quired two hours. There was obtained 157 g. (60% of theory) of 2,2-dichloro-1,1-difluoro-1-phenoxyethane boiling at 71.0–71.5° at 4 mm.

The Addition of Phenol to 2-Chloro-1,1-difluoroethylene. The reaction of 1.15 moles of olefin with 2.5 moles of phenol and 1.5 moles of potassium hydroxide dissolved in 450 ml. of acetone was carried out at room temperature. There was obtained 72 g. of 2-chloro-1,1-difluoro-1-phenoxyethane. In addition, in this case, there was obtained a considerable forecut (73 g.) which was a mixture of the saturated and the vinyl ether.

1,1-Dichloro-2-fluoro-2-phenoxyethylene.—The addition of phenol to *unsym*-dichlorodifluoroethylene at a higher temperature and with the separation of the product by a different procedure than that described above resulted in a dehydrofluorinated product.

Phenol (3.0 moles) was dissolved in 300 ml. of acetone and 0.64 mole of potassium hydroxide added. To this solution was added 1.5 moles of dichlorodifluoroethylene over a three-hour period; a marked temperature rise was noted. After the addition of the olefin, acetone was distilled from the mixture to a distillate temperature of 70°, the remainder cooled and sufficient base added to convert all the phenol to its salt. The mixture was then steam distilled, and the ether separated, washed and dried. By fractionation through a 10-inch column packed with glass helices, there was obtained 193 g. (62% of theory) of 1,1-dichloro-2-fluoro-2-phenoxyethylene.

1-Chloro-1,2-difluoro-2-phenoxyethylene.—The saturated ether $C_6H_5OCF_2CHClF$ resisted dehydrofluorination under the previously noted conditions of preparation or of steam distillation. When 23 g. of 2-chloro-1,1,2-trifluoro-1-phenoxyethane was refluxed for 24 hours with a 33% aqueous solution of potassium hydroxide, no appreciable reaction occurred. The recovered, unreacted ether was then refluxed with an excess of powdered base until all evidence of reaction had stopped. The difluorovinyl ether having the properties listed in Table I was isolated by distillation.

Proof of Structure of Chlorotrifluorophenoxyethane.—A considerable number of hydrolyses of the arylalkyl ethers were carried out before a satisfactory procedure was developed. Phenoxychlorotrifluoroethane (0.5 mole) was mixed with 100 ml. of sulfuric acid (96%) in a three-neck glass flask equipped with a reflux condenser and stirrer. The mixture was heated 45 minutes on a steam-bath, cooled to room temperature, 50 ml. of ethanol added and refluxed for 15 minutes. The mixture was poured onto ice and the organic layer washed with cold sodium hydroxide solution and with water and dried. Fractionation gave 11 g. of ethyl chlorofluoroacetate, boiling at 130–131°, $n^{25}D$ 1.3931, d^{25}_{4} 1.227. This hydrolysis indicates that the ether was 2-chloro-1,1,2-trifluoro-1-phenoxyethane.

Acknowledgment.—The authors wish to express their thanks to the Office of Naval Research for providing funds for this research under Contract N8onr503.

GAINESVILLE, FLORIDA RECEIVED APRIL 30, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

A New Evaluation of Electrical Effects of Groups on the Benzene Ring

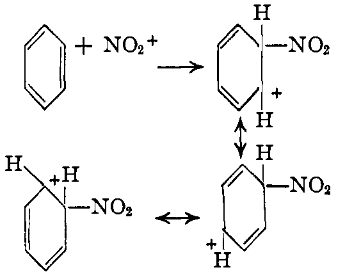
BY CHARLES C. PRICE

Based on an arbitrary but reasonable model, estimates of the energy of interaction between dipole charges in a substituent group and the positive charge placed on the ring in the intermediate complex for normal electrophilic benzene substitution indicate a magnitude capable of accounting for very marked orientation and activation (or deactivation) of the ring. These considerations can be extended to account for a parallel influence of the same groups in polarizing the ground state of the ring or of a carbon–carbon double bond. It is recognized that this electrical effect is not the sole nor necessarily the most important effect operating to influence reactivity or electron distribution.

