[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Reaction of Organometallic Compounds with Diazonium Salts.[1] Synthesis of Arylazoalkanes

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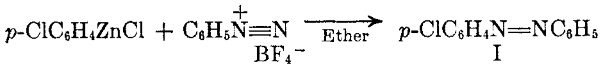
It has been found that alkyl- and aryl-zinc chlorides react with aryldiazonium fluoborates suspended in ether to give unsymmetrical azo compounds. Organo lithium, magnesium, cadmium, and mercury compounds give greatly reduced yields as do attempts to carry out the reaction as a homogenous reaction in pyridine. No significant amounts of biaryls, reported by Oda to be products of certain of these reactions, can be obtained even when cobalt chloride is added to the reaction medium. Methylmagnesium iodide reacts with a suspension of benzenediazonium fluoborate in ether to give iodobenzene.

It appears that very few studies have been made of the reaction of aryldiazonium salts with organometallics such as the Grignard reagent. Those which have been made have led to contradictory results. Thus, Hodgson and Marsden[3] found that the addition of the zinc chloride double salts of several diazonium chlorides to methyl-, ethyl-, or phenyl-magnesium bromide in refluxing ether gave azo compounds in low yields. Oda,[4] on the other hand, reported that some of these same reagents reacted at 0° in ether to yield 6–31% of the theoretical amount of biphenyls or alkylbenzenes formed with loss of nitrogen and, furthermore, the products were said to be independent of the order of mixing of reagents. These reactions have now been reinvestigated.

The reaction of *p*-chlorophenylmagnesium bromide with the zinc chloride double salt of benzenediazonium chloride was carried out under conditions which, according to Oda,[4] led to the biphenyl. The neutral fraction was separated and chromatographed to yield 22% of the theoretical amount of *p*-chloroazobenzene (I). No *p*-chlorobiphenyl was detected. When, instead of the zinc chloride double salt, a suspension of benzenediazonium fluoborate in ether was used, a small amount of biphenyl and a considerable amount of triphenylhydrazine were isolated. The latter, amounting to about 50% of the recovered neutral fraction, may have resulted from the further reaction of phenylmagnesium bromide with azobenzene initially formed. No azobenzene was isolated, however. The use of *p*-chlorophenyllithium with benzenediazonium fluoborate suspended in ether gave an oil which on chromatography showed at least six colored bands but no azo-compounds, or biphenyls could be isolated.

The observation that the zinc chloride double salts gave consistently more satisfactory results than the fluoborates suggested that the zinc chloride might be playing a fundamental role in the reaction by converting the Grignard reagent to an organozinc compound.[5] The reaction of *p*-chlorophenylzinc chloride with a suspension of benzenediazonium fluoborate in ether therefore was examined. The yield of *p*-chloroazobenzene (I) was estimated by examination of the ultraviolet spectrum of the neutral fraction to be 35%.



$$p\text{-ClC}_6\text{H}_4\text{ZnCl} + \underset{\text{BF}_4^-}{\text{C}_6\text{H}_5\overset{+}{\text{N}}\equiv\text{N}} \xrightarrow[\text{Ether}]{} \underset{\text{I}}{p\text{-ClC}_6\text{H}_4\text{N}{=}\text{NC}_6\text{H}_5}$$

The use of di-*p*-chlorophenylcadmium gave only 16% of the azo compound (I) and diphenylmercury gave no reaction even after 76 hours in refluxing ether.

Initially, it seemed desirable to have a solvent which would dissolve both the diazonium salt and the organometallic compound. It was found that benzenediazonium fluoborate was reasonably soluble in pyridine at 0°. Furthermore there was no immediate irreversible reaction of diazonium salt with the solvent since the addition of β-naphthylamine after 45 minutes at 0° gave the azo coupling product in 80% yield. Grignard reagents, also, are known not to undergo irreversible destruction in pyridine at room temperature and below.[6] Benzenediazonium fluoborate dissolved in pyridine was treated with *p*-chlorophenylzinc chloride in ether but no crystalline products could be obtained by chromatography. Ultraviolet analysis of the neutral product indicated that not more than 4% of *p*-chloroazobenzene (I) was obtained, as compared with the 35% yield obtained previously with the ether suspension. Reactions with aryllithium and arylmagnesium bromide in pyridine as the solvent were equally unrewarding. The remaining experiments therefore were carried out by adding

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[1] Taken from the Ph. D. Thesis of Joanne Arnheim Ursprung, University of Illinois, 1956.

