Registry No.—*cis*-1,1-Dimethyl-1-hydroxy-3-pentene 19639-96-4; *trans*-1,1-dimethyl-1-hydroxy-3-pentene, 19639-97-5; 5-hydroxypentene-1, 821-09-0.

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Aluminum Chloride Catalyzed Arylation of Ferrocene with Hydrazines

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The phenylation of aromatic hydrocarbons with diazonium salts proceeds by electrophilic substitution in the case of haloborates,[1] or radical substitution in the case of chlorides.[1,2] In the latter instance, the presence of aluminum chloride changes the character of the reaction to that of electrophilic substitution,[3] and it would appear that, in common with the former, phenyl cation ($C_6H_5^+$) is generated *via* loss of molecular nitrogen by an SN1 mechanism.

We report a new arylation process in which nitrogen is displaced from the aromatic ring very likely by a concerted displacement mechanism in aluminum chloride catalyzed reactions of arylhydrazines with ferrocene. This appears at the same time to be not only the first indisputable example of the arylation of ferrocene by an ionic mechanism, but also the first arylation of the neutral species.

Beckwith and Leydon[4] have convincingly demonstrated that arylation of ferrocene with diazonium salts (and N-nitrosoacetanilide) proceeds by free-radical attack on ferricinium ion,[5] rather than ionic substitution of the neutral species.[6] Thus

$$\text{FcH} + \text{ArN}_2^+ \longrightarrow \text{FcH}^+ + \text{ArN}_2\cdot$$

$$\text{ArN}_2\cdot \longrightarrow \text{Ar}\cdot + \text{N}_2$$

$$\text{FcH}^+ + \text{Ar}\cdot \longrightarrow [\text{FcArH}]^+ \longrightarrow \text{FcAr} + \text{H}^+$$

This mechanism, besides explaining why ferrocene (FcH) is unaffected by radicals or aryldiazonium salts under experimental conditions precluding the formation of ferricinium ion, explains why diazonium salts do not react with ferricinium ion in the absence of free ferrocene.

We have verified that in contrast to the behavior of aromatic hydrocarbons,[1] ferrocene reacts with *o*-tolyldiazonium fluoroborate[7] by radical rather than electrophilic substitution. Complete inhibition was obtained when the reaction was conducted in the presence of an excess of powdered zinc to preclude the formation of ferricinium ion.

In the present work (Table I), *o*- and *p*-tolyl-, *p*-bromophenyl-, and *α*-naphthylferrocenes were obtained as sole monoarylated products of the reactions of the corresponding hydrazines in *n*-heptane, establishing the ring carbon atom formerly connected to hydrazine nitrogen as the point of attachment of the ferrocene moiety. A reaction with zinc present to reduce any ferricinium ion formed, but otherwise identical with that producing phenylferrocene in 34% yield (Table I), gave the product in 29% yield. This served to establish that attack of aryl radical on ferricinium ion, generated as follows, is not part of the reaction mechanism.[8]

$$\text{FcH} + \overset{\delta+}{\text{ArNHNH}_2}\cdot\overset{\delta-}{\text{AlCl}_3} \longrightarrow \text{FcH}^+ + \text{Ar}\cdot + \text{H}_2\text{NNHAlCl}_3^-$$

TABLE I

ARYLATION OF FERROCENE (FcH) WITH HYDRAZINES[a]

Ar in $ArNHNH_2$	Molar ratio, $FcH:ArNHNH_2:AlCl_3$	Product (yield, %[b])	Recovd FcH, %
C_6H_5	1:1:1	C_6H_5Fc (4)	77
C_6H_5	1:1:2	C_6H_5Fc (20)	66
C_6H_5	1:2:2	C_6H_5Fc (36)	56
C_6H_5	1:2:3	C_6H_5Fc (34)[c,d]	52
C_6H_5 (HCl)[e]	1:2:3	C_6H_5Fc (23)	54
o-$CH_3C_6H_4$	1:2:3	*o*-$CH_3C_6H_4Fc$ (14)	52
p-$CH_3C_6H_4$(HCl)[e]	1:2:3	*p*-$CH_3C_6H_4Fc$ (7)	33
p-BrC_6H_4	1:2:3	*p*-BrC_6H_4Fc (19)[f]	46
α-$C_{10}H_7$	1:2:3	*α*-$C_{10}H_7Fc$ (16)	60

