bond was more likely to occur than in others. It is evident from Table III that the greater the absorption coefficient for the band at 2.93μ the greater is the amount of heterolytic cleavage of the N–Br bond and subsequent ring bromination. No bromination studies have been conducted with N-bromodifluoroacetamide but it might be expected to give a slightly less amount of ring bromination than N-bromomonochloroacetamide. Thus, it may be possible to predict in a qualitative manner the chemical activity of an N-bromoacetamide from spectroscopic studies.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Organotin Compounds Containing an Azo Linkage

BY HENRY GILMAN AND SANDERS D. ROSENBERG

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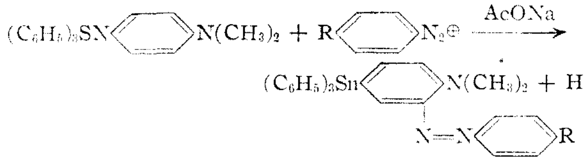
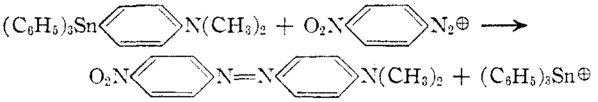
Some organotin compounds containing an azo linkage have been prepared by treating triphenyl-*m*- and triphenyl-*p*-dimethylaminophenyltin with appropriate diazonium salts. Their preparation and replacement of substituents by the diazonium cation in the course of the diazo-coupling reaction are described.

Organometallic compounds of silicon,[1] tin[2] and lead[3] containing an azo linkage have been prepared. It was found[1] that when trimethyl- and triphenyl-*p*-dimethylaminophenylsilane were treated with *p*-nitrobenzenediazonium salt the dye isolated in both cases was 4-dimethylamino-4′-nitroazobenzene. The latter is formed by the replacement of the trimethylsilyl and triphenylsilyl groups by the diazonium cation during the diazo-coupling reaction. Trimethyl- and triphenyl-*m*-dimethylaminophenylsilane, however, showed normal behavior toward diazonium salts, and gave a series of azo dyes in good yields. In contrast with its silicon analog, triphenyl-*p*-dimethylaminophenyltin reacted normally with *p*-nitrobenzenediazonium salt.[2] In order to explore the scope and limitations of this reaction, some additional organotin compounds containing an azo linkage have been synthesized with a view to their examination as carcinogenic agents[2] and for their substantivity as dyes.[1]

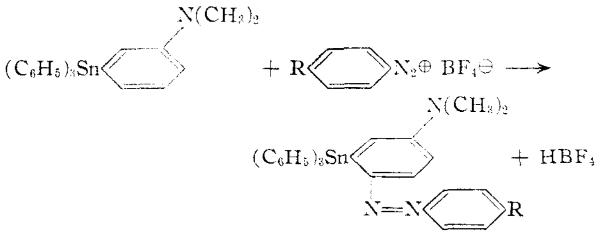
In the method previously reported,[2] triphenyl-*p*-dimethylaminophenyltin reacted with the *p*-substituted benzenediazonium salt in an acetate buffered solution. This method was extended to prepare compounds where R was —Br and —Cl as well as $—NO_2$ but the yields were very low, and in the case where R was $—SO_3H$, no reaction took place. Therefore a new method of preparation was sought. An improved procedure was found in the use of *p*-substituted benzenediazonium fluoborates which are stable solids and can be isolated, dried and weighed. A buffered solution was no longer used, and the coupling reaction was carried out in a dioxane–water solution.



