through a small Vigreux column. The product, 18.9 g. (70%), b.p. 130–140° (1.5 mm.), was 2,3-diacetoxy-2-cyclohexen-1-one (VIII) which possibly also contained some 2,6-diacetoxy-2-cyclohexen-1-one (XII) derived from another tautomeric form of dihydropyrogallol.

2-Acetoxy-3-(6-methoxy-2-naphthyl)-2-cyclohexen-1-one (IX). A solution of 6-methoxy-2-naphthylmagnesium bromide in a mixture of 300 ml. of dry ether and 300 ml. of dry benzene was prepared as described above from 4.86 g. of magnesium and 45 g. of 2-bromo-6-methoxynaphthalene. The Grignard reagent was filtered through glass wool and added over a 2-hr. period to a solution of 18.9 g. of VIII in 200 ml. of dry ether cooled with an ice bath. After another hour at 0–5°, the complex was decomposed by the addition of 600 ml. of saturated ammonium chloride solution. The organic layer was separated, washed with ammonium chloride solution, then with water, was filtered through anhydrous sodium sulfate, and the solvents were removed under vacuum without heating. The residue was chromatographed on 80 times its weight of silica gel. The column was developed with benzene and eluted with mixtures of benzene and ethyl acetate. Elution with 90% benzene–10% ethyl acetate gave material which was purified by digesting with boiling hexane, decanting the liquor, and evaporated to dryness. The residue was crystallized twice from methanol to give pure 2-acetoxy-3-(6-methoxy-2-naphthyl)-2-cyclohexen-1-one (IX), m.p. 116–117°.

Anal. Calcd. for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.67; H, 5.78.

2-Hydroxy-3-(6-methoxy-2-naphthyl)-2-cyclohexen-1-one (X). A solution of 0.50 g. of IX in 10 ml. of methanol was treated with 0.5 ml. of hydrochloric acid and warmed on a hot plate for 0.7 hr. Cooling and filtration gave 0.35 g. (80%) of pure 2-hydroxy-3-(6-methoxy-2-naphthyl)-2-cyclohexen-1-one (X), m.p. 174–176°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.40; H, 6.15.

ω-(6-Methoxy-2-naphthoyl)butyric acid (XI). a. *By oxidation of X.* A solution of 0.10 g. of X in 100 ml. of acetone was treated with 0.5 g. of magnesium sulfate and 0.12 g. of potassium permanganate and this mixture was stirred at room temperature for 2 hr. Then it was treated with 0.5 g. of sodium bisulfite and 1.0 ml. of hydrochloric acid, filtered, and the filtrate was evaporated to dryness. The residue was twice crystallized from acetone to give pure ω-(6-methoxy-2-naphthoyl)butyric acid (XI), m.p. 173–175.5°; mixed with X, m.p. 154–162°.

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.69; H, 5.95.

b. *From glutaric anhydride and methoxynaphthalene.* A mixture of 7.5 g. of glutaric anhydride and 9.5 g. of 2-methoxynaphthalene was added to a solution of 16 g. of aluminum chloride in 60 g. of nitrobenzene cooled in an ice bath. After the ice had melted, the reaction mixture was allowed to stand at room temperature for 64 hr. Aqueous hydrochloric acid was added and the mixture was extracted with ether. The organic layer was washed with water and filtered through anhydrous sodium sulfate. The solvents were removed by vacuum distillation and the residue was subjected to a short path distillation at 0.3 mm. and 250°. The distillate was crystallized three times from acetone to give pure XI, m.p. 175–177.5°, mixed with that from (a) above, m.p. 174.5–177°.

CHICAGO 80, ILL.