[a] Solvent: *n*-heptane. [b] Based on starting ferrocene. [c] In the presence of powdered zinc, the yield was 29%. [d] 1,1′-Diphenylferrocene (<1%) was also obtained. A reaction in *n*-octane gave 2% of this compound besides 26% of C_6H_5Fc. [e] The hydrazine was employed as the hydrochloride. [f] Also isolated was 1,1′-bis(*p*-bromophenyl)ferrocene (1%).

The results are consistent with an ionic mechanism involving direct displacement by ferrocene on the benzene ring, with simultaneous removal of hydrazide ion by aluminum chloride. Thus

$$\text{FcH} + \overset{\delta+}{\text{ArNHNH}_2}\cdot\overset{\delta-}{\text{AlCl}_3} \longrightarrow [\text{FcArH}]^+[\text{H}_2\text{NNHAlCl}_3]^- \longrightarrow \text{FcAr} + \text{H}_2\text{NNHAlCl}_2 + \text{HCl (by-product)}$$

Alkylated ferrocenes were not produced in attempted reactions of methyl- or *t*-butylhydrazines, raising the interesting question of whether or not the attack of ferrocene on aryl may initially involve the ring π system of each.[9,10] The displacement of hydrazide ion from arylhydrazines may be grossly related to Friedel–

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(1) G. A. Olah and W. S. Tolgyesi, *J. Org. Chem.*, **26**, 2053 (1961), and references cited therein.

(2) The free-radical nature of the Gomberg-Bachman reaction, in which the arylating agent is a diazonium salt and base, is well recognized [C. Rüchardt and E. Merz, *Tetrahedron Letters*, 2431 (1964); E. L. Eliel, J. G. Saha, and S. Meyerson, *J. Org. Chem.*, **30**, 2451 (1965); G. Binsch and C. Rüchardt, *J. Amer. Chem. Soc.*, **88**, 173 (1966)], although perhaps not as well understood [G. R. Chalfont and M. J. Perkins, *ibid.*, **89**, 3054 (1967)].

(3) G. A. Olah in "Friedel–Crafts and Related Reactions," Vol. I, G. A. Olah, Ed., Interscience Publishers, London, 1963, pp 66, 67, and references therein.

(4) A. L. J. Beckwith and R. J. Leydon, *Tetrahedron*, **20**, 791 (1964).

(5) W. F. Little and A. K. Clark, *J. Org. Chem.*, **25**, 1979 (1960).

(6) M. Rosenblum, W. G. Howells, A. K. Banerjee, and C. Bennett, *J. Amer. Chem. Soc.*, **84**, 2726 (1962), concluding that ferrocene is relatively inert toward attack by free radicals, proposed that arylferrocenes are formed *via* intramolecular decomposition of a ferrocene–diazonium salt charge-transfer complex.

(7) W. F. Little, C. N. Reilley, J. D. Johnson, K. N. Lynn, and A. P. Sanders, *ibid.*, **86**, 1376 (1964).

(8) Ferricinium ion could not be detected on work-up of the reaction mixtures, except for trace amounts when the aluminum chloride was present in excess of the hydrazine. R. L. Schaaf and C. T. Lenk, *J. Org. Chem.*, **28**, 3238 (1963), have discussed the oxidation of ferrocene by aluminum chloride.

