[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

SILICON-CONTAINING AZO DYES

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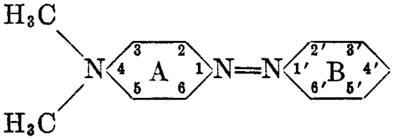
The relation between chemical constitution and the carcinogenic action of the azo dyes has not been as extensively investigated as in the case of polynuclear hydrocarbons. However, from the studies of the carcinogenic action of *p*-aminoazobenzene and its derivatives, it was found that methyl groups greatly enhance the potency of the parent azo dye, provided these groups occupy certain positions. For example, 4-N,N-dimethylaminoazobenzene (I) and its 2′-, 3′-, and 4′-methyl derivatives as well as 2-methyl- and 2,2′-dimethyl derivatives were found to possess carcinogenic potency (1). It was, therefore, thought to be of interest to study the carcinogenic action of some trimethylsilyl and triphenylsilyl derivatives of (I), to compare the effect of an R_3Si group with a methyl group from the point of view of carcinogenic potency of the respective azo dyes. The second purpose was to examine the substantivity of these dyes for textile fibers, in order to find out if the substitution of the R_3Si group has any favorable effect on their substantivity. We, therefore, have synthesized several silicon-containing azo dyes, which are reported in this paper.



I

The only silicon-containing azo compound reported in the literature is 4,4-′ bis(triethylsilyl)azobenzene, obtained by the reduction of 4-nitrophenyltriethylsilane with zinc and sodium hydroxide (2).

The preparation of the trimethylsilyl and triphenylsilyl derivatives of (I) met with certain difficulties. For example, attempts to prepare derivatives of (I) with an R_3Si group in the benzene ring B have not been successful. The reaction of organolithium derivatives of aniline with the appropriate chlorosilanes yielded polymeric products rather than the trimethylsilyl- and triphenylsilylaniline required for coupling with dimethylaniline. Furthermore, the reduction of *p*-nitrophenyltrimethylsilane with hydrogen under pressure using Raney nickel as a catalyst is reported to give only a low over-all yield of the corresponding amine.[1] Therefore, our preliminary study was restricted to the preparation of dyes having an R_3Si- substituent in the benzene ring A.

The silicon-containing azo dyes were prepared by coupling organosilicon compounds with selected diazonium salts. The organosilicon compounds were synthesized by the action of trimethylsilyl chloride and triphenylsilyl chloride

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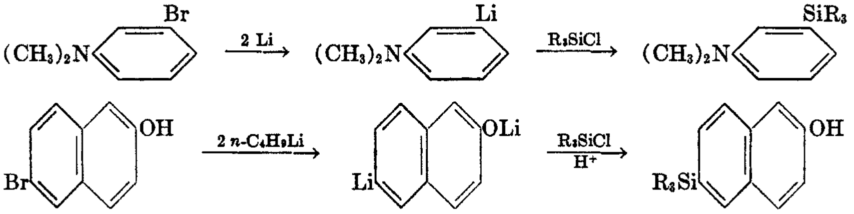
[1] Unpublished studies by Dr. R. A. Benkeser.

on the organolithium derivatives of dimethylaniline and 2-naphthol (3). The lithium compounds of dimethylaniline were prepared by the direct action of lithium on the corresponding bromodimethylanilines (4) and those of 2-naphthol were obtained by the halogen-metal interconversion reaction of *n*-butyllithium with the bromonaphthols (5).



A notable difference was observed in the behavior of *ortho*-, *meta*-, and *para*-substituted dimethylanilines toward diazonium salts. *p*-Trimethylsilyl- and *p*-triphenylsilyl-dimethylaniline coupled readily with the *p*-nitrobenzenediazonium salt; but the dye isolated in both cases was N,N-dimethyl-4-(*p*-nitrophenylazo)aniline in about 80% yield. The latter is evidently formed by the replacement of trimethylsilyl and triphenylsilyl groups by the diazonium cation, during the diazo-coupling reaction. Several examples of the replacement of substituents in the diazo-coupling reaction have been recorded in the literature. The earliest ones are the replacement of the carboxyl group during diazo-coupling with 2-hydroxy-1-naphthoic acid and *p*-hydroxybenzoic acid (6). Later, it was observed that halogen and sulfonyl groups in the 1-position of 2-naphthol are also replaced by the diazonium ion (7). Similarly, organolead groups (R_3Pb-) have been found to be replaced by the diazonium cation (8). During our work we have observed that bromine or the carboxyl group *para* to the tertiary amino group in *p*-bromodimethylaniline and *p*-dimethylaminobenzoic acid, respectively, is replaced to some extent.