A number of years ago,[1] it was suggested that one of the effects of polar or dipolar substituents attached to a benzene ring is to polarize the unsaturation, *i.e.*, the π-electrons of the aromatic nucleus as a simple consequence of the electric field generated by electric poles or dipoles in the substituent group. At that time, the electric force operating on an electron between the carbon holding the substituent and the ortho-carbons was calculated and called the "polarizing force." It is the purpose of the present paper to reconsider this electrical effect in more general terms, as applied to intermediate ionic complexes as well as to the starting material, and to express the resulting electrical influence in energy terms. This has been done by setting up arbitrary but reasonable models for the intermediate ionic states from which the magnitude of the major coulombic interactions have been calculated.[2]

In the process of substitution in benzene, such as nitration, for example, it is now generally accepted that the mechanism involves primary attack on the ring by a cationic, electrophilic fragment of the substituting reagent.[3]

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$



Hughes and Ingold have not only presented conclusive evidence that the nitro cation attacks the ring, but that this process occurs without a change in the number of ions. That the subsequent elimination of a proton was not involved in a rate-determining step has been substantiated by Melander's[4] observation that hydrogen and tritium are replaced at identical rates. This evidence supports the concept that the ionic complex is a stable intermediate and that there would therefore be ample

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(1) Price, *Chem. Revs.*, **29**, 37 (1941).

(2) Ri (Ree) and Eyring, *J. Chem. Phys.*, **8**, 433 (1940), have previously treated electrical effects on nitration from a different viewpoint, by considering that the activation energy for the process will be influenced directly by a simple coulombic interaction in the transition complex between the charge on the nitro cation ($e_n = 4.8 \times 10^{-10}$ e.s.u.) and the charge (e_x) induced by a substituent group, x, on the carbon atom of the ring being attacked by the nitro cation.

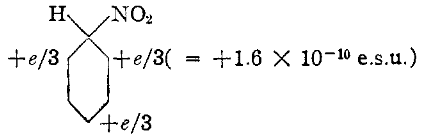
$$k_x = ae^{-(\Delta F_0 + e_x e_n/rD)RT}$$

(3) See, *e.g.*, Hughes and Ingold, *Nature*, **163**, 599 (1949).

(4) Melander, *ibid.*, **163**, 599 (1949).

opportunity for development of the charge distribution substantially as indicated.

This intermediate ionic complex may be represented more simply as

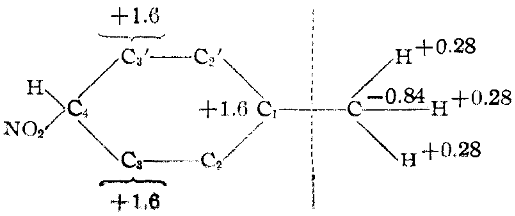


with the carbon atoms para and ortho to the entering nitro cation carrying equal positive charges, equivalent to one-third of an electronic unit of charge.

In the absence of steric effects significantly changing the entropy of formation of this intermediate ion, a principal orienting influence must be the effect of substituent groups attached to the various atoms in the ring on the stability of this intermediate. Certainly one such influence will be the normal resonance stabilization, especially important when a group such as an amino or hydroxyl group is attached to one of the carbon atoms bearing the positive charge in the intermediate complex.

It is, however, not the purpose here to consider the important role played by resonance which, in some instances, is the major factor, but to evaluate a second influence, the interaction of electric dipoles in a substituent group with the charges placed on the ring in the intermediate ionic complex. If these dipoles in the substituent have their negative end directed toward the ring, it is qualitatively obvious that placing a positive charge in the ring will be easier, that the energy of the intermediate will be decreased by coulombic interaction and that therefore attack by the nitro cation will be favored. Conversely, if the positive ends of dipoles in a substituent are directed toward the ring, then the energy of the intermediate will be increased and attack by a nitro cation will be retarded. Furthermore, the influence of a dipole in a substituent group will be quantitatively different depending on whether the group is directly attached to one of the ring carbon atoms holding a positive charge or one of those in between. The group will of course exert an *electrical* orienting influence favoring attack by the nitro cation at a position giving the intermediate of minimum electrical energy.

