4,4′-Dimethoxydiphenyliodonium Iodide (Potassium Iodate).—To a well-stirred mixture of 20.0 g. (101 mmoles) of sodium iodate and 200 ml. of acetic acid kept below 10° there was added during one hour a solution of 50 ml. (457 mmoles) of anisole, 50 ml. of acetic anhydride and 25 ml. of sulfuric acid. After the reaction mixture had been stirred overnight at room temperature, it was poured onto 500 ml. of ice-water and extracted with five 100-ml. portions of ether. Two treatments with charcoal were followed by addition of 40 g. of potassium iodide in water to give 5.2 g. (11.1 mmoles, 11%) of **4,4′-dimethoxydiphenyliodonium iodide**, m.p. 179–182° (dec.), lit.[5] 180°.

Thermal decomposition of this salt gave *p*-iodoanisole, m.p. 50–52° after crystallization from methanol; no depression on admixture with an authentic sample.

4,4′-Diacetamidodiphenyliodonium Iodide (Potassium Iodate).—To a vigorously stirred solution of 83.4 g. (0.618 mole) of acetanilide and 50 ml. of sulfuric acid in 300 ml. of acetic acid and 100 ml. of acetic anhydride cooled with a water-bath to 20°, 66.0 g. (0.309 mole) of potassium iodate was added over 2.5 hours. After an additional 24 hours of stirring (negative starch–iodide test) the reaction mixture was diluted with 500 ml. of ice water and insoluble material was removed by filtration. Addition of a small amount of sodium sulfite was followed by 150 g. of potassium iodide in water. The precipitate was collected, washed with alcohol and with ether until the washings were colorless, and dried *in vacuo* to give 77.0 g. (0.148 mole, 47.7%) of **4,4′-diacetamidodiphenyliodonium iodide**, m.p. 173° (dec.), lit.[6] 176.5°.

Anal. Calcd. for $C_{16}H_{16}I_2N_2O_2$: I^-, 24.30. Found: I^-, 24.22.

Thermal decomposition of this salt gave *p*-iodoacetanilide, m.p. 184° after crystallization from alcohol, no depression on admixture with an authentic sample.

3,3′-Dinitrodiphenyliodonium Salts (Iodyl Sulfate).—To a stirred cold suspension of iodyl sulfate (0.30 mole) in 400 ml. of sulfuric acid there was added during two hours 147.6 g. (1.20 moles) of nitrobenzene. After the reaction mixture had been stirred at room temperature for six days, it was poured onto 2500 g. of ice. The precipitate was collected, washed with water and crystallized from water (charcoal) to give 70.7 g. (0.151 mole, 25.2%) of **3,3′-dinitrodiphenyliodonium bisulfate**, m.p. 165–167° (dec.), lit.[7] 168.5°. From the combined mother liquors by the addition of 60 g. of sodium bromide in water there was obtained 46.6 g. (0.103 mole, 17.2%) of **3,3′-dinitrodiphenyliodonium bromide**, m.p. 178–179° (dec.). The combined yield of iodonium salts was thus 42.4%.

From other reaction mixtures there were also isolated the **3,3′-dinitrodiphenyliodonium chloride**, m.p. 203–205° (dec.), lit.[7] 214°, and **3,3′-dinitrodiphenyliodonium iodide**, m.p. 127–128°, lit.[7] 130.5°.

3,3′-Dicarboxydiphenyliodonium Iodide (Iodyl Sulfate).—To a suspension of iodyl sulfate prepared from 3.85 g. (15.2 mmoles) of iodine, 10.0 g. (46.4 mmoles) of potassium iodate and 40 ml. of sulfuric acid and kept below 10° there was added 1 ml. of acetic anhydride and 19.0 g. (156 moles) of benzoic acid. After being stirred for 8 hours in an ice-bath and for 15 hours at room temperature (negative starch–iodide test), the mixture was treated with 200 ml. of water below 25°. An ether-soluble precipitate was removed by filtration and the filtrate was extracted with ether. To the clear solution there was added 12.9 g. of potassium iodide and a few mg. of sodium bisulfite in 25 ml. of water. The precipitate was collected, washed with water and with ether and dried *in vacuo* to give 20.2 g. (40.6 mmoles, 53%) of **3,3′-dicarboxydiphenyliodonium iodide**, m.p. about 120° (dec.).

The structure of this salt is shown by its conversion at its m.p. to *m*-iodobenzoic acid, m.p. 184–185° after crystallization from aqueous acetic acid, no depression on admixture with an authentic sample.

BROOKLYN 2, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Diaryliodonium Salts. II. The Phenylation of Organic and Inorganic Bases[1,2]

BY F. MARSHALL BERINGER, ARTHUR BRIERLEY, MILTON DREXLER, E. MELVIN GINDLER AND CHARLES C. LUMPKIN

RECEIVED DECEMBER 15, 1952

Our results, taken with those in the literature, show that under relatively mild conditions organic and inorganic bases effect nucleophilic displacements on the 1-carbons of diphenyliodonium ions to form new bonds with carbon, hydrogen, oxygen, sulfur, selenium, nitrogen, phosphorus, arsenic, antimony and the halogens. Thus iodonium salts show promise as general phenylating agents.