Next, in order to study empirically the comparative ease of replacement of different substituents, a few competitive coupling reactions were carried out. First, only one equivalent of *p*-nitrobenzenediazonium salt was allowed to react competitively with one equivalent of dimethylaniline and one of *p*-triphenylsilyldimethylaniline in acetic acid solution. From the reaction mixture the products isolated were N,N-dimethyl-4-(*p*-nitrophenylazo)aniline (70%) and *p*-triphenylsilyldimethylaniline (90%). This indicates that the diazonium cation replaces a proton in preference to the triphenylsilyl group. When the reaction was repeated in dilute sodium hydroxide-acetone mixture as a solvent, the same two compounds were isolated, but the yield of the dye was 50%. Similar competitive coupling reactions, when carried out in acetic acid with mixtures of the same silicon compound and each of *p*-dimethylaminobenzoic acid and *p*-bromodimethylaniline separately, gave no conclusive results. Some tarry products were isolated from the reaction mixtures and the separation of the constituents was not possible. The *p*-nitrobenzenediazonium salt, therefore, was allowed to react separately with *p*-bromodimethylaniline and *p*-dimethylaminobenzoic acid.

TABLE I

SILICON-CONTAINING AZO DYES

NO.	AMINE DIAZOTIZED	TIME OF COUPLING REACTION, HR.[a]	COLOR OF DYE	M.P., °C., (Uncorr.)	YIELD, %	FORMULA	ANALYSIS			
							Si, %		N(Cl or S[b]), %	
							Calc'd	Found	Calc'd	Found
	COUPLER: *m*-TRIMETHYLSILYLDIMETHYLANILINE									
1	Aniline[c]	1	Orange	110	60	$C_{17}H_{23}N_3Si$[e]	9.43	9.24	14.13	
2	*p*-Nitroaniline	1	Red-violet	192	95	$C_{17}H_{22}N_4O_2Si$[e]	8.19	7.98	16.38	16.70
3	2,4-Dinitroaniline[d]	2	Blue-violet	238–240	36	$C_{17}H_{21}N_5O_4Si$	7.23	6.94	18.09	
4	2-Chloro-4-nitroaniline[c]	0.5	Blue-violet	205–206	77	$C_{17}H_{21}ClN_4O_2Si$	7.44	7.45	9.43^{Cl}	9.39
5	2,6-Dichloro-4-nitroaniline[d]	1	Blue-violet	146	66	$C_{17}H_{20}Cl_2N_4O_2Si$	6.98	7.23	17.28^{Cl}	17.55
6	2,4-Dinitro-6-chloroaniline[d]	3	Blue-violet	158	35	$C_{17}H_{20}ClN_5O_4Si$	6.65	6.73	16.63	17.02
7	2-Trifluoromethyl-4-nitroaniline[d]	1.5	Blue-violet	223–224	83	$C_{18}H_{21}F_3N_4O_2Si$[e]	—	—	13.66	13.90
8	2-Methylsulfonyl-4-nitroaniline[d]	2	Blue-violet	243–244	69	$C_{18}H_{24}N_4O_4SSi$	6.67	6.47	7.62^{S}	7.61
9	2,4-Bis(methylsulfonyl)aniline[d]	1.5	Deep red	217–218	51	$C_{19}H_{27}N_3O_4S_2Si$	6.18	5.93	9.27	9.53
10	2-Hydroxy-4-nitroaniline[d]	10	Blue-violet	225–226	14	$C_{17}H_{22}N_4O_3Si$	7.82	8.11	15.64	
11	Sulfanilic acid[f]	1	Orange	251 d.	87	$C_{17}H_{23}N_3O_3SSi$	7.43	7.21	8.49^{S}	8.53
12	Metanilic acid[f]	1	Red-brown	240–241 d.	70	$C_{17}H_{23}N_3O_3SSi$	7.43	7.10	8.49^{S}	8.26
13	Sulfanilamide	1	Red-brown	213	75	$C_{17}H_{24}N_4O_2SSi$	7.45	7.71	8.51^{S}	8.54
14	Anthranilic acid[c]	9	Red	242 d.	53	$C_{18}H_{23}N_3O_2Si$[g]	8.21	7.98	12.31	12.60
15	*p*-Aminobenzoic acid[c]	2	Orange	240–241 d.	65	$C_{18}H_{23}N_3O_2Si$[h]	8.21	8.14	12.31	12.33
	COUPLER: *m*-TRIPHENYLSILYLDIMETHYLANILINE									
16	Aniline	2	Orange	193–194	50	$C_{32}H_{29}N_3Si$	5.8	6.07	8.70	
17	*p*-Nitroaniline	1	Brown-red	205–206	95	$C_{32}H_{28}N_4O_2Si$	5.31	5.28	10.62	10.64
18	2,4-Dinitroaniline[i]	1	Blue-violet	213–214	44	$C_{32}H_{27}N_5O_4Si$	4.88	4.88	12.21	11.92
19	2-Chloro-4-nitroaniline	2	Blue-violet	233–234	65	$C_{32}H_{27}ClN_4O_2Si$	4.98	5.22	9.96	10.26
20	2,6-Dichloro-4-nitroaniline	1	Garnet	230–231	53	$C_{32}H_{26}Cl_2N_4O_2Si$	4.69	4.92	9.38	9.71
21	2-Methylsulfonyl-4-nitroaniline[i]	3	Blue-violet	263	37	$C_{33}H_{30}N_4O_4SSi$	4.62	4.84	9.24	9.37
22	2,4-Bis(methylsulfonyl)aniline	3	Red-brown	235–236	20	$C_{34}H_{33}N_3O_4S_2Si$	4.38	4.51	6.57	6.81

