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REDUCTION OF DIAZONIUM SALTS WITH SILYL AND STANNYL HYDRIDES

A NEW ROUTE FOR THE REPLACEMENT OF AMINO-GROUPS OF AROMATIC AMINES BY HYDROGEN

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Abstract—Diazonium salts are reduced by silyl or stannyl hydrides in ethers and acetonitrile to give the corresponding arenes with elimination of the diazonium group, thus providing a new route for replacement by hydrogen of the amino group attached to an aromatic nucleus. The treatment of *p*-chloro- and *p*-methoxybenzenediazonium fluoroborates with tri-n-butyltin deuteride resulted in the formation of chlorobenzene and anisole containing only about 40% of deuterium. The reduction of benzene- and *p*-chlorobenzenediazonium fluoroborates with tri-n-butyltin hydride in a mixture of acetonitrile and benzene (1:2) afforded biphenyl (8·4%), 1,4-dihydrobiphenyl (about 1%), and 4-chlorobiphenyl (16·8%). These findings indicate that aryl radicals are involved as intermediates.

THE diazonium group is replaced by hydrogen in the presence of a variety of reducing agents, of which ethanol and hypophosphorous acid are the most common reagents. Generally moderate yields of reduction-products are obtained, although the formation of by-products such as aryl ethers and tarry substances is always observed.[1] Reduction of diazonium salts by water-miscible ethers such as tetrahydrofuran and dioxan in the presence of sodium acetate is another method for replacing the diazo group by hydrogen.[2] These reactions are usually carried out in aqueous media, in which the diazonium salts are prepared, and only a few reactions in non-hydroxylic media are known. One is the reduction of diazonium fluoroborates (which are stable at room temperature and can be isolated easily and dried for use in non-aqueous media) with sodium borohydride in methanol or dimethylformamide[3] and another is the reduction with tertiary amines in acetonitrile.[2]

It has now been found that the reduction of diazonium salts with silyl and stannyl hydrides in ethers or acetonitrile proceeds smoothly to afford reduction-products in good yields, providing thus a new route for replacement by hydrogen of the amino group attached to an aromatic nucleus.

RESULTS AND DISCUSSION

Diazonium fluoroborates were reduced with tri-n-butyltin hydride either in ethers or in acetonitrile. The results are summarized in Tables 1 and 2. The reduction in THF proceeded smoothly to completion within 1 hr at room temperature. The yields were satisfactory except in the case of *p*-nitrobenzenediazonium fluoroborate, in which further reduction of the nitro group decreased the yield of nitrobenzene.

TABLE 1. REDUCTION OF DIAZONIUM SALTS WITH TRI-n-BUTYLTIN HYDRIDE IN ETHERS

Diazonium salt	Conditions[a]	Product (yield, %[b])
4-Nitrobenzenediazonium fluoroboroborate	THF, r.t., 20 min	Nitrobenzene (52)
4-Chlorobenzenediazonium fluoroborate	ether, refl., 1·5 hr	Chlorobenzene (89)
Benzenediazonium fluoroborate	THF, r.t., 1 hr	Benzene (100)
4-Methylbenzenediazonium fluoroborate	ether, refl., 4 hr	Toluene (87)
4-Methoxybenzenediazonium fluoroborate	ether, refl., 10 hr	nil
	THF, r.t., 50 min	Anisole (94)
Naphthalene-2-diazonium fluoroborate	THF, r.t., 20 min	Naphthalene (81)
Naphthalene-2-diazonium chloride[c]	THF, 0–3°, 40 min[d]	Naphthalene (66[e])
2-Carboxybenzenediazonium chloride	THF, r.t., 30 min	Benzoic acid (98[f])
Benzenediazonium-2-carboxylate	THF, r.t., 1 hr[h]	Tri-n-butyltin benzoate (100%[g])

[a] Under nitrogen atmosphere. THF stands for tetrahydrofuran, r.t. for room temperature, and refl. for heated under reflux.