While alkyl halides may be used for the alkylation of bases, the more inert aryl halides react with bases only at elevated temperatures of 200–300°.[3] Such high temperatures not only necessitate the use of pressure equipment but also limit the reactions to compounds that can withstand such drastic conditions. In a search for a group more susceptible to nucleophilic displacement, attention was drawn to the 'onium salts, the positive charges in which should facilitate polar fission of the bonds to the aromatic systems. Consideration was given to the common aromatic 'onium salts: diazonium, ammonium, phosphonium, sulfonium and iodonium salts.

Thus it is well known that the diazonium group may be displaced by water, alcohol, iodide ion, thiourea, thiosulfate ion and sulfide ion without catalysts and by chloride ion, bromide ion,[4] nitrite ion and cyanide ion with the aid of copper catalysts. Limitations on the generality of the displacement of the diazonium group by bases are offered by the following common reactions: with hydroxide ion to give a diazotate, with sulfite or bisulfite ions to give a hydrazine group, with phenoxide ion to give an azophenol and with acetoacetic ester to give a benzeneazo derivative, which rearranges to a phenylhydrazone.

Simple alkyl aryl ammonium ions with bases give displacement or elimination reactions with formation of alcohols or olefins and tertiary amines. With nitro or carbonyl groups in *o*- or *p*-positions, displacement of the ammonio group[3] may occur to give substituted phenyl derivatives of the bases.

---

(1) This paper is largely based on dissertations submitted by Milton Drexler, E. Melvin Gindler and Charles C. Lumpkin in partial fulfillment of the requirements of the degree of Master of Science in Chemistry in June, 1952, and was presented in part at the 121st National Meeting of the American Chemical Society in Buffalo, N. Y., March 23–27, 1952; see Abstracts, p. 3K.

(2) For the first paper of this series see F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2705 (1953).

(3) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

(4) The second-order reaction of the *p*-nitrobenzenediazonium ion with bromide ion has been recently reported: E. S. Lewis and W. H. Hinds, THIS JOURNAL, **74**, 304 (1952).

Tetraarylammonium salts are as yet unreported. It appears, then, that ammonium ions are unsuitable for the introduction of aryl groups not bearing activating substituents.

Phosphonium salts are generally similar to ammonium salts, with the interesting difference that phosphorus can form a fifth covalent bond. Thus, tetraphenylammonium bromide with phenyllithium has been reported to give pentaphenylphosphorus.[5]

Alkyl aryl sulfonium salts are not suitable arylating agents as nucleophilic displacement occurs far more rapidly on an α-carbon of an alkyl group than on the aromatic ring. Triarylsulfonium salts are little known. The meager evidence available on their properties suggests a high stability and a low reactivity.

According to the literature iodonium salts have shown more promise as arylating agents. Other workers have reported the phenylation of halide ions,[6,7] sulfide ion,[8] sulfhydryl groups,[9] phenyl sulfide,[10] phenyl selenide,[10] triphenylphosphine,[10] triphenylarsine,[10] triphenylstibine,[10] pyridine,[10] aromatic amines[11] and phenyllithium.[5] Also, 3,3′-dinitrodiphenyliodonium nitrate has been converted by hydroxide ion to *m*-nitrophenol and *m*-nitroiodobenzene.[12]

The first paper of this series[2] reported the synthesis of a number of symmetrical and unsymmetrical diphenyliodonium salts. This paper reports the reactions of diphenyliodonium bromide and 2- and 3-nitrodiphenyliodonium bromide with a wide variety of organic and inorganic bases to give phenyl or nitrophenyl derivatives of the bases. All reactions were run in water or in one of the lower alcohols at reflux except those with organometallic compounds and lithium aluminum hydride, which were run in ether. In all these reactions one product was iodobenzene.

With first consideration given to the reactions of unsubstituted diphenyliodonium salts, it was found that diphenyliodonium bromide in a refluxing dilute, aqueous solution decomposed over several weeks to bromobenzene and iodobenzene.

Diphenyliodonium bromide reacted with benzoate, methoxide, phenoxide and *o*-carbomethoxyphenoxide ions to give phenyl benzoate, anisole, diphenyl ether and methyl *o*-phenoxybenzoate. Hydroxide ion in water gave a small amount of phenol and a large amount of diphenyl ether, presumably formed by further reaction of the initially formed phenol.

To the known reactions of diphenyliodonium salts with sulfide ion[8] and sulfhydryl groups[9] have now been added those with sulfite and *p*-toluenesulfinate ions to form sodium benzenesulfonate and phenyl *p*-tolyl sulfone. This latter reaction is similar to the known formation of sulfones by the reaction of alkyl halides with metal sulfinates.[13]

Nitrite ion with diphenyliodonium bromide gave nitrobenzene, while aniline and piperidine were converted in low yield[14] to diphenylamine and N-phenylpiperidine. Further, several sulfonamides (including saccharin) in the presence of base gave N-phenyl or N,N-diphenyl derivatives.

