strongest electron donor cobaltocene. The specific type of complex formed, on the other hand, is apparently dependent upon the donor–acceptor combination in question. In no case, however, does simple charge transfer between the π-cyclopentadienyl ring and π-acceptor appear evident.

Experimental[7]

General Procedure.—The complexes were prepared by mixing dry benzene solutions of the purified components, in varying quantities, and filtering the immediately precipitated products. The products then were slurried with additional dry benzene, filtered, and dried *in vacuo* at 25°. All operations were conducted in a drybox under an atmosphere of dry argon.

1:2 Nickelocene–*p*-Chloroanil.—This complex was obtained in 76% yield based on the nickelocene used. It is a dark brown solid which exhibits no change to 350° under argon, is soluble in water and benzene, slightly soluble in acetonitrile, and appears stable in air (melting point unchanged after 3 days in air); λ_{max}^{Nujol} 3.20 (w), 7.10 (m) new, 8.9, 9.0 doublet (m) new, 10.0 (m), 11.2 (s), and 12.6 μ (m) new. The infrared bands at 6.05, 13.35, and 14.10 μ, due to *p*-chloroanil, and that at 13.0 μ, due to nickelocene, were absent. The ultraviolet spectrum was $\lambda_{max}^{CH_3CN}$ 236 mμ (log ε 3.98), 249 (3.93), 256 (3.97), 269 (3.98), 289 (3.89), 310 (3.73), and 449 (3.11) new. Employing a conventional X-band electron spin resonance spectrometer with a 12-in. Varian magnet, the solid product at 25° gave a very weak signal corresponding roughly to about 10^{-7} spins per formula weight (see below), and a *g* value of 2.0084 with an approximate line width of 13 gauss.

Anal. Calcd. for $[C_{10}H_{10}Ni]\ [C_6Cl_4O_2]_2$: C, 38.8; H, 1.47; Cl, 41.8; Ni, 8.63. Found: C, 39.3; H, 1.96; Cl, 41.5; Ni, 8.65.

Cobaltocene–*p*-Chloroanil (1:1 and 1:2 Complexes.).—Use of a 1:1 mole ratio of the reactants results in the immediate precipitation of an olive green solid in 92% yield, based on cobaltocene. It decomposes at 105–110° under argon to a yellow solid. The cobalt and chlorine results correspond to a 1:1 complex, while the carbon and hydrogen results are somewhat high.[8] The solid product gave an e.s.r. signal corresponding roughly to about 0.02–0.2 spins per formula weight and a *g* value of 2.0059 with approximate line width of 10 gauss.

Anal. Calcd. for $[C_{10}H_{10}Co]\ [C_6Cl_4O_2]$: C, 44.2; H, 2.32; Cl, 32.7; Co, 13.6. Found: C, 45.7: H, 3.18; Cl, 32.7; Co, 13.6.

Use of a 1:2 ratio of the reactants, with standing for an hour in the drybox, results in a dark green solid in 78% yield, based on the cobaltocene. It decomposes at 228° to a black liquid under argon, is slightly soluble in water with some decomposition (recovered solid decomposes at 238°), insoluble in benzene, slightly soluble in acetonitrile, and appears stable in air; λ_{max}^{Nujol} 3.29 (m), 6.52 (s), 6.77 (s) new, 7.12 (s) new, 8.83 (s) new, 9.32 (w), 9.94 (m) new, 10.17 (s) new, 11.08 (s) new, 11.39 (w), 11.62 (m) new, 14.00 (m), and 14.75 μ (s) new. The infrared bands at 6.05, 8.01, 8.17, 8.35 (triplet), 9.0–9.2, 13.35, and 14.10 μ, due to chloroanil, and the band at 12.95 μ, due to cobaltocene, were absent. The ultraviolet spectrum was $\lambda_{max}^{CH_3CN}$ 260 mμ (log ε 4.54), 289 (3.84), 320 (3.69), 421 (3.43) new, and 448 (3.58) new. The solid gave a very strong e.s.r. signal corresponding roughly to about one spin per formula weight and a *g* value of 2.0060 with an approximate line width of 11 gauss.

Anal. Calcd. for $[C_{10}H_{10}Co]\ [C_6Cl_4O_2]_2$: C, 38.8; H, 1.47; Cl, 41.8; Co, 8.6. Found: C, 39.0; H, 1.53; Cl, 41.3; Co, 9.0.