(9) Nucleophilic attack of ferrocene on silicon and germanium *via* the ring π system was suggested previously.[10]

(10) G. P. Sollott and W. R. Peterson, Jr., *J. Amer. Chem. Soc.*, **89**, 5054, 6783 (1967).

Crafts arylation giving biphenyls, which appears to involve the displacement of halide ion from halobenzenes.[11] The latter reaction occurs as a minor side reaction to aluminum halide induced isomerization of the halobenzenes.

p-Tolylferrocene, formed by the reaction of the hydrochloride of *p*-tolylhydrazine, very likely was obtained in reduced yield since the reaction of phenylhydrazine hydrochloride, as compared with the free hydrazine, gave a lower yield of phenylferrocene (Table I). No tolylferrocene was obtained from *m*-tolylhydrazine, and this is attributed to the greater basicity of the aromatic nucleus of the latter, relative to *o*- and *p*-tolylhydrazines, by anology with the basicities of *o*-, *m*-, and *p*-xylenes.[12] It is suggested that with *m*-tolylhydrazine, nucleophilic attack by ferrocene is thus precluded. *p*-Methoxyphenylhydrazine also gave a negative result possibly for a similar reason, but additionally there is opportunity for coordination of aluminum chloride at the methoxy group, which could interfere with the course of the arylation reaction.

The reaction of *p*-bromophenylhydrazine produced 1,1′-bis(*p*-bromophenyl)ferrocene in trace amount (1%) in addition to the expected monosubstituted product (Table I). Reactions of phenylhydrazine in *n*-heptane occasionally gave traces of 1,1′-diphenylferrocene (<1%); a reaction in *n*-octane gave 2% of the disubstituted product, with a somewhat reduced yield of phenylferrocene. While it was indicated that certain arylferrocenes may be sufficiently nucleophilic to enter into a displacement reaction with arylhydrazines, an attempted reaction of phenylferrocene with phenylhydrazine to produce 1,1′-diphenylferrocene was unsuccessful.

No phenylferrocene was produced when aniline was used in place of phenylhydrazine. This is explainable from the standpoint that phenylhydrazine, with two adjacent nitrogen atoms bearing unshared electron pairs, is a stronger nucleophile than aniline.[13] It is suggested that aluminum chloride coordinates hydrazine nitrogen more effectively than nitrogen of aniline, providing an entity of appropriate electrophilic character. Similarly, reduced nucleophilicity of nitrogen can be advanced as explanation for the negative results obtained in the case of such compounds as N-nitrosoaniline, *sym*- and *unsym*-diphenylhydrazines, benzoylhydrazine, 1,5-diphenylcarbazide, phenylhydrazine-*p*-sulfonic acid, and 4-nitro- and 2,4-dinitrophenylhydrazines. Some of these compounds, moreover, possess additional sites for the coordination of aluminum chloride. A reaction employing the phenylhydrazone of benzophenone gave phenylferrocene in small quantity (2%).

In passing, the attempted reaction of 1,5-diphenylcarbazide produced over 10% of 1,1′-(1,3-cyclopentylene)ferrocene, a heterobridged compound previously prepared[14] from ferrocene and aluminum chloride in benzene. When other hydrazines were employed, this compound was not isolated except occasionally in trace amounts.

Although sufficiently nucleophilic benzenoid aromatic substrates could be expected to undergo arylation in the same manner as ferrocene, attempted reactions of such compounds as mesitylene, anisole, and 1,3-dimethoxybenzene with aluminum chloride complexed phenylhydrazine failed, as did benzene itself, to give the expected biphenyls.

With benzene as solvent, a reaction of ferrocene with phenylhydrazine gave phenylferrocene in sharply reduced yield compared to the reaction run in *n*-heptane. Substitution of aluminum bromide for the chloride in a reaction performed in *n*-heptane caused a substantial increase in yield, but an appreciable decrease was obtained when the bromide was present in molar excess of the hydrazine. No such decrease was observed when aluminum chloride was employed in molar excess of phenylhydrazine. In the latter case, doubling the reflux time failed to cause an increase in yield, while shortening the reflux time by more than half, produced only a slight decrease in yield.

