usual workup 2.95 g. (67%) of yellow acid, m.p. 247–250°, was obtained. Recrystallization from aqueous alcohol yielded (61%) of pale yellow 1-carboxybenzo[c]phenanthrene, m.p. 249.5–251.5°. From the neutral portion of the reaction products there was obtained 0.48 g. of benzo[c]phenanthrene.

Oxidation of methylbenzo[c]phenanthrenes. In a typical case, a mixture of 3.00 g. of 2-methylbenzo[c]phenanthrene, m.p. 79.6–81.0°, 5.50 g. of sodium dichromate dihydrate, and 100 ml. of water was enclosed in 450-ml. stainless steel bomb. The bomb was rocked and heated at 250° for 65 hr. On suitable workup of the contents 2.48 g. (74%) of yellow acid, m.p. 214–221°, and 0.56 g. (19%) of 2-methylbenzo-[c]phenanthrene, m.p. 78–80°, were obtained. Recrystallization of the crude acid from toluene afforded 2.15 g. (64%) of pale yellow 2-carboxybenzo[c]phenanthrene, m.p. 220–222°. 3-, 4-, 5-, and 6-methylbenzo[c]phenanthrene were oxidized similarly. These oxidations are remarkably clean as the crude reaction products are not deeply discolored and the recovery of pure acid and starting hydrocarbon is in the 85–95% region in most runs. The yields and properties of the acids are listed in Table I.

When the 1-methyl isomer was treated similarly for 15 hr., 0.62 g. (31%) was recovered and 0.97 g. (46%) of 1,8,9-naphthanthr-10-one,[5] m.p. 240–242°. The mixed m.p. with an authentic sample was not depressed. We were unsuccessful in attempts to prepare a 2,4-dinitrophenylhydrazone or an oxime from this ketone. The 1-acid dissolved in concentrated sulfuric acid to produce a deep red color. On pouring this solution into water 1,8,9-naphthanthr-10-one was formed.

The methyl esters were prepared from 2-, 3-, 4-, 5-, and 6-carboxybenzo[c]phenanthrene by acid-catalyzed esterification. Since the rate of esterification of the 1-isomer was very slow this ester was prepared with diazomethane. The properties of the methyl esters are listed in Table I.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF G. D. SEARLE & CO.]

Tricyclic Naphthalenic Steroid Analogs

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1-Acetyl-3-(6-methoxy-2-naphthyl)cyclohexane (IV), 1-acetoxyacetyl-3-(6-methoxy-2-naphthyl)cyclohexane (VI), and 1-acetyl-3-(6-hydroxy-2-naphthyl)cyclohexane (VII) have been prepared from 3-(6-methoxy-2-naphthyl)cyclohexanone.

Recently in the steroid field a great deal of interest has been evidenced in modifications of the naturally occurring substances and also in the preparation of synthetic analogs bearing a formal structural relationship to the cortical hormones. In an attempt to delineate the limits within which steroid activity might be found as well as to keep the synthetic and stereo-chemical problems to a minimum, we have prepared a series of naphthyl substituted cyclohexane derivatives oxygenated in such positions as formally to resemble some steroid molecules lacking the complete elements of ring C.

The starting material for our syntheses, 3-(6-methoxy-2-naphthyl)cyclohexanone, has been described by Novello and Christy.[2] However, our preparation of the immediate precursor of this compound, 3 - (6 - methoxy - 2 - naphthyl) - 2 - cyclohexen-1-one (I), differed from that reported.[2] Thus, in a simpler and more direct synthesis, treatment of the ethyl ether of dihydroresorcinol[3] with 6 - methoxy - 2 - naphthylmagnesium bromide gave a 46% yield of I. Whether the Grignard reagent adds normally to the ketone followed by hydrolysis of the enol ether and dehydration to give I, or whether addition takes place in the conjugate 1,4-manner followed by elimination of the elements of ethanol is uncertain since the same product results in either case. The 3-(6-methoxy-2-naphthyl)cyclohexanone was converted to its cyanohydrin (II), which was dehydrated with pyridine and phosphorus oxychloride to give 1-cyano - 3 - (6 - methoxy - 2 - naphthyl)cyclohexene (III), probably as a mixture of double bond isomers. Reduction in the presence of palladium-on-carbon, followed by treatment with methylmagnesium bromide and subsequent hydrolysis of the intermediate imine gave 1-acetyl-3-(6-methoxy-2-naphthyl)cyclohexane (IV), obtained in 57% over-all yield from the starting ketone. Compound IV existed in two polymorphic forms, but apparently was a pure racemate, and is therefore thought to be the *cis* isomer (the most stable form, with both substituents on the cyclohexane ring in equatorial positions).