Cobaltocene–*sym*-trinitrobenzene was obtained in 95% yield. It is a brown solid, m.p. 125°, stable in air, slightly soluble in acetonitrile, and moderately soluble in water with apparent hydrolysis (recovered solid, m.p. 115°); λ_{max}^{Nujol} 3.28 (m), 6.29 (m) 6.60 (w), 8.20 (s) new, 9.65 (m) new, 10.0 (w), 11.60, 11.74 doublet (m) new, 12.93 (w), and 13.65 μ (w). The infrared absorption patterns in 6.5–7.5- and 13–16-μ regions were markedly different from those of *sym*-trinitrobenzene. The bands at 5.46 and 9.36 μ, due to *sym*-trinitrobenzene, were absent. The ultraviolet spectrum was $\lambda_{max}^{CH_3CN}$ 262 mμ (log ε 4.95) and 427 (3.61) new. The solid gave an e.s.r. signal corresponding roughly to about 0.05 spins per formula weight and a *g* value of 2.0051 with a line width of about 16 gauss.

Anal. Calcd. for $[C_{10}H_{10}Co]\ [C_6H_3N_3O_6]$: C, 47.7; H, 3.26; N, 10.4; Co, 14.7. Found: C, 47.3; H, 3.37; N, 10.2; Co, 14.3.

Ferrocene–*p*-Benzoquinone.—The resistivity of 1:1, 1:2, and 2:1 molar ratios was measured at 25–160° between copper electrodes under nitrogen. In every case, the 1:2 complex of ferrocene to *p*-benzoquinone showed a substantially lower resistance than the 1:1 and 2:1 mixtures at comparable temperatures. The 1:1 mixture exhibited a greater resistance than the 2:1 mixture at 120–125°. At all other temperatures, its resistance was also less than that of the 2:1 mixture. In all cases, the resistance was found to decrease in an essentially reversible manner with an increase in temperature. The 1:1 complex appears to form at about 105° and melts at 116–125°. Its resistivity at 120° is approximately 6.3 × 10^8 ohm-cm. All attempts to isolate a stable complex at 25° failed.

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[7] All melting points were determined in a sealed capillary tube under argon and are uncorrected.

[8] Possibly owing to some residual cobaltocene.

Ullmann Condensation

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Although the Ullmann condensation[1] has been used as a synthetic tool for over 50 years, its mechanism has received little attention. We recently undertook a mechanism study and herein report the results of the first phases of the work.[2]

A series of competitive reactions between a variety of unactivated aromatic halides were carried out with potassium phenoxide in diglyme solvent ($CH_3OCH_2CH_2OCH_2CH_2OCH_3$) catalyzed by copper salts. The product ratios were determined by gas chromatographic techniques. These ratios when corrected for statistical, analytical, and concentration errors were used to construct the relative rate sequence described in Table I. These results are essentially what one might expect from a nucleophilic aromatic substitution.[3,4]

The slight retardation due to a methyl substituent,[5] the activation due to substitution of an additional halo group,[5] and the slightly higher reactivity of the *meta* dihalo *vs.* the *para* dihalo compounds[6] appear to be typical of nucleophilic aromatic substitution. The same applies to the higher reactivity of the β- *vs.* α-naphthalenes.[7]

The halogen mobilities provide another interesting clue to the mechanism. They are in the order, I ~ Br > Cl >> F, and the differences are somewhat larger than those usually observed for nucleophilic

[1] The Ullmann condensation, the copper-catalyzed reaction between aromatic halides and alkali metal phenoxides or anilines to yield aryl ethers or arylamines, should be distinguished from the Ullmann coupling reaction used to form biaryls from aromatic halides [see A. R. Surrey, "Name Reactions in Organic Chemistry," Academic Press, New York, N. Y., 1954].

[2] A more detailed kinetic study will be reported later.

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TABLE I

RELATIVE RATES

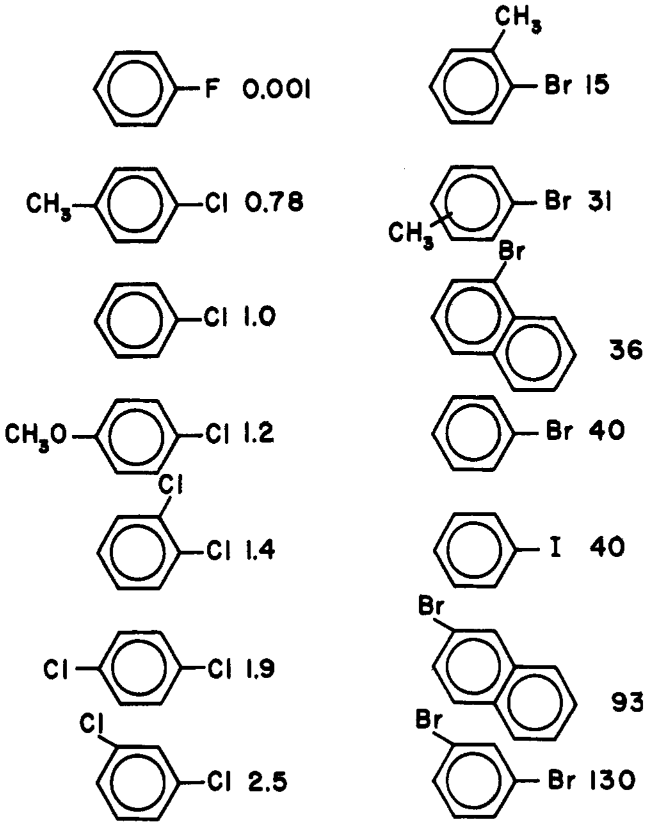

TABLE II

HALOGEN MOBILITIES[a]