Beckwith and Leydon[15] have recently reported that oxidation of a mixture of ferrocene and arylhydrazine with silver oxide or benzoquinone produces arylated ferrocenes. The mechanism of this reaction appears to involve free-radical substitution of ferricinium ion,[15] and is, therefore, essentially different from the mechanism of the process reported here.

Experimental Section

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected.

p-Methoxyphenylhydrazine was prepared by reduction of the diazonium salt obtained from *p*-anisidine. *t*-Butylhydrazine hydrochloride was prepared from hydrazine and *t*-butyl chloride.[16] The phenylhydrazone of benzophenone was prepared by standard procedure. All other hydrazines and derivatives were available commercially. *o*- and *m*-tolyl-, α-naphthyl-, and *t*-butylhydrazines were liberated from the hydrochlorides by treatment with aqueous alkali, then extracted with ether and distilled or crystallized.

Reactions of Ferrocene with Arylhydrazines. General Method.—In the molar ratios indicated in Table I, ferrocene (0.1 mole), anhydrous aluminum chloride, and the arylhydrazine (or hydrochloride), the last added dropwise or in small quantities over 10 min, were refluxed 20 hr in *n*-heptane (300 ml) under nitrogen. After evaporation of the solvent from the heptane phase, the residue was combined with the heptane-insoluble reaction solids, and the aggregate was hydrolyzed with water cautiously with cooling. The solids were collected by suction filtration, air-dried, and extracted by refluxing in *n*-heptane. The insoluble solids were discarded, and the filtered extract was chromatographed on a 70-cm column of activated alumina (80–200 mesh). Elution with *n*-heptane afforded unchanged ferrocene. [Continued elution with heptane removed any 1,1′-(1,3-cyclopentylene)ferrocene occasionally present in trace amount; *cf.* the attempted reaction of ferrocene with 1,5-diphenylcarbazide, below.] Elution next with benzene–heptane (1:2 by volume) produced the monoarylated ferrocene. Any 1,1′-diarylated ferrocene was eluted last with benzene. The arylated products were crystallized several times from petroleum ether (30–60°).[17]

Products.—Yields and recovered ferrocene are given in Table I. The products gave satisfactory elemental analyses and were identified as phenylferrocene, mp 110–111° (lit.[7] 110–111°); 1,1′-diphenylferrocene, mp 151–152° (lit.[18] 154°); *o*-tolylferrocene, mp 52.5–53° (lit.[7] 50–52°); *p*-tolylferrocene, mp 136–137° (lit.[7] 140–142°); α-naphthylferrocene, mp 100–101.5°[17] (lit.[16]

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[11] G. A. Olah and M. W. Meyer, *J. Org. Chem.*, **27**, 3464 (1962), and references therein.

[12] H. C. Brown and J. D. Brady, *J. Amer. Chem. Soc.*, **74**, 3570 (1952).

[13] P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. II, W. A. Benjamin, Inc., New York, N. Y., 1966, p 120.

[14] S. G. Cottis and H. Rosenberg, *Chem. Ind.* (London), 860 (1963).

[15] A. L. J. Beckwith and R. J. Leydon, *Australian J. Chem.*, **19**, 1381 (1966).

[16] O. Westphal, *Ber.*, **74B**, 759 (1941).

[17] α-Naphthylferrocene was crystallized from benzene-ether and recrystallized first from ether, then from petroleum ether (30–60°).

[18] P. L. Pauson, *J. Amer. Chem. Soc.*, **76**, 2187 (1954).

96–97°);[19] *p*-bromophenylferrocene, mp 121.5–123° (lit.[7] 122–123°).