[2] We are indebted to the General Electric Company for the Fellowship held by one of us (J.A.U.) during the year 1954–1955.

[3] Hodgson and Marsden, *J. Chem. Soc.*, 274 (1945).

[4] Oda and Nakano, *Repts. Inst. Chem. Res., Kyoto Univ.*, **19**, 91 (1949) [*Chem. Abstr.*, **45**, 7543h (1951)]; Oda, *Mem. Fac. Eng. Kyoto Univ.*, **14**, 195 (1952) [*Chem. Abst.*, **48**, 1935c (1952)].

[5] Bamberger and Tichvinsky [*Ber.*, **35**, 4179 (1902)] had found that diethylzinc reacted with phenyldiazonium chloride at −15° to give a mixture of products which included N-ethylbenzidine, N,N′-diethylphenylhydrazine, and N-ethyl-N-phenylhydrazine.

[6] See Cope, *J. Am. Chem. Soc.*, **60**, 2215 (1938).

the organozinc chloride to a suspension of the aryldiazonium fluoborate in ether.

The effects obtained by changing substituents on the two aryl rings are summarized in Table I. Since the reaction appeared to be interfered with by the formation of a number of colored side-products, it was considered that attack on the aromatic nucleus might be responsible for the rather poor yields of azo compound. The mesityl compounds were examined, therefore, in the hope that sufficient substitution of the rings by alkyl groups might correct this difficulty. It is seen in Table I that this hope was not realized.

TABLE I

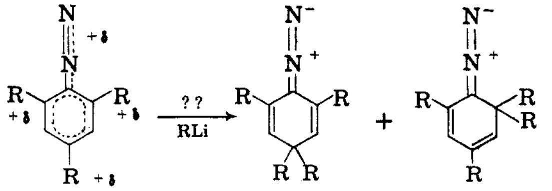
YIELDS IN THE REACTION

$Ar_1N_2^+ BF_4^- + Ar_2ZnCl \longrightarrow Ar_1N{=}NAr_2$

Ar_1	Ar_2	Yield, %
Phenyl	*p*-Chlorphenyl	35[a]
p-Chlorophenyl	Phenyl	10[a]
Phenyl	*p*-Methoxyphenyl	20[b]
p-Methoxyphenyl	Phenyl	2[c]
Phenyl	Mesityl	8[d]
Mesityl	Phenyl	0[e]

[a] Estimated from a determination of purity of total isolated acid-insoluble solid by the infrared spectrum. [b] Estimated from a determination of purity of total isolated acid-insoluble solid by the ultraviolet spectrum. [c] Approximately 10% of an oil was obtained which was shown by ultraviolet analysis to contain only about 20% of the product. [d] Chromatography yielded an oil from which the yield was determined by ultraviolet analysis. [e] Ether extraction of the neutral fraction followed by evaporation of the ether left a very small amount of yellow oil which was not examined further.

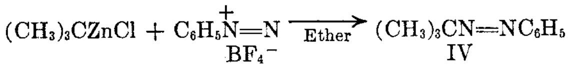
In spite of the adverse effect of substituents in the aromatic ring on the yields of azo compounds it appears likely that the multitude of colored side products and the low yields of azo compounds as well as the unfavorable effect of solvent may be due to the intervention of a reaction in which the organometallic compound attacks the *ortho* or *para* positions of the aromatic ring of the diazonium ion. It is seen that such reactions would lead to diazocyclohexadienes (II and III).



II III

It is evident that even when R = methyl such products are possible and might be expected to undergo further rapid reaction with the organometallic compound to yield a complex mixture. Some analogy is provided by the observation that halogen *para* to the diazonium group undergoes nucleophilic replacement by bromide or thiocyanate ion.[7] Such replacements presumably involve intermediates analogous to those postulated above. In none of these studies were the biphenyls to be anticipated from the work of Oda[4] found.

