[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP AT MELLON INSTITUTE, PITTSBURGH, PA., SPONSORED BY THE CORNING GLASS WORKS AND THE DOW CORNING CORPORATION]

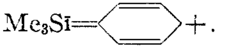
The Nitration of Trimethylphenylsilane

BY JOHN L. SPEIER

RECEIVED DECEMBER 1, 1952

The nitration of trimethylphenylsilane with 90% fuming nitric acid in acetic anhydride revealed the trimethylsilyl group to be a very weak ortho–para director. A competitive nitration of trimethylphenylsilane and benzene under similar conditions indicates that the trimethylsilyl group is a very slightly activating substituent on the benzene ring.

Recently Benkeser and Brumfield[1] reported that they obtained a 30/40/30 ratio of ortho/meta/para isomers of nitrophenyltrimethylsilane by nitrating trimethylphenylsilane with cupric nitrate trihydrate in acetic anhydride at 30–40°. A 24% yield of nitrobenzene was obtained by cleavage of the phenyl ring from the silicon. They showed that *o*-nitrophenyltrimethylsilane was more difficult to cleave than either of the other isomers. If the nitrobenzene had been formed by cleavage of only the meta nitro isomer, the ratio 30/40/30 would be 22/56/22 and the Me_3Si group would have to be considered a meta director in this case. A group such as Me_3Si should direct strongly ortho–para during nitration if it released electrons to the ring. One should ordinarily predict that any group with a semi-metallic atom such as silicon would release electrons to the phenyl ring more readily by induction than would a carbon atom in a group such as CH_3 or $(CH_3)_3C$.

On the other hand the Me_3Si group might well be meta directing if it can enter resonance states such as . Such states are possible as silicon may enter covalent states above the tetracovalent.

A third condition is one in which the trimethylphenylsilane exists as a resonance hybrid, the inductive effect of silicon being toward the ring (+ I) but counteracted to an unknown extent by the resonance effect out of the ring (−T).

This last view is supported by the values determined for the dipole moments of trimethylphenylsilane and similar structures[2–4] and by the ionization constants and reactivities of the *m*- and *p*-trimethylsilylbenzoic acids.[2]

Trimethylphenylsilane was nitrated with 90% fuming nitric acid in acetic anhydride at 0–10° and at 25–70°. The products were separated very satisfactorily in a 13 mm. Podbielniak "Heligrid" column of 100 or more theoretical plates. The products are listed in Table I.

From these data the ratios of isomers *o/m/p* are 26.6/41.7/31.6 at 0–10° and 32.5/34.7/32.7 at 25–70°. At both temperatures nitration proceeded to completion and some nitrobenzene formed, at 0–10° a much smaller amount, however. Since the origin of the nitrobenzene is unknown, its presence influences the reliability of the ratios found. If it forms by cleavage of a phenyl group from silicon followed by nitration of the benzene so formed, it is of no importance in our calculations. However, if it forms by the preferential cleavage of any one isomer of nitrophenyltrimethylsilane, its presence is important. Bird and Ingold[5] have discussed the effects of nitrating agent, medium and temperature on the distribution of isomers in similar cases. They found that temperature is the only important influence on the distribution of isomers. The changes with temperature noted by them were similar to but considerably smaller than the variations with temperature noted in Table I. The differences in degree may be due to the preferential cleavage of certain nitro isomers, and thus the results at the lowest temperature are likely to be the best. It should be noted that in neither of the cases in this work did sufficient nitrobenzene result to cast doubt upon the fact that the Me_3Si group is slightly ortho–para directing. If all the nitrobenzene formed by cleavage of only *m*-nitrophenyltrimethylsilane (an unlikely case) the ratios *o/m/p* should be 25.5/46.6/30.2 and 27.7/42.6/27.9. These ratios also indicate the Me_3Si group to be a weak ortho–para director.

TABLE I

PRODUCTS FROM THE NITRATION OF $Me_3SiC_6H_5$

	Mole percentage yields			
	$Cu(NO_3)_2{\cdot}3H_2O$ in Ac_2O[1]		HNO_3 in Ac_2O	
Nitration temp., °C.	30–40	30–40	25–70	0–10
$Me_3SiC_6H_5$	5.3	8	0	0
$C_6H_5NO_2$	24.7	23	13	6.8
o-$Me_3SiC_6H_4NO_2$	20.6	18	27.7	25.5
m-$Me_3SiC_6H_4NO_2$	23.1	24.7	29.6	39.8
p-$Me_3SiC_6H_4NO_2$	17.7	17.3	27.9	30.2
Total	91.4	91.0	98.2	102.3

To determine if the Me_3Si group was ring activating or deactivating a competitive nitration was carried out in which equimolar amounts of benzene and trimethylphenylsilane competed for an insufficient amount of nitric acid. Table I indicated that as the temperature of the nitration mixture was lowered, the quantity of nitrobenzene by-produced by cleavage of trimethylphenylsilane or of

TABLE II

PRODUCTS FROM COMPETITIVE NITRATION OF BENZENE AND TRIMETHYLPHENYLSILANE IN ACETIC ANHYDRIDE AT −10 TO −3°

	Grams	Moles
Benzene	60	0.77
$Me_3SiC_6H_5$	101.5	.68
$C_6H_5NO_2$	26.4	.21
$Me_3SiC_6H_4NO_2$	65.1	.32

---

(1) R. A. Benkeser and P. E. Brumfield, THIS JOURNAL, **73**, 4770 (1951).