[b] Yield estimated by VPC unless otherwise stated.

[c] Prepared from β-naphthylamine hydrochloride and isoamyl nitrite (Experimental).

[d] Tin hydride was added over a period of 5 min.

[e] Overall yield based on β-naphthylamine hydrochloride.

[f] The product, which contained a small amount of tri-n-butyltin benzoate, was treated with dilute alkali in order to hydrolyze the benzoate and the recovered acid was weighed.

[g] By weighing the isolated material.

[h] Tin hydride was added over a period of 15 min.

TABLE 2. REDUCTION OF DIAZONIUM SALTS WITH TRI-n-BUTYLTIN HYDRIDE IN ACETONITRILE[a]

Diazonium salt	Product (yield, %[b])
4-Nitrobenzenediazonium fluoroborate	Nitrobenzene (31)
4-Methylbenzenediazonium fluoroborate	Toluene (37)
4-Methoxybenzenediazonium fluoroborate	Anisole (71)
Naphthalene-2-diazonium fluoroborate	Naphthalene (25)

[a] Tin hydride was added over a period of 15 min and the mixture was stirred for an additional hr at room temp under N_2.

[b] Yield estimated by VPC.

The use of diethyl ether as a solvent retarded the reaction. *p*-Methoxybenzenediazonium fluoroborate, which was converted into anisole within 1 hr in THF at room temperature, was practically unchanged in ether after prolonged heating under reflux. The presence of electron-withdrawing substituents in the benzene nucleus generally facilitated the replacement of the diazo group by hydrogen. The end point of reaction is readily noticed by the disappearance of diazonium fluoroborates, which are insoluble in ethers. This is one of the advantages of this procedure besides the relatively short reaction time required.

In acetonitrile, in which diazonium fluoroborates are soluble, the reaction proceeds vigorously, but yields of reduction-products were less satisfactory and formation of some tarry matter was observed.

Diazotization of β-naphthylamine hydrochloride with isoamyl nitrite in THF and subsequent reduction of the resulting diazonium salt with tri-n-butyltin hydride yielded naphthalene in 66% yield. This procedure is recommended for the simplicity of operation.

The use of triethylsilane in acetonitrile, which was found to be a milder reducing agent than tri-n-butyltin hydride, also gave satisfactory yields of reduction-products, although it took much longer (overnight reaction) to complete the reduction at room temperature (Table 3). The triethylsilane procedure offers some advantage over that with tri-n-butyltin hydride, in that triethylsilane is stable, non-toxic and easily available, and no further reduction of the nitro group was observed in the reduction of *p*-nitrobenzenediazonium fluoroborate.

TABLE 3. REDUCTION OF DIAZONIUM SALTS WITH TRIETHYLSILANE

Diazonium salt	Solvent	Conditions[a]	Product (yield, %[b])
4-Nitrobenzenediazonium fluoroborate[c]	CH_3CN	r.t., overnight	Nitrobenzene (72)
4-Chlorobenzenediazonium fluoroborate	CH_3CN	r.t., overnight	Chlorobenzene (70)
4-Methylbenzenediazonium fluoroborate	CH_3CN	r.t., overnight	Toluene (25)
4-Methoxybenzenediazonium fluoroborate	CH_3CN	r.t., overnight	Anisole (90)
2-Carboxybenzenediazonium chloride	THF	refl., 2 hr	Benzoic acid (78[d])
Benzenediazonium-2-carboxylate	CH_2Cl_2	refl., 2 hr	Phenyltriethylsilane (29[e]) Triethylsilyl benzoate (9[e])

[a] Under nitrogen atmosphere. r.t. stands for room temperature, and refl. for heated under reflux.

[b] Yield estimated by VPC unless otherwise stated.

[c] Use of phenylsilane increased the yield of nitrobenzene (82%).

[d] The product, which contained a small amount of triethylsilyl benzoate, was treated with dilute alkali in order to hydrolyze the benzoate, and the recovered acid was weighed.