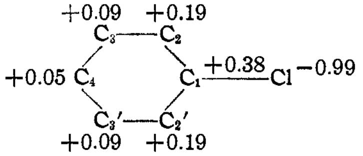
It is the purpose of this paper to propose a procedure for evaluating the relative magnitude of these electrical interactions, using charges for atoms in the substituent groups based on accepted bond moments,[1] locating all charges at the center of the atoms involved, arranged according to established molecular geometry. Using toluene as an example, we may consider the model below for para substitution.



For the purpose of our calculation, we may presume that the interaction of the charges within the ring (all charges to the left of the dotted line) will remain essentially constant regardless of the substituent group. Also, the interaction of charges in the reactive group will be the same in the initial molecules and the intermediates. The charge interactions of consequence to the influence of the substituent on the substitution process are those interactions occurring *across* the dotted line, *i.e.*, those between charges in the various atoms of the substituent with the charge placed on the three atoms of the ring in the intermediate ionic complex.

Essentially, this approach involves an evaluation of the perturbation of the energy of the π-electron system of the intermediate ionic complex, by an approximation of the direct interaction of the unperturbed π-electron system with the field generated by a substituent group. An alternative approach[5] involves an influence of the substituent on the π-ionization potential of the various atoms in the ring. The approximation reported herein has the advantage of easier quantitative interpretation. A subtle difference between them is that our picture involves a possible distortion of the axial symmetry of the p-orbitals; that of Wheland and Longuet-Higgins changes the π-electron energy but not the axial symmetry of the p-orbitals.

The case of halogen substitution is not susceptible to quantitative treatment on the basis of the simplifying assumption that we can estimate charge interactions as though the charges were located at the center of the atoms, since the interaction of the charge placed on C_1 by the attacking cation and by the C_1–Cl dipole would become infinite. In this case, it is of perhaps some interest to consider qualitatively the perturbing electrical influence on the π-electrons on the basis of the following model for the σ-electron skeleton of chlorobenzene based on the presumption that the inductive effect spreads the charge so that each succeeding carbon atom has one-half that of the preceding one.



Evaluated at a point in a π-orbital one-half a carbon–carbon bond length, *i.e.*, 0.77 Å., above C_1 or C_2, it turns out that an electron will be stabilized to a greater extent on either of these carbon atoms in chlorobenzene than will an electron at a corresponding position on a carbon in benzene. Because of the strong field effect of the negative chlorine atom, the significant feature of the calculation is that the perturbing stabilization will be 50% greater in the π-orbital on C_2 than on C_1. Evaluated at a point considerably closer than 0.77 Å. to C_1 and C_2, the stabilizing electric field becomes greater on C_1 than on C_2. The qualitative picture of the perturbation of the π-bond is therefore a shift of electron density *toward* C_1 close to the bond axis, a shift of electron density *away from* C_1 further

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(5) See, *e.g.*, Wheland, THIS JOURNAL, 64, 900 (1942); Longuet-Higgins, *J. Chem. Phys.*, 18, 265, 275, 283 (1950),

out from the bond axis. Since chemical reaction with the π-electrons, or their outside electrical influence, will be governed largely by their distribution in the outer part of their orbitals, the model proposed does qualitatively account for the *o,p*-orientation and the normal observed electron distribution in chlorobenzene.

Although a means exists for calculating the effect of the solvent medium on the effective dielectric constant between the charges interacting,[6] because of the approximate nature of the treatment and especially since for the important charge interactions, those acting at the shorter distances, the contribution of the dielectric medium will be small, the dielectric constant has been assumed to be unity.[7]

The distances separating the charges have been estimated from accurate model drawings based on established bond distances and bond angles. For atoms which may occupy different position with respect to each other, such as the hydrogen atoms in toluene and the meta-carbon atoms of the ring, the electrical interaction in the closest and most distant positions have been averaged.

On the basis of such considerations the total energy of electrical interaction for a number of groups with the positive charge distributed on the three atoms of the ring has been calculated as the sum of individual effects, $E = \Sigma e_b e_s / r$, where e_b is the charge on the benzene ring (1.6×10^{-10} e.s.u. at carbons 1, 3 and 3′ or 2,2′ and 4), e_s is the charge on each atom in the substituent (evaluated from bond moments) and r is the distance separating each pair of atoms involved. The results are given in Table I.

