malate reaction go through a minimum at about $D = 30$, similarly to the results observed in the three symmetrical diesters for the saponification of the second ester group.

**Salt Effects.** Runs 11 and 12 Table III were carried out under similar environmental conditions as in run 4 except for the addition of an inert electrolyte. On comparing the results of runs 4 and 11 it is observed that there is an appreciable positive primary salt effect on the rate constants $k_3$ and $k_4$ when a small quantity of an inert electrolyte is used. However, on using large quantities of an inert electrolyte, a large negative primary salt effect in the rate constants $k_3$ and $k_4$ is observed (see runs 4 and 12). Such complete reversal of primary salt effects is compatible with the behavior of the activity coefficients of an ion as one goes from a solution of low ionic strength to a solution of high ionic strength. It emphasizes the hazards of mechanistic interpretation of reactions in solutions which are highly swamped with an inert electrolyte, a practice which is all too common.

**Acknowledgments.** We wish to express our appreciation to E. I. du Pont de Nemours and Company for the Du Pont Fellowship held by F. Kundell from 1965 to 1966, U. S. Air Force for financial aid, General Research Board of the University of Maryland for a grant applicable to computer time, Computing Science Center of the University of Maryland and National Aeronautics and Space Administration Grant Ns G-398 for computer time, and Professor James Stewart and Mr. Alfred Beam of the University of Maryland for assistance in the development of the computer program used in this research.

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# *ortho*-Substituent Effects in Polarography[1a]

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*Contribution from the Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania.* *Received January 25, 1967*

**Abstract:** A series of substituted bromo- and iodobenzenes were polarographically reduced to investigate the *ortho* effect. It was found that the *ortho* effect could be interpreted as the result of two phenomena: (1) that the inductive effect of an *ortho* substituent is proportional to, but greater than, the inductive effect of that substituent in the *para* position; (2) that the resonance interaction of a substituent is hindered when it is adjacent to a bulky group such as the halides. Using these principles, the *ortho* half-wave potentials were correlated with the *meta* and *para* half-wave potentials and the Hammett function.

A number of studies have been performed to determine the effect of substituent groups on the electrochemical reduction of aromatic compounds. In many cases it has been noted that *ortho*-substituted compounds are much easier to reduce than would have been predicted. For example, the half-wave potential of a reducible aromatic compound is almost always lower for the *ortho*-substituted compound than for the *meta* or *para* isomers. Furthermore, many electron-donating groups aid, rather than hinder, reduction when they are placed in the *ortho* position. The abnormal polarographic behavior has been termed the "*ortho* effect."

These low half-wave potentials were first observed for compounds such as *o*-hydroxybenzaldehyde[2] and *o*-nitrophenol[3] and were attributed to hydrogen bonding. However, the *ortho* effect was subsequently observed to be a rather general phenomenon, often occuring in cases such as the reduction of *o*-chloroiodobenzene,[4] where there are no hydrogens involved. A recent review[5] points out the wide occurrence of marked positive shifts in cases where hydrogen bonding is unacceptable as an explanation, and states that the contribution of the formation of hydrogen bonds to the shift of half-wave potential cannot be taken as proven in any case so far reported.

This same review notes that *ortho* enhancement of reduction is a fairly consistent phenomenon in various systems, but no explanation of this effect is offered. For the most part, quantitative studies have concentrated on compounds with substituents in the *meta* and *para* positions and avoided the problems of the *ortho* case. We believe that the *ortho* effect can be explained as a change in the electron density at the reaction site due to a decrease in the resonance contribution and an increase in the inductive contribution for a substituent in the *ortho* position. Since no previous experimental work had been specifically concerned with *ortho* compounds, it was necessary that a reaction series be thoroughly investigated under controlled conditions to properly evaluate these effects. The phenyl halides were studied because their reaction is not sensitive to pH.[6]

## Experimental Section

**Instrumentation.** Polarograms were obtained using an operational amplifier polarograph similar in design to that of Kelley,

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(1) (a) Presented in part at the 127th Meeting of the Electrochemical Society, San Francisco, Calif., May 1965. This article is based on a thesis submitted by W. W. Hussey in partial requirement for the Ph.D. degree to Lehigh University, June 1965. (b) National Science Foundation Graduate Fellow, 1963-1965. (c) Person to whom correspondence should be addressed.