A simple example of the formation of a carbon–carbon bond was afforded by the reaction of diphenyliodonium bromide with cyanide ion to give benzonitrile. Reactions potentially more useful in synthesis were those with Grignard reagents or organolithium compounds to give alkyl or aryl substituted benzenes. In spite of insolubility of diphenyliodonium bromide in ether, the reactions were exothermic and vigorous. Diphenyliodonium bromide with lithium aluminum hydride gave benzene.

There are strong indications that with a few possible exceptions[15] the reactions of diphenyliodonium salts with bases proceeded by nucleophilic rather than by radical attack on the 1-carbons of the diphenyliodonium salts to give iodobenzene and the phenyl derivatives of the bases. First, the reactions[16] were faster with strong bases than with weak and in general parallelled the efficiencies of reaction with the similarly charged ethylenesulfonium ions.[17] Also, in no case were benzene and biphenyl, the expected by-products of a radical chain reaction involving phenyl radicals, found. Finally, while mercaptans are known to be efficient terminators of radical chain reactions, the phenylation of several sulfhydryl groups has been reported.[9]

To provide further tests for this mechanistic hypothesis and to enlarge the scope of the phenylation reaction, 2- and 3-nitrodiphenyliodonium bromide[2] were investigated. In all cases the attack of the bases occurred at the 1-carbons of the rings bearing the nitro groups, with formation of iodobenzene. The rates of reaction apparently increased in the order: unsubstituted $<$ 3-nitro $<$ 2-nitrodiphenyliodonium bromide (as did yields, in general). This enhanced reactivity on introduction of a nitro group was expected, on the basis that there would be more interaction of an electron-withdrawing group with a ring electron-rich in the transition state (during nucleophilic attack) than with a ring neutral in

---

(5) G. Wittig and M. Rieber, *Ann.*, **562**, 187 (1949).

(6) C. J. M. Fletcher and C. N. Hinshelwood, *J. Chem. Soc.*, 596 (1935); H. J. Lucas, E. R. Kennedy and C. A. Wilmot, THIS JOURNAL, **58**, 157 (1936).

(7) R. B. Sandin, M. Kulka and R. McCready, *ibid.*, **59**, 2014 (1937).

(8) C. Hoffman and V. Meyer, *Ber.*, **27**, 509 (1894); R. B. Sandin, F. T. McClure and F. Irwin, THIS JOURNAL, **61**, 2944 (1939).

(9) R. B. Sandin, R. G. Christiansen, R. K. Brown and S. Kirkwood, *ibid.*, **69**, 1550 (1947).

(10) L. G. Markarova and A. N. Nesmeyanov, *Bull. acad. sci. U. S. S. R., Classe sci. chim.*, 617 (626 in English) (1945); *C. A.*, **40**, 4686 (1946).

(11) L. G. Markarova, *Invest. Akad. Nauk, U. S. S. R., Otdel. Khim. Nauk*, 741 (1951); *C. A.*, **46**, 7532 (1952).

(12) D. Vorlander, *Ber.*, **58B**, 1893 (1925).

(13) P. Allen, Jr., L. S. Karger, D. Haygood, Jr., and J. Shrensel, *J. Org. Chem.*, **16**, 767 (1951).

(14) The superior yields reported with diphenyliodonium fluoroborate[11] may be due to the low nucleophilicity of the fluoroborate ion.

(15) Reactions of diphenyliodonium salts in which free radicals may be operative are those with mercury, tellurium and antimony (references 8, 9 and 10) and that with pyridine in the presence of sodium hydroxide to give mixed phenylpyridines: R. B. Sandin and R. K. Brown, THIS JOURNAL, **69**, 2253 (1947).

(16) Rough rates of reaction were measured by disappearance of halide ion, by recovery of diphenyliodonium salts from interrupted reactions and by concomitant steam distillation of iodobenzene (and other water-insoluble products) from reactions run in water.

(17) A. G. Ogston, E. R. Holliday, J. St. L. Philpot and L. A. Stockin, *Trans. Faraday Soc.*, **44**, 45 (1948). See especially Table 2 for tabulation of "competition factors" in the opening of ethylenesulfonium ions.

the ground state.[18] The activating effect of nitro groups in the *o*- and *p*-positions of phenyl halides is well known[3]; the enhanced reactivity of the substituted ring in 3-nitrodiphenyliodonium bromide is one of the few examples[19] of which the authors are aware in which the nitro group has been shown to activate a *m*-position.

After three days in refluxing water 2- and 3-nitrodiphenyliodonium bromide were completely decomposed to iodobenzene and 2- and 3-nitrobromobenzene, which serves as a proof of structure for these salts. With methoxide and benzoate ions the corresponding nitroanisoles and nitrophenyl benzoates were obtained. In contrast to the results with the unsubstituted salt the nitrodiphenyliodonium salts gave with aqueous hydroxide ion good yields of the nitrophenols. Carbon–nitrogen bonds were formed by reaction with nitrite ion and with dimethylamine, while sodium sulfite gave sodium nitrobenzenesulfonates. The reaction with cyanide ion gave nitrobenzonitriles without rearrangement, in contrast to the von Richter reaction.[3]

An especially interesting reaction is the formation of nitrophenylmalonic esters from sodioöxalacetic ester and the nitrodiphenyliodonium bromides. The structures of the products were shown by conversion to the nitrophenylmalonic acids, the nitrophenylacetic acids and the nitrobenzoic acids.