It was found that when triphenyl-*p*-dimethylaminophenyltin was treated with *p*-nitro- and *p*-bromobenzenediazonium fluoborate, replacement of the triphenyltin group by the diazonium cation occurred. This result is in agreement with that obtained for the silicon analog. Other examples of replacement of substituents in the diazo-coupling reaction have been reported; the replacement of the carboxyl group during diazo-coupling with 2-hydroxy-1-naphthoic acid and *p*-hydroxybenzoic acid,[4] replacement of halogen and sulfonyl groups in the 1-position of 2-naphthol by the diazonium ion,[5] partial replacement of bromo and carboxyl groups in *p*-substituted dimethylaniline and complete replacement of the trimethylsilyl group in 1-trimethylsilyl-2-naphthol.[1,6]



Triphenyl-*m*-dimethylaminophenyltin coupled in the normal manner with diazonium fluoborates and the azo dyes were isolated in good yields. In preparations where R was $-NO_2$, $-Br$ or $-CO_2H$, the reaction was successful, but where R was $—N(CH_3)_2$, no reaction took place. This might be expected as the diazonium ion is an electrophilic reagent, and its cationoid reactivity will be enhanced by electron-attracting and reduced by electron-releasing substituents in the para position on the benzene ring. The structure proof for this series of compounds was carried out by reductive



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(1) S. V. Sunthankar and H. Gilman, *J. Org. Chem.*, **15**, 1200 (1950); see also B. N. Dolgov and O. K. Panina, *J. Gen. Chem. (U.S.S.R.)*, **18**, 1129 (1948) [*C. A.*, **43**, 1737 (1949)].

(2) H. Gilman and C. E. Arntzen, *J. Org. Chem.*, **15**, 994 (1950).

(3) H. Gilman and C. G. Stuckwisch, THIS JOURNAL, **64**, 1007 (1942); **72**, 4553 (1950).

(4) R. Nietzki and A. L. Guiterman, *Ber.*, **20**, 1274 (1887); H. Limpricht, *Ann.*, **263**, 237 (1891).

(5) J. T. Hewitt and H. V. Mitchell, *J. Chem. Soc.*, **89**, 1167 (1906).

(6) See K. H. Saunders, "The Aromatic Diazo Compounds," 2nd Edition, Edward Arnold and Co., London, 1949, p. 221, for a more complete review of the replacement reaction.

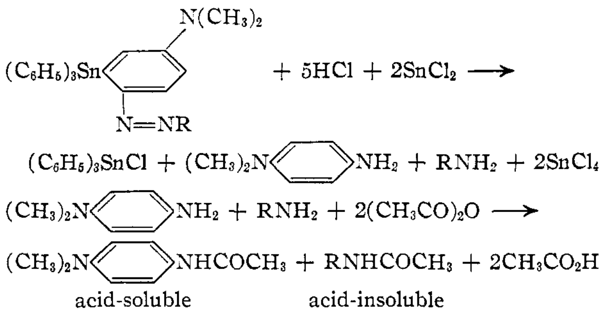
TABLE I

COUPLING WITH TRIPHENYL-*p*-DIMETHYLAMINOPHENYLTIN

Coupling agent	Product identified	Yield or recovery, %	M.p., °C.	Color	Sn, % Calcd.	Sn, % Found
p-Nitrobenzenediazonium chloride	Triphenyl-4-dimethylamino-3-(4'-nitrophenylazo)-phenyltin[a]	24.0	187–189	Gold	...	...
p-Bromobenzenediazonium chloride	Triphenyl-4-dimethylamino-3-(4'-bromophenylazo)-phenyltin[b]	16.8	170–172	Brown	18.17	18.36
p-Chlorobenzenediazonium chloride	Triphenyl-4-dimethylamino-3-(4'-chlorophenylazo)-phenyltin[b]	4.5	162–165	Brown	19.47	19.58
p-Sulfobenzenediazonium chloride	Triphenyl-*p*-dimethylaminophenyltin[c]	62.7	132–134	....	...	...
p-Nitrobenzenediazonium fluoborate	4-Dimethylamino-4'-nitroazobenzene[c]	45.7	228–231	Red	...	...
p-Bromobenzenediazonium fluoborate	4-Dimethylamino-4'-bromoazobenzene	45.3	151–153	Orange	...	...