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Reaction of Diarylzinc Reagents with Aryldiazonium Salts.[1] Direct Formation of *cis*-Azo Compounds

DAVID Y. CURTIN AND JOHN L. TVETEN[2]

Received September 22, 1960

Benzenediazonium, *p*-nitrobenzenediazonium, *p*-chlorobenzenediazonium, and *p*-methoxybenzenediazonium fluoborate have been found to react with diphenylzinc in dimethylformamide solution to give the corresponding *trans*-azo compounds, I, II, III, and IV. Yields were greater than 90% of I, II, and III and 72% of IV. The diphenylzinc could be prepared either from diphenylmercury and zinc in toluene or from phenyllithium and sublimed zinc bromide in ether. Preliminary observations indicate that the reaction to form I is 77% complete in one minute at 0° with the concentrations employed and 100% complete in fifteen minutes.

When diphenylmercury is added to the dimethylformamide, the product mixture, analyzed by the method of Dewar and Urch,[9] is shown to contain *cis*-azobenzene as well as *trans*, the amount of *cis*-isomer being as high as 80% of the product. The fraction of *cis*-product increases with increasing diphenylmercury.

Although it was found by Hodgson and Marsden[3] that azo compounds could be formed in low yields by the reaction of Grignard reagents in diethyl ether with aromatic diazonium zinc chloride double salts, the use of diazonium fluoborates in the reaction gave negligible yields of azo compound.[4a] The possibility that the reactions of the zinc chloride double salts involved an organozinc intermediate led to a study[4a] of certain reactions of aryl and alkylzinc chlorides[5] with suspensions of benzenediazonium fluoborates in ether which were

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(1) Supported in part by a grant (G-4467) from the National Science Foundation. This work is taken from the Ph.D. thesis submitted by John Lowell Tveten to the University of Illinois, 1960.

(2) Lubrizol Corporation Fellow, 1958–1959. Minnesota Mining and Manufacturing Company Fellow, 1959–1960.

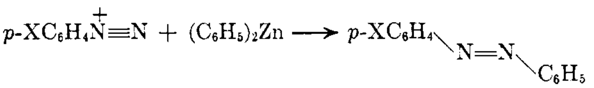
(3) H. H. Hodgson and E. Marsden, *J. Chem. Soc.*, 274 (1945).

(4)(a) D. Y. Curtin and J. A. Ursprung, *J. Org. Chem.*, **21**, 1221 (1956). (b) E. Bamberger and M. Tichvinsky, *Ber.*, **35**, 4179 (1902).

(5) The structure of the "alkylzinc chloride" prepared from the Grignard reagent and zinc chloride is still debatable but recent evidence suggests that it is, in fact a zinc chloride complex of the dialkylzinc [see A. B. Garrett, A. Sweet, W. L. Marshall, D. Riley, and A. Touma, *Rec. Chem. Progress*, 155 (1952); R. E. Dessy, *J. Am. Chem. Soc.*, **82**, 1580 (1960)].

found to give azo compounds in yields of 45% or less. Attempts to carry out these reactions in pyridine solution resulted in even poorer yields of azo compounds.[4a] In spite of these discouraging observations and also a previous report[4b] that benzenediazonium chloride added to diethylzinc in diethyl ether at −15° followed by heating under reflux gave a mixture of products (not including benzeneazoethane) a further investigation of the reactions of zinc reagents with aromatic diazonium fluoborates was undertaken.

Dimethylformamide was selected as a suitable solvent for the reaction. Diphenylzinc, prepared in excess from the reaction of diphenylmercury with zinc in xylene[6] and treated with a solution of benzenediazonium fluoborate, gave *trans*-azobenzene (*trans*-I) which could be isolated by steam distillation in 95% yield. *p*-Nitrobenzenediazonium fluoborate and *p*-chlorobenzenediazonium fluoborate gave the corresponding *trans*-azo compounds II and III in similar yields. *p*-Methoxybenzenediazonium fluoborate gave the *trans*-azo compound IV in only 72% yield.