The reaction of benzenediazonium fluoborate with aliphatic organozinc chlorides was also studied. *tert*-Butylzinc chloride reacted with the diazonium salt suspended in ether to give benzeneazo-*tert*-butane (IV) in 40% of the theoretical amount.



$$(CH_3)_3CZnCl + \underset{BF_4^-}{C_6H_5\overset{+}{N}{=}N} \xrightarrow{\text{Ether}} \underset{\text{IV}}{(CH_3)_3CN{=}NC_6H_5}$$

The evidence for the structure of this compound was primarily the ultraviolet spectrum which showed a band at 415 mμ with a molecular extinction coefficient of 151. These values may be compared with the spectrum reported[8] for benzeneazomethane (λ_{max} 397 mμ, ε 159). The reaction of *tert*-butylmagnesium bromide with benzenediazonium

$$C_6H_5N_2^+ BF_4^- + (CH_3)_3CZnCl \longrightarrow C_6H_5N{=}NC(CH_3)_3$$

fluoborate suspended in ether also yielded the azo compound (IV) although in only 20% yield as estimated from the ultraviolet spectrum of the crude product.

Benzylzinc chloride yielded the azo compound which was not isolated, however, but estimated to be formed in 35% yield by isomerization to benzaldehyde phenylhydrazone and then conversion of the latter to the 2,4-dinitrophenylhydrazone. Benzylmagnesium chloride gave only 14% of the 2,4-dinitrophenylhydrazone when it was allowed to react with benzenediazonium fluoborate suspended in ether and the product was isolated as above.

Methylmagnesium iodide gave little benzeneazomethane but instead reacted with benzenediazonium fluoborate suspended in ether to give a 50% yield of iodobenzene. Benzenediazonium chloride had previously been reported to yield iodobenzene when treated with methyl iodide in the presence of zinc-copper.[9] The present example is perhaps more striking since the replacement of nitrogen by iodine occurs even in the presence of the preformed methyl Grignard reagent which is thus present in a relatively large concentration.

An attempt to carry out the reaction of triphenylvinylzinc chloride with benzenediazonium fluoborate gave, on hydrolysis of the reaction mixture, triphenylethylene (34% yield) as the only isolable product. Apparently much of the vinyl zinc compound had failed to react with the azo compound.

In an effort to explain the discrepancy between the formation of diaryls reported by Oda[4] and the formation of azo compounds found in the present work it was postulated that perhaps Oda's magnesium contained small amounts of metal impurities

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[7] Hantzsch and Hirsch, *Ber.*, **29**, 947 (1896).

[8] Ramart-Lucas, *Bull. soc. chim. France*, **4**, 481 (1937).

[9] Oddo, *Gazz. chim. ital.*, **20**, 635 (1890).

which catalyzed the reaction in which nitrogen is lost. Since cobalt chloride has been shown to have a dramatic effect on other Grignard reactions,[10] it was added in 0.1 *molar* amount to the reaction of benzenediazonium fluoborate with *p*-chlorophenylzinc chloride. The only product which could be identified, however, was *p*-chloroazobenzene in 8% yield when the reaction mixture was separated by chromatography.

EXPERIMENTAL[11]

Preparation of the benzenediazonium fluoborates. These salts are prepared by the method used by Flood[12] and Roe.[13] Ammonium fluoborate (a 20% aqueous solution) was added to the diazotized amine in aqueous acid solution and the diazonium fluoborate which precipitated was collected, washed several times with ice-cold methanol and then with ether, and dried. It was used without further purification.

Reaction of benzenediazonium chloride–zinc chloride double salt with p-chlorophenylmagnesium bromide. *p*-Chlorophenylmagnesium bromide, prepared from 0.7 g. (0.029 g.-atom) of magnesium and 5.36 g. (0.028 mole) of *p*-chlorobromobenzene in 70 ml. of anhydrous ether was added slowly to a solution of 5 g. (0.026 mole) of benzenediazonium chloride–zinc chloride double salt in 50 ml. of anhydrous ether at 0° in a nitrogen atmosphere, according to the method of Oda.[4] At the end of 24 hours in the cold the orange-red mixture was poured onto ice-water containing 15 ml. of concentrated hydrochloric acid, extracted with ether, and the ether was evaporated to yield a black solid (4.12 g.). A portion of this material (1.47 g.) was chromatographed on alumina using cyclohexane as the eluent to yield 450 mg. of orange azo compound (I), m.p. 78–84°. Recrystallization from ethanol raised its m.p. to 87–88.5°. The m.p. previously recorded[14] is 90–91°. The product (I) thus amounted to 1.25 g. or 22% of the theoretical.