[a] Crystallized from chloroform–ethanol pair. [b] Crystallized from petroleum ether (b.p. 77–120°). [c] Product identified by a mixed melting point with an authentic specimen.

cleavage using stannous chloride and hydrochloric acid.[3] The following equations outline the reactions involved



Separation and identification of the dimethylaminoacetanilide showed the relative positions of the dimethylamino and azo groups in the original compound.

In the preparation of triphenyl-*m*-dimethylaminophenyltin it was found that if the reaction were permitted to take place at the reflux temperature of ether, the only product isolated was tetraphenyltin. Apparently disproportionation[7] takes place under these relatively mild conditions.

Experimental

Triphenyltin Chloride.[8]—In a one-liter flask, equipped with an air condenser, were placed 118.0 g. (0.276 mole) of tetraphenyltin, which had been air-dried at 120° for 12 hours, and 33.4 g. (0.128 mole) of anhydrous stannic chloride. The flask was placed in an oil-bath which was then slowly heated to 220 ± 10° and maintained there for one hour. The flask was shaken occasionally. After the mass had cooled it was extracted with 500 ml. of petroleum ether (b.p. 77–120°), treated with Norit, and filtered hot. On cooling, 92.8 g. (65.6%) of triphenyltin chloride melting at 104–106°[9] was recovered. This reaction was repeated many times over a wide range of concentrations, and the yields were consistently between 60 and 70%.

Triphenyl-4-dimethylamino-3-(4'-nitrophenylazo)-phenyltin.—This compound was prepared as previously outlined.[2] In a one-liter beaker, surrounded by an ice-bath and equipped with a magnetic stirrer, were placed 3.5 g. (0.007 mole) of triphenyl-*p*-dimethylaminophenyltin,[2] 4.1 g. of sodium acetate, 75 ml. of ethyl acetate and 50 ml. of water, A solution containing 0.007 mole of *p*-nitrobenzenediazonium chloride, to which enough sodium acetate had been added to neutralize the excess hydrochloric acid, was added dropwise, with vigorous stirring. A red color formed almost immediately. The solution was stirred for two hours, the ice-bath was removed and the mixture allowed to stand overnight. The water, in which a red oil was suspended, was decanted, and the red mass was digested twice with 25-ml. portions of ethanol, leaving a brown solid. The solid was dissolved in a minimum amount of refluxing chloroform, then ethanol was added at reflux until a trace of solid precipitated from solution. On cooling, 1.1 g. (24.0%) of triphenyl-4-dimethylamino-3-(4'-nitrophenylazo)-phenyltin,[9] bright gold gilt in color, melting at 187–189° was recovered. This method was used for all reactions where *p*-substituted benzenediazonium chlorides were used as the coupling agent.

***m*-Bromodimethylaniline.**—This compound was prepared by a modification[10] of the method previously reported.[11] In a two-liter flask were placed 100 g. (0.581 mole) of *m*-bromoaniline (Eastman Kodak Co. white label) and 100 ml. of water. The flask was partially immersed in a running water-bath, and 70 ml. (91.0 g., 0.72 mole) of freshly redistilled dimethyl sulfate was added dropwise with good stirring. Ten minutes after the addition was completed the solution was neutralized with 150 ml. of saturated sodium carbonate solution. A second and third addition of 70 ml. of dimethyl sulfate were made followed by neutralization with sodium carbonate solution (care was taken to make the reaction mixture strongly basic after the third addition). The mixture was then extracted with 500 ml. of ether, and the ether layer dried over sodium sulfate. To the water layer was added 500 ml. of saturated potassium iodide solution, and a voluminous white solid precipitated. The solid was filtered off and air-dried. The ether was removed by distillation from a water-bath and the residue digested with 150 ml. of saturated sodium carbonate solution. The resulting mixture was poured into the potassium iodide mother liquor, and the precipitate thus formed was filtered off and air-dried. The solids were combined (158.5 g.) and distilled at water-pump pressure [122.5° (15 mm.), 136° (22 mm.)]; the total distillate was collected in one fraction. The distillate partially solidified on standing. The entire fraction was redistilled under reduced pressure [78° (1.0 mm.)] and two cuts were taken. Both fractions had the same index of refraction, $n^{17.1}_D$ 1.6011. Total yield of *m*-bromodimethylaniline was 79.2 g. (68.2%).