23	Sulfanilic acid	2	Maroon	253–254 d.	85	$C_{32}H_{29}N_3O_3SSi$	4.97	4.65	7.46^N 5.68^S	7.23 5.41
24	Metanilic acid	2	Maroon	260 d.	80	$C_{32}H_{29}N_3O_3SSi$	4.97	4.75	5.68^S	5.35
25	Sulfanilamide	2	Scarlet	224	90	$C_{32}H_{30}N_4O_2SSi$	4.98	5.21	7.47	7.28
26	Anthranilic acid	10	Red	254–255	10	$C_{33}H_{29}N_3O_2Si$	5.32	5.17	7.98	7.62
27	*p*-Aminobenzoic acid	2	Orange-red	274–275	70	$C_{33}H_{29}N_3O_2Si$	5.32	5.12	7.98	8.17

NAPHTHOL AZO DYES

COUPLER: 6-TRIMETHYLSILYL-2-NAPHTHOL

28	*p*-Nitroaniline	1	Orange-red	234–235	83	$C_{19}H_{19}N_3O_3Si$	7.68	7.48	11.51	11.38
29	Benzidine[j] (disazo dye)	2	Violet	314–315	70	$C_{38}H_{38}N_4O_2Si_2$	8.78	8.48	8.78	8.57
30	*o*-Dianisidine[i] (disazo dye)	2	Violet-blue	291–292	62	$C_{40}H_{42}N_4O_4Si_2$	8.41	8.70		

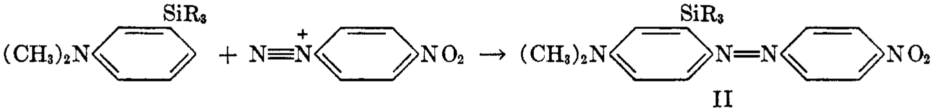
COUPLER: 6-TRIPHENYLSILYL-2-NAPHTHOL

31	*p*-Nitroaniline	2	Orange-red	316–317 d.	75	$C_{34}H_{25}N_3O_3Si$	5.08	5.31	7.62	7.61
32	Sulfanilamide	2	Orange-red	312–313	50	$C_{34}H_{27}N_3O_3SSi$	4.78	4.92	7.18	7.32
33	Benzidine[j] (disazo dye)	2	Violet	359–360	90	$C_{68}H_{50}N_4O_2Si_2$	5.54	5.46	5.54	5.50
34	*o*-Dianisidine[i] (disazo dye)	2	Blue	340	60	$C_{70}H_{54}N_4O_4Si_2$	5.23	5.27	5.23	5.52

[a] The times selected for many of these reactions were arbitrary and in slow coupling, the reactions were carried out for several hours at room temperature. [b] The figures in this column stand for the N%, unless otherwise indicated by superscript for chlorine or sulfur. [c] Diazotized by the method (A). [d] Diazotized by the method (B). [e] Final purification of the dye was done by the chromatographic method. [f] Crystallized from acetone. [g] Crystallized from chloroform. [h] Diazotized according to the procedure given by Fierz-David and Blangey (19). [i] Crystallized from benzene. [j] Crystallized from chlorobenzene.

