

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Additivity of Electrical Effects in Aromatic Electrophilic Substitutions as Determined by Desilylation Reactions

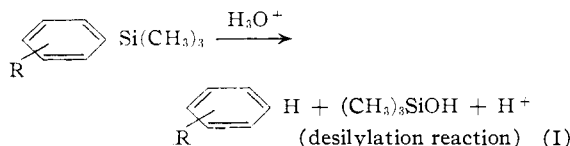
BY ROBERT A. BENKESER, RICHARD A. HICKNER, DONALD I. HOKE AND OWEN H. THOMAS

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A series of mono- and di-*m*-substituted phenyltrimethylsilanes have been synthesized and the rates of desilylation by acid have been determined. The rates of cleavage of the disubstituted compounds as calculated from partial relative rates agree well with the observed values. As would be expected, serious discrepancies occur when the rate is accelerated by steric factors. The observation that the rates of desilylation of the 3,5-dialkyl compounds can be calculated accurately from the rates of the monoalkyl series leads to the conclusion that no pronounced steric effect is operating in these cases.

There has been considerable interest over a period of years in the additive effects of substituents in aromatic electrophilic substitution reactions.¹⁻³ It is now generally conceded that electrical effects of substituents are indeed additive for reactions whose variation in rate is dependent solely on changes in the energy of activation. This has been found to be the case⁴⁻⁶ generally with *m*- and *p*-substituents, since such groups do not markedly affect the entropy of activation. Thus, the additive effects of two substituents on the rate of alkaline hydrolysis of substituted ethyl benzoates has been demonstrated.⁷ Similarly, Condon⁸ has shown the feasibility of calculating the rates of chlorination of polymethylbenzenes from a knowledge of the relative rates of chlorination of toluene at various positions.

Since the desilylation (reaction I below) of substituted aryltrimethylsilanes has been shown to be a convenient tool for measuring the rate of electrophilic attack at a particular position in an aromatic ring,⁴⁻¹² it was of interest to see whether the additivity of electrical effects could be demonstrated by means of this reaction.



Since the rates of desilylation of the isomeric trimethylsilylsilanes already had been determined,⁹ it was necessary only to determine the rates of cleavage of the three isomeric trimethyltolylsilanes to determine the additive effect of methyl groups. As a further check on the method, the rates of cleavage of *m*-methoxyphenyltrimethylsilane and 3,5-dimethoxyphenyltrimethylsilane were determined as well. Similarly, *m*-bromophenyltrimethylsilane and 3,5-dibromophenyltrimethylsilane were

- (1) (a) A. E. Bradfield and B. Jones, *J. Chem. Soc.*, 1006 (1928); (b) B. Jones, *ibid.*, 1831 (1935); 418 (1942); 676 (1942).
- (2) F. J. Stubbs and C. Hinshelwood, *ibid.*, 571 (1949).
- (3) J. Shorter and F. J. Stubbs, *ibid.*, 1180 (1949).
- (4) C. K. Ingold and W. S. Nathan, *ibid.*, 222 (1936).
- (5) D. P. Evans, J. J. Gordon and H. B. Watson, *ibid.*, 1430 (1937).
- (6) E. Tommila and C. N. Hinshelwood, *ibid.*, 1801 (1938).
- (7) B. Jones and J. Robinson, *ibid.*, 3845 (1955).
- (8) F. E. Condon, *THIS JOURNAL*, **70**, 1963 (1948); see also H. C. Brown and L. M. Stock, *ibid.*, **79**, 1421, 5171 (1957).
- (9) R. A. Benkeser and H. R. Krysiak, *ibid.*, **76**, 6353 (1954).
- (10) R. A. Benkeser, R. A. Hickner and D. I. Hoke, *ibid.*, **80**, 2279 (1958).
- (11) R. A. Benkeser, W. Schroeder and O. H. Thomas, *ibid.*, **80**, 2283 (1958).
- (12) C. Eaborn, *J. Chem. Soc.*, 4858 (1956).

prepared. Unfortunately, however, the latter compound proved to be too insoluble and, hence, its rate of cleavage could not be determined.

In a previous study¹⁰ concerned with the electrical effect of *m*-alkyl substituents, it was noted that the rate of desilylation reactions varied in a regular manner, completely predictable on the basis of the inductive effect of the *m*-substituted alkyl groups (*i.e.*, *m*-*t*-butyl > *m*-isopropyl > *m*-ethyl > *m*-methyl). These findings were in sharp contrast to the results of other workers¹³⁻¹⁵ who had utilized the rates of solvolysis of *t*-carbinyl chlorides to study the electrical effects of *m*-alkyl substituents. In the latter instances, the rates of solvolysis were *reversed* from the order which would be predicted on the basis of the inductive effect of the alkyl groups.¹⁶

Several proposals were offered in a previous paper¹⁰ to explain this discrepancy. For example, it was suggested that a bulky group in the *m*-position might exert a buttressing effect on the hydrogen in the adjacent *o*-position. In the case of desilylation, this strain would be relieved in the transition state (Fig. A below) and hence steric acceleration of rate would be observed as the *m*-substituent is varied from methyl to *t*-butyl.

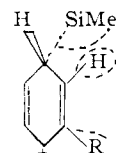
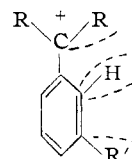


Fig. A.

It would be predicted that this same buttressing effect should *decrease* the rates of carbinyl chloride solvolysis. A gradual increase in bulk of the *m*-substituent would cause an increased buttressing of the *o*-hydrogen, thus gradually interfering more and more with the coplanarity of the carbonium ion intermediate.