Demethylation of IV with pyridine hydrochloride gave a 52–58% yield of 1-acetyl-3-(6-hydroxy-2-naphthyl) cyclohexane (VII), obtained as a mixture of racemates.

1 - Hydroxy - 3 - (6 - methoxy - 2 - naphthyl)-1-cyclohexanecarboxylic acid (V) was considered to be a likely intermediate for the preparation of analogs containing the "dihydroxyacetone" side chain of cortisone. Accordingly the cyanohydrin II was hydrolyzed with hydrochloric acid to give V, but the yield was so poor that this route was abandoned.

Compound IV was allowed to react with ethyl oxalate in the presence of sodium methoxide and the sodium enolate of the condensation product was treated with iodine to yield crude 1-iodoacetyl-3-

(1) Vick Chemical Co., Greensboro, N. C.

(2) F. C. Novello and M. E. Christy, *J. Am. Chem. Soc.*, **75**, 5431 (1953).

(3) G. F. Woods and I. W. Tucker, *J. Am. Chem. Soc.*, **70**, 2174 (1948).

(6-methoxy-2-naphthyl)cyclohexane. Treatment with potassium acetate converted this to 1-acetoxyacetyl-3-(6-methoxy-2-naphthyl)cyclohexane (VI). The over-all yield on this conversion was very poor, but only one preparation of VI was carried out, and some improvement could undoubtedly be effected with further experimentation.

An extension of the method of preparing I led to the synthesis of two other compounds with added oxygen substitution in the D ring. Dihydropyrogallol[4] was converted to its diacetate by treatment with pyridine and acetyl chloride. Depending on which tautomeric form of dihydropyrogallol was acetylated, the product would be 2,3-diacetoxy-2-cyclohexen-1-one (VIII), 2,6-diacetoxy-2-cyclohexen-1-one (XII) or a mixture of these compounds. The product actually obtained was evidently largely VIII for treatment with 6-methoxy-2-naphthylmagnesium bromide gave 2-acetoxy-3-(6-methoxy-2-naphthyl)-2-cyclohexen-1-one (IX), rather than either 3-acetoxy-2-(6-methoxy-2-naphthyl)-2-cyclohexen-1-one, or 2,6-diacetoxy-3-(6-methoxy-2-naphthyl)-cyclohexanone, which would have been expected to be formed from XII. Compound IX could be hydrolyzed with methanolic hydrogen chloride to yield 80% of 2-hydroxy-3-(6-methoxy-2-naphthyl)-2-cyclohexen-1-one (X). The structure of X was proved by permanganate oxidation to ω-(6-methoxy-2-naphthoyl)butyric acid, rather than 6-methoxy-2-naphthoic acid, which would have been expected as an oxidation product of the isomeric 3-hydroxy-2-(6-methoxy-2-naphthyl)-2-cyclohexen-1-one. An authentic sample of XI was prepared from glutaric anhydride and 2-methoxynaphthalene by treatment with aluminum chloride in nitrobenzene.

We are greatly indebted to our colleagues of the Division of Biological Research who assayed compounds I, IV, V, VI, VII, IX, and X for anti-flammatory, mineralocorticoid, and glucocorticoid activity. Whereas some anti-inflammatory activity was observed in these compounds, the order of activity was generally low, suggesting much greater structural dependence than is characteristic, for example, of estrogenic activity which remains substantial throughout a wide spectrum of molecular alterations.