A study of the kinetics and energetics of these and related reactions is now under way and will be reported later.

Acknowledgment.—The senior author (F. M. B.) is glad to acknowledge the experimental contributions of Emil J. Geering and Erwin Sommer.

Experimental[20]

Thermal Decomposition in Water.—After a mixture of 15.0 g. (41.6 mmoles) of diphenyliodonium bromide[2] and 500 ml. of water had boiled under reflux for three weeks, 1.3 g. (3.6 mmoles) of the bromide was recovered. The oil separated from the water by ether extraction was dried and distilled to give 5.22 g. (33.2 mmoles, 87% yield based on unrecovered bromide) of bromobenzene, b.p. 155–157°, and 6.65 g. (32.6 mmoles, 86%) of iodobenzene, b.p. 74–76° at 25 mm.

Three days of reflux in water converted 2-nitrodiphenyliodonium bromide[2] in 91% yield to *o*-nitrobromobenzene, m.p. 43°,[21] and 3-nitrodiphenyliodonium bromide[2] in 87% yield to *m*-nitrobromobenzene, m.p. 54–55°.[21]

Reactions with Sodium Hydroxide.—A mixture of 10.00 g. (27.7 mmoles) of sodium hydroxide in 50 ml. of water was boiled for 13 minutes, cooled, and treated with 70 ml. of ether and 30 ml. of water to give a colorless solid (diphenyliodonium bromide, 1.0 g. after crystallization). The original filtrate was separated into ethereal and aqueous layers, which were cross-washed. From the ether layer there was obtained, besides iodobenzene, 1.78 g. (10.4 mmoles, 84% yield based on unreacted bromide) of diphenyl ether; m.p. of derived 4,4′-dibromodiphenyl ether 53.5–54.5°.[21] From the aqueous layer there was obtained by bromination 0.30 g. (0.9 mmole, 3.4%) of *s*-tribromophenol, m.p. 95–96°.[21]

To a boiling solution of 3.0 g. (7.4 mmoles) of 2-nitrodiphenyliodonium bromide 1.48 g. (37 mmole) of sodium hydroxide in 20 ml. of water was rapidly added, and the solution was refluxed for one hour. From the aqueous layer there was obtained 0.788 g. (5.6 mmoles, 76%) of *o*-nitrophenol, m.p. 44°.[21] A similar reaction with 3-nitrodiphenyliodonium bromide gave 0.745 g. (5.4 mmoles, 72%) of *m*-nitrophenol, m.p. 95°.[21]

Reactions with Alkoxides.—Diphenyliodonium bromide (50.2 g., 139 mmoles) was added to 160 mmoles of sodium methoxide in 250 ml. of anhydrous methanol, and the mixture was refluxed for 30 minutes. Neutralization and standard work-up gave 10.15 g. (94 mmoles, 67%) of anisole, b.p. 153–156°, n^{20}D 1.5182–1.5223, characterized as 2,4-dinitroanisole, m.p. 86.5–87°.[21]

After a mixture of 3.0 g. (7.4 mmoles) of 2-nitrodiphenyliodonium bromide and 2.0 g. (37 mmoles) of sodium methoxide in 300 ml. of methanol had been refluxed for three hours, 250 ml. of methanol was removed by distillation. Water was added and distilled until no more iodobenzene came over. From the residue there was obtained 0.807 g. (5.27 mmoles, 71%) of *o*-nitroanisole, identified by conversion to *o*-methoxyacetanilide, m.p. 84°.[21] A similar reaction with 3-nitrodiphenyliodonium bromide gave 0.482 g. (3.15 mmoles, 43%) of *m*-nitroanisole, m.p. 37.5–38.5°.[21]

Reactions with Phenoxides.—To a solution of 250 mmoles of sodium methoxide in 300 ml. of methanol there was added 23.5 g. (250 mmoles) of phenol and 18.0 g. (50 mmoles) of diphenyliodonium bromide. After the reaction mixture had been refluxed for 24 hours, the ether-soluble product was collected and distilled under reduced pressure to give 6.5 g. (38 mmoles, 76%) of diphenyl ether, b.p. 250–251°, identified by formation of the 4,4′-dibromo derivative, m.p. 54°.[21]

To 157 mmoles of sodium methoxide in 300 ml. of methanol were added 25.1 g. (165 mmoles) of methyl salicylate and 10.0 g. (30 mmoles) of diphenyliodonium bromide, and the reaction was stirred at 65° for 16 hours. After removal of most of the methanol by distillation, water and ether were added. The residue from the ether extract was saponified with hot aqueous sodium hydroxide. Acidification gave crude *o*-phenoxybenzoic acid, which was crystallized from aqueous alcohol to give 2.8 g. (13.2 mmoles, 44%) of *o*-phenoxybenzoic acid, m.p. 113°, lit.[22] 113°; neut. equiv., 213 (theoretical, 214). Treatment with excess hot bromine water gave a solid which was crystallized from acetic acid to give a tribromo derivative, m.p. 176°; lit.[23] 176°.