TABLE I

ELECTRICAL INTERACTION OF DIPOLES IN SUBSTITUENTS WITH THE CHARGE ON THE RING OF THE INTERMEDIATE IONIC COMPLEX FOR ELECTROPHILIC SUBSTITUTION ON BENZENE

Group	E^a para	E^a meta	ΔE^a $(p - m)$
$\mathrm{CH_3}$	−4.5	−2.8	−1.7
$\mathrm{C(CH_3)_3}$	−3.5	−1.9	−1.6
$\mathrm{CH_2Cl}$	5.0	3.3	1.7
$\mathrm{CHCl_2}$	9.7	5.6	4.1
$\mathrm{CCl_3}$	12.0	7.7	4.3
CHO	12.7	8.9	3.8
$\mathrm{CF_3}$	16.5	10.7	5.8
CN	26.6	20.7	5.9
$\mathrm{NH_2}^{(-)b,c}$	−20.2	−11.0	−9.2
$\mathrm{NH_2}^{(\perp)c,d}$	−20.5	−12.2	−8.3
$\mathrm{NO_2}^{(-)b,c}$	34.8	19.8	15.0

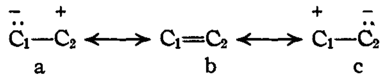
[a] These values are in kcal./mole; all should be divided by the effective dielectric constant, which should have a value between 1 and 2.[6] [b] For model with $-\mathrm{NH_2}$ group in plane of benzene ring. [c] The small $\mathrm{C_1-N}$ dipole has been neglected in estimating these values for the amino and nitro group. [d] For model with $-\mathrm{NH_2}$ group perpendicular to plane of benzene ring.

It is of striking interest that, even for a group with such small polar character as the methyl group, the magnitude of the electrical interaction stabilizing the cationic intermediate complex is sufficient to account adequately for the known activating influence of methyl. The estimated factor of −4.5 kcal./mole in activation energy would account for an increase in rate at 25° of 1700-fold. Toluene has been reported to brominate 400-fold faster than benzene.[8b]

The estimated difference, $\Delta E_{(p-m)}$, of −1.7 kcal./mole would account for a factor of 20 in rate at 25°. This is in satisfactory agreement with the observed 4% meta-isomer formed from nitration of toluene.

It is of some interest that the values for E_p and E_m are less negative for *t*-butyl than for methyl. This offers a possible explanation for the Baker–Nathan effect,[8] observations indicating a greater "electron-release" by methyl than *t*-butyl.[9]

In addition to an electrical effect on the ionic complex, it seems that there will be a parallel effect in the initial molecule leading to polarization of the π-electrons of the ring (or an adjacent double bond). We normally consider that a double bond may have contributions from ionic character, represented as



$$\underset{a}{\overset{-}{\ddot{C}_1}-\overset{+}{C_2}} \longleftrightarrow \underset{b}{C_1=C_2} \longleftrightarrow \underset{c}{\overset{+}{C_1}-\overset{-}{\ddot{C}_2}}$$

In the absence of polarizing electrical influence, the two polar forms will contribute equally and the bond will be non-polar. If, however, we attach to atom $\mathrm{C_1}$ a methyl group, the negative field of the methyl group will make form c more stable, form a less stable. Form c will thus contribute more to the structure, and we may say that the electrical effect of the methyl group on $\mathrm{C_1}$ has polarized the double bond. A group with a positive field would similarly induce polarization in the opposite direction. In a conjugated system, such as benzene, these induced charges will, by simple resonance, show up on alternate carbon atoms.

In conclusion, it should be stated clearly that it is not the intention to convey the impression that the electrical effect described herein is the sole or necessarily the most important effect operating to influence reactivity or electron distribution. The approximate evaluation presented does indicate that the electrical effects can, in many instances, be an important contribution.

It should be pointed out further that the complex depicted is not a transition state, and its energy of formation is not the energy of activation. In the transition state the charges on the ring will all be

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(6) Kirkwood and Westheimer, *J. Chem. Phys.*, **6**, 506 (1938).

(7) Perhaps at least as reasonable a value for the dielectric constant would be $D = 2$, approximately the value for benzene itself. This would halve the energy values listed in Table I.

(8) (a) Baker and Nathan, *J. Chem. Soc.*, 519, 1840 (1935); (b) Berliner and Bondhus, THIS JOURNAL, **68**, 2355 (1946); **70**, 854 (1948).