The yields of the azo dye, N,N-dimethyl-4-(*p*-nitrophenylazo)aniline, obtained by the partial replacement of bromine and the carboxyl group during coupling, were 18% and 54%, respectively. From the yields of the azo dye, obtained under similar conditions, the ease of replacement of the substituents seems to decrease in the order H > SiR_3 > COOH > Br. It will be noted that, due to the similar electronegativities of hydrogen and silicon, both are displaced by the diazonium cation with relative ease.

m-Trimethylsilyl- and *m*-triphenylsilyl-dimethylaniline, however, showed normal behavior towards diazonium salts and gave a series of azo dyes in very good yields. The color of the dyes, obtained from these two compounds and the respective diazonium salts, was of almost the same tone but a comparison of the visual color of some of these dyes with that of unsubstituted dyes shows that the substitution of trimethylsilyl and triphenylsilyl groups in the azo dyes has a general bathochromic effect on the color. However, the exact effect can not be judged unless determined by spectroscopic methods. In general, the trimethylsilyl derivative coupled more readily than the triphenylsilyl compound, and this may be attributed to steric effects. A notable difference was observed in their reaction with certain diazonium salts containing functional groups in the *o*-position to the diazo group. For example, the diazonium sulfates obtained from 2-hydroxy-4-nitroaniline, 2,4-dinitro-6-chloroaniline, and 2-trifluoromethyl-4-nitroaniline coupled readily with the trimethylsilyl compound but failed to react with the triphenylsilyl derivative, even though the reaction was carried out for a prolonged time.



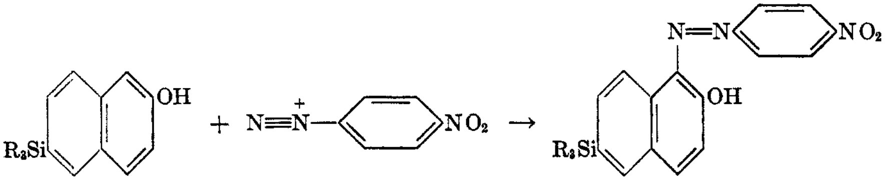
II

Since the diazonium ion is an electrophilic reagent, its cationoid reactivity will be increased by electron-attracting (−E) and decreased by electron-releasing (+E) substituents in the molecule. The nitro and trifluoromethyl groups are strongly electron-attracting and therefore, 2,4-dinitro-6-chlorobenzenediazonium ions and 2-trifluoromethyl-4-nitrobenzenediazonium ions should be very reactive. It seems, therefore, that their failure to couple with the triphenylsilyl compound may be due to the steric effect between the triphenylsilyl, and nitro and trifluoromethyl groups respectively, which happen to be in the *ortho* positions to the azo linkage being formed. The general low reactivity of 2-hydroxy-4-nitrobenzenediazonium ions may be due to both the +E effect of the hydroxyl group and the steric effect. Moreover, the diazonium salt obtained from 2-hydroxy-4-nitroaniline when added to water forms an internal diazo oxide, which couples with difficulty. It is also likely that the triphenysilyl group has more deactivating effect on the *ortho* position than has the trimethylsilyl group. The difference in reactivity due to the steric effect is also observed in the reaction of diazonium salts from anthranilic acid and *p*-aminobenzoic acid. The diazonium salt from anthranilic acid coupled with both the compounds but gave low yields, especially with the triphenylsilyl compound; whereas the dyes from *p*-aminobenzoic acid were obtained in good yields. That the steric effects, however, are not the only considerations will be observed from the reaction of the diazonium salts from 2-methylsulfonyl-4-nitroaniline and 2,4-bis(methylsulfonyl)aniline with both the silicon compounds. In both cases, the bulky methylsulfonyl group which is in the *o*-position to the diazo group would be expected to offer more steric hindrance. Perhaps the activation of the diazonium cation may be increased considerably by the (−E) effect of the methylsulfone group. A comparison of the reactivity of the diazonium salts from 2-methylsulfonyl-4-nitroaniline and 2-trifluoromethyl-4-nitroaniline also reveals that the activation due to the substituent effect of methylsulfonyl group is, probably, more than that of the trifluoromethyl group, assuming the steric effect is the same in both cases.

o-Trimethylsilyl- and *o*-triphenylsilyl-dimethylaniline did not couple with the *p*-nitrobenzenediazonium salt even though the reaction was carried out for several hours. It has been reported that dimethylaniline substituted with the nitro- (9), methyl (10), and chloro- (11) groups in the *ortho*-position does not show any tendency to couple with the diazonium salt. We have found that *o*-bromodimethylaniline also fails to react with the diazonium salt. There are several other observations reported in the literature which show that *ortho*-substituted dimethylaniline is much less reactive than dimethylaniline in electrophilic substitutions. For example, *o*-nitrodimethylaniline, N,N-dimethyl-*o*-toluidine, and *o*-N,N-dimethylamino-*p*-xylene do not form *p*-nitroso derivatives by the action of nitrous acid (12). *o*-Chlorodimethylaniline is similarly indifferent to aqueous nitrous acid (9). The low reactivity of the above amines is also exhibited by the difficulty of their reactions with benzaldehyde and formaldehyde (12).