Reaction with Sodium Benzoate.—A solution of 5.0 g. (13.8 mmoles) of diphenyliodonium bromide and 10.0 g. (69 mmoles) of sodium benzoate in 100 ml. of water was refluxed for two hours, cooled and extracted with ether. Removal of the ether gave a residue from which iodobenzene was removed by steam distillation. Crystallization of the residue from petroleum ether gave 1.1 g. (5.5 mmoles, 40%) of phenyl benzoate, m.p. 71°.[21]

A solution of 3.0 g. (7.4 mmoles) of 2-nitrodiphenyliodonium bromide and 5.34 g. (37 mmoles) of sodium benzoate in 300 ml. of water was refluxed for three hours, while iodobenzene was collected in a Barrett receiver. From the residue there was isolated 1.46 g. (6.32 mmoles, 85%) of *o*-nitrophenyl benzoate, m.p. 59°.[21] A similar reaction with 3-nitrodiphenyliodonium bromide gave 1.00 g. (4.33 mmoles, 59%) of *m*-nitrophenyl benzoate, m.p. 95°.[21]

Reaction with Sodium Nitrite.—A solution of 20.0 g. (55.2 mmoles) of diphenyliodonium bromide and 19.1 g. (280 mmoles) of sodium nitrite in 200 ml. of water was refluxed for five hours. The nitrobenzene and iodobenzene were collected in the usual way and separated by virtue of the solubility of the former in concentrated sulfuric acid. Regeneration from this solution gave 4.5 g. (36.6 mmoles, 66%) of nitrobenzene, identified by formation of *m*-dinitrobenzene, m.p. 89–89.5°.[21]

A solution of 3.0 g. (7.4 mmoles) of 2-nitrodiphenyliodonium bromide and 2.56 g. (37 mmoles) of sodium nitrite in 300 ml. of water was refluxed for three hours, while iodo-

---

[18] Similarly it might be expected that electron-donating substituents would deactivate a ring to nucleophilic attack. This has been realized with the 4-methoxydiphenyliodonium halides, both with their thermal decomposition (reference 7) and with their reaction with aqueous sodium sulfite to give iodobenzene and *p*-iodoanisole in the ratio of 1:19. A similar cleavage of the 4-methyl analog gave iodobenzene and *p*-iodotoluene in the ratio of 1:4.

[19] Sodium methoxide converted *m*-nitrofluorobenzene to *m*-nitroanisole [A. F. Holleman and J. W. Beckman, *Proc. K. Akad. Wetensch. Amsterdam*, **6**, 327 (1903)] and 1,3,5-trinitrobenzene to 3,5-dinitroanisole [A. F. Holleman and F. E. von Haeften, *Rec. trav. chim.*, **40**, 67 (1921)].

[20] Melting points were taken in a modified Hershberg apparatus. Boiling points are not corrected.

[21] No depression of melting point was observed on admixture with an authentic sample.

[22] F. Ullmann and M. Zlokasoff, *Ber.*, **38**, 2111 (1905).

[23] C. Arbenz, *Ann.*, **257**, 76 (1890).

benzene was collected in a Barrett receiver. From the residue there was obtained 1.044 g. (6.21 mmoles, 84%) of *o*-dinitrobenzene, m.p. 117°.[21] A similar reaction with 3-nitrodiphenyliodonium bromide gave 0.772 g. (4.59 mmoles, 62%) of *m*-dinitrobenzene, m.p. 89–90°.[21]

Reactions with Sulfonamides.—To a refluxing stirred mixture of 300 ml. of benzene, 100 ml. of water and 11.0 g. (30 mmoles) of diphenyliodonium bromide there was added dropwise a solution of 5.19 g. (60 mmoles) of *p*-toluenesulfonamide in 50 ml. of 1.2 *N* sodium hydroxide. After five hours at reflux the reaction mixture was cooled. The residue from evaporation of the washed benzene extract was crystallized from alcohol to give 4.4 g. (13.6 mmoles, 45%) of N,N-diphenyl-*p*-toluenesulfonamide, m.p. 140–141°.[21]

Diphenyliodonium bromide (14.4 g., 40 mmoles) was added to a solution of 10.2 g. (44 mmoles) of benzenesulfonanilide in 100 ml. of ethanol and 200 ml. of 0.25 *N* potassium hydroxide. After seven hours at reflux the reaction mixture was extracted with ether. The residue from evaporation of the washed extract was crystallized from ethanol to give 7.0 g. (2.26 mmoles, 56%) of N,N-diphenylbenzenesulfonamide, m.p. 124–125°.[21]

Diphenyliodonium bromide (7.2 g., 20 mmoles) was added to a solution of 4.0 g. (22 mmoles) of N-methyl-*p*-toluenesulfonamide in 70 ml. of ethanol and 200 ml. of 0.25 *N* potassium hydroxide. After the reaction mixture had been refluxed for five hours, iodobenzene was removed by steam distillation. Evaporation of the washed ether extract gave a residue which was crystallized from aqueous ethanol to give 2.7 g. (10.3 mmoles, 52%) of N-methyl-N-phenyl-*p*-toluenesulfonamide, m.p. 94–95°.[21]