(2) G. Semerano and V. Capitanio, *Gazz. Chim. Ital.*, 70, 490 (1940).

(3) M. J. Astle and W. V. McConnel, *J. Am. Chem. Soc.*, **65**, 35 (1943).

(4) E. L. Colichman and S. K. Liu, *ibid.*, 76, 913 (1954).

(5) P. Zuman, *Collection Czech. Chem. Commun.*, 27, 648 (1962).

(6) P. J. Elving and C. S. Tang, *J. Am. Chem. Soc.*, **74**, 6109 (1952).

*et al.*[7] A three-electrode system was used with a calomel reference electrode. Solutions were deaerated with prepurified nitrogen prior to analysis. The current–potential curves were recorded on an x-y recorder (Model HR 291, Houston Instrument Co.)

**Reagents.** Substituted bromo- and iodobenzenes were obtained from Distillation Products Inc., Rochester, N. Y., and Columbia Organic Chemical Corp., Columbus, S. C. Reagent grade chemicals were used without further modification. Tetramethylammonium chloride was obtained from J. T. Baker Chemical Co., Phillipsburg, N. J., and recrystallized twice from methanol. Lithium perchlorate was prepared by the neutralization of reagent grade lithium carbonate with perchloric acid (both from J. T. Baker). The resulting solution was acidified and boiled to remove carbon dioxide. The pH was then adjusted to 7.0 with lithium hydroxide and diluted to make a stock solution of 2.5 *M* lithium perchlorate.

## Results

Thirty-five substituted iodobenzenes were reduced at the dme in 1 *M* $LiClO_4$ and 0.1 *M* $(CH_3)_4NCl$. The half-wave potentials recorded are shown in Table I.

Table I. Half-Wave Potentials of Substituted Iodobenzenes

| Iodobenzene | $-E_{1/2}$ in $LiClO_4$, v | $-E_{1/2}$ in $(CH_3)_4NCl$, v |
|---|---|---|
| Iodobenzene | 1.655 | 1.467 |
| *o*-Methyl- | 1.688 | 1.495 |
| *m*-Methyl- | 1.673 | 1.483 |
| *p*-Methyl- | 1.687 | 1.497 |
| *o*-Ethyl- | 1.685 | 1.478 |
| 2,6-Dimethyl- | 1.718 | 1.516 |
| 2,4-Dimethyl- | 1.718 | 1.527 |
| *o*-Phenyl- | 1.570 | 1.327 |
| *p*-Phenyl- | 1.622 | 1.413 |
| *o*-Amino- | 1.565 | 1.416 |
| *m*-Amino- | 1.650 | 1.463 |
| *p*-Amino- | 1.710 | 1.529 |
| *o*-Hydroxy- | 1.535 | 1.391 |
| *m*-Hydroxy- | 1.637 | 1.463 |
| *p*-Hydroxy- | 1.700 | 1.520 |
| *o*-Methoxy- | 1.567 | 1.393 |
| *m*-Methoxy- | 1.603 | 1.421 |
| *p*-Methoxy- | 1.672 | 1.488 |
| *o*-Ethoxy- | 1.587 | 1.405 |
| *p*-Ethoxy- | 1.672 | 1.488 |
| *p*-Cyano- | 1.417 | 1.287 |
| *o*-Trifluoromethyl- | 1.343 | 1.190 |
| *m*-Trifluoromethyl- | 1.517 | 1.343 |
| *p*-Trifluoromethyl- | 1.515 | 1.351 |
| *o*-Fluoro- | 1.374 | 1.205 |
| *p*-Fluoro- | 1.593 | 1.420 |
| *o*-Chloro- | 1.375 | 1.203 |
| *m*-Chloro- | 1.509 | 1.337 |
| *p*-Chloro- | 1.557 | 1.388 |
| *o*-Bromo- | 1.322 | 1.153 |
| *m*-Bromo- | 1.482 | 1.318 |
| *p*-Bromo- | 1.550 | 1.383 |
| *p*-Iodobenzoic acid | 1.505 | 1.377 |
| *o*-Iodobenzyl alcohol | 1.555 | 1.396 |
| *p*-Iodobenzyl alcohol | 1.636 | 1.456 |

The half-wave potentials of 24 substituted bromobenzenes reduced in 0.1 *M* $(CH_3)_4NCl$ are shown in Table II to within ± 10 mv. The accuracy with which the bromobenzene half-wave potentials can be determined is limited by the fact that many of them reduce at potentials above −2.00 v and are too close to the decomposition potential of the supporting electrolyte to form a good diffusion plateau.