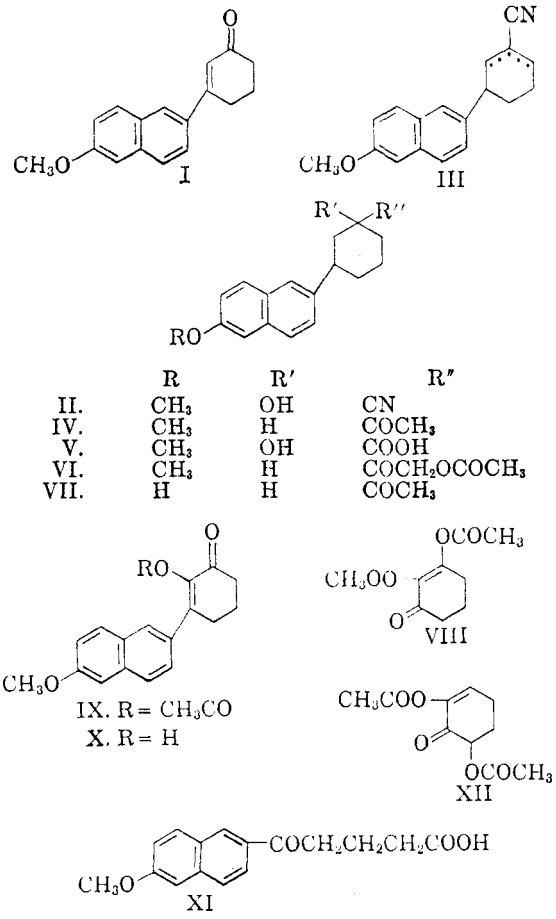
EXPERIMENTAL[5]

3-(6-Methoxy-2-naphthyl)-2-cyclohexen-1-one (I)[2]. A crystal of iodine and 0.8 g. of ethyl iodide in 10 ml. of dry ether was added to 15.3 g. of magnesium turnings, under an atmosphere of nitrogen. As the mixture was stirred, reaction commenced, and a solution of 147 g. of 2-bromo-6-methoxynaphthalene in a mixture of 600 ml. of dry ether and 350 ml. of dry benzene was added. Total addition took 1 hr., during which time the mixture was heated at reflux temperature. A subsequent 46 hr. of refluxing completed the preparation of the Grignard reagent. Then a solution of 57 g. of dihydroresorcinol ethyl ether[3] in 250 ml. of dry ether was added, and after addition was complete, the solution was heated at reflux temperature for 2 hr. Then a mixture of 100 ml. of sulfuric acid and 400 ml. of water was added cautiously. The solvents were removed by steam distillation. Water was decanted from the tarry residue, which was then dissolved in a mixture of ether and benzene and washed several times with water. The solvents were removed by distillation and the residue was vacuum dried to give about 100 g. of crude product. A small portion of this material was subjected to a short path distillation at 0.5 mm. and 260°. The most volatile distillate had m.p. 67–70°, and probably is 2-methoxynaphthalene. The remaining distillate was digested with boiling methanol, filtered, and cooled. The precipitate was collected by filtration and crystallized twice more from a mixture of benzene and hexane to give pure 3-(6-methoxy-2-naphthyl)-2-cyclohexen-1-one (I), m.p. 140.6–141.6°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39; Found: C, 80.72; H, 6.39.

The bulk of the crude product was chromatographed on 100 times its weight of silica gel. The column was developed with benzene and eluted with mixtures of benzene and ethyl acetate. The desired product, I, 48 g. (46%), was obtained by elution with 95% benzene–5% ethyl acetate. About 6 g. of a reduction product, 3-(6-methoxy-2-naphthyl)cyclohexanone,[2] m.p. 119.6–121.6°, was also obtained by elution with 98% benzene–2% ethyl acetate.

1-Cyano-1-hydroxy-3-(6-methoxy-2-naphthyl)cyclohexane (II). A mixture of 0.96 g. of 3-(6-methoxy-2-naphthyl)cyclohexanone,[2] 3.0 g. of potassium cyanide, and 15 ml. of ethanol was heated at reflux temperature as 3.0 ml. of glacial acetic acid was added dropwise. Refluxing was continued for 0.5



(4) B. Pecherer, L. M. Jampolsky, and H. M. Wuest, *J. Am. Chem. Soc.*, **70**, 2587 (1948).