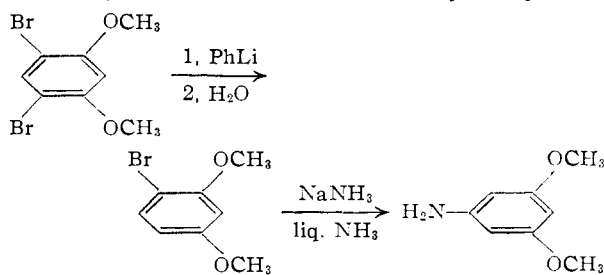
- (13) V. J. Shiner and C. J. Verbanic, *THIS JOURNAL*, **79**, 369 (1957).
- (14) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *ibid.*, **79**, 1897 (1957).
- (15) E. Berliner and M. M. Chen, *ibid.*, **80**, 343 (1958).
- (16) There is some uncertainty as to the position of the *t*-butyl group in these solvolysis studies (see refs. 14 and 15). Otherwise there is general agreement that the rates follow the sequence *m*-CH₃ > *m*-Et > *m*-*i*-Pr.

It seemed desirable to test this attractive hypothesis, which, if correct, would nicely rationalize the diverse results noted in the desilylation and carbonyl chloride solvolyses. It should be noted that both of these reactions have been put forth as reliable methods for determining electrical effects at a particular ring position.^{9,14} Only in the case of aromatic compounds containing *m*-substituted alkyl groups have the two methods given markedly different results.

It would be predicted that if the desilylation reaction were indeed sterically accelerated by bulky groups in the *m*-position, this effect would be even more pronounced with *two* such bulky groups located in the 3,5-positions to the trimethylsilyl group. Accordingly, the 3,5-dimethyl-, diethyl-, diisopropyl- and di-*t*-butylphenyltrimethylsilanes were synthesized, and the rate of cleavage of the trimethylsilyl group from each of these compounds was determined.

Preparation of Compounds.—The synthesis of the tolyltrimethylsilanes was accomplished in conventional fashion. The physical constants of these compounds are listed in Table I.

The synthesis of the 3,5-dimethoxy- and 3,5-dibromophenyltrimethylsilane proved difficult and many approaches were attempted before a satisfactory synthesis was achieved. The following sequence shows the route which was employed in the synthesis of the 3,5-dimethoxy compound.



The 3,5-dimethoxyaniline was converted by the Sandmeyer reaction to the bromo compound which, in turn, was coupled (*via* its organolithium derivative) with trimethylchlorosilane to form 3,5-dimethoxyphenyltrimethylsilane.

There are several points of interest in this synthesis. It was found that monobromination of *m*-dimethoxybenzene could be achieved by the use of dioxane dibromide and a short reaction time. However, the over-all yield was better if the compound was first dibrominated and then one of the halogens removed by selective interconversion¹⁷ with phenyllithium and then hydrolysis.

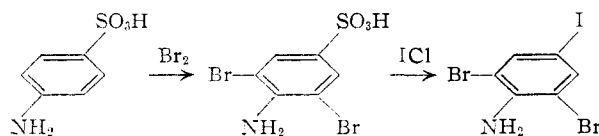
The cine' substitution reaction¹⁸ with sodium amide proved very useful in obtaining the 1,3,5-arrangement of groups. It resulted in a 59% yield of product with no trace of the direct substitution product.

Of particular interest was the diazotization of 3,5-dimethoxyaniline and its conversion to the bromo compound *via* the Sandmeyer route. When the amine was diazotized with hydrochloric acid, and then potassium iodide was added in the tradi-

tional manner to obtain the iodo compound, only a very low yield of product was realized. Only the HBr-CuBr combination produced reasonable yields of product.

Two procedures were employed to obtain the 3,5-dibromophenyltrimethylsilane. The over-all yield of product was comparable by either route.

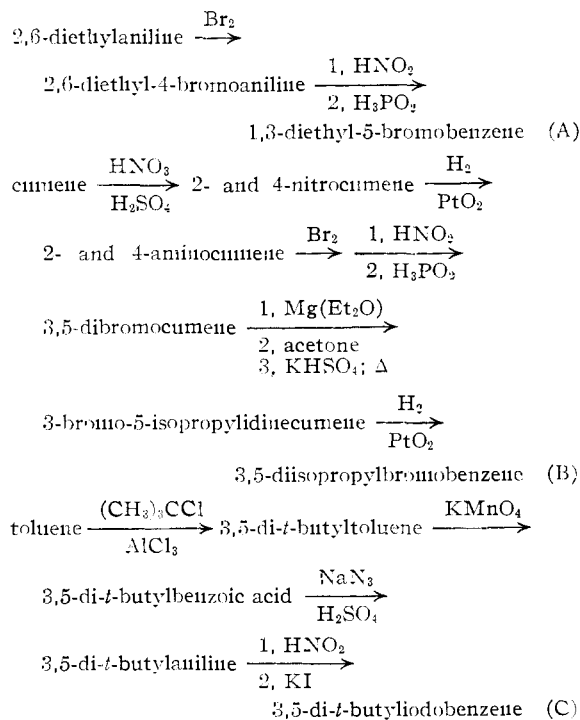
Method A. The 2,6-dibromo-4-iodoaniline was



then deaminated to form 3,5-dibromoiodobenzene. The iodine in the latter compound was selectively interconverted¹⁷ with *n*-butyllithium and then coupled with trimethylchlorosilane to form the product.

Method B. Anthranilic acid was dibrominated and then deaminated to form 3,5-dibromobenzoic acid. A Schmidt reaction converted the latter to 3,5-dibromoaniline which, in turn, was converted to 3,5-dibromoiodobenzene *via* a Sandmeyer reaction. From this point the sequence was the same as that described in method A.