A mixture of 7.2 g. (20 mmoles) of diphenyliodonium bromide, 20.5 g. (10 mmoles) of sodium saccharinate, 150 ml. of ethanol and 400 ml. of water was refluxed for 24 hours. The crystals obtained from the cold reaction mixture and those obtained by concentration of the mother liquor were combined and crystallized from 200 ml. of ethanol to give 3.9 g. (15.0 mmoles, 75%) of N-phenylsaccharin, m.p. 189–190°, reported 189–190°[24] and 190.5°.[25] Alkaline hydrolysis of N-phenylsaccharin gave *o*-sulfanilinobenzoic acid (benzenesulfonanilide-2-carboxylic acid), m.p. 155–156°, lit.[25] 156°.

Reactions with Amines.—Diphenyliodonium bromide (10.0 g., 28 mmoles) was treated with aniline under three conditions: with 5.5 g. (59 mmoles) of aniline and 100 ml. of water at reflux for three hours to give 4.7 g. (23 mmoles, 82%) of iodobenzene, 3.5 g. (22 mmoles, 79%) of bromobenzene and a trace of diphenylamine, m.p. 52–53°[21]; with 30 ml. (330 mmoles) of aniline and 100 ml. of water at reflux for 24 hours to give 1.3 g. (7.7 mmoles, 27%) of diphenylamine, m.p. 52.5–53°[21]; and with 5.5 g. (59 mmoles) of aniline at 130–140° for 1.5 hours to give 0.68 g. (5.1 mmoles, 18%) of diphenylamine, m.p. 51–53°.[21]

Similarly, 45 g. (125 mmoles) of diphenyliodonium bromide with 37 ml. of piperidine and 250 ml. of water at reflux for four hours gave 3.07 g. (19.0 mmoles, 15%) of N-phenylpiperidine, b.p. 118–123° at 10 mm., hydrobromide m.p. 232°, lit.[26] 235°.

2-Nitrodiphenyliodonium bromide (3.0 g., 7.4 mmoles) with 83 ml. of 20% aqueous dimethylamine (equivalent to 1.67 g. of dimethylamine, 37 mmoles) and 300 ml. of water at reflux for three hours gave 1.01 g. (6.15 mmoles, 83%) of 2-nitro-N,N-dimethylaniline, identified as the hydrochloride, m.p. 172°.[21] A similar reaction with 3-nitrodiphenyliodonium bromide gave 0.53 g. (3.19 mmoles, 43%) of 3-nitro-N,N-dimethylaniline, m.p. 60–61°.[21]

Reactions with Sodium Sulfite and Sodium *p*-Toluenesulfinate.—A mixture of 10.6 g. (84 mmoles) of sodium sulfite, 7.6 g. (21 mmoles) of diphenyliodonium bromide and 75 ml. of water was refluxed for one hour and evaporated to dryness. The residue was extracted with hot absolute methanol, which was evaporated to give 3.6 g. (20 mmoles, 95%) of sodium benzenesulfonate, S-benzylthiuronium derivative m.p. 145.5–146.5°.[21]

Similar reactions with 2- and 3-nitrodiphenyliodonium bromide gave 79% of sodium *o*-nitrobenzenesulfonate (characterized as *o*-nitrobenzenesulfonyl chloride, m.p. 69°, and as *o*-nitrobenzenesulfonamide, m.p. 190°) and 60% of sodium *m*-nitrobenzenesulfonate (characterized as the S-benzylthiuronium derivative, m.p. 141°[21]).

A mixture of 17.55 g. (50 mmoles) of diphenyliodonium bromide and 7.61 g. (50 mmoles) of sodium *p*-toluenesulfinate in 100 ml. of ethanol and 25 ml. of water was refluxed for four hours, diluted with 50 ml. of ethanol and 350 ml. of hot water, and cooled. The precipitate was extracted with four 125-ml. portions of hot heptane. The residue was crystallized from methanol to give 6.83 g. (19.2 mmoles) of diphenyliodonium bromide. From the heptane extract there was obtained 4.00 g. (17.2 mmoles, 56% yield based on unrecovered diphenyliodonium bromide) of phenyl *p*-tolyl sulfone, m.p. 127–127.5°,[21] diamond-shaped plates from ethanol–water.

Reactions with Sodium and Potassium Cyanide.—Diphenyliodonium bromide (15.0 g., 41.5 mmoles) was added to a solution of 3.50 g. (54 mmoles) of potassium cyanide in 15 ml. of water and 50 ml. of ethanol. After the mixture had been refluxed for 6.5 hours, 100 ml. each of water and ether were added, and the layers were separated and cross-washed. The residue from evaporation of the ether layer was treated with 50 ml. of 75% sulfuric acid containing 2.0 g. of sodium chloride for 30 minutes at 150° and for three hours at 190°. By a standard work-up, including crystallization from water, there was obtained 1.18 g. (9.6 mmoles, 23%) of benzoic acid, m.p. 121–122°.[21]

A mixture of 3.0 g. (7.4 mmoles) of 2-nitrodiphenyliodonium bromide, 1.83 g. (37 mmoles) of sodium cyanide and 300 ml. of water was refluxed for three hours, the iodobenzene formed being removed in a Barrett receiver. The reaction mixture was then treated with 20 ml. of concentrated hydrochloric acid and refluxed for two hours. By usual procedures, including crystallization from water, there was obtained 0.715 g. (4.28 mmoles, 58%) of *o*-nitrobenzoic acid, m.p. 147.5°,[21] neut. equiv. 167.7 (theoretical, 167.1). A similar reaction with 3-nitrodiphenyliodonium bromide gave 0.585 g. (3.50 mmoles, 47%) of *m*-nitrobenzoic acid, m.p. 141°,[21] neut. equiv. 168 (theoretical, 167.1).