Reaction of phenylmagnesium bromide with benzenediazonium fluoborate. Phenylmagnesium bromide, prepared from 0.82 g. (0.034 g.-atom) of magnesium, 5.86 g. (0.038 mole) bromobenzene, and 50 ml. of anhydrous ether, was added to 5 g. (0.026 mole) of benzenediazonium fluoborate suspended in 100 ml. of anhydrous ether in an ice-salt bath. After 24 hours of stirring and cooling, the reaction mixture was decomposed in a mixture of ice, water, and concentrated hydrochloric acid. The mixture was filtered, and the ether layer was separated and dried. Evaporation of the ether gave 1.5 g. of dark oil. Solution of 700 mg. of this oil in *n*-hexane and chromatography on alumina using as eluents hexene, hexane-ether mixtures and finally ether and gave 54 fractions of which 60 mg. was biphenyl, identified by a mixture m.p.; 60 mg. was an orange oil which was not further purified; and the remaining 434 mg. was triphenylhydrazine which after two recrystallizations from ethanol had m.p. 140–142° (dec.). The previously reported m.p.[15] was 142° (dec.).

Anal. Calc'd for $C_{18}H_{16}N_2$: N, 10.7. Found: N, 10.7.

The infrared spectrum showed an NH band at 3360 cm.$^{-1}$.

Reaction of p-chlorophenyllithium with benzenediazonium fluoborate. The lithium reagent was added to 0.96 g. (0.005 mole) of the benzenediazonium fluoborate in 40 ml. of anhydrous ether as in the reaction above. Extraction of the neutral product from aqueous acid as before and evaporation of the ether gave a dark red oil, amounting to 0.607 g. When this material was chromatographed on alumina using an eluents cyclohexane, cyclohexane-ether mixtures, and finally ether, several colored bands were obtained. The fraction which came off the column where *p*-chloroazobenzene was expected amounted only to 20 mg. and so was not further purified.

Reaction of p-chlorophenylzinc chloride with benzenediazonium fluoborate. The organozinc compound was prepared by adding 1.1 g. (0.011 mole) of freshly fused anhydrous zinc chloride with 50 ml. of anhydrous ether to a solution of *p*-chlorophenylmagnesium bromide prepared from 0.29 g. (0.012 g.-atom) of magnesium and 2.1 g. (0.011 mole) of *p*-chlorobromobenzene in 30 ml. of anhydrous ether. The resulting solution was forced with nitrogen into an equilibrated dropping-funnel from which it was added slowly to a suspension of 1.92 g. (0.01 mole) of benzenediazonium fluoborate in 50 ml. of anhydrous ether cooled in an ice-salt bath. After 6 hours the reaction mixture was poured onto a mixture of ice, water, and concentrated hydrochloric acid and the neutral fraction was extracted with ether. The ether extracts were dried and the ether was evaporated to yield a brown solid (0.914 g., 42%) of *p*-chloroazobenzene (I). The infrared absorption spectrum of this crude product was obtained and a calculation based on the assumption that Beer's law holds using the band at 1157 cm.$^{-1}$, found in the spectrum of an authentic sample of I, indicated the crude product to contain 82% of I. The total yield of I is thus estimated to be about 35%.

Reaction of di-p-chlorophenylcadmium with benzenediazonium fluoborate. The cadmium reagent was prepared from *p*-chlorophenylmagnesium bromide [from 0.29 g. (0.012 g.-atom) of magnesium and 2.1 g. (0.011 mole) of *p*-chlorobromobenzene in 30 ml. of anhydrous ether] by treatment with 1.1 g. (0.05 mole) of anhydrous cadmium chloride dried at 110° to constant weight. After 50 minutes under reflux the mixture was forced under nitrogen pressure into an equilibrated dropping-funnel from which it was added slowly to a suspension of 1.92 g. (0.01 mole) of benzenediazonium fluoborate in 50 ml. of anhydrous ether at room temperature. (An attempted reaction in the cold yielded no acid-insoluble product). After 5.5 hours, when the addition was completed, the reaction mixture was poured into ice, water, and concentrated hydrochloric acid and the ether extract gave, after evaporation of the ether, 0.544 g. of black solid amounting to 25% of the theoretical weight of *p*-chloroazobenzene. The comparison of the infrared spectrum with that of an authentic sample and a calculation made from the intensity of the band at 1157 cm.$^{-1}$ of a 10% solution in carbon tetrachloride indicated that the yield of *p*-chloroazobenzene was approximately 16%.

