until the eluate gave a negative silver nitrate test for chloride ion. The resin was then thoroughly washed with distilled water until the washings were neutral. It was then dried in an oven for several hours at about 40° and kept in a vacuum desiccator for 24 hr. before use.

C. 1-*p*-Tolyl-4-carbethoxy-4′-phenylazetidin-2-one (IV).—Ethyl N-(*p*-tolyl)-α-chloroacetamidophenylacetate (0.69 g.) was dissolved in absolute ethanol (10 ml.) and the resin (0.88 g.) was added to it and the contents were stirred by means of a magnetic stirrer for 2 hr. at room temperature. The reaction mixture was then filtered and the resin was washed once with a little absolute alcohol. The resin gave a positive test for chloride ion. The filtrate was evaporated in a vacuum desiccator leaving behind a colorless viscous liquid. Maceration of this liquid with petroleum ether (b.p. 90–120°) afforded a colorless crystalline material (0.56 g., 90%). Recrystallization from petroleum ether afforded colorless crystals, m.p. 49–50°. The infrared spectrum had peaks at 5.65 μ owing to the β-lactam carbonyl and 5.72 μ owing to the carbonyl of the ester group.

Anal. Calcd. for $C_{19}H_{19}NO_3$: C, 73.54; H, 6.12; N, 4.51. Found: C, 73.48; H, 6.13; N, 4.45.

Synthesis of 1-Phenyl-5,5′-dicarbethoxypyrrolidin-2-one (VI). **A. Diethyl Anilinomalonate** (III).—A mixture of 9.3 g. of freshly distilled aniline and 11.95 g. of diethyl bromomalonate was placed in a round-bottomed flask fitted with a two-way stopcock and evacuated to 40-mm. pressure. The reaction mixture was then allowed to stand at 70° in an oven for 8 hr. Extraction of the solid cake with ether afforded a residue of 8.6 g. of aniline hydrobromide which corresponded to 100% conversion. The ethereal solution was washed with 2 *N* hydrochloric acid and then with distilled water. Removal of the solvent after drying the solution over anhydrous magnesium sulfate afforded the anilinomalonate as colorless crystalline solid, m.p. 44–45°, yield 11.9 g. (95%).

B. Diethyl ω-Bromopropionilidomalonate (V).—A mixture of diethyl anilinomalonate (5.0 g.), β-bromopropionic acid (5.0 g.), and phosphorus trichloride (2.5 ml.) was refluxed in dry benzene solution for about 4 hr. The cooled reaction mixture was decanted and the benzene solution was thoroughly washed with distilled water. The dried solution was distilled to remove as much solvent as possible. The residue obtained was a pale yellow viscous liquid which soon solidified. Recrystallization from petroleum ether (b.p. 60–80°) afforded colorless plates, m.p. 51–52°, yield 85%. The infrared spectrum shows peaks at 5.75 μ owing to the carbonyl of the ester groups and at 6.0 μ owing to the carbonyl of the open-chain amide function. A flame test indicated the presence of halogen.

C. 1-Phenyl-5,5′-dicarbethoxypyrrolidin-2-one (VI).—An absolute ethanolic solution of diethyl ω-bromopropionilidomalonate (0.78 g.) was treated with the resin (0.88 g.) and stirred magnetically at room temperature for a period of 2 hr. The resin was filtered off and washed with little absolute alcohol. The resin gave a positive test for bromide ion. The alcoholic solution was carefully evaporated in a vacuum desiccator, leaving a pale yellow liquid. It had a refractive index of 1.5135 at 30° and was halogen free (yield 85%). The refractive index agreed well with that of an authentic sample. A small portion of the liquid was hydrolyzed with potassium hydroxide giving the monoacid, 1-phenyl-5-carboxy-5′-carbethoxypyrrolidin-2-one, m.p. 150–151°. There was no depression in a mixture melting point with a sample prepared by the conventional method. The infrared spectrum had peaks at 5.75 and 5.70 μ.