1,1′-Bis(*p*-bromophenyl)ferrocene had mp 195–196°; ν_{max}^{Nujol} 1110 and 1000 absent (no unsubstituted ferrocene ring), 860–800 (*para*-disubstituted benzene ring) obscured by a strong complex band at 819 cm^{-1} (ferrocene out-of-plane C–H bending). *Anal.* Calcd for $C_{22}H_{16}Br_2Fe$: C, 53.27; H, 3.25; Br, 32.22; Fe, 11.26. Found: C, 53.16; H, 3.26; Br, 32.26; Fe, 11.65.

Reactions under Modified Conditions.—Summarized in Table II are reactions of ferrocene (FcH), phenylhydrazine, and anhydrous aluminum chloride employed in the molar ratios indicated. The reactions were performed based on the general method above, except for the modification specified.

TABLE II

Molar ratio	Modification	% of phenylferrocene, 1,1′-diphenylferrocene, recovd FcH
1:2:3	Powdered Zn (1 g-atom) present	29, 0, 65
1:2:3	Solvent: *n*-octane	26, 2, 60
1:1:2	Solvent: benzene	4, 0, 74
1:1:2	40-hr reflux	19, 0, 56
1:1:2	6-hr reflux	18, 0, 76
1:1:1	$AlBr_3$ replaced $AlCl_3$	18, 0, 67
1:1:2	$AlBr_3$ replaced $AlCl_3$	12, 0, 30

Attempted Reactions of Ferrocene with Hydrazines and Other Compounds.—Procedures were similar to those of the general method above. The following reactants were refluxed in *n*-heptane with ferrocene (FcH) and anhydrous aluminum chloride in the molar ratios (FcH:reactant:$AlCl_3$) indicated, with negative results except in the case of benzophenone phenylhydrazone which yielded 2% of phenylferrocene: aniline (1:1:2), N-nitrosoaniline (1:1:2), *p*-methoxyphenylhydrazine (1:2:3), *sym*-diphenylhydrazine (1:2:3), *unsym*-diphenylhydrazine (1:2:3), benzoylhydrazine (1:1:2), phenylhydrazine-*p*-sulfonic acid (1:2:3), 4-nitrophenylhydrazine (1:2:3), 2,4-dinitrophenylhydrazine (1:1:2), benzophenone phenylhydrazone (1:1:2), methylhydrazine (1:2:3), *t*-butylhydrazine (1:2:3).

m-Tolylhydrazine (1:2:3) yielded 1.5 g of orange needles upon elution of the chromatographic column with benzene and crystallization from *n*-heptane, mp 295° dec, ν_{max}^{Nujol} 1106 and 1003 (unsubstituted ferrocene ring) and 761 cm^{-1} (aromatic C–H?). *Anal.* Calcd for $C_{17}H_{16}Fe$ (*m*-tolylferrocene): C, 73.93; H, 5.84; Fe, 20.22. Found: C, 70.21; H, 3.21; Fe, 27.14.

1,5-Diphenylcarbazide (1:1:2) yielded 14% of 1,1′-(1,3-cyclopentylene)ferrocene, mp 138–139° from 30–60° petroleum ether (lit.[14] 140°), undepressed by admixture with an authentic sample.[14]

Attempted Reaction of Phenylferrocene with Phenylhydrazine.—Phenylferrocene (0.1 mole), phenylhydrazine, and anhydrous aluminum chloride (molar ratio, 1:2:3) were refluxed in *n*-heptane employing procedures similar to those of the general method above. No 1,1′-diphenylferrocene was detected upon election of the chromatographic column as above.

Attempted Reactions of Benzenoid Aromatics with Phenylhydrazine.—Using procedures based on the general method above, mesitylene and 1,3-dimethoxybenzene were refluxed, in place of ferrocene, with phenylhydrazine and anhydrous aluminum chloride in a 1:2:2 molar ratio. Benzene and anisole were refluxed with phenylhydrazine (0.2 mole) and aluminum chloride (0.3 mole), using excess of the aromatic compound as solvent in place of *n*-heptane. No biphenyl derivative was detected upon elution of the chromatographic columns with solvents as above, or with chloroform or methanol.