***m*-Dimethylaminophenyllithium.**—In a 250-ml. flask were place 0.8 g. (0.09 g. atom plus 20%) of sliced lithium wire and 50 ml. of ether. To this was added, with good stirring, at a rate to maintain gentle reflux, 9.0 g. (0.045 mole) of *m*-bromodimethylaniline in 40 ml. of ether. The mixture was refluxed for 0.5 hour after addition was completed, cooled and then decanted through a glass wool plug into a 250-ml. graduated dropping funnel. The yield was determined by titration of a 1-ml. aliquot with standard acid using phenolphthalein as the indicator, and usually was between 97 and 105%.[12]

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(7) G. Calingaert, H. Soroos and V. Hnizda, THIS JOURNAL, **63**, 1107 (1940); G. Calingaert and H. A. Beatty, Chap. 24 in Gilman's "Organic Chemistry," 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1943; H. Gilman and H. W. Melvin, THIS JOURNAL, **71**, 4050 (1949).

(8) Private communication from Dr. Bullard, Eastman Kodak Company.

(9) The product was identified by a mixed melting point with an authentic specimen. All melting points are uncorrected.

(10) This method was developed by S. V. Sunthankar and the authors.

(11) H. Gilman and I. Banner, THIS JOURNAL, **62**, 344 (1940).

(12) Yields in excess of 100% were attributed to the presence of small amounts of *m*-bromo-N-methylaniline in the halide used.

TABLE II

COUPLING WITH TRIPHENYL-*m*-DIMETHYLAMINOPHENYLTIN

Coupling agent	Product identified	Yield or recovery, %	M.p., °C.	Color	Sn, % Calcd.	Found
p-Nitrobenzenediazonium fluoborate[14]	Triphenyl-3-dimethylamino-6-(4'-nitrophenylazo)-phenyltin[a]	66.6	205	Green[c]	19.17	19.18
p-Bromobenzendiazonium fluoborate[15]	Triphenyl-3-dimethylamino-6-(4'-bromophenylazo)-phenyltin[a]	48.6	199–200	Red	18.17	18.01
p-Carboxybenzenediazonium fluoborate[14]	Triphenyl-3-dimethylamino-6-(4'-carboxyphenylazo)-phenyltin[b]	47.8	d. 358	Red	19.20	19.37
p-Dimethylaminobenzenediazonium fluoborate[16]	Triphenyl-*m*-dimethylaminophenyltin[d]	85.0	90–91	....	...	...

[a] Crystallized from petroleum ether (b.p. 77–120°). [b] Extracted with petroleum ether (b.p. 77–120°). [c] Green when crystalline but red when amorphous. [d] Product identified by a mixed melting point with an authentic specimen.

Triphenyl-*m*-dimethylaminophenyltin.—In a 500-ml. flask was placed 15.0 g. (0.039 mole) of triphenyltin chloride in 200 ml. of ether. The flask was immersed in a running water bath, and 0.046 mole of *m*-dimethylaminophenyllithium in 84 ml. of ether was added to the flask, dropwise and with good stirring. The mixture was stirred for one hour after addition; color test I[13] was negative at the end of this time. The reaction mixture was hydrolyzed by the addition of 150 ml. of water to the reaction flask, and the ether layer was dried over sodium sulfate. The ether was removed by distillation from a steam-bath leaving an oil. The oil was dissolved by vigorous refluxing in 25 ml. of chloroform plus 100 ml. of methanol. On cooling, 12.3 g. (67.1%) of crude product melting at 87–91° was recovered. The solid was recrystallized from 25 ml. of chloroform plus 100 ml. of methanol to yield 10.4 g. of triphenyl-*m*-dimethylaminophenyltin melting at 90–91°. Concentration of the mother liquor led to the recovery of 1.2 g. of product melting at 89–91°; total yield was 11.6 g. (63.4%).