A rational interpretation of this general inactivity of *ortho*-substituted dimethylaniline can be given by taking into account its resonance interaction. The *o*-substituents in dimethylaniline crowd the tertiary amino group to a serious extent in the planar arrangement and thus disturb the planarity between the tertiary amino group and the benzene ring. This increases the energies of the contributing polar structures and diminishes their resonance interaction. Consequently the *p*-position, which is activated mainly by the resonance effect of the amino group, becomes less reactive towards electrophilic reagents.

Silicon-containing naphthols also showed a similar behavior toward *p*-nitrobenzenediazonium chloride. 1-Trimethylsilyl-2-naphthol, when reacted with *p*-nitrobenzenediazonium chloride, gave the azo dye 1-(*p*-nitrophenylazo)-2-naphthol. Since in 2-naphthol, the carbon in the 1-position is the only center of attack for the diazonium ion, the coupling takes place with the elimination of the trimethylsilyl group. 6-Trimethylsilyl- and 6-triphenylsilyl-2-naphthol, however, coupled with the different diazonium compounds and gave silicon-containing



III

dyes in good yields. Only the dyes from sulfanilic acid could not be obtained in pure form due to their high solubilities in water. 3-Trimethylsilyl- and 3-triphenylsilyl-2-methoxynaphthalene, however, did not couple with *p*-nitrobenzenediazonium chloride, although 2-methoxynapthhalene has been reported to couple with *p*-nitrobenzenediazonium chloride (13).

Action of acid-cleaving agents on the azo dyes. The action of acid-cleaving agents on the azo dyes was studied with a double purpose, first, to study the stability of the carbon-silicon bond in the azo dyes and, second, to remove the R_3Si-group to establish the structural position of the azo linkages.

It has been found that hydrogen chloride in acetic acid is a convenient reagent for the cleavage of organosilicon compounds (14). However the azo dyes (II, $R=CH_3$) and (II, $R=C_6H_5$) were unaffected when dry hydrogen chloride gas was bubbled through their refluxing acetic acid solutions for a long period. The dye (II, $R=C_6H_5$), being a tetraaryl silane derivative, would be expected to be much less susceptible to the acid cleavage since it has been observed that the tetraarylsilanes are much more resistant to acid cleavage than the trialkylarylsilanes (14); but the resistance of the dye (II, $R=CH_3$), containing the trimethylsilyl group, to acid cleavage warrants some discussion. The acid cleavage of organosilicon compounds involves a nucleophilic displacement on silicon by Cl^- accompanied by an electrophilic attack by proton on carbon and rupture of the C-Si bond. The acid cleavage of the C-Si bond should, therefore, be considerably influenced by the substituents in the aromatic ring. From the studies of the hydrogen chloride cleavage of organosilicon compounds, the order of the ease of cleavage of the groups is *p*-anisyl > *p*-dimethylaminophenyl > *p*-tolyl > *p*-chlorophenyl (14). Interestingly, this order is in essential agreement with the σ-constants of the substituents in the benzene ring (15). Since in the dye (II, $R=CH_3$) there are two groups having opposite effects, and since it is more resistant to the acid cleavage than *m*-trimethylsilyldimethylaniline, it is probable that the *p*-nitrobenzeneazo group has a more pronounced electronic effect than the *m*-dimethylamino group of σ-value (-0.211) (15). Furthermore, the azo linkage is *ortho* to the C-Si bond and therefore, steric effects may play a major role in the deactivation of the *ortho*-position.

Both the dyes (II, $R=CH_3$ and $R=C_6H_5$), however, were quite susceptible to acidic reducing agents. By the action of tin, or stannous chloride, and hydrochloric acid reduction of the azo linkage to amino groups and simultaneous cleavage of the C-Si bond took place. For structure proof, the dye (II, $R=CH_3$) was reduced with tin and hydrochloric acid. *p*-Aminodimethylaniline, obtained as one of the products, indicated that the azo linkage in the dye is *para* to the tertiary amino group and *ortho* to the trimethylsilyl group.