The synthesis of the 3,5-dialkylphenyltrimethylsilanes is summarized in the sequences



In each of the above sequences, the 3,5-dialkylhalobenzene produced was converted to the trimethylsilyl derivative by treatment with sodium (A and B above) or *n*-butyllithium (C), then by trimethylchlorosilane.

In general, the above reactions were straightforward with few exceptions. In the nitration of cumene (sequence B) small amounts of the 3-nitrocumene conceivably could be formed. However, the infrared spectrum of the final silane showed the absence of any bands associated with an

(17) R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 352.

(18) J. F. Bunnett and R. El Zahler, *Chem. Revs.*, **49**, 382 (1951).

arrangement other than that of the 1,3,5-isomer. 3,5-Di-*t*-butyliodobenzene (sequence C) failed to react with sodium in a trial run. The failure of 3,5-di-*t*-butylbromobenzene to react with magnesium or lithium has been noted previously by other workers.¹⁹ The halogen-metal exchange of the iodide with *n*-butyllithium then subsequent coupling with trimethylchlorosilane proceeded smoothly. However, a persistent iodine impurity (possibly formed by oxidation of lithium iodide) was removed only after several distillations and washings with aqueous thiosulfate. In reality, the yield of silane was likely 50-60%, but the losses inherent in several distillations reduced the final yield to 30%.

Rate Determinations.—The rates of desilylation were followed by a volume expansion method⁹ employing dilatometers. The various cleaving media that were employed are listed in Tables II to IV. It will be noted that the methyl and *t*-butyl compounds (see Table IV) were run in the usual cleaving medium (glacial acetic acid, 2.35 molar in hydrogen chloride and 7.23 molar in water) as well as in a medium which was 1.17 molar in hydrogen chloride and 3.62 molar in water. The latter medium allowed higher concentrations of the silane resulting in a greater rise in the dilatometer as well as providing an added check on the results.

The rate results are listed in Tables II to V. It will be noted that the partial relative rates listed (P.R.R.) were obtained by dividing each rate constant by the rate constant for trimethylphenylsilane.

TABLE I

PHYSICAL CONSTANTS AND YIELDS OBTAINED FOR THE ISOMERIC TRIMETHYLTOLYLSILANES AND TRIMETHYLPHENYLSILANE

Product (R = Me ₃ Si-)	Found	Reported	B.p., °C.	Yield, %
R-Benzene	1.4901	1.4901 ^a	169-169.5	
<i>o</i> -R-Toluene	1.5034	1.5025 ^b	196-197	67
<i>m</i> -R-Toluene	1.4922	1.4922 ^b	189-189.5	31
<i>p</i> -R-Toluene	1.4915	1.4912 ^b	192	53

^a J. D. Roberts, E. A. McElhill and R. Armstrong, *THIS JOURNAL*, **71**, 2923 (1949). ^b H. A. Clark, A. F. Gordon, C. W. Young and M. J. Hunter, *ibid.*, **73**, 3798 (1951).

TABLE II

RATE CONSTANTS AND PARTIAL RELATIVE RATES (P.R.R.) OF TRIMETHYLARYLSILANES

Compound (R = Me ₃ Si-)	Rate constant × 10 ³ , min. ⁻¹	P.R.R.
R-Benzene ^a	0.0890 ± 0.0005	1.00
<i>o</i> -R-Toluene ^a	1.40 ± .01	15.7
<i>m</i> -R-Toluene ^a	0.195 ± .008	2.19
<i>p</i> -R-Toluene ^a	1.27 ± .01	14.3
R-Benzene ^b	3.96 ± .06	1.00
<i>m</i> -R-Bromobenzene ^b	0.0751	0.0189
R-Benzene ^c	6.23 ± 0.03	1.00
<i>m</i> -R-Anisole ^c	3.95 ± .03	0.633

^a Cleaving medium was glacial acetic acid which was 0.80 molar in *p*-toluenesulfonic acid and 3.2 molar in water. ^b Cleaving medium was glacial acetic acid which was 2.49 molar in hydrogen chloride and 8.2 molar in water. ^c Cleaving medium was glacial acetic acid which was 3.1 molar in hydrogen chloride and 9.62 molar in water.

(19) P. D. Bartlett, M. Roha and R. M. Stiles, *THIS JOURNAL*, **76**, 2349 (1954).

TABLE III
CORRELATION OF EXPERIMENTAL AND PREDICTED RATES OF CLEAVAGE

Compound (R = Me ₃ Si-)	Rate, $k \times 10^{-3}$ min. ⁻¹		P.R.R.		P.R.R. obsd./ P.R.R. calcd.
	Obsd.	Calcd.	Obsd.	Calcd.	
2-R- <i>p</i> -Xylene	3.09	3.06	34.8	34.4	1.01
4-R- <i>m</i> -Xylene	24.6	20.0	277	225	1.23
2-R- <i>m</i> -Xylene	300	21.9	3380	246	13.7
4-R- <i>o</i> -Xylene	2.98	2.79	33.6	31.3	1.07
3-R- <i>o</i> -Xylene ^b	73.6	27.0	94	34.4	2.7
3,5-Dimethoxy-R- benzene	2.17	2.49	0.348	0.400	0.87

^a The rate constants for the trimethylxylylsilanes were determined in a previous study. ^b The cleaving medium was glacial acetic acid which was 0.587 molar in hydrogen chloride and 1.81 molar in water.