Treatment of p-chlorobenzenediazonium fluoborate with diphenylmercury. A suspension of 2.27 g. (0.01 mole) of *p*-chlorobenzenediazonium fluoborate in 50 ml. of anhydrous ether was treated under reflux with a suspension of 1.36 g. (0.005 mole) of diphenylmercury, which had been recrystallized from benzene, into 30 ml. of anhydrous ether. After 76 hours under reflux evaporation of the ether gave 1.3 g. of diphenylmercury (96% recovery).

Reaction of p-chlorophenylzinc chloride with benzenediazonium fluoborate in pyridine. To a solution of *p*-chlorophenylmagnesium bromide prepared from 0.3 g. (0.012 g.-atom) of magnesium and 2.2 g. (0.012 mole) of *p*-chlorobromobenzene in 50 ml. of anhydrous ether was added a solution of 1.6 g. (0.012 mole) of freshly fused anhydrous zinc chloride and 50 ml. of anhydrous ether. The reaction mixture was forced with nitrogen pressure into an equilibrated

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[10] Kharasch and Fuchs, *J. Am. Chem. Soc.*, **65**, 504 (1943).

[11] All melting points are corrected. Microanalyses were carried out by Mr. Joseph Nemeth, Miss Katherine Pih, Mrs. Ester Fett, and Mrs. Lucy Chang at the University of Illinois. Infrared spectra were measured by Miss Helen Miklas, Mrs. Rosemary Hill, and Mr. James Brader. Ultraviolet spectra were obtained by Miss Geradine Meerman.

[12] Flood, *Org. Syntheses*, Coll. Vol. **1**, 295 (1943).

[13] Roe, *Org. Reactions*, **5**, 193 (1949).

[14] Jacobson and Loeb, *Ber.*, **36**, 4090 (1903).

[15] Busch and Hobein, *Ber.*, **40**, 2100 (1907).

dropping-funnel from which it was added slowly to a solution of 1.92 g. (0.01 mole) of benzenediazonium fluoborate in 70 ml. of anhydrous pyridine cooled in an ice-salt bath. The reaction mixture was stirred for 15 minutes after the addition was completed and was poured into a mixture of ice-water–pyridine. The solution was acidified by the addition of 80 ml. of concentrated hydrochloric acid, the neutral fraction extracted with ether, and the ether extracts washed and dried and the ether evaporated. A brown oil (0.313 g.) was obtained. Examination of the infrared spectrum and a calculation using Beer's law and the 1157 cm.$^{-1}$ band indicated that it was only about 30% *p*-chloroazobenzene (I) or that the over-all yield of azo compound (I) was only 4%.

Replacement of the zinc compound by *p*-chlorophenyllithium or with *p*-chlorophenylmagnesium bromide gave no detectable amount of azo compound (I).

Reaction of phenylzinc chloride with p-chlorobenzenediazonium fluoborate. Phenylmagnesium bromide prepared from 0.3 g. (0.012 g.-atom) of magnesium and 1.8 g. (0.012 mole) of bromobenzene in 30 ml. of anhydrous ether was treated with 1.64 g. (0.012 mole) of freshly fused anhydrous zinc chloride in 30 ml. of anhydrous ether under reflux. The mixture was forced with nitrogen pressure into an equilibrated dropping-funnel from which it was added to a suspension of 2.27 g. (0.01 mole) of *p*-chlorobenzenediazonium fluoborate in 50 ml. of anhydrous ether kept at ice-salt bath temperature after which the reaction was stirred for 18 hours and worked up as before to give 0.3 g. or 18% of a black solid, shown by the infrared spectrum to be only about 57% *p*-chloroazobenzene. The total yield is therefore only about 10% of the azo compound (I).