In the case of the naphthol azo dyes, the dye (III, $R=CH_3$) was cleaved smoothly by passing hydrogen chloride into its refluxing acetic acid solution. The product obtained was 1-(*p*-nitrophenylazo)-2-naphthol, indicating that the coupling takes place in the 1-position of the naphthalene ring. The dye (III, $R=C_6H_5$), however, was unaffected by this reagent, even though 6-triphenylsilyl-2-naphthol was cleaved smoothly by dry hydrogen chloride in acetic acid.

This gives further support to the assumption of the stabilization of the C-Si bond by the *p*-nitrobenzeneazo group.

The carcinogenic action and the dyeing properties of the dyes will be reported elsewhere.

EXPERIMENTAL

o-Triphenylsilyldimethylaniline. To a solution of 21 g. (0.071 mole) of triphenylchlorosilane dissolved in 100 ml. of ether was added 0.075 mole of *o*-dimethylaminophenyllithium [prepared from 20 g. (0.1 mole) of *o*-bromodimethylaniline and 1.8 g. (0.26 g.-atom) of lithium in 90% yield]. The reaction was instantaneous and Color Test I (16) was negative after the addition of the organolithium compound. The mixture was hydrolyzed by pouring into water. The ethereal layer was separated and dried over sodium sulfate. Ether was removed and the residue (18 g.) of m.p. 80–90°, which was contaminated with some oily compound, was purified by crystallization from ethanol; the yield of the pure compound was 10 g. (39%); m.p. 95.5°.

Anal. Calc'd for $C_{26}H_{25}NSi$: N, 3.69; Si, 7.39.
Found: N, 4.00 Si, 7.33.

The *meta-* and the *para*-isomers were prepared in a similar manner (17, 18).

m-Trimethylsilyldimethylaniline. To 16 g. (0.148 mole) of trimethylchlorosilane in 50 ml. of ether was added an ethereal solution of 0.14 mole of *m*-dimethylaminophenyllithium [prepared from carefully purified *m*-bromodimethylaniline (30 g., 0.15 mole) and lithium (2.3 g., 0.33 g.-atom) in 92% yield]. The reaction was prompt and Color Test I was negative just after the addition of the organolithium compound. The mixture was hydrolyzed and worked up in the customary manner. The yield of the crude product was 21 g. (77%). The liquid was purified by distillation under reduced pressure, b.p. 86–87° (1.0 mm.). The yield of pure *m*-trimethylsilyldimethylaniline was 14 g. (52%); d_4^{20} 0.9124; n_D^{20} 1.5257; MR_D 64.91 (calc'd MR_D 64.99).

Anal. Calc'd for $C_{11}H_{19}NSi$: Si, 14.51. Found: Si, 14.23.

o-Trimethylsilyldimethylaniline. This compound was prepared as in the previous case. The yield was 45%. It boiled at 65–65.5° (1.0 mm.); d_4^{20} 0.9324; n_D^{20} 1.5080; MR_D 62.16 (Calc'd MR_D: 64.99). The product, however, did not analyze correctly for silicon; probably it forms an azeotrope.

Anal. Calc'd for $C_{11}H_{19}NSi$: Si, 14.51. Found: Si, 11.65.

The *para*-isomer was prepared in a similar way (14).

PREPARATION OF THE AZO DYES

The diazotizations of the amines and their coupling reactions with the silanes were carried out by the customary procedures. The following are typical examples:

Diazotization of the amines. The amines containing one functional group were diazotized by the usual procedure, using hydrochloric acid and sodium nitrite (19). The aniline derivatives containing more than one negative group were diazotized by the nitrosyl sulfuric acid method (20).

Method (A). *p*-Nitroaniline (1.4 g., 0.01 mole) was added to 3 ml. of conc'd hydrochloric acid and 3 ml. of water. The mixture was warmed to 70° and then cooled to 0°, by keeping in ice. Three ml. of hydrochloric acid and 3 ml. of water were added. The mixture was stirred occasionally. A 20% solution of 0.7 g. (0.011 mole) of sodium nitrite was added and the mixture was kept in ice for 15–20 minutes. The diazonium salt solution was diluted by adding 10 g. of ice. Excess of nitrous acid was destroyed by adding urea and the resulting solution was used for coupling.