TABLE IV

RATE CONSTANTS AND PARTIAL RELATIVE RATES (P.R.R.) OF *m*-ALKYLPHENYLTRIMETHYLSILANES

<i>m</i> -Alkyl group	Rate constant × 10 ³ , min. ⁻¹	P.R.R.
H ^a	3.84 ± 0.03	1
CH ₃ ^a	8.31 ± .19	2.16
C ₂ H ₅ ^a	8.54 ± .13	2.22
<i>i</i> -C ₃ H ₇ ^a	9.08 ± .26	2.36
<i>t</i> -C ₄ H ₉ ^a	10.8 ± .02	2.81
H ^b	1.46 ± .01	1
CH ₃ ^b	3.13 ± .04	2.14
<i>t</i> -C ₄ H ₉ ^b	4.37 ± .04	2.99

^a Cleaving medium was glacial acetic acid which was 2.35 molar in hydrogen chloride and 7.23 molar in water. ^b Cleaving medium was glacial acetic acid which was 1.17 molar in hydrogen chloride and 3.62 molar in water.

TABLE V

CORRELATION OF EXPERIMENTAL AND PREDICTED RATES OF CLEAVAGE OF 3,5-DIALKYLPHENYLTRIMETHYLSILANES

<i>m</i> -Alkyl group	Rate constant × 10 ³ , min. ⁻¹	P.R.R.		P.R.R. obsd./ P.R.R. calcd.
		Obsd.	Calcd.	
H ^a	3.84	1
CH ₃ ^a	15.5 ± 0.01	4.04	4.67	0.87
C ₂ H ₅ ^a	18.3 ± .3	4.77	4.93	.96
<i>i</i> -C ₃ H ₇ ^a	19.7 ± .1	5.13	5.57	.92
<i>t</i> -C ₄ H ₉ ^a	29.1 ± .3	7.60	7.90	.96
H ^b	1.46	1
CH ₃ ^b	6.29 ± 0.16	4.30	4.57	.94
<i>t</i> -C ₄ H ₉ ^b	11.6 ± .1	7.97	8.92	.90

^{a, b} See notes in Table IV.

Discussion

The predicted and observed rate constants for six disubstituted compounds are listed in Table III. The agreement is generally good except in the case of 2-trimethylsilyl-*m*-xylene and 3-trimethylsilyl-*o*-xylene. An acceleration in rate is to be expected in these two cases since the desilylation results in a relief of steric strain (Fig. A).

The observed and calculated rates for the 3,5-dialkylphenyltrimethylsilanes in Table V are in good agreement. It can be deduced from these results that the substituents in the two *m*-positions do not cause an increased buttressing effect, or, if such an effect is in operation, it is small and lies within the experimental error. It should be kept in mind that an error of 3% in measuring the rate of the mono alkyl series becomes an error of 9% in

calculating the value for the disubstituted compounds since the square of the partial relative rate is involved. However, the results clearly indicate that the increase in rate observed in desilylations as the *m*-alkyl substituent is varied from methyl to *t*-butyl is *not steric in origin* but can be attributed most satisfactorily to the inductive effect of the alkyl substituent.

It will be noted that in all cases the calculated rates for the *m*-dialkyl series are *greater* than the observed values. It is difficult to attach any significance to the trend since all the values are well within experimental error. If the trend is real it may indicate a *small* effect caused by steric hindrance to solvation in the transition state.²⁰

The rates of cleavage of the methoxy and bromo compounds are both considerably less than for the unsubstituted phenyltrimethylsilane. This, again, would be predicted on the basis of the inductive effects of these groups.

It appears, therefore, that the results of desilylations follow closely the pattern of aromatic electrophilic substitution reactions. Electrical effects appear to be additive in desilylations, with serious discrepancies in predicted rates arising only in those cases where severe steric factors provide an undue acceleration to the rate of cleavage.

Experimental

m-Dimethoxybenzene was prepared in a 96% yield (crude product) by the method of Ullman.²¹

2,4-Dimethoxybromobenzene—*m*-Dimethoxybenzene was brominated²² in 83% yield. The product melted at 137–138°. This was converted to 2,4-dimethoxybromobenzene (b.p. 141–142° (14 mm.)) in 76% yield by treatment with phenyllithium.²³

3,5-Dimethoxyaniline.—2,4-Dimethoxybromobenzene (205 g., 0.95 mole) was added dropwise over a 45-minute period to a solution of sodium amide²⁴ in liquid ammonia prepared from 45 g. (1.9 g. atoms) of sodium and 2 l. of liquid ammonia. The mixture was stirred for three hours and then hydrolyzed by addition of 100 g. (1.9 moles) of ammonium chloride. Benzene (500 ml.) was then added and the ammonia allowed to evaporate overnight. The benzene solution was washed with 100 ml. of water then extracted with excess 6 *N* hydrochloric acid. The acid extracts were made basic with strong sodium hydroxide solution, cooled and extracted with ether. The ether extracts were dried with Drierite, filtered and the ether distilled off. The residue was distilled under reduced pressure and the portion boiling 137° (3 mm.) was collected. The yield was 86 g. (59%).

The hydrochloride and acetyl derivatives of the amine were prepared in the usual manner; hydrochloride, m.p. 209° dec. (reported²⁵ 210° dec.); acetyl, m.p. 155–156° (reported²⁶ 156°).

3,5-Dimethoxyiodobenzene.—3,5-Dimethoxyaniline (17 g., 0.11 mole) was diazotized in the usual manner using 11 g. (0.16 mole) of sodium nitrite in 25 ml. of water and 45 ml. of hydrochloric acid in 200 ml. of water. The addition of sodium nitrite was discontinued when nitrous acid was present in excess as indicated by starch-iodide paper. After

10 minutes, a solution of 20 g. (0.12 mole) of potassium iodide in 50 ml. of water was added with stirring and the mixture allowed to stand overnight. It was then made basic with strong sodium hydroxide and steam distilled. The distillate was extracted with ether and the ether evaporated. The yield of white crystals was 2 g. (7%). This was recrystallized from aqueous ethanol, m.p. 74–75°.