Reaction type	I	Br	Cl	F
Ullmann condensation	40[b]	40	1	~10^{-3}
E2	190	41	1	
SN2	80	30 to 40	1	
SN1	100	25 to 60	1	~10^{-5}

[a] The data for E2, SN2, and SN1 reactions were obtained from C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 339. [b] More precise kinetic measurements show the I:Br ratio to be about 3.

aromatic substitution. We believe these results point to a rate-determining step involving carbon–halogen bond cleavage. Our data are summarized in Table II and are compared with similar data for reactions known to involve carbon–halogen bond cleavage in the rate step.

Experimental

Competitive Reactions.—In a flask equipped with a stirrer, condenser (fitted with azeotrope adapter), thermometer, and gas inlet were placed 0.025 mole of KOH, 0.05 mole of phenol, and 10 ml. of toluene. The mixture was heated under a small nitrogen flow at 100–115° until all of the water was removed. To this mixture was added 10 ml. of diglyme (practical grade[8]) and 0.1 mole each of the haloaromatics (usually two), followed by 0.1 g. of $CuCl_2$. The solution was then refluxed at 160° for 15 hr. The reaction mixture was poured into ice–water, extracted into CCl_4, dried, and the CCl_4 solution was used directly for gas chromatographic analysis.

The following runs were made and are reported with corrected product ratios: fluorobenzene *vs.* *p*-chlorotoluene 1:~1000, chlorobenzene *vs.* *p*-bromotoluene 1:31, iodobenzene *vs.* *p*-bromotoluene 1:0.77, chlorobenzene *vs.* *p*-chloroanisole 1:1.2, bromobenzene *vs.* *p*-bromotoluene 1:0.78, chlorobenzene *vs.* *p*-dichlorobenzene 1:1.9, bromobenzene *vs.* *m*-dibromobenzene 1:3.2, bromobenzene *vs.* α-bromonaphthalene 1:0.9, α-bromonaphthalene *vs.* β-bromonaphthalene 1:2.6, *o*, *m*-, and *p*-bromotoluene 1:2:2, *o*-, *m*-, and *p*-dichlorobenzene 1:1.7:1.3.

Gas Chromatographic Analysis.—The gas chromatographic analyses were performed on an F and M Model 1720 instrument equipped with a 1 m. × 0.25 in. column packed with Anakrom ABS (50–60 mesh) impregnated with 2% *m*-bis[*m*-(*m*-phenoxyphenoxy)phenoxy]benzene. The column temperature was programmed between 100 and 300°, the detector block containing a hot filament was kept at 285°, and the injection block was kept at 287°. The eluent was helium, the flow rate was 30 ml./min., and the pressure was maintained at 50 p.s.i.g.

An Ott compensating planimeter was used to measure peak areas, and standard mixtures were run concurrently to provide correction factors.

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[8] Matheson, Coleman and Bell.

The Facile Isomerization of 4-Methylene-2-oxazolidinones to 4-Methyl-4-oxazolin-2-ones

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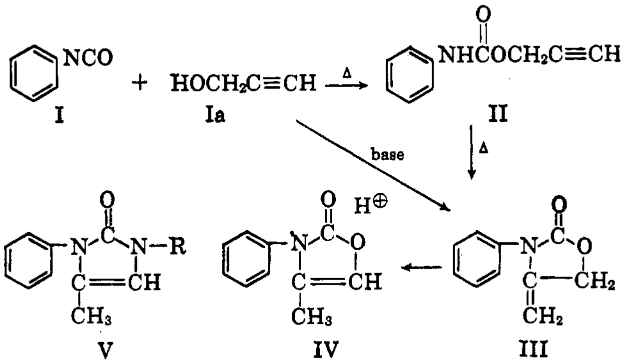
We have shown that heating propargyl alcohol with phenyl isocyanate to 65° gave the carbanilate (II). Furthermore, heating the same reactants or the preformed carbanilate (II) to 160° gave the cyclized 4-methylene-2-oxazolidinone[1] (III). Other investigators obtained III directly from I and Ia using catalytic amounts of pyridine,[2] sodium acetate,[3,4] potassium hydroxide,[5] and sodium methoxide.[6] This did not seem reasonable since we have shown that the treatment of propynylureas with strong acid or strong base gave the 4-methyl-imidazolin-2-one[7,8] (V) containing an endocyclic double bond in contrast to the exocyclic double bond of III. It was equally puzzling to note that Sisido, *et al.*,[5] obtained the endocyclic analog (IV) in the reaction of I and Ia with base, but a footnote states



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