Method (B). 2,4-Dinitroaniline (1.83 g., 0.01 mole) was added to 20 ml. of glacial acetic acid and the mixture was heated to 70°, then cooled by keeping in ice. The amine acetate which separated was added as a slurry to a nitrosyl sulfuric acid solution. In order to prepare the latter, 0.8 g. (0.011 mole) of sodium nitrite was added to 5.5 ml. of conc'd sulfuric acid (*d*, 1.84) and the mixture was heated to 70 ° and then cooled to 10°. During the addition of the amine acetate to nitrosylsulfuric acid, the temperature of the mixture was not allowed to rise above 15°. The diazonium salt was kept in ice for 30 minutes, with occasional stirring. Fifteen grams of ice were added. The excess of nitrous acid was destroyed by adding urea. The diazonium salt solution was added to the solution of the coupler through a filter paper.

N,N-Dimethyl-4-(p-nitrophenylazo)-3-(trimethylsilyl)aniline. To a solution of 1.93 g. (0.01 mole) of *m*-trimethylsilyldimethylaniline in 50 ml. of glacial acetic acid was added a filtered solution of 0.01 mole of *p*-nitrobenzenediazonium chloride and the mixture was stirred for half an hour, keeping the temperature of the reaction mixture below 10°. Sodium acetate was added to neutralize the mineral acid and to hasten the coupling reaction. After stirring for about 15 minutes more, the brown-red dye was collected; 3.25 g. (95%), m.p. 188–190°. The dye was crystallized from alcohol; the pure product melted at 192°.

1-(p-Nitrophenylazo)-6-trimethylsilyl-2-naphthol. To a solution of 3 g. (0.014 mole) of 6-trimethylsilyl-2-naphthol in 100 ml. of ethanol and 10 ml. of 20% sodium hydroxide was added an aqueous solution of *p*-nitrobenzenediazonium chloride, prepared from 2.1 g. (0.015 mole) of *p*-nitroaniline, and the mixture was stirred for 2 hours. The red-orange product (2.5 g., m.p. 234–235°) was collected and crystallized from acetic acid to give a pure dye melting at 235°. From the filtrate, 1.0 g. of the product was recovered making the total yield 70%.

Purification of the dyes. In most of the cases, the dyes separated from the coupling reactions in pure crystalline form. The dyes were further purified by crystallization from ethanol. Acetic acid was also found to be a suitable solvent for crystallization. In certain cases, however, the dyes had to be finally purified by chromatographic methods. The chromatographic separations were done by a usual procedure on a column of alumina (Fisher Adsorption Alumina, 80–200 mesh), using chloroform as a solvent. The dyes adsorbed on the alumina column were eluted by using chloroform containing 2–5% of methanol.

Coupling reaction of p-nitrobenzenediazonium acetate with p-triphenylsilyldimethylaniline. To an ice-cold solution of *p*-triphenylsilyldimethylaniline (3 g., 0.008 mole) in 100 ml. of glacial acetic acid and 50 ml. of acetone was added dropwise a filtered aqueous solution of 0.008 mole of *p*-nitrobenzenediazonium acetate. The reaction mixture was stirred for two hours, keeping the temperature below 10°. A thick garnet-colored precipitate, which separated, weighed 2 g. (92.5%), m.p. 160–172°. It was crystallized twice from acetic acid; the pure product, 1.7 g. (78.6%) had a m.p. and a mixed m.p. with N,N-dimethyl-4-(*p*-nitrophenylazo)aniline of 230–231°. From the acetic acid filtrate was recovered triphenylsilanol, 1.6 g. (72.7%), m.p. 135–140°. On crystallization from petroleum ether (b.p. 80–100°), its m.p. and mixed m.p. with triphenylsilanol was 152–153°.

The coupling reaction of *p*-nitrobenzenediazonium acetate with *p*-trimethylsilyldimethylaniline, carried out in a similar way, gave the dye, N,N-dimethyl-4-(*p*-nitrophenylazo)aniline, in about 80% yield.

Competitive coupling reaction of p-nitrobenzenediazonium acetate with dimethylaniline and p-triphenylsilyldimethylaniline. To a solution of 2.5 g. (0.0066 mole) of *p*-triphenylsilyldimethylaniline and 0.81 g. (0.0066 mole) of dimethylaniline in 100 ml. of ethanol, 50 ml. of acetic acid, and 100 ml. of acetone, was added dropwise a filtered solution of *p*-nitrobenzenediazonium acetate, prepared from 0.92 g. (0.0066 mole) of *p*-nitroaniline. The mixture was stirred for 3 hours, at 0–5°. The red-brown product was collected (3.5 g.). It was extracted with petroleum ether (b.p., 80–100°). The dye, insoluble in the petroleum ether, weighed 1.2 g. (70%) and melted at 225–230°. On crystallization from glacial acetic acid, it melted at 230–231°. The m.p. was not depressed when the compound was mixed with N,N-dimethyl-4-(*p*-nitrophenylazo)aniline. The weight of silicon compound recovered was 2.21 g. (88.5%). On crystallization from petroleum ether (b.p., 80–100°), it melted at 146–147°. The mixed m.p. with *p*-triphenylsilyldimethylaniline was 146–147°.