Anal. Calcd. for C₈H₉IO₂: C, 36.39; H, 3.44. Found: C, 36.57; H, 3.39.

3,5-Dimethoxybromobenzene was prepared in 50% yield following the directions of Dean and Whalley.²⁷ The product melted at 63–65° (reported²⁷ 66°).

3,5-Dimethoxyphenyltrimethylsilane.—A solution of 38 g. (0.18 mole) of 3,5-dimethoxybromobenzene in anhydrous ether was added, with stirring, to a solution of *n*-butyllithium at 0° prepared in the usual manner from 34 g. (0.25 mole) of *n*-butyl bromide and 3.5 g. (0.5 g. atom) of lithium.¹⁷ The mixture was stirred for 15 minutes, and then a solution of 27 g. (0.25 mole) of trimethylchlorosilane in ether was added, with stirring, at 0°. The mixture was stirred for one hour while it was allowed to warm to room temperature. When Color Test I²⁸ was negative, the mixture was filtered and hydrolyzed by pouring into ice-water. The ether layer was separated, dried with Drierite and distilled through a Widmer column. The portion boiling at 130–133° (15 mm.) was collected and redistilled through a Todd continuous wire spiral column. There was obtained 14 g. (27%) of a liquid boiling at 129.5–130.0° (12 mm.), *n*_D²⁰ 1.5080, *d*₄²⁰ 0.9878; *MR* found 63.47, *MR* calcd. 62.94.

Anal. Calcd. for C₁₁H₁₈O₂Si: C, 62.84; H, 8.57. Found: C, 62.75; H, 8.77.

3,5-Dibromiodobenzene. **Method A**.—2,6-Dibromo-4-iodoaniline was prepared by the method of Sudborough and Lakhumalani²⁹ in yields of 40–70%, m.p. 145–146° (reported 147–148°). This was deaminated following a procedure similar to that described in ref. 30 for the preparation of 1,3,5-tribromobenzene.³⁰ The yield of dibromiodobenzene after recrystallization from aqueous acetic acid was 12 g. (40%), m.p. 122.5–123.5° (reported³¹ 124.8°).

Method B.—3,5-Dibromoanthranilic acid was prepared by the method of Ullman and Kopetschni.³² This was deaminated by a method similar to that described in ref. 30 for the preparation of 1,3,5-tribromobenzene.³⁰ The 3,5-dibromobenzoic acid was recrystallized from aqueous ethanol. The yield was 66% (based on anthranilic acid) of material melting at 212–214° (reported³³ 219–220°).

The 3,5-dibromobenzoic acid (78 g., 0.28 mole) was added to a mixture of 110 ml. of fuming sulfuric acid (20%), 24 ml. of concentrated sulfuric acid and 200 ml. of chloroform. Sodium azide (21 g., 0.32 mole) was added, with stirring, while the temperature was kept at 40–45°. The mixture was poured slowly onto crushed ice and allowed to stand for at least one hour. The solid was filtered and recrystallized from aqueous ethanol. There was obtained 35 g. (50%) of 3,5-dibromoaniline which melted at 55–56° (reported³⁴ 56–57°).

The 3,5-dibromoaniline (69 g., 0.28 mole) was dissolved in 150 ml. of concentrated sulfuric acid and the solution cooled to –5°. A solution of nitrosylsulfuric acid, prepared by dissolving 19 g. (0.28 mole) of sodium nitrite in 240 ml. of concentrated sulfuric acid at 0°,³⁵ was added and the solution again cooled to –5°. Phosphoric acid (350 ml., 85%) was then added, with stirring, while the temperature was maintained at ±2°. The mixture, which was a thick paste at this point, was stirred for an additional 0.5 hour and then was poured onto 100 g. of crushed ice. A solution of 46 g. (0.28 mole) of potassium iodide in 250 ml. of water was added with rapid stirring. The mixture was allowed to stand

(20) W. A. Schubert and W. M. Schubert, *THIS JOURNAL*, **76**, 4625 (1954); W. M. Schubert and W. A. Sweeney, *J. Org. Chem.*, **21**, 119 (1956); W. A. Schubert, J. Robins and J. L. Haun, *THIS JOURNAL*, **79**, 910 (1957); see also C. C. Price and D. C. Lincoln, *ibid.*, **73**, 5386 (1951).

(21) F. Ullman, *Ann.*, **327**, 116 (1903).

(22) M. Honig, *Ber.*, **11**, 1041 (1878).

(23) G. Wittig, V. Pockels and H. Dröge, *ibid.*, **71**, 1903 (1938).

(24) T. H. Vaughn, R. R. Vogt and J. A. Nieuwland, *THIS JOURNAL*, **56**, 2120 (1934).

(25) R. Seka and W. Fuchs, *Monatsh.*, **57**, 63 (1931); *C. A.*, **25**, 1816 (1931).

(26) S. H. Oakeshott and S. G. P. Plant, *J. Chem. Soc.*, 489 (1927).

(27) N. B. Dean and W. B. Whalley, *ibid.*, 4639 (1954).

(28) H. Gilman and F. Schultz, *THIS JOURNAL*, **47**, 2002 (1925).

(29) J. J. Sudborough and J. V. Lakhumalani, *J. Chem. Soc.*, **111**, 41 (1917).

(30) G. H. Coleman and W. F. Talbot, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 592.

(31) G. Korner and Contardi, *Atti Accad. Lincei*, **22**, 1 829 (1913); *C. A.*, **8**, 75 (1914).

(32) F. Ullman and E. Kopetschni, *Ber.*, **44**, 426 (1911).