(5) Melting points are uncorrected. Analyses were performed by Dr. R. T. Dillon and associates.

hr. at which time an additional 0.5 ml. of acetic acid was added and the hot solution was poured into a large volume of ice and water. The resulting mixture was extracted with ether, the organic layer was washed with water, and the ether was removed by distillation. The residue was crystallized twice from a mixture of benzene and hexane to give 1-cyano-1-hydroxy-3-(6-methoxy-2-naphthyl)cyclohexane (II) as a mixture of racemates, m.p. 113–134°.

Anal. Calcd. for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81. Found: C, 76.78; H, 6.79.

1-Cyano-3-(6-methoxy-2-naphthyl)cyclohexene (III). A solution of 1.07 g. of II in 15 ml. of pyridine was treated with 2.0 g. of phosphorus oxychloride and then heated at reflux temperature for 0.5 hr. The hot reaction mixture was cautiously poured into a beaker of chipped ice and 20 ml. of hydrochloric acid, and the product was extracted with ether. The organic layer was washed with water, filtered through anhydrous sodium sulfate, and the ether removed by distillation. The residue was crystallized from *n*-hexane and then recrystallized three times from methanol to give 1-cyano-3-(6-methoxy-2-naphthyl)cyclohexene (III) as a mixture of isomers, m.p. 102–110°.

Anal. Calcd. for $C_{18}H_{17}NO$: C, 82.09; H, 6.51. Found: C, 82.05; H, 6.38.

1-Acetyl-3-(6-methoxy-2-naphthyl)cyclohexane (IV). Hydrogenation of a solution of 0.95 g. of III in 30 ml. of ethanol in the presence of 0.1 g. of potassium hydroxide and 2.0 g. of 5% palladium-on-carbon was complete in 6 hr. The reduction mixture was neutralized with hydrochloric acid, filtered to remove the catalyst, and the filtrate was evaporated under nitrogen. The residue was chromatographed on 40 times its weight of silica gel. The column was developed and eluted with mixtures of benzene and *n*-hexane. Elution with 80% benzene-20% hexane gave fairly pure 1-cyano-3-(6-methoxy-2-naphthyl)cyclohexane, m.p. 102–106°. A solution of 0.27 g. of this material in 20 ml. of dry benzene was added to a solution of 1.0 g. of methylmagnesium bromide in 10 ml. of benzene. After the resulting solution had been heated at reflux temperature for 3 hr., a mixture of 10 ml. of hydrochloric acid and 20 ml. of water was added. Brief heating was required to hydrolyze the magnesium salt of the intermediate imine. The organic layer was separated and the aqueous portion extracted with ether. The combined organic layers were washed with water and evaporated under nitrogen. The residue was crystallized from hexane to give pure 1-acetyl-3-(6-methoxy-2-naphthyl)cyclohexane (IV). This compound was obtained in two polymorphic forms, m.p. 72.4–73.4°, and m.p. 83.0–83.6°, mixed m.p. 83.0–84.0°. The infrared spectra of these two forms were identical when taken in chloroform solution, but were somewhat different when obtained from a pressed potassium bromide disc.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found: C, 80.61; H, 7.89.

A subsequent preparation of IV from 7.7 g. of 3-(6-methoxy-2-naphthyl)cyclohexanone without purification of any of the intermediate products gave 5.1 g. (57%) of pure material, which was isolated by chromatographing on 700 g. of silica gel and eluting with 98% benzene–2% ethyl acetate. An earlier fraction eluted with 100% benzene gave also 1.3 g. of colorless crystals, m.p. 75–79.5°. This substance is believed to be 3-(6-methoxy-2-naphthyl)-1-methylcyclohexene, a mixture of isomers derived from 3-(6-methoxy-2-naphthyl)cyclohexanone which had not formed a cyanohydrin but did react with methyl magnesium bromide, and was subsequently dehydrated.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.74; H, 8.08.