$$p\text{-}XC_6H_4\overset{+}{N}{\equiv}N + (C_6H_5)_2Zn \longrightarrow p\text{-}XC_6H_4N{=}NC_6H_5$$

trans-I. X = H
II. X = NO_2
III. X = Cl
IV. X = CH_3O

A more convenient procedure for synthetic work was obtained by carrying out the reaction in ether and preparing the zinc reagent by treatment of phenyllithium with zinc bromide. A reaction carried out for fifteen minutes at 0° of an excess of zinc reagent[7] with a suspension of benzenediazonium fluoborate in diethyl ether gave *trans*-azobenzene in 99% yield. This procedure was readily adapted to the preparation of *trans*-benzeneazo-*t*-butane (V). *t*-Butylmagnesium chloride was treated with anhydrous zinc bromide (one-half molar equivalent) to give a zinc reagent to which was added benzenediazonium fluoborate at 0°. The azo compound V was obtained in a yield of 97%. Attempts to prepare benzeneazomethane

$$C_6H_5N_2^+ + [(CH_3)_3C]_2Zn \longrightarrow \underset{\text{V}}{(CH_3)_3CN{=}NC_6H_5}$$

by a similar method, however, have thus far been unsuccessful, and only dark tars were obtained.

Preliminary observations have shown that the reaction of diphenylzinc with phenyldiazonium fluoborate in xylene-dimethylformamide (1:2) at 0° is very fast. Thus a reaction with 0.03*M* diazonium salt and 0.1*M* diphenylzinc was 77% complete after one minute and 100% complete after fifteen minutes. It might be noted that it was convenient to use excess diphenylzinc in order to allow for any accidental hydrolysis or other loss which might have occurred. Since azobenzene has been reported[8] to react with diphenylzinc in refluxing ether, its behavior toward an equimolar amount of diphenylzinc under the reaction conditions was examined. It was found that after two hours at 0° there was no evidence of reaction and 93% of the azobenzene employed could be recovered.

With the hope that the use of dimethyl formamide as the solvent might make possible the formation of azo compounds from the Grignard reagent, this reaction was re-examined. However, phenylmagnesium bromide failed to give appreciable amounts of azobenzene. Diphenylmercury failed to react with benzenediazonium fluoroborate and could be recovered in 84% yield.

In certain reactions of benzenediazonium fluoborate in dimethylformamide with diphenylzinc which had been prepared from diphenylmercury in xylene, it was noted that the amount of *trans*-azobenzene isolated on steam distillation of the product was more than should have been present according to an ultraviolet spectroscopic examination of the crude product. This discrepency suggested the possibility that part of the product was *cis*-azobenzene which isomerized during the steam distillation to the *trans*-isomer. The reaction mixtures were therefore analyzed by comparing their absorbancies in the ultraviolet at thirteen wave lengths between 300 and 330 mμ, using the method of Dewar and Urch.[9] The assumption that *cis*- and *trans*-azobenzene were the only species present which had absorption in this region was confirmed by the fact that linear plots were obtained. Furthermore, the calculated amount of azobenzene agreed well with the amount of *trans*-isomer obtained after steam distillation (in which any *cis*-isomer present was converted to *trans*).[10] By using the ultraviolet spectral analysis it was found that only those runs with excess diphenylmercury gave the *cis* product. The fraction of *cis*-azobenzene increased when more diphenylmercury was present and when 0.03 mole of diphenylzinc in xylene was treated with 0.15 mole of diphenylmercury and then added to 0.01 mole of benzenediazonium fluoborate 80% of the azobenzene formed was shown by the ultraviolet spectral analysis to be the *cis*-isomer.

No *cis*-product was obtained when diphenylmercury was added to diphenylzinc in diethyl ether at 0° and the diazonium salt was added to

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(6) K. A. Kozeschkow, A. N. Nesmejanow, and W. I. Petrosow, *Ber.*, **67B**, 1138 (1934).

(7) The zinc reagent was prepared by adding one-half the molar amount of anhydrous zinc bromide (sublimed) to phenyllithium in ether. Zinc bromide rather than zinc chloride was employed because it is easier to prepare and maintain in anhydrous condition.

(8) H. Gilman and J. C. Baile, *J. Org. Chem.*, **2**, 84 (1937).

(9) M. J. S. Dewar and D. S. Urch, *J. Chem. Soc.*, 345 (1957).