(33) J. F. Bunnett, M. M. Rauhut, D. Knutson and G. B. Bussell, *THIS JOURNAL*, **76**, 5755 (1954).

(34) R. G. Shephard, *J. Org. Chem.*, **12**, 275 (1947).

(35) L. H. Welsh, *THIS JOURNAL*, **63**, 3277 (1941).

overnight, and then the solid was filtered and recrystallized from acetic acid. There was obtained 46 g. (46%) of 3,5-dibromiodobenzene melting at 122–123° (reported³¹ 124.8°).

3,5-Dibromophenyltrimethylsilane.—A solution of 34 g. (0.094 mole) of 3,5-dibromiodobenzene in anhydrous ether was added to a solution of 0.09 equivalent of *n*-butyllithium¹¹ in anhydrous ether at –30°. The temperature was kept at –30 ± 2° during this period. After the addition, the solution was stirred for 15 minutes, then 20 g. (0.18 mole) of trimethylchlorosilane was added, with stirring, at –25°. The mixture was then allowed to stand at room temperature until Color Test I²⁸ was negative. It then was filtered and hydrolyzed with 200 ml. of cold water. The ether layer was separated and washed with three 25-ml. portions of 10% sodium thiosulfate solution and two 25-ml. portions of water. The ether solution was dried with Drierite, the ether distilled off, and the residue distilled through a Todd continuous wire spiral column. The material boiling at 112.0–112.2° (4 mm.) was collected. This solidified at room temperature and was recrystallized from aqueous ethanol. There was obtained 9 g. (33%) of white needles melting at 40–41°.

Anal. Calcd. for C₉H₁₂Br₂Si: C, 35.08; H, 3.93. Found: C, 35.01; H, 4.13.

Trimethyl-*m*-bromophenylsilane.—*m*-Dibromobenzene (50 g., 0.212 mole), prepared in 51% yield by the hypophosphorus acid deamination of 2,4-dibromoaniline, was treated with magnesium turnings (0.20 g. atom, 4.8 g.) to form the mono-Grignard in 200 ml. of anhydrous ether. The reaction was continued with external heating until all the magnesium had disappeared. At this point approximately 100 ml. of ether was distilled off under an atmosphere of nitrogen. Trimethylchlorosilane was then added immediately to the Grignard, and external heating was applied. Refluxing was continued for ten hours. At this time hydrolysis with cold water was accomplished. Ether extraction followed and the combined extracts were washed with aqueous potassium carbonate and finally with water. The combined extracts were dried overnight with Drierite. The ether and hexamethyldisiloxane were distilled off and the remaining product fractionated under vacuum in a Todd continuous wire spiral column. There was obtained 5 g. of material boiling at 75° (1 mm.), *n*_D²⁰ 1.5282, *d*₄²⁰ 1.219, *n*_D²⁵ (reported³⁶) 1.5290; *MR* calcd. 57.78, *MR* found 57.91.

Trimethyl-*m*-anisylsilane.—A solution of 35 g. (0.25 mole) of *m*-chloroanisole and 27 g. (0.25 mole) of trimethylchlorosilane in 150 ml. of anhydrous ether was added to a well stirred suspension of 12 g. (0.52 g. atom) of sodium sand in 150 ml. of anhydrous ether. This mixture was stirred and refluxed a total of 10 hours and allowed to stand at room temperature without stirring for 20 hours. At the end of this period it was cooled in an ice-bath and hydrolyzed by the dropwise addition of 100 ml. of cold water. The ether layer was separated, dried with Drierite, and distilled through a Widmer column. The portion boiling at 217–220° was redistilled through a Todd continuous wire spiral column. The yield was 23 g. (50%), b.p. 218.0–218.5°, *n*_D²⁵ 1.5015 (reported³⁷ *n*_D²⁰ 1.5020).

Trimethyltolylsilanes.—All of the isomeric trimethyltolylsilanes and trimethylphenylsilane were prepared by reaction of the appropriate aryllithium compound and trimethylchlorosilane in the usual manner. The physical constants obtained for these compounds are summarized in Table I.

3,5-Dimethylphenyltrimethylsilane.—A sample prepared previously in this Laboratory was used¹¹; *n*_D²⁰ 1.4946.

2,6-Diethyl-4-bromoaniline.—The procedure employed was adapted from that of Snyder, *et al.*,³⁸ for an isomeric compound. Bromine (32 g., 0.2 mole) was added to a stirred solution of 30 g. (0.2 mole) of 2,6-diethylaniline³⁹ in 100 ml. of methanol and 20 ml. of glacial acetic acid at 10–15° over a 1-hour period. Stirring was continued for an additional 30 minutes. The solvents were evaporated under reduced pressure and the hydrobromide was collected by vacuum filtration. The free amine was regenerated by treatment with aqueous sodium hydroxide. The amine was taken up in

ether and dried over magnesium sulfate. Distillation through a 12-inch Vigreux column gave 26.8 g. (53%) of amine boiling at 130–134° (3 mm.), *n*_D²⁰ 1.5846. The amine darkened rapidly upon standing. A sample was converted to the acetyl derivative (m.p. 181–182°) for analysis.

Anal. Calcd. for C₁₂H₁₆NOBr: C, 53.35; H, 5.97. Found: C, 53.10; H, 6.02.

1,3-Diethyl-5-bromobenzene.³⁸—The amine was deaminated in 60% yield by hypophosphorous acid. The product was distilled through a Widmer column and boiled at 76–78° (3 mm.), *n*_D²⁰ 1.5380 (reported³⁸ b.p. 115–119° (17 mm.).