Table II. Half-Wave Potentials of Substituted Bromobenzenes

| Bromobenzene | $-E_{1/2}$ in $(CH_3)_4NCl$, v | Bromobenzene | $-E_{1/2}$ in $(CH_3)_4NCl$, v |
|---|---|---|---|
| Bromobenzene | 2.07 | *p*-Methoxy- | 2.10 |
| *o*-Methyl- | 2.12 | *o*-Ethoxy- | 1.99 |
| *m*-Methyl- | 2.09 | *p*-Ethoxy- | 2.10 |
| *p*-Methyl- | 2.11 | *o*-Trifluoromethyl- | 1.67 |
| *p*-Phenyl- | 1.99 | *m*-Trifluoromethyl- | 1.89 |
| *o*-Amino- | 2.01 | *p*-Trifluoromethyl- | 1.90 |
| *m*-Amino- | 2.07 | *o*-Fluoro- | 1.69 |
| *p*-Amino- | 2.15 | *p*-Fluoro- | 2.00 |
| *o*-Hydroxy- | 1.97 | *o*-Chloro- | 1.69 |
| *m*-Hydroxy- | 2.06 | *m*-Chloro- | 1.87 |
| *p*-Hydroxy- | 2.14 | *p*-Chloro- | 1.96 |
| *o*-Methoxy- | 1.93 | 3,4-Dichloro- | 1.77 |

## Discussion

An examination of the half-wave potentials of the *meta*- and *para*-substituted compounds in Tables I and II shows that they are markedly affected by substituents in a manner consistent with the electronegativity rule of reduction potentials. *ortho* substituents (other than alkyl) cause bromo- and iodobenzene to be reduced more easily than *para*- or *meta*-substituted isomers.

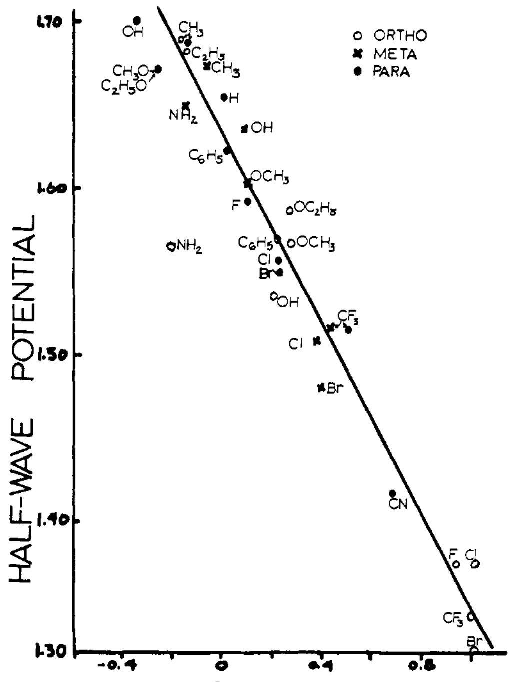

Figure 1. Half-wave potentials of substituted iodobenzenes in 1.0 *M* $LiClO_4$ *vs.* sce plotted against $\sigma$ values.

Since the data for *meta* and *para* substituents are correlated by Hammett constants, it is attractive to treat the effect of the *ortho* substituent as a perturbation due to an increased inductive effect and in some cases a steric inhibition of resonance. Equation 1 has been found to generate $\sigma_o$ values that correlate the data for *ortho* substituents (Figures 1–3).

$$\sigma_o = 2.4\sigma_{I,p} + (1 - \text{steric-hindrance factor})\sigma_{R,p} \quad (1)$$

The value 2.4 was obtained by curve fitting and the

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[7] M. T. Kelley, D. J. Fisher, and H. C. Jones, *Anal. Chem.*, 32, 1262 (1960).