Reaction of p-methoxyphenylzinc chloride with benzenediazonium fluoborate. To 3.84 g. (0.02 mole) of benzenediazonium fluoborate suspended in 100 ml. of anhydrous ether at ice-salt bath temperature was added *p*-methoxyphenylzinc chloride, in ether, prepared as was the phenylzinc chloride as in the reactions described above. After 18 hours of stirring the reaction mixture was poured into a saturated solution of ammonium chloride and extracted with ether. Removal of the ether yielded 2.0 g. of dark brown solid. A portion (239 mg.) of this solid, dissolved in cyclohexane, was chromatographed on alumina using cyclohexane as the eluent. Orange material (100 mg., m.p. 45°) was obtained. The recorded m.p. for *p*-methoxyazobenzene[16] is 54°. The ultraviolet spectrum in cyclohexane showed λ_{max} 338 mμ, ϵ 16,667 and λ_{max} 440 mμ, ϵ 860. The reported values[16] are λ_{max} 338 mμ, ϵ 24,700 and λ_{max} 440 mμ, ϵ 860. A calculation using the intensity of the band at 338 mμ and the assumption that Beer's law was obeyed indicates that the product was approximately 67% *p*-methoxyazobenzene. The total yield is thus 0.83 g. or 20% of the theoretical amount.

Reaction of phenylzinc chloride with p-methoxybenzenediazonium fluoborate. Phenylzinc chloride prepared from 0.6 g. (0.024 g.-atom) of magnesium, 3.8 g. (0.24 mole) of bromobenzene, and 3.3 g. (0.024 mole) of freshly fused anhydrous zinc chloride in 90 ml. of anhydrous ether was added to a suspension of 4.28 g. (0.02 mole) of *p*-methoxybenzenediazonium fluoborate in 100 ml. of anhydrous ether cooled in an ice-salt bath. The reaction mixture became yellow almost immediately and at the end of 22 hours in the cold was deep orange. It was decomposed by treatment with saturated ammonium chloride and extraction with ether. Evaporation of the ether left 305 mg. of red-brown oil. The ultraviolet spectrum showed a band at 345 mμ with ϵ 5,606. Calculation indicates that this corresponds to a 2% yield.

Reaction of mesitylzinc chloride with benzenediazonium fluoborate. Mesitylzinc chloride was prepared by treating an equivalent amount of mesitylmagnesium bromide with 5.5 g. (0.04 mole) of freshly fused anhydrous zinc chloride under reflux for 0.5 hour. The suspension of mesitylzinc chloride was forced with nitrogen pressure into an equilibrated dropping-funnel from which it was added slowly to a suspension of 3.4 g. (0.02 mole) of benzenediazonium fluoborate in 70 ml. of anhydrous ether cooled in an ice-salt bath. The reaction mixture was stirred in the cold for 20 hours. Then it was decomposed by treatment with saturated ammonium chloride solution. Extraction with ether and evaporation of the ether left 1.11 g. of red-brown oil. A 500-mg. aliquot of this oil dissolved in cyclohexane and chromatographed on alumina yielded 155 mg. of red oil. The ultraviolet spectrum of this oil showed a maximum at 325 mμ with ϵ 10,600. This corresponds to a yield of about 8% of azo compound.

Reaction of phenylzinc chloride with mesitylenediazonium fluoborate. Phenylzinc chloride was prepared as before from 3.8 g. (0.024 mole) of bromobenzene, 0.58 g. (0.024 g.-atom) of magnesium, and 0.024 mole of freshly fused anhydrous zinc chloride in 100 ml. of absolute ether and added to a suspension of 4.4 g. (0.02 mole) of mesitylenediazonium fluoborate in 70 ml. of anhydrous ether cooled in an ice-salt bath. After 24 hours of stirring in the cold there was no apparent color change. The reaction was, therefore, stirred at room temperature for 48 hours longer. Although there was still little change in color the mixture was decomposed by treatment with saturated ammonium chloride. Extraction with ether and evaporation of the ether left such a small quantity of yellow oil that it was not examined further.