[e] By weighing the isolated material.

Benzenediazonium-2-carboxylate with tri-n-butyltin hydride gave tri-n-butyltin benzoate quantitatively, whereas, with triethylsilane, it yielded triethylphenylsilane as a major product together with a little triethylsilyl benzoate. Tri-n-butyltin and triethylsilyl benzoates are normal reduction products and in keeping with the findings with diazonium fluoroborates. The formation of triethylphenylsilane suggests that benzyne, which is generated on decomposition of benzenediazonium-2-carboxylate,[4] is able to add triethylsilane to afford phenyltriethylsilane.

The usefulness of this method for synthetic purposes having been thus established, an attempt was made to extend it to the preparation of deuteriated compounds. *p*-Chloro- and *p*-methoxy-benzenediazonium fluoroborates were treated with tri-n-butyltin deuteride. The results summarized in Table 4 show that the chlorobenzene and anisole formed contained only about 40% of deuterium, when the diazonium salts were treated with a slight excess of the tin deuteride. Although the use of more of the tin deuteride resulted in increasing incorporation of deuterium in anisole, the original purpose was defeated. These findings, however, indicate that the incorporation of hydrogen takes place from molecules of solvent competing with that from

the tin deuteride, and it seems highly probable that aryl radicals are involved as intermediates. This is supported by the experiments, in which benzene- or *p*-chlorobenzene-diazonium fluoroborates were reduced with tri-n-butyltin hydride in a mixture of acetonitrile and benzene; the formation of biphenyl (8·4%) and 1,4-dihydrobiphenyl (about 1%) or of 4-chlorobiphenyl (16·8%) clearly indicates the generation of phenyl or *p*-chlorophenyl radicals and their subsequent attack on benzene.[5]

TABLE 4. REDUCTION OF DIAZONIUM FLUOROBORATES WITH TRI-n-BUTYLTIN DEUTERIDE

Diazonium salt (mmol)	Deuteride (mmol)	Solvent (ml)	Product, Deuterium included (%[a])
4-Methoxybenzenediazonium fluoroborate (10)	12	THF (50)	Anisole (40·0)
	23	THF (50)	Anisole (59·4)
	15	CH_3CN (25)	Anisole (44·3)
	12[b]	CH_3CN (20)	Anisole (42·7)
4-Chlorobenzenediazonium fluoroborate (10)	12	ether (75)	Chlorobenzene (37·8)
	14[c]	DMF (6)	Chlorobenzene (3·8)

[a] Measured by mass spectrometry with an ionization voltage of 12 volts.
[b] Reduction with triphenyltin deuteride.
[c] Reduction with $NaBD_4$.

The mechanism of the present reduction is not certain except that aryl radicals are involved as mentioned. In this connection it is of interest to note the behaviour of phenyldiazene reported by Huang and Kosower;[6] phenyldiazene decomposes bimolecularly yielding benzene and nitrogen, and a mechanism involving the formation of radical reaction partners within a solvent cage was suggested. However, part of the phenyl radicals escape the cage to yield benzene by hydrogen abstraction from the solvent, as is evidenced by the fact that only 72% of deuterated benzene was obtained from phenyldiazene-1-*d*.[6] These observations together with our results suggest that aryldiazenes may possibly be formed initially by the reduction of diazonium salts with metal hydrides, subsequently to decompose giving rise to arenes,

$$ArN_2BF_4 + (n\text{-}Bu)_3SnH \rightarrow ArN{=}NH + BF_3 + (n\text{-}Bu)_3SnF$$

$$ArN{=}NH \rightarrow ArH + N_2$$

The participation of aryl radicals is also important.

$$Ar\cdot + SH\ (Solvent) \rightarrow ArH + S\cdot$$

$$Ar\cdot + (n\text{-}Bu)_3SnH \rightarrow ArH + (n\text{-}Bu)_3Sn\cdot$$

As for the source of the aryl radicals, a route which does not pass through aryldiazenes cannot be excluded. The fact that incorporation of deuterium did not occur in the present experiments to the same extent as with phenyldiazene-1-*d* may indicate the existence of such a route.