**Table III.** Calculation of *ortho* Values for Iodobenzenes[a]

| Group | Radius | SF | (1 − SF) | $2.4_{\mathrm{I},p} + (1 - \mathrm{SF})_{\mathrm{R},p}$ | $\sigma_o$ |
|---|---|---|---|---|---|
| $CH_3$ | 1.73 | 0.52 | 0.48 | 2.4(−0.05) + 0.48(−0.11) | −0.17 |
| $NH_2$ | 1.56 | 0.41 | 0.59 | 2.4( 0.10) + 0.59(−0.76) | −0.21 |
| OH | 1.45 | 0.34 | 0.66 | 2.4( 0.25) + 0.66(−0.60) | 0.20 |
| $OCH_3$ | 1.47 | 0.35 | 0.65 | 2.4( 0.25) + 0.65(−0.51) | 0.27 |
| $OC_2H_5$ | 1.47 | 0.35 | 0.65 | 2.4( 0.25) + 0.65(−0.51) | 0.27 |
| $CF_3$ | 2.15 | 0.78 | 0.22 | 2.4( 0.41) + 0.22(+0.09) | 1.00 |
| F | 1.39 | 0.31 | 0.69 | 2.4( 0.52) + 0.69(−0.44) | 0.95 |
| Cl | 1.89 | 0.61 | 0.39 | 2.4( 0.47) + 0.39(−0.25) | 1.03 |
| Br | 2.11 | 0.75 | 0.25 | 2.4( 0.45) + 0.25(−0.22) | 1.03 |
| $C_2H_5$ | 1.79 | 0.55 | 0.45 | 2.4(−0.05) + 0.45(−0.10) | −0.16 |
| $C_6H_5$ | 2.20 | 0.80 | 0.20 | 2.4( 0.10) + 0.20(+0.09) | 0.22 |

[a] SF = steric factor.

steric-hindrance factor was determined as outlined below. The values of $\sigma_{\mathrm{I},p}$ and $\sigma_{\mathrm{R},p}$ are from Taft.[8]

It is difficult to determine precisely what this steric-hindrance factor should be. The interference will obviously increase with the size of the groups involved.

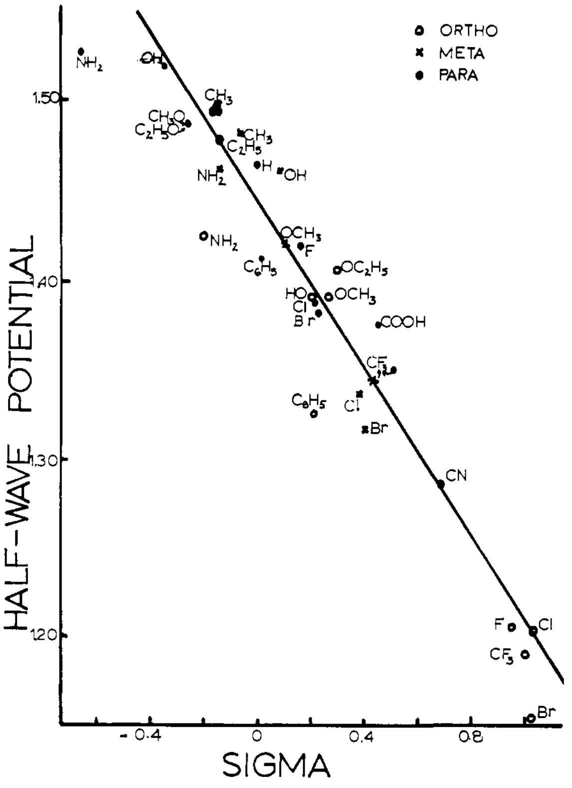

Figure 2. Half-wave potentials of substituted iodobenzenes in 0.1 *M* $(CH_3)_4NCl$ *vs.* sce plotted against $\sigma$ values.

One estimate of the size of the various groups has been obtained from data on the resolvability of *ortho*-substituted biphenyls.[9] Using the iodic group radii derived from the *ortho*-substituted biphenyls and bond lengths, it was found that groups with radii of less than 0.95 A did not interfere with the *ortho* group, while two *o*-iodo groups overlap by 0.80 A. The fraction of an angstrom unit with which a group overlapped the reacting group was used as the measure of steric hindrance. This steric hindrance has no units and is a crude adjustment coefficient, not absolute but relative in nature.