(10) The equilibrium in the thermal isomerization of azobenzene lies far to the *trans* side [see R. J. Corruccini and E. G. Gilbert, *J. Am. Chem. Soc.*, **61**, 2925 (1939)].

the resultant mixture. This may be due in part to the relatively low solubility of diphenylmercury in ether. A separate experiment indicated that the solubility in anhydrous ether at 0° is about 3 g./100 ml., which would indicate that about 0.02 mole of diphenylmercury was present in the reaction with 0.026 mole diphenylzinc, provided that the solubility in the reaction mixture is comparable to the solubility in ether alone.

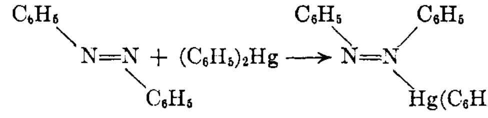
These results are summarized in Table I. Although the mechanism by which diphenylmercury is able to alter the stereochemistry of the azobenzene formed is not at all clear from the present work a few additional observations are pertinent. The possibility arises that the effect of diphenylmercury might be to isomerize *trans*-azobenzene to a more stable *cis*-azobenzene-diphenylmercury complex. Such an explanation is untenable since *trans*-azobenzene when allowed to stand with

TABLE I

EFFECT OF DIPHENYLMERCURY ON THE STEREOCHEMISTRY OF THE REACTION OF DIPHENYLZINC WITH BENZENEDIAZONIUM FLUOBORATE

Amount of Diphenylzinc, Moles	Amount of Diphenylmercury, Moles	% of *cis*-Azobenzene[a]	Total Yield, %
0.030	0.00	0.00	72
0.030	0.03[b]	21.6	78
0.030	0.03[c]	26.9	65
0.015	0.075[b]	78.5	74
0.026	0.130[d]	0.0	88

[a] % *trans* = 100 − % *cis*. [b] Diphenylmercury was added to diphenylzinc in dimethylformamide and then the diazonium salt added. [c] Diphenylmercury was added to the diazonium salt in dimethylformamide and then diphenylzinc added. [d] This reaction was carried out as a heterogeneous reaction in diethyl ether.



diphenylmercury in dimethylformamide undergoes no such isomerization as shown by the ultraviolet absorption spectrum. This leaves the supposition that the effect of diphenylmercury is on the mechanism of the coupling reaction itself. It might be considered that diphenylmercury and diphenylzinc could react initially to give a new reagent, $C_6H_5H_9^+$ Zn $(C_6H_5)_3^-$ or $C_6H_5Zn^+$ $Hg(C_6H_5)_3^-$. Although somewhat analogous complexes have been observed with other metals, diphenylmercury has been reported to form no complex in a detectable amount with phenyllithium.[11] Preliminary attempts to obtain spectral evidence for a complex between diphenylmercury and benzenediazonium fluoborate in dimethylformamide were thwarted by the decomposition of the diazonium salt. It will be noted that the results in Table I show that the ratio of *cis*- to *trans*-azobenzene is unchanged by changing the order of mixing the reagents. Work to obtain more detailed information about the reaction leading to *cis*-azo compounds is being continued.

EXPERIMENTAL[12]

Preparation of the benzenediazonium fluoborates. These salts were prepared by addition of 20% aqueous ammonium fluoborate to the aqueous acidic solution of the diazotized amine.[13] The salts were filtered and washed with cold methanol and ether and dried without further purification. Benzenediazonium fluoborate so obtained was white with m.p. 100° dec. *p*-Nitrobenzenediazonium fluoborate was obtained as yellow crystals, m.p. 154° dec. The methoxy compound was light grey, m.p. 142–143° dec. and the *p*-chlorodiazonium fluoborate was obtained as a tan solid, m.p. 139° dec.