Reactions with Ethyl Sodioöxalacetate.—At the time of writing no clean-cut reaction had been obtained with diphenyliodonium bromide or chloride. The reaction is under continuing investigation.

A mixture of 10.0 g. (24.7 mmoles) of 2-nitrodiphenyliodonium bromide and 27.0 g. (123 mmoles) of ethyl sodiooxalacetate[27] in 300 ml. of water was refluxed for three hours, while 4.0 g. (19.6 mmoles, 79%) of iodobenzene was collected in a Barrett receiver. The ether extract of the chilled reaction mixture was washed with aqueous sodium carbonate and with water, dried and distilled to give 4.72 g. (16.8 mmoles, 68%) of ethyl *o*-nitrophenylmalonate, sapn. equiv., 141.3 (theoretical, 140.6). Saponification of the ester with 20% methanolic potassium hydroxide gave *o*-nitrophenylmalonic acid, m.p. 132° (lit.[28] 132°), neut. equiv. 112.6 (theoretical, 112.5). Decarboxylation gave *o*-nitrophenylacetic acid, m.p. 138° (lit.[28] 138°), neut. equiv. 181.7 (theoretical, 181.1). When the original displacement was carried out in *t*-butyl alcohol, there was obtained 78% of iodobenzene and 62% of ethyl *o*-nitrophenylmalonate.

A similar reaction with 3-nitrodiphenyliodonium bromide (in water) gave 4.17 g. (20.4 mmoles, 83%) of iodobenzene and 3.2 g. (11.4 mmoles, 46%) of ethyl *m*-nitrophenylmalonate, sapn. equiv. 141 (theoretical, 140.6). Saponification gave *m*-nitrophenylmalonic acid, m.p. 112°, neut. equiv. 112.8 (theoretical, 112.5), decarboxylated to *m*-nitrophenylacetic acid, m.p. 117–118° (lit.[29] 117°), neut. equiv. 182 (theoretical, 181.1). *m*-Nitrophenylmalonic acid was oxidized by alkaline permanganate to *m*-nitrobenzoic acid, m.p. 141°,[21] neut. equiv. 167.2 (theoretical, 167.1). When the original arylation was carried out in *t*-butyl alcohol, there was obtained 73% of iodobenzene and 45% of ethyl *m*-nitrophenylmalonate.

Reactions with Organometallic Compounds and Lithium Aluminum Hydride.—To an ethereal solution of methylmagnesium iodide prepared from 32.0 g. (225 mmoles) of methyl iodide and 5.2 g. (214 mg.-atoms) of magnesium and cooled in an ice-bath there was added portionwise 50.0 g. (138 mmoles) of diphenyliodonium bromide. After the exothermic reaction the mixture was worked up in the usual way to give 7.43 g. (80.6 mmoles, 59%) of toluene, b.p. 109–111°, 0.46 g. (2.9 mmoles, 2%) of bromobenzene, b.p.

---

[24] R. List and M. Stein, *Ber.*, **31**, 1648 (1898).

[25] I. Remsen and C. E. Coates, Jr., *Am. Chem. J.*, **17**, 311 (1895).

[26] J. von Braun, *Ber.*, **40**, 3920 (1907).

[27] A research sample of this salt from U. S. Industrial Chemicals, Inc., is acknowledged with appreciation.

[28] J. Bedson, *J. Chem. Soc.*, **37**, 91 (1935).

[29] K. Gabriel and V. Borgmann, *Ber.*, **16**, 2066 (1883).

154–157°, and 24.4 g. (119 mmoles, 87%) of iodobenzene, b.p. 75–77° at 25 mm. A sample of the toluene was oxidized by alkaline permanganate to benzoic acid, m.p. 120–121°.[21]

Similar reactions run on a smaller scale with ethylmagnesium bromide, phenylmagnesium bromide and phenyllithium[5] gave ethylbenzene, b.p. 134–137° (37%, characterized as 4-ethylbenzoylbenzoic acid, m.p. 121–122°, lit.[30] 122°), and biphenyl, m.p. 69–70°[21] (33% and 46%).