The greatest deviation of Figures 1–3 is exhibited by the amino group, which is to be expected since the *para* value from which the *ortho* value was derived deviated as well. For most of the substituents it can be seen that the *ortho* effect is largely the result of the increased inductive effect, with the decrease in resonance helping. The case of the alkyl groups is one where the two effects cancel each other. The increased inductive effect hinders the alkyl reduction, while the decrease in resonance aids the reduction.

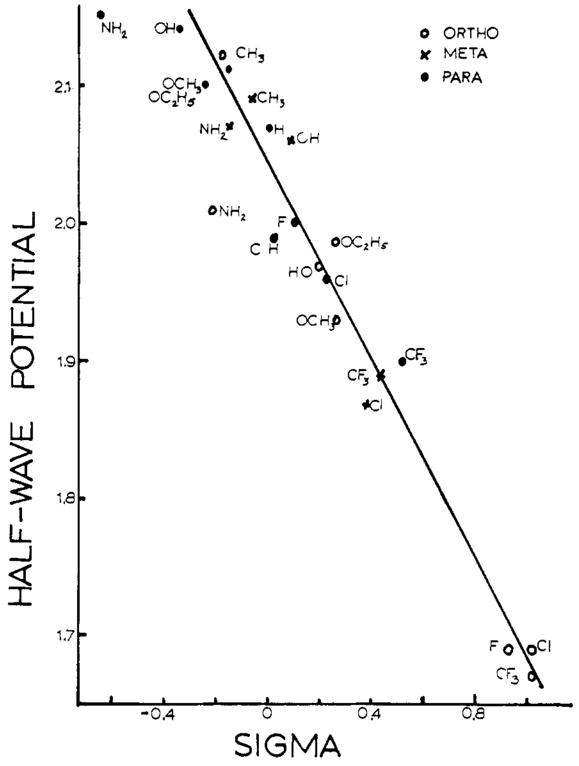

Figure 3. Half-wave potentials of substituted bromobenzenes in 0.1 *M* $(CH_3)_4NCl$ *vs.* sce plotted against $\sigma$ values.

It must be remembered that the *ortho* $\sigma$ values calculated above are not universal substituent constants, but reflect the case of the phenyl halides. The method should be applied to other reduction systems, but several factors must be considered. Obviously, steric hindrance of resonance will vary with the size and shape of the reacting group. The coefficient for the increased

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(8) R. W. Taft, Jr., N. C. Deno, and P. S. Skell, *Ann. Rev. Phys. Chem.*, **9**, 292 (1958).

(9) L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963.

**Table IV.** Calculations of *ortho* Values for Bromobenzenes[a]

| Group | Radius | SF | (1 − SF) | $2.4_{\mathrm{I},p} + (1 - \mathrm{SF})_{\mathrm{R},p}$ | $\sigma_o$ |
|---|---|---|---|---|---|
| $CH_3$ | 1.73 | 0.48 | 0.52 | 2.4(−0.05) + 0.52(−0.11) | −0.18 |
| $NH_2$ | 1.56 | 0.38 | 0.62 | 2.4( 0.10) + 0.62(−0.76) | −0.23 |
| OH | 1.45 | 0.32 | 0.68 | 2.4( 0.25) + 0.68(−0.60) | 0.19 |
| $OCH_3$ | 1.47 | 0.33 | 0.67 | 2.4( 0.25) + 0.67(−0.51) | 0.26 |
| $OC_2H_5$ | 1.47 | 0.33 | 0.67 | 2.4( 0.25) + 0.67(−0.51) | 0.26 |
| $CF_3$ | 2.15 | 0.74 | 0.26 | 2.4( 0.41) + 0.26(+0.09) | 1.01 |
| F | 1.39 | 0.29 | 0.71 | 2.4( 0.52) + 0.71(−0.44) | 0.94 |
| Cl | 1.89 | 0.57 | 0.43 | 2.4( 0.47) + 0.43(−0.25) | 1.02 |
| Br | 2.11 | 0.71 | 0.29 | 2.4( 0.45) + 0.29(−0.22) | 1.02 |
| $C_2H_5$ | 1.79 | 0.52 | 0.48 | 2.4(−0.05) + 0.48(−0.10) | −0.17 |
| $C_6H_5$ | 2.20 | 0.78 | 0.22 | 2.4( 0.10) + 0.22(+0.09) | 0.22 |

