acid (55 g), at 15°, and the mixture was kept at 15° for 6 h.

Experiments (38)—(40). In experiment (38), nitric acid (11·25 g) was added dropwise to acetic anhydride (31·5 g, 0·31 mol) at room temperature, and the mixture was allowed to reflux spontaneously (*ca.* 100°); it was then set aside to cool to room temperature. It was then added with vigorous stirring to a solution of *m*-tolyltrimethylsilane (8·20 g, 0·050 mol) in acetic acid (27·5 g, 0·46 mol) at 15°, and the mixture was maintained at 15° for 6 h; work-up was as before. The medium was: nitric acid (0·125 mol) in 12·4 g (20 wt-%) of acetic anhydride and 50 g (80 wt-%) of acetic acid.

In experiment (39), similar quantities of materials were used, but the nitrating mixture was made up at 15° and added to the arylsilane solution at 120°. In experiment (40), the nitrating mixture was made up at 15° and nitrous fumes from a refluxing mixture of nitric acid and acetic anhydride were bubbled through it before use.

Experiment (41). Nitric acid (5 ml) was added dropwise during 20 min to a vigorously stirred solution of *m*-tolyltrimethylsilane (8·2 g, 0·05 mol) in acetic anhydride (8·3 ml), initially at room temperature. The temperature rose to 110° during the addition and was maintained there for a total of 6 h.

Experiments (42) *and* (43). In experiments (42) and (43), nitric acid (22·5 g) was added dropwise to acetic anhydride (63·3 g, 0·62 mol) at 15°. The mixture was cooled to 0°, and nitrous fumes from the decomposition of a solution of nitric acid in acetic anhydride were passed in for 10 min. The mixture was added during 1 h to a vigorously stirred solution of *p*-chlorophenyltrimethylsilane (18·4 g, 0·10 mol) in acetic acid (56 g, 0·93 mol) at 100° or 110°, a cold finger cooled with solid carbon dioxide being fitted to the top of the water condenser to retain nitrous fumes. The mixture was kept at 100° or 110° for 6 h. The medium consisted of nitric acid (0·25 mol) in acetic anhydride (20 wt-%) and acetic acid (80 wt-%).

Experiment (44). Nitric acid (5·0 ml) was added dropwise without cooling during 20 min to *p*-chlorophenyltrimethylsilane (9·2 g, 0·050 mol) in acetic anhydride (8·3 ml), initially at room temperature. The temperature rose to 90° and was kept there for 6 h.

Experiment (45). Experiment (45) was identical with experiment (42), except that *m*-chlorophenyltrimethylsilane was used.

Experiments (46)—(50). In experiment (46), nitric acid (22·5 g) was added dropwise to acetic anhydride (63·3 g, 0·62 mol) maintained at 0°. The mixture was added with vigorous stirring to phenyltrimethylsilane (15·0 g, 0·10 mol) in acetic acid (55 g, 0·92 mol) maintained at 15°. The mixture was kept at 15° for a total of 6 h. The medium consisted of nitric acid (0·25 mol) in acetic anhydride (20 wt-%) and acetic acid (80 wt-%).

Experiment (47) was similar, except that nitrous fumes were bubbled through the nitrating mixture for 10 min at 0° before use. In experiment (48), urea (1 g) was added to the nitric acid, which was then warmed briefly to 50° and cooled before use. In experiment (49) the nitrating mixture was made up at 15° but then heated to 110°, kept there for 1 min, and cooled to 15° before use. In experiment (50) the nitrating mixture was made up at 15° but was added to the arylsilane solution at 120°.

Experiment (51). Nitric acid (10 ml) was added during 20 min to a vigorously stirred solution of phenyltrimethylsilane (15·0 g, 0·10 mol), initially at room temperature. The temperature rose to 90°, and was kept there for 6 h.

Experiment (52). Nitrogen oxides (15·6 g), generated by decomposition of lead nitrate and trapped as a bluish solid on a cold finger cooled with solid carbon dioxide, were dissolved in acetic anhydride (63 g) to give a deep blue solution, which later became green. This was added to phenyltrimethylsilane (15·0 g, 0·10 mol) in acetic acid (55 g) at room temperature, and the mixture was set aside at room temperature for 24 h.

Experiment (53). This was identical with experiment (35), except that phenyltrimethylsilane was used.

Competition between p-*Tolyl- and Phenyl-trimethylsilane.*—A solution of 4·7 g, of nitrogen oxides [see under experiment (52)] in acetic anhydride (63 g) was added dropwise to a solution of phenyltrimethylsilane (15 g, 0·10 mol) and *p*-tolyltrimethylsilane (0·82 g, 0·0050 mol) in acetic acid (55 g) at 15°. The mixture was maintained at 15° for 5 h, and then cooled and added to sodium hydroxide (96 g) in water (400 ml), with strong cooling. Ether extraction (150 ml, then 6 × 50 ml) was followed by evaporation of the ether, and addition of acetic acid (40 ml) to the residue. Sulphuric acid (30 ml of 10M-acid) was then added, and the mixture was immersed in an oil-bath at 85° for 30 min so that unchanged phenyl- and *p*-tolyl-trimethylsilane would be converted into benzene and toluene, respectively. The mixture was neutralized with addition to aqueous alkali, with strong cooling, the internal standard (tridecane, 2·0 ml) was added; the organic products were extracted with ether and the usual g.l.c. analysis was carried out.

The analysis showed that 5·5 mmol of nitrobenzene and 3·7 mmol of *p*-nitrotoluene had been produced. The reactivity of the *p*-tolyl- compared to the phenyl-compound is thus [log (0·13/0·50)]/[log (9·45/10·0)],[27] *i.e.* 48·4.

In an experiment identical except that 3·9 g of the nitrogen oxides were used, 5·0 and 3·4 mmol of nitrobenzene and *p*-nitrotoluene, respectively, were found, corresponding with a reactivity ratio of 49·0.

Conversion of p-*Nitroso- to* p-*Nitro-toluene.*—Nitric acid (4·5 g) was added dropwise to acetic anhydride (5·0 g). The mixture was cooled to 15°, and *p*-nitrosotoluene (0·5 g) was added. After 2 min at 15° the mixture was added to aqueous sodium carbonate with strong cooling; work-up and analysis was carried out as described above for nitration products. The g.l.c. analysis showed that no *p*-nitrosotoluene remained and the sole product detected was *p*-nitrotoluene, which was formed in high but undetermined yield.

When the same work-up was applied to a solution of *p*-nitrosotoluene in 80% acetic acid, the g.l.c. analysis revealed only unchanged *p*-nitrosotoluene.

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[27] C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 1927, 2918.