pies of activation for the reactions in methanol solution relative to other solvents.

In the light of the reactivity pattern displayed in methanol solution, the similar behavior of piperidine to that of ethyl acetate, as noted above, indicates that the former solvent is not sufficiently protic to promote any appreciable specific solvent–substrate interaction.

Since the reaction rates are different functions of the solvent depending on both the activating group and its position relative to the reaction site, the activating power of the nitro group relative to that of the aza group also depends on the solvent, as shown by the k_{NO_2}/k_{aza} ratios reported in Table II, which display variations of more than one order of magnitude. In particular, the lowest values were obtained for the reactions in methanol solution, where a major contribution to this effect comes from the greater H-bonding interaction observed with the N-heteroaromatic substrates. It is of interest to note that, on comparing the reactivity of the nitrobenzene with that of the pyridine series in methanol, the k_{NO_2}/k_{aza} ratio is greater at the ortho than at the para positions,[18] but the reverse is true for the corresponding fused-ring systems considered here.

Experimental Section

Materials.—2-Chloro-1-nitronaphthalene, mp 95.5–96.5° (lit.[16] mp 99°), and its 4-chloro-1-nitro isomer, mp 84.5–85.5° (lit.[19] mp 87°), were prepared from the appropriate nitronaphthylamines by the methods of Hodgson and Walker[20] and of Bassilios and Shawky,[21] respectively. The products expected from the reactions under kinetic investigation were prepared by refluxing the chloronitronaphthalenes in neat piperidine for about 2 hr: 4-nitro-1-piperidinonaphthalene, mp 75–76° (lit.[22] mp 76°), and 1-nitro-2-piperidinonaphthalene, mp 63.5–64° (red needles from methanol).

Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.3; H, 6.3; N, 10.9. Found: C, 70.5; H, 6.4; N, 11.0.

Dimethyl sulfoxide (Erba-RP) was purified by allowing it to percolate slowly in the dark through a 1-m column filled with molecular sieve "Bayer T10" (Schuchardt), water content *ca.* 30 ppm. Methanol,[23] piperidine,[24] toluene,[25] and ethyl acetate[26] were purified as in the given references.

Product Analyses.—The mixtures from the kinetic measurements were analyzed by tlc. Single spots were found except in the high-temperature reactions of 4-chloro-1-nitronaphthalene in toluene solution after 57% reaction at 140°, 62% at 150°, 69% at 160°, and 84% at 180°. No further investigation on the byproducts was made.

Kinetic Measurements.—The general procedure used has been described previously.[3,23,24] The reaction rates were followed by analyzing for the displaced chloride ion. Samples were quenched in 10 ml of 2 *N* nitric acid (3 *N* when piperidine was the solvent); sufficient acetone was added to dissolve any organic material; and the homogeneous solutions were titrated by the potentiometric method.[3,27] The rate constants were obtained graphically from second-order or pseudo-first-order plots. All the second-order rate constants were corrected for the thermal expansion of the solvent. Activation energies and entropies were calculated from the *k* values at four or five temperatures, using the least-squares method. Values of *k* are accurate to ±2.5% or better, energies of activation to ±0.4 kcal/mol, and values of $\Delta S^{\ddagger}$ to ±1 unit.

Registry No.—I, 4185-63-1; II, 612-62-4; III, 605-61-8; IV, 611-35-8; 1-nitro-2-piperidinonaphthalene, 7711-41-3.

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Reduction of Diazonium Fluoroborates in Dimethylformamide, Catalyzed by Rhodium Complexes

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Received June 19, 1970

I wish to report on a novel reduction of aromatic diazonium fluoroborates to arenes by DMF, a reaction which is catalyzed by $RhCl(CO)(PPh_3)_3$ (RCCP) and $RhCl(PPh_3)_3$ (RCTP) at room temperature and at 80°

$$ArN_2{}^+BF^{-}{}_4 \xrightarrow{\text{Rh complex, DMF}} ArH$$

Electron-attracting substituents appear to favor this reduction, whereas, in the one observed case of a strong electron-donating substituent (OMe), no reduced product was observed. Ortho substitution (NO_2, CO_2Et, Me) did not appear to affect significantly the yield of reduced product. In fact, in the case of the 2-methyl-4-nitrobenzenediazonium salt, the reduction competed successfully with the spontaneous cyclization to 6-nitroindazole.[1]

Addition of small amounts of water or formic acid to the DMF lowered the yields of the reduction products. Reduction was not observed in the absence of the Rh complex.

Only traces of fluorinated compounds were detected in the products by elemental analysis, vpc, or tlc, whether the reactions were carried out at room temperature or at 80°[2] (see Table I).