Preparation of trans *azo compounds I-V from substituted benzenediazonium fluoborates and diphenylzinc.* (*a*) *In dimethylformamide.* To a solution of diphenylzinc[6] in 100 ml. of xylene, prepared from 10.65 g. (0.03 mole) of diphenylmercury[14] and 58.86 g. (0.900 mole) of granulated zinc, was added 150 ml. of freshly dried dimethylformamide and the resulting solution cooled to 0°. A solution of 1.92 g. (0.01 mole) of benzenediazonium fluoborate in 25 ml. of cold dimethylformamide was added over a period of 1 min. After stirring at 0° for 2.5 hr., the reaction mixture was hydrolyzed with 175 ml. of water containing 25 ml. of concd. hydrochloric acid and steam distilled. The distillate was extracted with ether and the extracts dried over magnesium sulfate and concentrated. Attempts to remove the xylene from the product under reduced pressure resulted in codistillation of some of the colored material. The xylene was therefore removed by chromatography on 1 lb. of "acid-washed" aluminum oxide which had been heated 12 hr., at 125°. The xylene was removed from the column with hexane and anhydrous ether used to elute the colored fraction. Upon drying and evaporation of the solvent, the yield was 1.72 g. of *trans*-azobenzene, m.p. 61–66°, or 95% based on the diazonium salt used. One recrystallization from ethanol gave 1.67 g. (92%) of product melting at 67–68°, and a mixed melting point with an authentic sample of azobenzene showed no depression. The infrared spectra of both crude and purified azobenzene were identical with a spectrum of authentic material. A reaction similar to that above except that the diphenylzinc was prepared from zinc bromide (sublimed at 340°, 0.5 mm. pressure) and the scale doubled gave a 75% yield of *trans*-azobenzene, m.p. 66.5–68.5°, with an infrared spectrum identical with those obtained previously.

A reaction like the first described above but employing *p*-methoxybenzenediazonium fluoborate and a reaction time

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(11) G. Wittig, F. J. Meyer, and G. Lange, *Ann.*, **571**, 167 (1951).

(12) All melting points are corrected. Microanalyses were carried out by Mr. J. Nemeth, Miss C. Higham, Miss J. Liu, and Mrs. A. Bay. The infrared spectra were determined with a Perkin-Elmer Model 21 spectrophotometer by Mr. P. McMahon, Mr. W. Dalton, Mr. D. Johnson, Miss C. Luebke, and Mrs. M. Verkade. Ultraviolet measurements were made with a Cary model 14 M recording spectrophotometer with 1-cm. cells. Spectra and other data will be available in the Ph.D. thesis of J. L. T., Univ. Microfilms, Ann Arbor, Mich.

(13) D. T. Flood, *Org. Syntheses*, **Coll. Vol. II**, 295 (1943); A. Roe, *Org. Reactions*, **5**, 193 (1949).

(14) H. O. Calvery, *Org. Syntheses*, **Coll. Vol. I**, 228 (1941).

of 15 min. at 0° gave an oil on chromatography which crystallized on cooling in a Dry Ice bath to give a 72% yield of *trans-p*-methoxyazobenzene (IV), m.p. 53–54° (lit.[15] m.p. 53°), ultraviolet spectrum, λ_{max} 343 mμ, ϵ 2.47×10^4. Another run on one-third the scale above gave 50% of IV.

A similar reaction with *p*-nitrobenzenediazonium fluoborate for 15 min. gave on chromatography a red solid which was recrystallized from petroleum ether (Dry Ice bath) to yield 97% of *trans-p*-nitroazobenzene (II), m.p. 133–135.5° (lit.[16] m.p. 134°), ultraviolet spectrum, λ_{max} 330 mμ, ϵ, 2.38×10^4. A second (identical) reaction gave an amount of II, estimated from the ultraviolet spectrum to be 83% of the theoretical but after an unsatisfactory steam distillation (due to the low volatility of II) only 57% of II was isolated.

A reaction with *p*-chlorobenzenediazonium fluoborate on the same scale as before for 15 min. at 0° but with the diphenylzinc prepared from phenyllithium and sublimed zinc bromide (340°, 0.5 mm.) in ether, gave a red solid which after chromatography was recrystallized from ethanol to give 96% of *trans-p*-chloroazobenzene (III), m.p. 89–91.5° (lit.[17] m.p. 90–91°), ultraviolet spectrum, λ_{max} 322 mμ, ϵ, 2.10×10^4.

