prepared by reaction of the appropriate amine with isobutylene sulfide. Since these compounds are new to the literature and provide further examples of the isobutylene sulfide–amine reaction, the syntheses are described in the Experimental section.

## Experimental[8]

**1-Dimethylamino-2-propanethiol** (I). A. **Addition of Hydrogen Sulfide to Dimethylallylamine.**—A mixture of 325 g. (3.8 moles) of dimethylallylamine,[5] 450 g. (13.2 moles) of hydrogen sulfide, and 4 g. of sulfur was heated in an autoclave under autogenous pressure at 85° for 5 hr. Distillation of the reaction mixture under reduced pressure through a 2-ft. column packed with glass helices gave 80–85 g. (18%) of I, b.p. 55° at 47 mm., $n^{20}_{D}$ 1.4558. Analysis of this product by gas–liquid chromatography (Carbowax 20 on Teflon, programmed between 100° and 250°) indicated 100% purity.

B. **Reaction of Dimethylamine with Propylene Sulfide.**—This reaction, according to the procedure of Hansen,[4] gave a 47% yield of 1-dimethylamino-2-propanethiol, b.p. 70° at 88 mm., $n^{20}_{D}$ 1.4557; lit.[4] (as the other isomer) b.p. 71° at 88 mm., $n^{20}_{D}$ 1.4538. Treatment of the free base with hydrochloric acid, followed by recrystallization of the product from a mixture of 2-propanol and heptane, gave the amine hydrochloride, m.p. 166–167°, lit.[4] (as the other isomer) m.p. 167°.

*Anal.* Calcd. for $C_5H_{14}ClNS$: C, 38.57; H, 9.06; N, 9.00; S, 20.59. Found: C, 38.61; H, 9.17; N, 8.95; S (as mercaptan), 19.3.

**2-(Benzylthio)-1-methylethylamine.**—Propylenimine (1 mole, 57 g.) was added slowly to a stirred solution of 124 g. (1 mole) of benzyl mercaptan in 200 ml. of tetrahydrofuran at room temperature. A very slight temperature rise occurred. The solution was allowed to stand at room temperature for 2 days and then was heated under reflux for 3 hr. The volatile materials were removed by distillation from a steam bath, leaving 150 g. of a pale yellow oil. The latter was distilled *in vacuo* through a 15-in. Vigreux column, giving, after a small forecut of unchanged benzyl mercaptan , 100 g. (55%) of the desired amino sulfide, b.p. 78–80° at 0.2 mm., $n^{20}_{D}$ 1.5597.

*Anal.* Calcd. for $C_{10}H_{15}NS$: C, 66.24; H, 8.34; N, 7.73. Found: C, 66.2; H, 8.3; N, 7.3.

**2-(Benzylthio)-*N*,*N*,1-trimethylethylamine.**—A solution of 90 g. (0.5 mole) of 2-(benzylthio)-1-methylethylamine in 130 g. (2.5 moles) of 95% formic acid was prepared with cooling; to this was added 115 ml. (1.5 moles) of commercial 37% aqueous formaldehyde. The clear solution was heated on a steam bath until the evolution of carbon dioxide was vigorous (*ca.* 2–3 min.). The heat was removed until the reaction had subsided (*ca.* 10 min.), and then heating was resumed (steam bath) for 10 hr. After cooling, 80 ml. of 12 *N* hydrochloric acid was added, and the solution was stripped at 100° under aspirator pressure. The residue was dissolved in 100 ml. of water, and the solution was made basic by the addition of a solution of 50 g. of sodium hydroxide in 200 ml. of water. The organic layer (oil) was separated, and the aqueous layer was extracted twice with ether. The ether extracts were combined with the oil, and the solution was washed well with water. After drying over potassium carbonate, the ether was distilled. The dark-colored residual oil was distilled under a high vacuum to give the desired amine in an 88% yield (92 g.), b.p. 80° at 0.1 mm., $n^{20}_{D}$ 1.5401.

*Anal.* Calcd. for $C_{12}H_{19}NS$: C, 68.84; H, 9.15; N, 6.69. Found: C, 68.72; H, 9.20; N, 6.4.