A few other solvents were tested, *viz.*, dimethylacetamide (DMA), acetonitrile, and, in one case, formamide. Only in formamide was the same reduction process observed. This points to the formyl hydrogen of DMF or formamide as the source of the hydrogen involved in the reduction.[3] An ir study of RCCP has shown that a hydrido–rhodium complex may be an intermediate in this reaction; a solution of RCCP in DMF develops, in addition to the C=O peak at 1970 cm^{-1},[4] a peak at 2100 cm^{-1}, which is transformed within 24 hr into a broad envelope with a maximum at 2150 cm^{-1}. On the other hand, a similar solution of RCCP in DMA showed only the initial peak at 1970

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[1] K. v. Auwers and E. Frese, *Ber.*, **58**, 1369 (1925).

[2] In experiments with the diazonium fluoroborate derived from ethyl-3-amino-2-naphthoate in DMF with RCCP for 2 days at room temperature, the product (30% yield) after work-up was a mixture of 17% 2-naphthoic acid and 13% 3-fluoro-2-naphthoic acid. This result agrees with a previous report from this laboratory [J. Blum, *Israel J. Chem.*, **4**, 158 (1966)] in which also *p*-tolyl- and 1-naphthyldiazonium fluoroborates reacted with RCTP in DMF to give *p*-fluorotoluene and 1-fluoronaphthalene. We are unable, at this time, to rationalize this divergence in results.

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TABLE I

CATALYTIC REDUCTION OF DIAZONIUM FLUOROBORATE, $ArN_2 \cdot BF_4$ (TO ArH)

Ar	Registry no.	Solvent[a]	Catalyst	Temp,[d] °C	% yield of ArH[b]
$2\text{-}NO_2 \cdot C_6H_4$	365-33-3	DMF	RCCP		43
$3\text{-}NO_2 \cdot C_6H_4$	586-36-7	DMF	RCCP		34
$4\text{-}NO_2 \cdot C_6H_4$	456-27-9	DMF	RCCP		50
$4\text{-}NO_2 \cdot C_6H_4$		DMF	RCTP		23
$4\text{-}NO_2 \cdot C_6H_4$		DMA	RCCP		0
$3\text{-}Cl \cdot C_6H_4$	14874-10-3	DMF	RCCP		75
$3\text{-}Cl \cdot C_6H_4$		DMF	RCTP		50
$3\text{-}Cl \cdot C_6H_4$		DMA	RCCP		0
$4\text{-}Cl \cdot C_6H_4$	673-41-6	DMF	RCCP		47
$2\text{-}CO_2Et \cdot C_6H_4$	28912-87-0	DMF	RCCP		54
$2\text{-}CO_2Et \cdot C_6H_4$		CH_3CN	RCCP		0
$4\text{-}CO_2Me \cdot C_6H_4$	369-48-2	DMF	RCCP		44
$4\text{-}CH_3 \cdot C_6H_4$	459-44-9	DMF	RCCP		10 }[c] + trace ArF
$4\text{-}CH_3 \cdot C_6H_4$		DMF	RCTP		7
$4\text{-}MeO \cdot C_6H_4$	18424-07-2	DMF	RCCP		10
$2\text{-}CH_3\text{-}, 4\text{-}NO_2 \cdot C_6H_4$	15278-77-0	DMF	RCCP		61
$2\text{-}CH_3\text{-}, 4\text{-}NO_2 \cdot C_6H_4$		Formamide	RCCP		23
$3\text{-}NO_2\text{-}, 4\text{-}Me \cdot C_6H_4$	28912-92-7	DMF	RCCP		42
$C_{10}H_7$	28912-93-8	DMF	RCCP		16
$C_{10}H_7$		DMF	RCCP	80	20
$C_{10}H_7$		CH_3CN	RCCP		0
$C_{10}H_7$		CH_3CN	RCCP	80	0
$C_{10}H_7$		DMF	RCTP		20
$C_{10}H_7$		DMF	RCTP	80	22
$C_{10}H_7$		CH_3CN	RCTP		0
$C_{10}H_7$		CH_3CN	RCTP	80	0

[a] All solvents were dried over CaH_2 and distilled. [b] Yields based on vpc or tlc and elemental analyses. [c] Only by vpc. [d] Room temperature unless otherwise specified.

cm^{-1} and no new peaks in the 2700–1800-cm^{-1} region. The hydrido-complex $RhH(CO)(PPh_3)_3$ in DMF has peaks at 2450 cm^{-1} (RhH) and 1970 cm^{-1} (C=O), with no new peaks appearing even after prolonged standing.

Experimental Section

A mixture of 2 mmol of ArN_2BF_4 and 0.12 mmol of RCCP or RCTP in 5 ml of dry solvent was left at room temperature for 2 days, or at 80° for 1 day. The reaction mixture was poured into water and extracted with benzene or ethyl acetate and the extract was washed with 3 *N* NaOH and water and dried over $MgSO_4$. The crude products were chromatographed on a short column of silica gel or alumina, after which they were checked by vpc or tlc and elemental analysis. The ir spectra were run on a Perkin-Elmer Model 137 NaCl spectrophotometer.

Registry No.—RCCP, 28912-94-9; RCTP, 14694-95-2.

Acknowledgment.—Sincere thanks are due to Professor E. D. Bergmann and to Dr. J. Blum for valuable discussion and to the Hebrew University for a postdoctoral research grant.