Reaction of tert-butylzinc chloride with benzenediazonium fluoborate. A solution estimated by titration to be 0.1 *molar* in *tert*-butylmagnesium chloride[17] was forced with nitrogen pressure into an equilibrated dropping-funnel and added to 16.4 g. (0.1 mole) of freshly fused anhydrous zinc chloride in 150 ml. of anhydrous ether. A copious white precipitate was formed. After 0.5 hour the reaction mixture was shaken vigorously and forced with nitrogen pressure in an equilibrated dropping-funnel in such a way that the white precipitate was also forced out. This suspension, presumably *tert*-butylzinc chloride in ether, was added slowly to a suspension of 19.2 g. (0.1 mole) of benzenediazonium fluoborate in 120 ml. of anhydrous ether cooled in an ice-salt bath. The reaction mixture was stirred for 22 hours after completion of addition. At the end of this time it was decomposed by treatment with 50 ml. of saturated ammonium chloride solution. Extraction with ether and removal of the ether by distillation and then steam-distillation of the product yielded a yellow oil which was distilled under reduced pressure. The fraction with b.p. 50–54° at 0.2 mm. amounted to 6.32 g. (40%) of benzeneazo-*tert*-butane. A fraction with b.p. 52–54° (0.2 mm.) showed a maximum at 415 mμ (ϵ 151) in the visible spectrum.

Anal. Calc'd for $C_{10}H_{14}N_2$: C, 74.1; H, 8.7; N, 17.3. Found: C, 74.3; H, 8.8; N, 17.5.

Reaction of tert-butylmagnesium chloride with benzenediazonium fluoborate. The reaction carried out as above but without the addition of zinc chloride was allowed to proceed for 22 hours and decomposed with 50 ml. of saturated ammonium chloride solution. Extraction with ether, evaporation of the ether and steam-distillation gave an oil which was distilled at 0.5 mm. through a Holzmann column. A total of 3.8 g., b.p. 56–90° was obtained, which was estimated by the intensity of the absorption maximum at 420 mμ to amount to about a 20% yield.

Reaction of benzylzinc chloride with benzenediazonium fluoborate. To 0.1 mole of benzylmagnesium chloride[18] in ether was added 16.4 g. (0.1 mole) of freshly fused anhydrous zinc chloride in 60 ml. of anhydrous ether. A copious fine precipitate was formed so that the suspension was forced over into an equilibrated dropping-funnel with nitrogen.

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(16) Burawoy, *J. Chem. Soc.*, 1865 (1937).

(17) Puntambeker and Zoellner, *Org. Syntheses*, Coll. Vol. 1, 524 (1941).

(18) Gilman and Catlin, *Org. Syntheses*, Coll. Vol. 1, 4 (1941).

Then it was added slowly to a suspension of 19.2 g. (0.1 mole) of benzenediazonium fluoborate and 120 ml. of anhydrous ether cooled in an ice-salt bath. The reaction mixture was stirred for 22 hours and decomposed with 50 ml. of saturated ammonium chloride solution. Extraction with ether and removal of the ether gave a red-brown precipitate amounting to 17.5 g. This was converted to benzaldehyde 2,4-dinitrophenylhydrazone when a 1.0-g. aliquot was dissolved in 95% ethanol and treated with a solution of 2,4-dinitrophenylhydrazine.[19] A yield of 0.59 g. (41%) was obtained. This amounts to an over-all yield of 35% of the theoretical amount of benzaldehyde phenylhydrazone from benzenediazonium fluoborate.

The 2,4-dinitrophenylhydrazone was recrystallized from 45% ethanol after which it had m.p. 236°, alone or mixed with authentic benzaldehyde 2,4-dinitrophenylhydrazone.

Reaction of methylmagnesium iodide with benzenediazonium fluoborate. To a suspension of 30 g. (0.16 mole) or benzenediazonium fluoborate and 150 ml. of anhydrous ether cooled in an ice-salt bath was added a solution of methylmagnesium iodide prepared from 25.6 g. (0.18 mole) of methyl iodide, 4.52 g. (0.19 g.-atom) of magnesium, and 70 ml. of anhydrous ether. Decomposition of the reaction mixture with ice-water containing 60 ml. of concentrated hydrochloric acid and extraction of the neutral product gave, on distillation through a Holzmann column under 15 mm. pressure, 15.2 g. (50%) of iodobenzene, b.p. 64-72°. Redistillation gave b.p. (20 mm.) 77-78.5°. The infrared spectrum of the liquid was identical with that of authentic iodobenzene.