**2-Dimethylamino-1-propanethiol** (II).—A solution of 75 g. (0.36 mole) of 2-(benzylthio)-*N*,*N*,1-trimethylethylamine in *ca.* 1000 ml. of liquid ammonia was prepared. To this, small pieces of sodium were added with stirring until the resulting blue coloration persisted for an hour; about 15 g. of sodium was required. Ammonium chloride (*ca.* 50 g.) was added, and the ammonia was evaporated. The residue was mixed with 300 ml. of 2-propanol under nitrogen, and the mixture was heated to boiling. After cooling in an ice bath, the mixture was filtered under nitrogen; the solids were washed twice with ether. The ether and alcoholic filtrate were combined and the solvents were removed. The residue was distilled through a short Vigreux column under reduced pressure giving 19 g. (45%) of the desired aminothiol, b.p. 70° at 70 mm., $n^{20}_{D}$ 1.4704; lit.[4] (as the other isomer) b.p. 78.5° at 70 mm., $n^{20}_{D}$ 1.4684. Conversion of the product to the hydrochloride gave, from a mixture of 2-propanol and heptane, small white crystals, m.p. 120–121°, lit.[4] (as the other isomer) m.p. 114–115°.

*Anal.* Calcd. for $C_5H_{14}ClNS$: C, 38.57; H, 9.06; N, 9.00; S, 20.59. Found: C, 38.6; H, 9.3; N, 8.9; S (as mercaptan), 19.1.

**1-(1-Piperidyl)-2-methyl-2-propanethiol.**—A solution of 44 g. (0.5 mole) of isobutylene sulfide[2] and 42.5 g. (0.5 mole) of piperidine was heated on a steam bath for 20 hr. Fractional distillation of the product gave a 71% yield of 1-(1-piperidyl)-2-methyl-2-propanethiol, b.p. 54.5° at 2.5 mm., $n^{20}_{D}$ 1.4842; lit.[2] b.p. 47° at 2.5 mm., $n^{20}_{D}$ 1.4840.

*Anal.* Calcd. for $C_9H_{19}NS$: C, 62.37; H, 11.05; N, 8.08; S, 18.5. Found: C, 62.31; H, 11.09; N, 7.8; S (as mercaptan), 17.6.

The hydrochloride (from 2-propanol) melted at 193–194°, lit.[2] m.p. 198–199°.

**1-*n*-Octylamino-2-methyl-2-propanethiol.**—A solution of 84.3 g. (0.57 mole) of *n*-octylamine in 180 ml. of benzene and 20 ml. of ethanol was heated under reflux, while a solution of 24.4 g. (0.28 mole) of isobutylene sulfide in 90 ml. of benzene and 10 ml. of ethanol was added dropwise over a period of 3 hr. After heating overnight, the reaction solution was fractionally distilled to give a 43% yield of the desired aminothiol, b.p. 105–108° at 0.25 mm., $n^{20}_{D}$ 1.4620. Treating a methanolic solution of the free base with concentrated hydrochloric acid, stripping the solution to dryness, and recrystallizing the residue from tetrahydrofuran gave 1-*n*-octylamino-2-methyl-2-propanethiol hydrochloride, m.p. 163–164.5°.

*Anal.* Calcd. for $C_{12}H_{28}ClNS$: C, 56.77; H, 11.11; N, 5.52; S, 12.63. Found: C, 56.8; H, 11.3; N, 5.8; S (as mercaptan), 12.93.

**1-*n*-Decylamino-2-methyl-2-propanethiol.**—A solution of 89 g. (0.57 mole) of *n*-decylamine and 25 g. (0.28 mole) of isobutylene sulfide was heated 20 hr. on a steam bath. The reaction solution was fractionally distilled through a 60-cm. column packed with glass helices to give a 66% yield of the desired aminothiol, b.p. 121° at 1 mm., $n^{20}_{D}$ 1.4642. This was converted to the hydrochloride in the same manner as described above for the *n*-octyl homolog, m.p. 151–153°.

*Anal.* Calcd. for $C_{14}H_{32}ClNS$: C, 59.65; H, 11.44; N, 4.97; S, 11.37. Found: C, 59.65; H, 11.3; N, 5.4; S (as mercaptan), 11.7.

**Acknowledgment.**—The authors are grateful to Mr. Vernon Thornton, Dr. R. S. Silas, and Miss Joy Yates of these laboratories for obtaining and interpreting the n.m.r. spectra.

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(8) All melting points are uncorrected.

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## Novel Complexes of Metallocenes with π-Acceptors

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The objective of this study was to investigate the possibility of preparing charge transfer complexes of metallocenes, where either the π-cyclopentadienyl ring as in I or the coordinated metal as in II might act as an electron donor to a π-acceptor, such as *p*-chloroanil or *sym*-trinitrobenzene. Though much work has been done on the synthesis of metallocinium salts of aromatic acids, such as the ferrocinium and nickelocinium picrates,[2,3]

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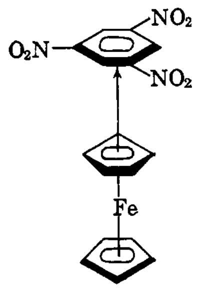
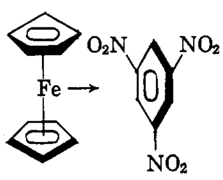
(1) To whom all inquiries should be addressed.