Attempted Preparation of *o*-Tolylferrocene from *o*-Tolyldiazonium Fluoroborate in the Presence of Zinc.—The method was based on the published procedure[7] except that powdered zinc (1 g-atom) was added to the methylene chloride solution of ferrocene (0.1 mole) prior to addition of the dry diazonium fluoroborate (0.1 mole) over 1 hr with cooling (water bath). After stirring of the mixture 2 hr at room temperature, no *o*-tolylferrocene was detected *via* chromatography on alumina, and ferrocene was recovered nearly quantitatively.

Registry No.—Aluminum chloride, 7446700; ferrocene, 102545; 1,1′-bis(*p*-bromophenyl)ferrocene, 12155-929; *m*-tolylferrocene, 12344364.

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[19] α-Naphthylferrocene, mp 93–95°, and β-naphthylferrocene, mp 137–142°, have been reported by K. Schlögl and H. Egger, *Monatsh.*, **94**, 1054 (1963); *Chem. Abstr.*, **60**, 13269*h* (1964).

The Selectivity of Benzyne. A New Approach Using the Reaction of Benzyne with Ambident[1] Nucleophiles

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In an attempt to find the optimum conditions for the reaction of bromobenzene with potassium anilide we varied the solvent as well as the ratio of aniline to potassium anilide. The results are summarized in Table I. As expected, we observed the well-known[2] increase in yield as the amount of free amine in the reaction mixture was increased. Most remarkable, however, was the observation that a dramatic change in product *composition* takes place as the ratio of aniline/anilide is changed. In each of the three solvents examined there was at least a tenfold increase in the carbon to nitrogen phenylation ratio (C/N) when an excess of aniline was present in the reaction mixture.

In order to subject this interesting phenomenon to a more systematic and quantitative examination we needed a reaction system in which higher and more consistent yields could be obtained. Reaction in dimethyl sulfoxide at 25° provided such data. As can be seen in Table II, 4-aminobiphenyl was now found as a product, in addition to 2-aminobiphenyl, diphenylamine, and small amounts of triphenylamine.

Discussion

An interesting question concerning the reactivity of benzyne is the degree of its selectivity among various nucleophiles. For example, it has been reported[3] that 9,10-phenanthryne in ether solution reacts with equal speed with piperidine and with lithium piperidide. On the other hand, benzyne generated in ethanol by the decomposition of benzothiadiazole dioxide was found to react with LiCl, LiBr, and LiI at relative rates of 1:8:65.[4]

It appeared to us that our data enable us to obtain an estimate of the relative rates of the reaction of benzyne[5] with aniline and with potassium anilide by a

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(1) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Amer. Chem. Soc.*, **77**, 6269 (1955).

(2) R. Huisgen and J. Sauer, *Chem. Ber.*, **92**, 192 (1959).

(3) W. Mack and R. Huisgen, *ibid.*, **93**, 608 (1960).

(4) G. Wittig and R. W. Hoffman, *ibid.*, **95**, 2729 (1962).

(5) (a) J. D. Roberts and F. Scardiglia [*J. Org. Chem.*, **23**, 629 (1958)] have shown that this reaction goes by way of a benzyne intermediate. They found that bromobenzene and potassium anilide in aniline as solvent gave a 60% yield of diphenylamine. They did not wish to investigate possible primary amine products. Using their reaction conditions we obtained a 50% yield of diphenylamine and a 5% yield of 2-aminobiphenyl. (b) Further evidence that this type of reaction proceeds by way of a benzyne intermediate in dimethyl sulfoxide solution as well can be found in the work of D. J. Cram, B. Rickborn, and G. R. Knox, *J. Amer. Chem. Soc.*, **82**, 6412 (1960).