(b) *In diethyl ether.* An ether solution of diphenylzinc was prepared by adding 121 ml. of $0.88N$ phenyllithium (0.106 mole) to 12.00 g. (0.053 mole) of freshly sublimed (340°, 0.5 mm.) zinc bromide. Dry ether (150 ml.) was added, the mixture cooled to 0°, and 3.26 g. (0.017 mole) of solid benzenediazonium fluoborate added quickly. After stirring for 15 min. the mixture was hydrolyzed with 500 ml. of water containing 20 ml. of concd. hydrochloric acid and extracted with ether. The ether fractions, when dried and concentrated, yielded a dark red oil. When chromatographed on 1 lb. of alumina the product was found to consist mainly of a large orange fraction which was removed from the column with ether and concentrated to an orange solid. Recrystallization from petroleum ether (b.p. 30–60°) gave 3.08 g. (99%) of *trans*-azobenzene, m.p. 68–69°. The infrared spectrum was identical with commercial azobenzene, and a mixed melting point was not depressed.

The reaction with di-*t*-butylzinc prepared from 2:1 molar amounts of *t*-butylmagnesium chloride and sublimed zinc bromide (3 moles of dialkylzinc per mole of diazonium fluoborate) was carried out as above. The chromatography gave a 97% yield of V, ultraviolet spectrum, λ_{max} 262 mμ, ϵ 8.74×10^3, infrared spectrum identical with that previously obtained.[4a] Distillation through a Holzmann column at 2.3 mm. gave extensive decomposition but a fraction b.p. 56–58° had the same infrared spectrum as obtained previously. A repetition of the experiment gave 89% of the azo compound V.

Quantitative determination of cis- *and* trans-*azobenzene* (*cis- and trans*-I). The pure isomers were prepared by the method of Hartley.[18] Commercial *trans*-azobenzene was purified by partial precipitation (five times) from acetone with water. It had m.p. 68.5–69° and differed from the *cis*-isomer in the infrared absorption spectrum with maxima at 685, 1152, 1218, and 1583 cm.$^{-1}$ The ultraviolet spectrum in ethanol showed λ_{max} 317 mμ, ϵ 2.22×10^4. The NMR spectra of the samples of *cis*- and *trans*-I described here have been discussed elsewhere.[19] *cis*-I prepared by irradiation of the *trans*-isomer and purified by four recrystallizations from pentane had m.p. 68.5–70°, m.p. of mixture with *trans*-I, 43–47°, infrared absorption at 695, 1510, 1578, and 1590 cm.$^{-1}$ The ultraviolet spectrum in ethanol showed λ_{max} 280 mμ, ϵ, 5.26×10^3. A sample kept for 6 months in the dark still contained 70% of the *cis*-isomer as indicated by the infrared spectrum. Solutions containing 2.010 mg. of *cis*-I in 100 ml. of absolute ethanol (c_c) and 0.690 mg. of *trans*-I in 100 ml. of ethanol (c_t) were used as standards for all the ultraviolet spectral determinations. Analyses were made by determining the spectrum using an expanded scale and employing the method of Dewar and Urch.[9]

Data at thirteen wave lengths at 2.5 mμ intervals from 300 to 330 mμ were plotted in each case. Because it was desirable to determine spectra in a medium containing small amounts of dimethylformamide and xylene (obtained by withdrawing aliquots and diluting with ethanol to the concentrations desired for spectral measurements), the effect of small amounts of these substances on the spectra was examined and found to be negligible above 287 mμ. Determination of the composition of known mixtures by the method described gave percentages which agreed with the theoretical to within 3% or better.