(9) It is of some interest to consider the source of the commonly-accepted reverse order of electron release, the dipole moments of methyl chloride (1.86), ethyl chloride (2.03), isopropyl chloride (2.18), and *t*-butyl chloride (2.15) (Wiswall and Smyth, *J. Chem. Phys.*, **9**, 356 (1940)). On the presumption that the carbon–chlorine bond moments remain constant in this series but that charge is distributed from the carbon atom holding the chlorine to adjacent carbons so that the charge on the second carbon is just half that on the first, we arrive at the following charge distributions:

$$\overset{+0.9}{\mathrm{CH_3}}-\overset{-0.9}{\mathrm{Cl}},\quad \overset{+0.3}{\mathrm{CH_3}}\overset{+0.6}{\mathrm{CH_2}}-\overset{-0.9}{\mathrm{Cl}}.\quad \overset{+0.23}{\mathrm{(CH_3)_2}}\overset{+0.45}{\mathrm{CH}}-\overset{-0.9}{\mathrm{Cl}},\quad \overset{+0.18}{\mathrm{(CH_3)_3}}\ \overset{+0.36}{\mathrm{C}}-\overset{-0.9}{\mathrm{Cl}}.$$

On the basis of these charge distributions, the calculated dipole moments are 1.87, 2.07, 2.21 and 2.18, respectively.

less fully developed than in the ionic intermediate. For this reason and because of the assumption of a dielectric constant of unity, the tabulated electrostatic energies represent maximum values in excess of those actually contributing to the reaction rates. Furthermore, the difference between the change in activation energy and the change in energy of the intermediate ion will be a function of the endothermicity of the process of its formation. The more endothermic the process, the more nearly will the change in activation energy approximate the change in energy of formation. As the process becomes more exothermic, the activation energy will decrease and changes in the energy of formation will have continuously smaller influence on the activation energy.[10]

[10] This relationship was pointed out to the author in a discussion with Professor Herbert C. Brown of Purdue University. The author is indebted to Professor Brown for permission to present this interpretation here. It will be discussed in detail by him in papers with his students reporting their work on directive effects.

NOTRE DAME, INDIANA RECEIVED MARCH 22, 1950

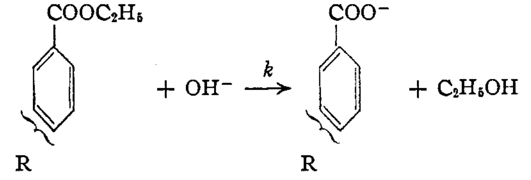
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Rates of Saponification of Ethyl *m*- and *p*-Toluate and *m*- and *p*-*t*-Butylbenzoate

BY CHARLES C. PRICE AND DWIGHT C. LINCOLN[1,2]

The effect of *t*-butyl groups in the meta and para position on the saponification of ethyl benzoate has been determined. Analyzed in terms of an "apparent" electrical effect, the influence seems anomalous. It has been suggested that the anomaly is due to the bulk effect of the large alkyl group decreasing solvation stabilization of the charged transition complex.

The nature of the influence of alkyl groups on reactivities of aromatic compounds has been the subject of a great deal of experiment and much controversial interpretation. It was the purpose of the investigation reported herein to obtain data on the difference between the influence of the methyl and *t*-butyl groups on a simple, well understood reaction, the saponification of an ester. We have therefore studied the rates of saponification of ethyl *m*- and *p*-toluate and *m*- and *p*-*t*-butylbenzoate in 56% by weight aqueous acetone at 25 and 40°.



R = Me or *t*-Bu

Experimental[3,4]

The *m*- and *p*-toluic acids were obtained from Monroe Scientific Service, Hilton, New York, and melted at 111–112° and 178–179°, respectively.

***m*-*t*-Butylbenzoic Acid.**—*t*-Butylbenzene was converted to *m*-bromo-*t*-butylbenzene by nitration, reduction, acetylation, bromination, hydrolysis, diazotization and treatment with hypophosphorous acid. The *m*-bromo-*t*-butylbenzene so obtained boiled at 116.5° at 27 mm., $n^{20}\text{D}$ 1.5343–1.5351 (lit.[5] b.p. 103–106° (17 mm.), $n^{20}\text{D}$ 1.5337).