1-Hydroxy-3-(6-methoxy-2-naphthyl)-1-cyclohexanecarboxylic acid (V). A mixture of 2.0 g. of crude II and 20 ml. of hydrochloric acid was heated in a pressure bottle at 100° for 15 hr., then cooled and made basic with potassium hydroxide. This mixture was washed with ether and then acidified with hydrochloric acid. The product was isolated by extraction with ether, washing the extracts with water, and removal of the ether by distillation. The residue was chromatographed on 30 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, followed by crystallization from benzene and sublimation at 0.5 mm. and 180° gave pure 1-hydroxy-3-(6-methoxy-2-naphthyl)-1-cyclohexanecarboxylic acid (V), m.p. 188.6–190.4°.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.89; H, 6.71. Found: C, 72.00; H, 6.66.

1-Acetoxyacetyl-3-(6-methoxy-2-naphthyl)cyclohexane (VI). A solution of 6.0 ml. of redistilled ethyl oxalate in 100 ml. of dry ether was added under a nitrogen atmosphere to 1.4 g. of sodium methoxide, followed by the rapid addition of a solution of 4.6 g. of crude IV in 400 ml. of dry ether and 150 ml. of benzene. The mixture was stirred and heated at reflux temperature for 4 hr., then was cooled and the sodium enolate of the condensation product was collected by filtration, rinsed with ether, and dried. This product, 3.5 g., was dissolved in 80 ml. of methanol and then under a nitrogen atmosphere at −15° was treated with a solution of 2.2 g. of iodine in 100 ml. of methanol. After 0.5 hr. at −15°, a solution of 0.23 g. of sodium in 10 ml. of methanol was added and the mixture was allowed to stand at room temperature for 0.5 hr. It was then filtered and the filtrate was poured into a large volume of water. The gummy precipitate of crude 1-iodoacetyl-3-(6-methoxy-2-naphthyl)cyclohexane was collected by filtration. This material was rinsed off the filter with acetone and was heated at reflux temperature for 5 hr. in a mixture of 6.1 ml. of acetic acid, 10.5 g. of potassium acetate, 125 ml. of water, and 500 ml. of acetone. After concentration to about 150 ml., this solution was poured into a large volume of water, extracted with ether, the organic layer was washed with water, and the ether was removed by distillation. The residue was subjected to a short path distillation at 0.5 mm. and 250° and the distillate was then chromatographed on 80 times its weight of silica gel. The column was developed with 60% benzene–40% hexane and eluted with mixtures of hexane, benzene and ethyl acetate. Elution with 98% benzene–2% ethyl acetate, followed by crystallization from methanol, sublimation at 0.5 mm. and 200°, and then two recrystallizations from methanol yielded pure 1-acetoxyacetyl-3-(6-methoxy-2-naphthyl)cyclohexane (VI), m.p. 130–131°.

Anal. Calcd. for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.12; H, 7.15.

1-Acetyl-3-(6-hydroxy-2-naphthyl)cyclohexane (VII). A mixture of 20 g. of purified pyridine hydrochloride and 2.0 g. of IV was heated at reflux temperature for 0.5 hr. The hot solution was poured over cracked ice and the product was isolated by extraction with ether, washing with water, and removing the ether by distillation. The residue was chromatographed on 100 times its weight of silica gel. The column was developed with benzene and eluted with mixtures of benzene and ethyl acetate. Elution with 95% benzene–5% ethyl acetate, followed by crystallization from ether gave 0.78 g. of 1-acetyl-3-(6-hydroxy-2-naphthyl)-cyclohexane (VII) as a mixture of racemates, m.p. 129–144°. An additional 0.21 g. (52% total yield), m.p. 128–141°, was obtained from the mother liquors by a short path distillation at 0.2 mm. and 210° followed by crystallization from ether. Another preparation of VII gave a 58% yield of material with m.p. 132–160°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.57; H, 7.51. Found: C, 80.68; H, 7.47.

2,3-Diacetoxy-2-cyclohexen-1-one (VIII). A solution of 16.3 g. of dihydropyrogallol[4] in 300 ml. of benzene and 23.7 g. of pyridine was treated dropwise with 23.6 g. of acetyl chloride. The reaction mixture was stirred at room temperature for 18 hr., after which the precipitated pyridine hydrochloride was removed by filtration and rinsed with ether. The combined filtrates were washed quickly with cold water, filtered through anhydrous sodium sulfate, and distilled

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

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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,[3] 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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(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)].