CLEAVAGE REACTIONS

Acid cleavage of m-trimethylsilyldimethylaniline. Dry hydrogen chloride gas was passed into a stirred, refluxing solution of 1.00 g. (0.0052 mole) of the silicon compound in 15 ml. of glacial acetic acid, for 24 hours. On cooling, the reaction mixture was neutralized with a saturated aqueous solution of sodium carbonate. The resulting mixture was extracted with ether. From the ether, 0.5 g. (80%) of dimethylaniline was recovered. It was identified by preparing its picrate of m.p. 159–161°; the mixed m.p. with the picrate of dimethylaniline was 160–161°. The dyes (II, R = CH_3 and R = C_6H_5), when treated in a similar manner with dry hydrogen chloride gas in glacial acetic acid, were unaffected and in both cases, the original dyes were recovered in more than 50% yields.

Acid cleavage of the azo dye (III, R = CH_3). Dry hydrogen chloride gas was passed into a refluxing solution of 1.00 g. of the azo dye (III, R = CH_3), in 100 ml. of glacial acetic acid for 18 hours. After 15 hours, the color of the solution changed from orange-red to brown-red. The reaction was continued for three hours more. The mixture was cooled and the crystalline azo dye was collected, 0.6 g. (75%), m.p., 249–250°, which was not depressed when the compound was mixed with 1-(*p*-nitrophenylazo)-2-naphthol. The dye (III, R = C_6H_5), when treated in a similar manner with dry hydrogen chloride gas, was unaffected.

Reductive cleavage of the azo dye (II, R = CH_3). The azo dye, 1.00 g., was heated on a steam-bath with 50 ml. of conc'd hydrochloric acid and 0.5 g. of tin powder. The dye was reduced slowly and the mixture became colorless after about one hour. The mixture was diluted with 200 ml. of water and filtered. The filtrate was made basic by adding solid sodium carbonate and the basic mixture was extracted with ether. The brown liquid obtained from ether was heated on a steam-bath with 5 ml. of acetic anhydride for 3 hours. The reaction product was poured into 200 ml. of water and the resulting solution was filtered to separate *p*-nitroacetanilide. The filtrate was neutralized with sodium bicarbonate. No precipitate separated. Therefore, the water from the filtrate was removed by slow evaporation, by blowing air over it at room temperature. The residue was extracted with ether. On removing ether, 0.2 g. of a colorless product was obtained, m.p. 80–90°. It was crystallized from water. The pure crystalline product melted at 129–130°. A mixed melting point of the compound with *p*-dimethylaminoacetanilide was 129–130°.

SUMMARY

1. The preparation of *o*-, and *m*-trimethylsilyl- and *o*-triphenylsilyl-dimethylanilines has been reported.

2. The *p*-nitrobenzenediazonium salt was found to couple with *p*-trimethylsilyl- and *p*-triphenylsilyl-dimethylaniline, and 1-trimethylsilyl-2-naphthol with the replacement of the R_3Si-group.

3. From the competitive coupling reaction and the replacement reactions, the ease of replacement of the substituents, during diazo-coupling, was found to decrease in the order: $H > R_3Si > COOH > Br$.

4. Several silicon-containing azo dyes have been synthesized by coupling *m*-trimethylsilyl- and *m*-triphenylsilyl-dimethylaniline, and 6-trimethylsilyl- and 6-triphenylsilyl-2-naphthol with selected diazonium salts, and their properties have been described.

5. The failure of *m*-triphenylsilyldimethylaniline to couple with certain diazonium salts from *ortho*-substituted aniline derivatives, such as 2,4-dinitro-6-chloro-, 2-hydroxy-4-nitro-, and 2-trifluoromethyl-4-nitro- has been attributed to the steric and substituent effects of the triphenysilyl group.

6. In the cleavage studies of the dyes with dry hydrogen chloride in glacial

acetic acid, it has been observed that the *p*-nitrobenzeneazo group stabilizes the carbon-silicon bond.

7. Reduction of two of the dyes with tin and hydrochloric acid was found to cleave the C-Si bond, and also to reduce the azo linkage to the corresponding amino products.

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