Anal. Calcd. for $C_{26}H_{25}NSn$: Sn, 25.24. Found: Sn, 25.28.

Run 2.—This run was carried out exactly as the first except that no running water bath was used, the *m*-dimethylaminophenyllithium was added at a rate to maintain vigorous reflux, and the mixture was refluxed for one hour after addition was completed. On hydrolysis some solid did not go into solution. The solid was filtered off, air-dried, and crystallized from petroleum ether (b.p. 77–120°) to yield 7.5 g. (60.0%) of tetraphenyltin[9] melting at 227–229°. No triphenyl-*m*-dimethylaminophenyltin was isolated from the ether layer.

Triphenyl-3-dimethylamino-6-(4'-nitrophenylazo)-phenyltin.—This preparation was carried out as the one for 4-dimethylamino-4'-nitroazobenzene; 8.0 g. (0.017 mole) of triphenyl-*m*-dimethylaminophenyltin in 100 ml. of dioxane reacted with 4.0 g. (0.017 mole) of *p*-nitrobenzenediazonium fluoborate in 500 ml. of a 50% water–dioxane solution. The deep red solid which precipitated on dilution of the reaction mixture with water was filtered off, air-dried, extracted with 400 ml. of petroleum ether (b.p. 77–120°) and filtered hot. On cooling, 5.7 g. of triphenyl-3-dimethylamino-6-(4'-nitrophenylazo)-phenyltin, green in color when crystalline and red when amorphous, melting at 205–206° was recovered. Concentration of the mother liquor led to the recovery of 1.3 g. of product melting at 205–205.5°; total yield was 7.0 g. (66.6%). This method was used for all reactions where *p*-substituted benzenediazonium fluoborates were used as the coupling agent.

Anal. Calcd. for $C_{32}H_{28}O_2N_4Sn$: Sn, 19.17. Found: Sn, 19.18.

Structure Proof for Triphenyl-3-dimethylamino-6-(4'-nitrophenylazo)-phenyltin.—In a 100-ml. flask were placed 4.0 g. (0.0065 mole) of the dye, 8.0 g. of stannous chloride, 10 ml. of water and 30 ml. of concd. hydrochloric acid. The mixture was stirred vigorously and warmed on a hot-plate until decolorized (*ca.* 3 hours). The solid residue was filtered off, and the filtrate was neutralized with 10% sodium hydroxide solution and extracted with ether. The ether layer was dried over sodium sulfate. After filtering the ethereal solution from the drying agent, the ether was removed by passing a gentle stream of air over the surface of the solution. The crude bases were warmed on a water-bath with 1.0 g. of acetic anhydride for 5 minutes. This solution was then diluted with 25 ml. of water and filtered. The filtrate was neutralized with sodium carbonate solution, and extracted with ether. The ether layer was dried and treated as before. The residue remaining on ether removal was crystallized from water to yield 0.4 g. (35.0%) of *p*-dimethylaminoacetanilide[9] melting at 131°.

Sodium *p*-(2'-Triphenylstannyl-4'-dimethylamino)-phenylazobenzoate.—In a 250-ml. beaker was placed 2.0 g. (0.00324 mole) of triphenyl-3-dimethylamino-6-(4'-carboxyphenylazo)-phenyltin in 100 ml. of ethanol. To this was added exactly 33.8 ml. of 0.096 *N* sodium hydroxide solution (0.00324 mole). The solution was then poured into a crystallization dish and the ethanol permitted to evaporate. A recovery of 2.0 g. (96.5%) of sodium *p*-(2'-triphenyl-4'-dimethylamino)-phenylazobenzoate, orange in color, was made. The salt is very slightly soluble in water.

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[13] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

[14] E. B. Starkey, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 225.

[15] G. Schiemann and R. Pillarsky, *Ber.*, **64**, 1340 (1931).

[16] G. Schiemann and W. Winkelmüller, *ibid.*, **66**, 727 (1933).