Effect of diphenylmercury on the stereochemistry of the reaction of diphenylzinc with benzenediazonium fluoborate. A series of reactions was carried out by the precedure (a) given above for the preparation of *trans*-azo compounds in dimethylformamide except that varying amounts of diphenylmercury were added. After 15 min. at 0° 2-ml. aliquots were withdrawn and diluted with absolute ethanol. Ultraviolet spectra were obtained immediately and analyzed by the method of Dewar and Urch[9] as described above.[20]

An attempt was made to isolate *cis*-I from the reaction mixture in which the ultraviolet analysis indicated that it was present in a yield of 58%. Chromatography of the product on alumina gave with hexane as an eluent two large red bands. The first was shown by its infrared spectrum to be *trans*-I. The second, obtained from the column by elution with 5% methanol in ether, was contaminated with dimethylformamide and was not positively identified as *cis*-I.

The selective reaction of diphenylketene with *cis*-I but not with *trans*-I has been previously reported.[21] It was confirmed in the present study that 0.50 g. of *cis*-azobenzene in 50 ml. of dry pentane reacted rapidly with 1.0 g. of diphenylketene to give 0.65 g. (63%) of the adduct, 4-keto-1,2,3,3-tetraphenyldimethylene-1,2-diimine, m.p. 175–176°. Under the same conditions no adduct was obtained from *trans*-I and 98% of the starting *trans*-I could be recovered. In an early stage of this investigation addition of diphenylketene to a reaction mixture carried out as above gave a 5% yield (based on diazonium salt) of the *cis*-I adduct, m.p. 174.5–176°, but the reaction with diphenylketene was not employed with the reactions known from the ultraviolet spectra to contain large amounts of *cis*-I. It may be noted that care was taken throughout to avoid as much as possible exposure of the product mixtures to light which might have interconverted *cis*- and *trans*-I.

Treatment of trans-azobenzene with diphenylmercury. To a mixture of 10 ml. of xylene and 20 ml. of dimethylformamide was added 0.15 g. of *trans*-azobenzene and 5.33 g. of diphenylmercury and the solution stirred for 20 min. in the dark at 25°. The ultraviolet spectrum (after dilution with ethanol) showed the *trans*-azobenzene absorption with no curve broadening nor loss of intensity.

Stability of trans-I to diphenylzinc. To a solution of di-

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[15] R. P. Zelinski and W. A. Bonner, *J. Am. Chem. Soc.*, 71, 1792 (1949).

[16] E. Bamberger and R. Hubner, *Ber.*, 36, 4082 (1903).

[17] P. Jacobson and A. Loeb, *Ber.*, 36, 4082 (1903).

[18] G. S. Hartley, *J. Chem. Soc.*, 633 (1938).

[19] D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem.* and *Ind.*, 1205 (1958).

[20] In the following table x_c and x_t are the concentrations of *cis*- and *trans*-I to be determined (x_1 and x_2 in the paper of Dewar and Urch) and c_C and c_t are the concentrations of the standard solution (c_c and c_2 in the reference cited). The slope, x_t/c_t and intercept, x_c/c_c and their probable errors were determined by the method of least squares (L. P. Hammett, *Introduction to the Study of Physical Chemistry*, McGraw-Hill, New York, 1952, p. 410).

[21] A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 184 (1941).

Moles of Diphenyl-zinc	Moles of Diphenyl-mercury	$x_t/c_t \times 10^2$	$x_c/c_c \times 10^2$	Yield trans-I, %	Yield cis-I, %
0.03[a]	—	63.0 ± 0.1	-1.2 ± 0.4	71.7	0
0.03[b, c]	0.03	104.8 ± 0.1	9.92 ± 0.6	59.6	16.5
0.03[c, d]	0.03	83.0 ± 0.1	10.5 ± 0.6	47.3	17.4
0.015[b, e]	0.075	55.8 ± 0.2	70.1 ± 1.2	15.8	58.1
0.026[a, f]	0.130	77.0 ± 0.2	-4.9 ± 0.9	87.5	0

[a] Diluted 1:1000. [b] Diphenylmercury was added to diphenylzinc in dimethylformamide and then the diazonium salt in dimethylformamide was added. [c] Diluted 1:500. [d] Diphenylmercury was added to the diazonium salt in dimethylformamide and then diphenylzinc added. [e] Diluted 1:250. [f] Carried out as a heteroegenous reaction in diethyl ether.

phenylmercury from 7.82 g. of diphenylmercury and 10.1 g. of zinc in 75 ml. of xylene and 200 ml. of dry dimethylformamide cooled to 0° was added 2.00 g. of *trans*-I and the reaction mixture stirred for 4 hr. Steam distillation and chromatography gave 1.85 g. of azobenzene, m.p. 67.5–70.5°, or 93% recovery. The infrared spectrum was identical with that of the starting material.