3,5-Diethylphenyltrimethylsilane.—The aryl bromide was coupled with trimethylchlorosilane by sodium in 77% yield by the procedure previously described.⁹ The silane was distilled through a Vigreux column and then fractionated through a continuous spiral Todd column. It boiled at 97° (7 mm.), *n*_D²⁰ 1.4936, *d*₄²⁰ 0.8620; *MR* found 68.60, *MR* calcd. 68.08.

Anal. Calcd. for C₁₃H₂₂Si: C, 75.63; H, 10.74. Found: C, 75.68; H, 10.43.

***o*- and *p*-Nitrocumene.**—Cumene was nitrated in a 60% yield according to the procedure of Hansch and Helmkamp.⁴⁰

3,5-Dibromocumene.—The isomeric nitrocumenes were reduced to the cumidines according to the procedure of Biel⁴¹ in 88% yield. The mixture of *o*- and *p*-cumidine boiled at 83–87° at 4 mm. This mixture (74 g., 0.55 mole) was dissolved in 350 ml. of methanol and 60 g. of glacial acetic acid. A solution of 176 g. (1.10 moles) of bromine in 250 ml. of glacial acetic was added at 10–15° with stirring over a 2-hour period. Stirring was continued for an additional 2 hours. The solvents were evaporated at reduced pressure and the free amine regenerated by aqueous sodium hydroxide.

The crude amine was dissolved in 600 ml. of glacial acetic acid, 40 ml. of water and 180 ml. of concd. hydrochloric acid. Diazotization was effected at 5–8° by 37 g. of sodium nitrite in 200 ml. of water. The diazonium solution was added to a cold solution of 540 ml. of 50% hypophosphorous acid (tech. grade) and 360 ml. of water. The mixture was allowed to stand at 0° for 16 hours and then at room temperature for 24 hours. The lower layer was separated and the aqueous layer extracted with several portions of ether. The combined layers were dried over calcium chloride. Two distillations through a 12-inch Vigreux column gave 86 g. (56% based on the cumidines) of 3,5-dibromocumene boiling at 90–91° (2 mm.), *n*_D²⁰ 1.5762, *d*₄²⁰ 1.6399; *MR* found 56.10, *MR* calcd. 55.62. A negative silver nitrate test indicated the absence of side-chain bromination.

Anal. Calcd. for C₉H₁₀Br₂: C, 38.88; H, 3.63. Found: C, 38.60; H, 3.68.

3,5-Di-*i*-propylbromobenzene.—A solution of 41.7 g. (0.15 mole) of 3,5-dibromocumene in 125 ml. of ether was added dropwise to 3.66 g. (0.15 g. atom) of magnesium turnings in 25 ml. of ether. Stirring was continued until the magnesium was essentially consumed. Acetone (8.7 g., 0.15 mole) was added so as to maintain gentle reflux. The reaction mixture was then stirred for an additional hour. Hydrolysis was effected by pouring onto chipped ice. The ethereal layer was separated and the aqueous layer extracted with two portions of ether. The combined ethereal solutions were concentrated by distillation. Three grams of powdered, fused potassium bisulfate and 0.5 g. of hydroquinone were added to the carbinol. The flask was fitted with a 12-inch Vigreux column fitted for vacuum distillation. The pressure was adjusted to 25 mm. and the pot temperature raised gradually until a mixture of water and the crude olefin distilled over. The crude olefin was dissolved in ether and washed successively with water, 5% aqueous sodium hydroxide and water. After drying over Drierite, the crude olefin was distilled through a Vigreux column to give 18.3 g. (51% based on dibromocumene) of product b.p. 112–114° (5 mm.), *n*_D²⁰ 1.5566.

A Parr hydrogenator was charged with 18.3 g. of olefin, 50 ml. of absolute ethanol and 0.15 g. of platinum oxide. The theoretical amount of hydrogen was absorbed rapidly from an initial pressure of 60 p.s.i. Distillation through a Vigreux column gave 13 g. (70%) of 3,5-di-*i*-propylbromobenzene which boiled at 109–110° (4 mm.), *n*_D²⁰ 1.5290.

(40) C. Hansch and G. Helmkamp, *ibid.*, **73**, 3080 (1951).

(41) J. H. Biel, *ibid.*, **71**, 1306 (1949).

(36) R. A. Benkeser and H. R. Krysiak, *THIS JOURNAL*, **76**, 599 (1954).

(37) R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 4528 (1953).

(38) H. R. Snyder, R. Adams and A. McIntosh, *ibid.*, **68**, 3282 (1941).

(39) A generous sample of this compound was supplied by Dr. Roy Sugimoto of the Ethyl Corporation, Detroit, Mich.

Anal. Calcd. for $C_{12}H_{17}Br$: C, 59.74; H, 7.06; Found: C, 59.56; H, 6.84.

3,5-Di-*i*-propylphenyltrimethylsilane.—The bromide was coupled with trimethylchlorosilane by sodium according to the procedure employed for the diethyl compound. The product, which was fractionated through a Todd column, boiled at 94–95° (3 mm.), n_D^{20} 1.4894, d_4^{20} 1.8605; *MR* found 78.60, *MR* calcd. 77.90.

Anal. Calcd. for $C_{15}H_{26}Si$: C, 76.84; H, 11.18. Found: C, 76.54; H, 11.00

3,5-Di-*t*-butyltoluene⁴² was prepared in 46% yield. The product, which was fractionated through a Todd column, boiled at 94.5–95° (5 mm.) (reported⁴² b.p. 98° (6 mm.).

3,5-Di-*t*-butylbenzoic Acid.⁴³—Oxidation of the di-*t*-butyltoluene gave the desired acid in 64% yield, m.p. 170–171.5° (lit.⁴³ m.p. 172°).