The Grignard reagent from 95 g. of this *m*-bromo-*t*-butylbenzene and 12 g. of magnesium in 500 ml. of ether was treated with carbon dioxide at −5 to 0°. After acidification with 6 *N* hydrochloric acid, the ether was extracted with portions of 10% sodium bicarbonate. Acidification of the combined extracts precipitated 60 g. of crude acid, purified by crystallization from "Skellysolve L" to yield 25 g. (32%), m.p. 127.2–127.6° (lit.[6] m.p. 127.0–127.6°).

***p*-*t*-Butylbenzoic Acid.**—*t*-Butylbenzene was converted in 85% yield to *p*-*t*-butylacetophenone, b.p. 137° (15 mm.) (lit.[7] b.p. 137–138° (16 mm.)). The acetyl group was converted to carboxyl in 96% yield by adding one mole of ketone to approximately 400 g. of potassium hypochlorite in 3.5 l. of water at 60° with stirring. The potassium hypochlorite solution was prepared by treating 500 g. of "H.T.H." (commercial 70% calcium hypochlorite) in 2 l. of warm water with 350 g. of potassium carbonate and 100 g. of potassium hydroxide in 1 l. of water. The precipitate of calcium carbonate was removed by filtration before use. The acid was precipitated by acidification and purified by crystallization from aqueous methanol, m.p. 166.0–166.3° (lit.[6] m.p. 165–165.6°).

Ethyl Esters.—All the esters were prepared by standard Fisher esterification with ethanolic hydrogen chloride and purified by distillation through a 90 × 1.2-cm. column with double glass spiral packing. A constant-boiling center fraction was taken for the samples employed in the rate experiments. Results are summarized in Table I.

TABLE I

PHYSICAL CONSTANTS FOR ETHYL ESTERS

Substituent	B.p. °C.	Mm.	$n^{20}\text{D}$
m-Methyl	105.6	11	1.5055
p-Methyl	102.6–102.8	8.5	1.5085
m-*t*-Butyl[a]	112.6–112.8	4.2	1.4994
p-*t*-Butyl[b]	117.0–117.8	5.0	1.5017

[a] *Anal.* Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.32; H, 8.86. [b] Marvel, Johnston, Meier, Mastin, Whitson and Himel, THIS JOURNAL, 69, 914 (1947), report b.p. 120–120.5° (4 mm.).

Rate Measurements.—In general, the procedure was that described by Tommila and Hinshelwood[8] and extended by Tommila.[9] Equal volumes of 0.1 *M* ester and alkali dissolved in 56% by weight (60% by volume) aqueous acetone were mixed at the desired temperature. Samples were withdrawn at timed intervals by means of a volumetric pipet, discharged into an excess of standard hydrochloric acid and the excess back-titrated with standard sodium hydroxide, using phenolphthalein as an indicator.

The alkali solution was prepared by diluting exactly 0.01 mole of carbonate-free sodium hydroxide solution from the stock solution of approximately 0.275 *N* with enough water to make 40 ml., assuming the volumes to be additive. This was then diluted to 100 ml. with acetone in a 100-ml. volu-

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[1] Eastman Kodak Company Fellow, 1947–1948. Present address: Hercules Powder Company, Wilmington, Delaware.

[2] Abstracted from part of a Ph.D. thesis presented to the University of Notre Dame by Dwight C. Lincoln.

[3] All melting points were recorded with a modified Hershberg apparatus (Fieser "Experiments in Organic Chemistry," D. C. Heath Co., New York, N. Y., 2nd Ed., 1941, p. 327) and correspond to corrected values.

[4] Microanalysis by Microtech Laboratories, Skokie, Illinois.

[5] Marvel, Allen and Overberger, THIS JOURNAL, 68, 1088 (1946).

[6] Serijan, Hipsher and Gibbons, *ibid.*, 71, 873 (1949).

[7] Mowry, Renoll and Huber, *ibid.*, 68, 1105 (1946).

[8] Tommila and Hinshelwood, *J. Chem. Soc.*, 1801 (1938).

[9] Tommila, *Ann. Acad. Sci. Fennicae*, Ser. A57, No. 13, 3 (1941); *C. A.*, 38, 6171 (1944).