To a well-stirred suspension of 4.0 g. (108 mmoles) of lithium aluminum hydride in 100 ml. of ether there was added 18.0 g. (49.8 mmoles) of diphenyliodonium bromide portionwise (rapid exothermic reaction). After the addition the reaction mixture was removed from the ice-bath, stirred overnight and treated with 50 ml. of water. Distillation of the ether extract gave 1.59 g. (20.3 mmoles, 41%) of benzene, b.p. 79–81° (characterized as *o*-benzoylbenzoic acid, m.p. 126–127°, lit.[30] 127–128°), 0.20 g. (1.3 mmoles, 2.6%) of bromobenzene and 8.21 g. (40.2 mmoles, 81%) of iodobenzene. Investigation of the aqueous layer showed that less than 1% of the iodine was converted to iodide ion.

BROOKLYN 2, N. Y.

---

[30] H. W. Underwood, Jr., and W. L. Walsh, THIS JOURNAL, **57**, 940 (1935).

[CONTRIBUTION OF THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

The Hydrolysis of Methoxysilanes. Dimethylsilanediol

BY SIMON W. KANTOR

RECEIVED JANUARY 19, 1953

A new method has been found for the preparation of organo silanols. This involves the hydrolysis of the corresponding methoxysilane with distilled water which allows the isolation of unstable silanols. Dimethylsilanediol, a white crystalline solid melting at 101°, has been prepared for the first time by the hydrolysis of dimethyldimethoxysilane with distilled water. The properties of this diol are described. Trimethylmethoxysilane has also been hydrolyzed with distilled water to give the trimethylsilanol–hexamethyldisiloxane azeotrope. Methyltrimethoxysilane and phenyltrimethoxysilane have also been hydrolyzed by distilled water, but in these cases the monomeric silanetriols have not been obtained. Instead, water and alcohol soluble materials have been obtained which are considered to be condensation products of the monomer.

Two general methods have been used to prepare silanols. Kipping and Hackford[1] obtained silanols R_3SiOH where the R's may be the same or different by the reaction of siloxanes with the desired Grignard reagent followed by hydrolysis of the magnesium complex. The second method, which has been used more extensively, involves hydrolysis of organochlorosilanes under carefully controlled conditions. Organosilanediols, $R_2Si(OH)_2$ where R is ethyl, *n*-propyl and *n*-butyl have been obtained in pure form by this method.[2] The failure to prepare dimethylsilanediol has been attributed to the rapid condensation of this compound even at 0°.[3] In this investigation it has been found that alkoxysilanes can be hydrolyzed by using neutral water to form silanols.

When a mixture of dimethyldimethoxysilane and excess water was heated at the boiling point, the organosilane slowly dissolved and very soon a clear solution was obtained. Evaporation of this solution at room temperature left a semi-solid which after washing with hot *n*-hexane gave the crystalline dimethylsilanediol in essentially pure form; the crystals had the appearance of white, shiny plates.

$$(CH_3)_2Si(OCH_3)_2 + 2H_2O \longrightarrow (CH_3)_2Si(OH)_2 + 2CH_3OH$$

Dimethylsilanediol is a white solid melting at 101° with condensation. Each successive fusion of the same sample lowers the melting point markedly. The diol is very sensitive to traces of acid or base, both of which condense it to polysiloxanes; the major part of the condensation product consists of hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane. Dimethylsilanediol has been kept for several weeks in an evacuated glass tube in liquid nitrogen. It will not keep very well in soft glass at room temperature, presumably because there is sufficient alkali from the glass to condense it. It is important that the hydrolysis of dimethyldimethoxysilane be carried out in glass which has been acid washed followed by many rinsings with distilled water, or preferably in quartz equipment. If this precaution is neglected, condensation will occur during the evaporation forming tetramethyldisiloxanediol-1,3.[4] The properties of dimethylsilanediol are very similar to those of the higher dialkylsilanediols.[2]

Trimethylmethoxysilane was also hydrolyzed with hot water, but in this case the trimethylsilanol–hexamethyldisiloxane azeotrope was obtained. It was not possible to carry this reaction out under any conditions which did not give the azeotrope. The use of quartz equipment which should contain a minimum of alkali did not help to stop the condensation of trimethylsilanol. Apparently prolonged heating at 100° will slowly condense trimethylsilanol to hexamethyldisiloxane.

When methyltrimethoxysilane was treated with hot water the hydrolysis proceeded with the formation of water soluble material along with some polymerization to a dense insoluble oil (monomethylpolysiloxane polymer, methyl-T-oil). This oil was insoluble in toluene and soluble in methanol. On heating, the methyl-T-oil condensed with loss of water to a brittle, transparent insoluble solid. The water solution obtained from the hydrolysis of methyltrimethoxysilane was unstable and slowly precipitated more T-oil on standing. Several attempts to isolate a monomeric silanetriol from the water solution have failed. Working in acid-washed glassware or even in quartz equipment has not helped in the isolation of methylsilanetriol. The water solution which is obtained from the hydrolysis of methyltrimethoxysilane probably

---

[1] F. S. Kipping and J. E. Hackford, *J. Chem. Soc.*, **99**, 138 (1911).

[2] P. D. George, L. H. Sommer and F. C. Whitmore, Paper presented before the division of Organic Chemistry, 109th Meeting, American Chemical Society, Atlantic City, April, 1946.

[3] E. G. Rochow, "An Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 69.

[4] G. R. Lucas and R. W. Martin, THIS JOURNAL, **74**, 5225 (1952).