3,5-Di-*t*-butylaniline.⁴⁴—A Schmidt reaction on the acid gave the amine (m.p. 52.5–54°) in 88% yield (lit.⁴⁴ m.p. 50.5–53°).

3,5-Di-*t*-butyliodobenzene was prepared in 33% yield according to the procedure described in the literature.⁴⁴ The iodide melted at 66–67° (lit.⁴⁴ m.p. 67–68°).

3,5-Di-*t*-butylphenyltrimethylsilane.—A solution of 25.25 g. (0.08 mole) of 3,5-di-*t*-butyliodobenzene in 75 ml. of ether

(42) J. Greuze, C. Ruinard, J. Soeterbroek, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **75**, 301 (1956).

(43) W. VanHartingsveldt, P. E. Verkade and B. M. Wepster, *ibid.* **75**, 349 (1956).

(44) J. Burgers, W. Van Hartingsveldt, J. Kuelen, P. Verkade, H. Visser and B. M. Wepster, *ibid.*, **75**, 1327 (1956).

was added at 0–10° to a solution of *n*-butyllithium prepared from 19.2 g. (0.14 mole) of *n*-butyl bromide and 2.00 g. (0.28 g. atom) of lithium wire. Stirring was continued at 0° for 15 minutes. The cooling was removed and 15.25 g. (0.14 mole) of trimethylchlorosilane in 25 ml. of ether was added dropwise. The mixture was stirred at room temperature for three hours then refluxed for four hours. Hydrolysis was effected by pouring onto crushed ice which was mixed with several grams of sodium bicarbonate. The ethereal layer was washed successively with several portions of water, aqueous sodium thiosulfate and finally water. The solution was dried over Drierite. Upon distillation, iodine distilled over with the product. The product was dissolved in 35–37° petroleum ether, washed with thiosulfate, dried, and distilled. This procedure was repeated three times before a product was obtained free from iodine. Final purification was achieved by distillation through a Todd column. The product boiled at 82–83° at 1 mm., n_D^{20} 1.4854, d_4^{20} 0.8573; *MR* found 87.75, *MR* calcd. 87.15.

Anal. Calcd. for $C_{17}H_{30}Si$: C, 77.80; H, 11.52. Found: C, 78.04; H, 11.62.

General Kinetic Procedure.—The purification of materials, thermostat, dilatometers and procedure were described in a previous paper from this Laboratory.⁹

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LAFAYETTE, IND.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

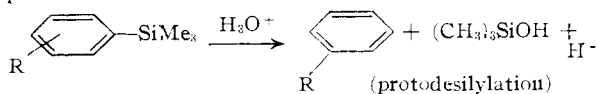
A New Method for Determining the Reactivity of a Particular Ring Position in an Aromatic System

BY ROBERT A. BENKESER, DONALD I. HOKE AND RICHARD A. HICKNER

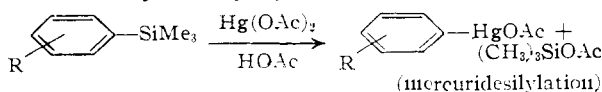
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It has been found that the trimethylsilyl group can be removed cleanly from an aromatic ring by mercuric acetate in glacial acetic acid (mercuridesilylation). The mercuriacetate enters the ring at the position originally occupied by the silicon group. The rates of mercuric acetate cleavage of the isomeric tolyl- and xylyltrimethylsilanes are reported. The relative order of the ease of cleavage of these compounds parallels closely that which was observed in protodesilylations, and can be rationalized in terms of a combined steric and electronic effect. A plot of $\log P_t/m_t$ vs. $\log p_t$ for mercuridesilylation obeys the linear "selectivity" relationship demonstrated by H. C. Brown and co-workers.

In previous publications from this Laboratory the protodesilylation¹ of various aryltrimethylsilanes was studied.² This reaction has been shown to resemble aromatic electrophilic substitution very closely and has proved to be a valuable tool in determining the electrical effect at a particular ring position in an aromatic nucleus.



We have found recently that cleavage of the trimethylsilyl group from an aromatic ring can be effected very cleanly by mercuric acetate in a sol-



(1) This term was introduced by Prof. C. Eaborn (*J. Chem. Soc.*, 1858 (1956)) to describe the acid-catalyzed removal of the trimethylsilyl group from an aromatic ring.

(2) (a) R. A. Benkeser and H. R. Krysiaik, *THIS JOURNAL*, **76**, 6353 (1954); (b) R. A. Benkeser, R. A. Hickner and D. I. Hoke, *ibid.*, **80**, 2279 (1958); (c) R. A. Benkeser, O. H. Thomas and W. A. Schroeder, *ibid.*, **80**, 2283 (1958); (d) R. A. Benkeser, R. A. Hickner, D. I. Hoke and O. H. Thomas, *ibid.*, **80**, 5789 (1958).

vent of glacial acetic acid. In such cases the trimethylsilyl group is replaced by a mercuriacetate group rather than by a proton. It was of interest to determine whether the results obtained in protodesilylations² could be correlated in any manner with the mercuridesilylation results. To test this point the isomeric tolyl- and xylyltrimethylsilanes were chosen for study since protodesilylations had been carried out on the members of both of these series previously. Table I lists all the compounds included in the present study along with their physical constants.

Table II lists the rate constants and partial relative rates (P.R.R.) for the tolyl series. These cleavages were carried out as pseudo first-order in silane, the mercuric acetate being present in ten-fold excess.

It was not possible to carry out cleavages in the xylyl series under the same conditions since the rates proved to be too rapid to follow. Consequently the latter were run pseudo first-order in mercuric acetate. The rate data for the xylyl series are listed in Table III.

It will be noted that the mercuridesilylation reaction provides a new synthetic route to aromatic