Stability of trans-I to benzenediazonium fluoborate. To 3.84 g. of benzenediazonium fluoborate in 75 ml. of xylene and 200 ml. of dimethylformamide at 0° was added 2.00 g. of *trans*-I. Examination of the ultraviolet initially and after 17 hr. at 0° showed no change in the concentration of azobenzene during that period. A further period of 6 hr. at room temperature during which time the diazonium salt underwent extensive decomposition also showed no loss of azo absorption.

Reaction of benzenediazonium fluoborate with phenylmagnesium bromide. To 100 ml. of dimethylformamide at 0° containing 1.34 g. of benzenediazonium fluoborate was added the Grignard reagent prepared from 2.20 g. of bromobenzene and 0.39 g. of magnesium turnings in 50 ml. of ether (filtered under nitrogen pressure). After 15 min. at 0° the mixture was acidified and steam distilled to yield only a few milligrams of red oil. Steam distillation of 3.0 g. of azobenzene in 100 ml. of dimethylformamide after acidification showed that 2.95 g. (98%) could be recovered.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

Ketone Synthesis by the Grignard Reaction with Acid Chlorides in Presence of Ferric Chloride

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A detailed analysis has been made, by use of gas chromatography, of the products of the reaction between a Grignard reagent and an acid chloride, in presence of ferric chloride. Under the most favorable conditions, there may be obtained yields of about 75% for a simple ketone and of about 50% for a δ-keto ester. Use of an ether-toluene solvent avoids the unworkable masses frequently encountered at −60° when ether alone is used as solvent. Yields in the reaction are lowered by two-fold or more if too dilute solutions are used. Yields are similarly lowered by presence of an ester group intermolecularly or intramolecularly. Yields of δ-keto esters are improved by use of larger amounts of ferric chloride and an excess of Grignard reagent. The data indicate that numerous complexes are formed, some of them irreversibly at −60°, between the reactants and the solvents for the reaction. In addition, ferric chloride forms a stable complex with five moles of capryl chloride.

Subsequent to the report[2] that use of a copper vessel leads to improved yields of ketones from the reaction of a Grignard reagent with an acid chloride, it was determined[3] that cuprous chloride is an effective catalyst for this synthesis. A later investigation[4] of the catalytic effects of various Lewis acids demonstrated that ferric chloride is the most effective of the several metallic halides that were tested. It was also learned that yields are improved, in the case of an unhindered ketone, by lowering the temperature. At −65° with ferric chloride catalyst, 2-hexanone was obtained in yields of 70–75%.

Two groups of investigators[4,5] who have proposed explanations of the remarkable catalytic effect of ferric chloride have suggested that the ferric chloride forms a coordination complex with oxygen in the acid chloride, and thus polarizes and activates the carbonyl group. It was later suggested[6] that any intermediate involving coordination of the ferric chloride with oxygen is inconsistent with the observed fact that ferric chloride specifically catalyzes the Grignard reaction with an acid chloride in great preference to other carbonyl groups. It was further suggested that the

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(2) C. J. Stehman, N. C. Cook, and F. C. Whitmore, *J. Am. Chem. Soc.*, **71**, 1509 (1949).

(3) N. C. Cook and W. C. Percival, *J. Am. Chem. Soc.*, **71**, 4141 (1949).

(4) W. C. Percival, R. B. Wagner, and N. C. Cook, *J. Am. Chem. Soc.*, **75**, 3731 (1953).

(5) R. T. Morrison and M. Wishman, *J. Am. Chem. Soc.*, **76**, 1059 (1954).

(6) J. Cason and E. J. Reist, *J. Org. Chem.*, **23**, 1668 (1958).