(2) G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, *J. Am. Chem. Soc.*, **74**, 2125 (1952).

(3) G. Wilkinson, P. L. Pauson, and F. A. Cotton, *ibid.*, **76**, 1970 (1954).



I



II

there have been no reports on their formation of intermediate $\pi$-complexes.

A common method for preparing metallocinium salts of organic acids consists of oxiding the metallocene with benzoquinone or air in the presence of the organic acid of interest.[2] It would seem logical to expect in these reactions the formation of an intermediate complex involving charge transfer between the metallocene and benzoquinone, with the latter ultimately yielding hydroquinone. In accord with this hypothesis, we have found that ferrocene, nickelocene, and cobaltocene react quite readily with benzoquinone and other $\pi$-acceptors to form a series of complexes.

The specific complexes isolated include 1:2 nickelocene–*p*-chloroanil, 1:1 and 1:2 cobaltocene–*p*-chloroanil, and 1:1 cobaltocene–*sym*-trinitrobenzene. In addition to these complexes, it was found that ferrocene forms complexes with *p*-benzoquinone, *p*-chloroanil, tetrachlorophthalic anhydride, and 1,2,4,5-tetracyanobenzene in the melt and in various solvents. It was not possible, however, to isolate stable complexes of ferrocene with these $\pi$-acceptors.

The properties of the isolable complexes range from those of high melting salts, in the case of 1:2 nickelocene–*p*-chloroanil and 1:2 cobaltocene–*p*-chloroanil, to relatively low melting charge transfer complexes, in the case of 1:1 cobaltocene–*p*-chloroanil and 1:1 cobaltocene–*sym*-trinitrobenzene. All of these substances are deeply colored solids, and they possess a new ultraviolet absorption band (in acetonitrile) which may be attributable to charge transfer interaction. In addition, they are all relatively stable in air, in contrast to the oxidative instability of nickelocene and cobaltocene, in particular.

The infrared spectra of these complexes (in Nujol) show bands similar to those of the free metallocenes (or metallocinium ions) but differ vastly from those of the free *p*-chloroanil and *sym*-trinitrobenzene. In particular, it appears that there is a marked interaction between the metal in the metallocene and carbonyl group (in chloroanil) or nitro group (in trinitrobenzene). The ultraviolet absorption spectra (in acetonitrile) show bands similar to those of both the metallocene and metallocinium ion for the chloroanil complexes, while only the metallocinium ion appears evident in the case of the trinitrobenzene complex. In each case a new absorption band is present in the region of 430–450 mμ which may be due to charge transfer interaction.

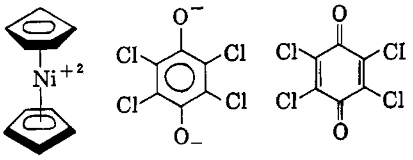
Electron spin resonance studies of the solids at 25° suggest in each case the presence of negative aromatic radicals, based on the $g$ values, though the spin concentration varies markedly with the complex in question. In particular, 1:2 cobaltocene–*p*-chloroanil gave a very strong e.s.r. signal, 1:2 nickelocene–*p*-chloroanil a very weak signal, and the 1:1 complexes gave signals of intermediate intensity.

Based on the e.s.r. results it appears that 1:2 cobaltocene–*p*-chloroanil may be formulated as a charge transfer radical ion salt, *viz.*, $\pi\text{-Cp}_2\text{Co}^{+}\text{CA}^{\overline{\cdot}}\text{CA}$. The other properties also appear, in the main, consistent with this formulation.

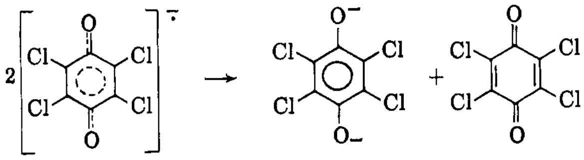
The 1:1 complexes, on a similar basis, would appear to be best represented as charge transfer complexes wherein there is only slight charge transfer in the solid state, *i.e.*, $\pi\text{-Cp}_2\text{Co}^{+\delta}\text{CA}\cdot^{-\delta}$. The presence of metallocinium ions in the acetonitrile solutions, on the other hand, as indicated by the ultraviolet spectra, may be attributable to the following dissociation.[4]

$$\pi\text{-Cp}_2\text{Co}^{+\delta}\text{TNB}^{-\delta} \longrightarrow \pi\text{-Cp}_2\text{Co}^{+} + \text{TNB}^{\overline{\cdot}}$$

The e.s.r. results obtained for 1:2 nickelocene–*p*-chloroanil are surprising in view of those obtained for the cobaltocene analog. In particular, it appears from these results that the nickelocene complex may be best represented by a structure, such as follows.