Anal. Calc'd for C_6H_5I: C, 35.5; H, 2.5. Found: C, 35.5; H, 2.6.

A reaction similar to that above except that the methylmagnesium iodide was treated with anhydrous zinc chloride before being added to the benzenediazonium salt gave a 13% yield of iodobenzene. No azo compound was obtained.

Reaction of triphenylvinylzinc chloride with benzenediazonium fluoborate. Triphenylvinylzinc chloride was prepared from triphenylvinyl bromide (7.04 g., 0.024 mole) and *n*-butyllithium (0.027 mole) in 173 ml. of ether at −20°.[20] After 15 minutes 3.3 g. (0.024 mole) of freshly fused anhydrous zinc chloride in 70 ml. of anhydrous ether was added and the reaction mixture refluxed for 0.5 hour. The resulting suspension was forced with nitrogen into an equilibrated dropping-funnel from which it was added slowly to a suspension of 3.84 g. (0.02 mole) of benzenediazonium fluoborate in 70 ml. of anhydrous ether at ice-salt bath temperatures. The reaction mixture slowly changed color from yellow to orange to brown. After 20 hours in the cold the mixture was poured into a saturated solution of ammonium chloride and the neutral fraction was extracted with ether. Evaporation of the ether gave an oil (4.24 g.) which on steam-distillation gave an orange semi-solid after extraction with ether and evaporation of the ether. A solution of 480 mg. of the original oil in cyclohexane was chromatographed on alumina using as eluents cyclohexane, cyclohexane-ether mixtures, and ether to give 280 mg. of a white crystalline solid, m.p. 53-54°. All other fractions were orange oils. Recrystallization of the white solid gave triphenylethylene, m.p. 66-67.5°. A mixture with an authentic sample, m.p. 69°, showed no depression. The estimated yield of triphenylethylene is thus 34%. No further purification of the colored fractions was attempted.

The stability of benzenediazonium fluoborate in pyridine. Benzenediazonium fluoborate (0.5 g., 0.026 mole) in 30 ml. of dry pyridine was allowed to stand for 45 minutes in an ice-salt bath after which time 0.37 g. (0.0026 mole) of β-naphthylamine was added to the solution. Extraction of the red solution with 500 ml. of water containing 0.2 g. of sodium hydroxide gave a precipitate which was collected by filtration. The benzeneazo-β-naphthylamine (0.53 g., m.p. 90-95°) amounted to 0.53 g. However, it is estimated that at least 0.1 g. was lost in the work-up and that the yield was about 80%. Recrystallization from 50% acetic acid gave product, m.p. 97-98°. The recorded[21] m.p. is 102-104°.

Reaction of p-chlorophenylzinc chloride with benzenediazonium fluoborate in the presence of cobalt chloride. p-Chlorophenylzinc chloride prepared from 2.64 g. (0.11 mole) of magnesium, 21.0 g. (0.11 mole) of *p*-chlorobromobenzene, and 16.4 g. (0.12 mole) of freshly fused anhydrous zinc chloride in 230 ml. of anhydrous ether was forced with nitrogen pressure into an equilibrated dropping-funnel from which it was added to a suspension of 19.2 g. (0.1 mole) of benzenediazonium fluoborate in 100 ml. of ether containing 1.3 g. (0.01 mole) of cobalt chloride (anhydrous; dried at 110° for 48 hours) in an ice-salt bath.[10] After 20 hours of stirring the solution was poured into saturated ammonium chloride and extracted with ether. Evaporation of the ether followed by sublimation or chromatography of the sample on activated alumina yielded, as the only identifiable product, *p*-chloroazobenzene. A calculation from the infrared spectrum indicated that the *p*-chloroazobenzene amounted to 8% yield. No *p*-chlorobiphenyl could be found.

The *infrared spectra* were obtained with a Perkin-Elmer Model 21 Spectrophotometer using 10% solutions in carbon tetrachloride in 0.1-mm. matched cells unless otherwise specified. Quantitative estimates were made using absorbancies and assuming Beer's Law to hold. Infrared curves are available in the Ph.D. Thesis of Dr. Joanne Ursprung and reported by Univ. Microfilms, Ann Arbor, Michigan.

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