EXPERIMENTAL

Materials. Diazonium fluoroborates,[7] benzenediazonium-2-carboxylate,[8] tri-n-butyltin hydride,[9] triethylsilane[10] and phenylsilane[11] were prepared according to directions described. Tri-n-butyltin deuteride, b.p. 72–74° (0·4 mm), and triphenyltin deuteride, b.p. 158° (0·3 mm), were prepared by reduction of the corresponding chlorides with LAD (CIBA Prods. Ltd., 99 atom % D).[9,12] No inclusion of the hydrides in the stannyl deuterides obtained was confirmed by the absence of an Sn-H stretching band (1812 cm^{-1}) in the IR spectra of the products.

Analysis of products. The yield of products was determined by VPC, reference being made to appropriate calibration curves, without any purification after the completion of reduction. The products were identified by comparison of their retention times and IR spectra with those of authentic samples.

Reductions of diazonium fluoroborates in ethers. A mixture of a diazonium fluoroborates (10 mmoles) and tri-n-butyltin hydride (12 mmoles) in diethyl ether (50 ml) was heated under reflux with stirring under N_2. When the insoluble fluoroborate had completely disappeared, the resulting ether soln was washed with water and dried over Na_2SO_4. Ether was removed by distillation and the crude product was purified in appropriate ways. A similar reduction was carried out in THF at room temp; after the completion of the reaction, the solvent was removed by distillation, water added to the residue, and organic materials extracted with ether. The ether extracts were worked up as described.

Reductions of diazonium fluoroborates in acetonitrile. Triethylsilane or tri-n-butyltin hydride (12 mmoles) was added with stirring to a soln of diazonium fluoroborate (10 mmoles) in 30 ml acetonitrile over a period of 15 min under N_2. The reaction was exothermic when the tin hydride was used, but the yield of reduction-product did not change even when the hydride was added very slowly at room temp. The reaction mixture was stirred for an additional hr, and the ppt of tri-n-butyltin fluoride was removed by filtration. The filtrate was worked up as described for the reduction in THF. When silyl hydride was used, it was necessary to allow the mixture to stand overnight to complete the reduction.

Replacement of the amino group of β-naphthylamine. A suspension of β-naphthylamine hydrochloride (5 mmoles) in 40 ml THF was cooled to −5° and diazotized by addition of isoamyl nitrite (8 mmoles) over a period of 5 min, and the mixture was stirred at 0° for an additional hr to complete the reaction. A soln of tri-n-butyltin hydride (12 mmoles) in 2 ml THF was added to the resulting diazonium soln over a period of 5 min at 0° and the mixture was stirred for a further 5 min at 0°. It was then diluted to 50·0 ml with THF and the yield of naphthalene (66%) was estimated by VPC on a 2 m column containing 15% Ucon oil LB-550-X on Chromosorb P at 198°.

Reductions of diazonium fluoroborates in a mixture of acetonitrile and benzene. Tri-n-butyltin hydride (12 mmoles) was added with stirring to a soln of benzene- or *p*-chlorobenzene-diazonium fluoroborates (10 mmoles) in a mixture of acetonitrile (15 ml) and benzene (30 ml) over a period of 10 min under N_2 at room temp. The mixture was stirred for an additional hr to complete the reduction and made up to 50·0 ml with benzene for VPC analysis. Benzenediazonium fluoroborate gave biphenyl (8·4%) and 1,4-dihydrobiphenyl (about 1%), which were estimated on a 2 m column containing 15% Apiezon grease on Chromosorb P at 186°, and *p*-chlorobenzenediazonium fluoroborate afforded chlorobenzene (40·0%) estimated on the same column at 128° and 4-chlorobiphenyl (16·8%) estimated on a 2 m column containing 15% Silicone grease on Chromosorb P at 172°.

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