[a] SF = steric factor.

inductive effect at the *ortho* position, which was treated as a constant, is an unknown combination of bond interaction and field effects. If the spatial configuration of the *ortho* substituent and the reaction site was substantially changed, it would probably affect the coefficient for the inductive effect, especially that portion which is due to field effects. Thus no system would necessarily have the same parameters as the phenyl halides unless it was completely analogous to their reduction.

There are several reducible aromatic systems in which substituent effects could be examined such as the benzyl halides, the benzyl carbonyls, and unsaturated systems such as styrene. In each of these cases, however, the reaction site is one carbon removed from the ring, and the bond between the ring and the reacting group is not broken. This is obviously a different situation from the phenyl halides which are reduced to benzene so that the bond between the aromatic nucleus and the halide atom is broken. Thus there is no reducible system which is completely analogous to the phenyl halides.

This treatment offers an explanation for a previously unexplained phenomenon, and further work on other systems is in progress to extend it.

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# The Crystal and Molecular Structure of $[Al(CH_3)_3]_2 \cdot C_4H_8O_2$

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*Received April 17, 1967*

**Abstract:** The crystal structure of $[Al(CH_3)_3]_2 \cdot C_4H_8O_2$ has been determined by three-dimensional, single-crystal, X-ray diffraction techniques. The compound crystallizes in the monoclinic space group C2/m, with two molecules per unit cell. The cell parameters are: $a = 18.84$, $b = 11.51$, $c = 6.79$ A, $\alpha = \gamma = 90°$, $\beta = 146° 15'$. The molecule, which has 2/m symmetry, contains the dioxane ring in the chair form with each oxygen atom bonded to an aluminum atom. The hybridization of the aluminum atoms is more nearly trigonal than tetrahedral. Structure solution was accomplished with the use of the symbolic addition procedure for phase determination.

As compounds of trivalent aluminum, the organoaluminum compounds are Lewis acids and will combine with Lewis bases to form molecular compounds or complex anions. When suitable electron donors (amines, ethers, or anions such as hydride or halide) combine with organoalanes, compounds containing four- or five[1]-coordinate aluminum are obtained. Bifunctional donors such as dioxane usually add 2 moles of trialkylalane.[2] Several neutral addition complexes have been studied by infrared[3] and nmr[4] techniques, but little is known in detail about their geometries. We wish to report the three-dimensional X-ray study of a neutral addition complex of trimethylaluminum, bis(trimethylaluminum) dioxanate.

## Experimental Section

The material was prepared by the addition of trimethylaluminum to an excess of dioxane. The excess dioxane was then pumped off under moderate vacuum and the complex sublimed out of the residue. Two types of crystals were observed: small, colorless, regular polyhedra which give a melting point of 173 ± 1°, and a small quantity of colorless needles of undetermined melting point. Single crystals of both materials were sealed in glass capillaries as the compounds are water and oxygen sensitive. We report here the unit cell and space group for both modifications and the three-dimensional structure of the crystals characterized as small, colorless, regular polyhedra.

Preliminary unit cell dimensions were determined from oscillation, Weissenberg (Cu Kα), and precession (Mo Kα) photographs. With the needle-like compound, the crystal system is orthorhombic. The systematic absences allow the space group to be Pnn2 or

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[1] A. R. Young, II, and R. Ehrlich, *Inorg. Chem.*, **4**, 1358 (1965).

[2] W. Brüser, K. H. Thiele, and H. K. Müller, *Z. Chem.*, **2**, 342 (1962).

[3] R. Tarao, *Bull. Chem. Soc. Japan*, **39**, 2126 (1966).

[4] A. P. Batalov and I. A. Korshunov, *Tr. po Khim. i Khim. Tekhnol.*, **3**, 501 (1960).