Significant charge transfer interaction may occur between the hydroquinone anion and quinone to yield the 1:2 composition. The formation of a nickelocinium salt containing the $\pi\text{-Cp}_2\text{Ni}^{+2}$ cation[3] may be due to the strong electron affinity of chloroanil or chloroanil radical ions, coupled with the driving force of nickel to achieve the inert gas configuration. The formation of the tetrachlorohydroquinone anion rather than two chloroanil radical ions would suggest that the following disproportionation is favored.



In conclusion, it appears that the ease of forming isolable complexes of metallocenes with $\pi$-acceptors correlates with the electron donor–acceptor properties of the components. Thus, whereas tetracyanoquinonedimethane gives isolable complexes with ferrocene,[5,6] nickelocene,[6] and cobaltocene,[5] the weaker $\pi$-acceptor *p*-chloroanil gives complexes with only nickelocene and cobaltocene, and the still weaker $\pi$-acceptor *sym*-trinitrobenzene gives an isolable complex only with the

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(4) It would in fact appear that, whereas the trinitrobenzene complex is essentially completely ionized in acetonitrile, the chloranil complexes dissociate to yield significant quantities of the free metallocene.

$$\pi\text{-Cp}_2\text{Co}^{+}\text{CA}^{\overline{\cdot}}\text{CA} \rightleftharpoons \pi\text{-Cp}_2\text{Co} + 2\ \text{CA}$$

(5) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962). The only complexes reported were the 1:2 metallocene–TCNQ complexes.

(6) Independently prepared at Melpar prior to the preceding publication. The 1:2 ferrocene–TCNQ complex decomposes at 134° and has an electrical resistivity of 6.95 ohm-cm. (pellet pressed at 17,000 p.s.i.). No melting point was reported by the previous workers for this substance.

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 $\pi$-cyclopentadienyl ring and $\pi$-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); $\lambda_{max}^{Nujol}$ 3.20 (w), 7.10 (m) new, 8.9, 9.0 doublet (m) new, 10.0 (m), 11.2 (s), and 12.6 $\mu$ (m) new. The infrared bands at 6.05, 13.35, and 14.10 $\mu$, due to *p*-chloroanil, and that at 13.0 $\mu$, due to nickelocene, were absent. The ultraviolet spectrum was $\lambda_{max}^{CH_3CN}$ 236 m$\mu$ (log $\epsilon$ 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; $\lambda_{max}^{Nujol}$ 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 $\mu$ (s) new. The infrared bands at 6.05, 8.01, 8.17, 8.35 (triplet), 9.0–9.2, 13.35, and 14.10 $\mu$, due to chloroanil, and the band at 12.95 $\mu$, due to cobaltocene, were absent. The ultraviolet spectrum was $\lambda_{max}^{CH_3CN}$ 260 m$\mu$ (log $\epsilon$ 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°); $\lambda_{max}^{Nujol}$ 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 $\mu$ (w). The infrared absorption patterns in 6.5–7.5- and 13–16-$\mu$ regions were markedly different from those of *sym*-trinitrobenzene. The bands at 5.46 and 9.36 $\mu$, due to *sym*-trinitrobenzene, were absent. The ultraviolet spectrum was $\lambda_{max}^{CH_3CN}$ 262 m$\mu$ (log $\epsilon$ 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.

**Acknowledgment.**—The authors wish to thank Dr. Hannibal DeSchmertzing for the elemental analysis, Mr. Lester Shubin for the spectroscopic measurements, and Mr. Van Townsend for the e.s.r. measurements.

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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.

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# Ullmann Condensation

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*Received August 22, 1963*

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 $\beta$- *vs.* $\alpha$-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

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[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.

[3] J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 394 (1951).

[4] W. G. Dauben, *J. Am. Chem. Soc.*, **70**, 2420 (1948).

[5] E. Berliner and L. C. Monack, *ibid.*, **74**, 1574 (1952).

[6] A. F. Holleman and W. J. DeMooy, *Rec. trav. chim.*, **35**, 27 (1915).

[7] E. Berliner, M. J. Quinn, and P. J. Edgerton, *J. Am. Chem. Soc.*, **72**, 5305 (1950).