(2) J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949).

(3) H. Soffer and T. De Vries, *ibid.*, **73**, 5817 (1951).

(4) H. Freiser, M. V. Eagle and J. L. Speier, *ibid.*, **75**, 2821 (1953).

(5) M. L. Bird and C. K. Ingold, *J. Chem. Soc.*, 918 (1938).

one of its nitro derivatives diminishes rapidly. Therefore the competitive nitration was carried out at −10° for the most part and permitted to rise overnight to only −3°. Under these conditions no detectable amount of cleavage occurred to complicate the analysis of the results shown in Table II.

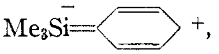
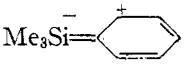
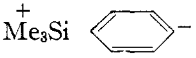
From the figures of Table II the relative reactivities of trimethylphenylsilane and benzene were calculated by the equation of Ingold, *et al.*[6,7]

$$k_{\mathrm{PhSiMe_3}}/k_{\mathrm{PhH}} = \log \frac{(\mathrm{PhSiMe_3})_f}{(\mathrm{PhSiMe_3})_i} \Big/ \log \frac{(\mathrm{PhH})_f}{(\mathrm{PhH})_i} = 1.64.$$

In this equation the subscripts i and f signify initial and final, the initial being taken in each case as equal to unity and the final being the fraction recovered or (1-fraction) reacted. The two are identical for the silicon compound in which a material balance of 100% was achieved. However, it seems likely that the 2% benzene unaccounted for was lost as benzene by evaporation during the experiment and that 1 − 0.21 = 0.79 is a better value for $\mathrm{PhH_f}$ than the value 0.77 actually found. However if 0.77 is used the ratio becomes 1.47.

Either of these values is more nearly unity than the similar values found for chlorobenzene[5] (0.0273), or toluene[7] (27) both at 0° in acetic anhydride. Thus one sees that the $\mathrm{Me_3Si}$ group has a very slight activating influence on the benzene ring and hence might be expected to have a very slight ortho-para directive influence.

The very considerable amount of ortho isomer formed is surprising in view of the fact that *t*-butylbenzene seems sterically hindered in the ortho position and yields practically all para substitution products.[8] One would not expect the $\mathrm{Me_3Si}$ group to be quite so nearly free of steric effects in view of the strong hindrance demonstrated by the similar $\mathrm{Me_3C}$ group.

The valuable procedure of calculating the rate of nitration for each position in a monosubstituted benzene relative to that for any position in benzene does not seem accurately applicable in the instance of this work, the data for relative rates having been determined at below 0° with the formation of no Si–C cleavage products and the distribution of products having been found above 0° accompanied by cleavage. However, the result calculated for the experiment at 0–10° by the method described[5] gives relative activity values for the ortho, meta and para positions of 1.3, 2.0 and 3.1, respectively, based on an activity of any position in benzene being equal to unity. These values probably are not very greatly in error. The corresponding values for toluene[5] are 43, 3 and 55. Thus the $\mathrm{Me_3Si}$ group activates the meta position $^2/_3$ as effectively as a $\mathrm{CH_3}$ group does but activates the para position only 3.1/55 as effectively. This is in agreement with the expectations based on a resonance model molecule such as ,  (2 forms) and  in which the first three forms nearly overcome the last.

Experimental nitration of trimethylphenylsilane was carried out by adding one mole (150 g.) to a solution of 1.5 moles, 105 g., of 90% fuming nitric acid in 458 g. of acetic anhydride. In the first experiment the addition was made at 25° (room temp.) and the mixture finally rose to about 70°. In the second the mixture was held at all times between 0–10°. After four hours in the first case and 18 hours in the second, the mixtures were dumped into a slurry of ice and 28% ammonia water, stirred vigorously until the ice had melted, extracted repeatedly with toluene, dried and distilled. Each product appeared as a very well defined plateau on the distillation graph. The nitrophenyltrimethylsilanes had the properties: ortho, b.p. 149° at 40 mm., $n^{25}\mathrm{D}$ 1.5290; meta, b.p. 161° at 40 mm., $n^{25}\mathrm{D}$ 1.5211; para, b.p. 166° at 40 mm., $n^{25}\mathrm{D}$ 1.5238 (for supercooled liquid), m.p. 36–37°. These properties are in substantial agreement with those reported[1] ortho, b.p. 117° at 10 mm., $n^{20}\mathrm{D}$ 1.5321; meta, b.p. 126° at 10 mm., $n^{20}\mathrm{D}$ 1.5239; para, b.p. 129° at 10 mm., m.p. 38–39°.

Competitive nitration was performed by adding a cold solution of 75 g., 1.05 moles, of 90% fuming nitric acid in 152 g. of acetic anhydride to a second cold solution of 78 g., 1 mole, of benzene, 150 g., 1 mole, of trimethylphenylsilane and 107 g. of acetic anhydride. The reaction mixture was held at about −10° during the addition and 2.5 hours thereafter. It was then placed in a refrigerator overnight. Seventeen hours later the temperature was −3°. It was then worked up as described.

PITTSBURGH, PA.

---

(6) C. K. Ingold and M. S. Smith, *J. Chem. Soc.*, 905 (1938).

(7) C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *ibid.*, 1959 (1931).

(8) L. F. Fieser, Gilman's "Organic Chemistry," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 142.