Acknowledgment.—The authors wish to express their sincere thanks to Professor Ajay K. Bose of Stevens Institute of Technology, Hoboken, New Jersey, for kindly supplying the infrared spectra of all the compounds sent to him and for his valuable suggestions.

Aromatic Fluorine Compounds. III.[1] Introduction of a Fluorine Atom into Substituted Aromatic Rings

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The gas phase decarboxylation of aromatic fluoroformates was successfully applied to substituted aromatic fluoroformates, containing substituents of sufficiently high thermal stability, such as bromine, fluorine, methyl, or trifluoromethyl. The method was also successful in the case of the polycyclic α-naphthyl fluoroformate. A polar reaction mechanism (S_Ni) is suggested. In the case of *p*-methoxyphenyl fluoroformate the corresponding fluoride could not be obtained.

In the preceding paper[1] a novel method has been described for introducing a fluorine atom into an aromatic ring by gas phase decarboxylation of phenyl fluoroformate or thiol fluoroformate. Yields of fluorobenzene as high as 90% have been achieved. In this paper the application of this method to nuclear-substituted aromatic compounds will be reported.

Eight different substituted aromatic fluoroformates were prepared and their decarboxylation was investigated. Table I gives the results of their preparation from the corresponding phenols and COFCl. When small amounts of a tertiary amine were used as a catalyst a nearly quantitative conversion of the starting material to the fluoroformate was obtained. The use of an organic solvent such as toluene or benzene in these reactions was advantageous. All reactions were carried out in stainless steel cylinders at over atmospheric pressures; however, a continuous process at atmospheric pressure should be applicable too. The purity of the COFCl was not critical. Impurities as high as 10% of $COCl_2$ and COF_2 did not influence the yield of fluoroformate so long as COFCl was used in excess. Table II shows the physical and spectral properties of these compounds. All of them are colorless lachrymatory liquids with a strong fluoroformate odor. Their thermal stability is higher than that of comparable chloroformates.

The high-temperature gas phase decarboxylation was investigated only in quartz tubes with Pt-gauze filling, since this system had previously given the best results for phenyl fluoroformate.[1] Table III shows the results of these reactions; however, no attempts were made to maximize the yields. Therefore, the yields of the corresponding substituted aryl fluorides, listed in Table III (ranging from 25 to 57%), could probably be increased by investigating the most favorable reaction conditions.

The new method is limited to substituents that exhibit a higher thermal stability than the fluoroformate group. In the case of *p*-methoxyphenyl fluoroformate,

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[1] For part II of this series, see K. O. Christe and A. E. Pavlath, *J. Org. Chem.*, **30**, 3170 (1965).

TABLE I

PREPARATION OF SUBSTITUTED AROMATIC FLUOROFORMATES FROM THE CORRESPONDING PHENOLS AND COFCl[a]

Phenol substituent	Reactants, mole		Solvent (ml.)	Reaction temp., °C.	Reaction time, hr.	% conversion[b] of phenol	% yield of fluoroformate[b]
	Phenol	COFCl					
2-Bromo	0.14	0.48	Benzene (40)	60	12	45	100
	0.14	0.57	Benzene (55)	100	24	99.9	100
4-Bromo	0.1	0.33	Toluene (50)	70	12	100	99.9
2-Fluoro	0.11	0.48	Benzene (50)	60	12	100	100
4-Fluoro	0.1	0.30	Toluene (50)	60	16	100	99
4-Trifluoromethyl	0.09	0.30	Toluene (50)	70	12	99	100
4-Methyl	0.11	0.33	Benzene (50)	60	15	100	99
4-Methoxy	0.1	0.30	Toluene (50)	60	18	100	99
α-Naphthyl fluoroformate	0.07	0.20	Toluene (50)	60	14	100	99

[a] All reactions were run in a 150-ml. stainless steel lecture bottle, using 0.5 ml. of NBu_3 as a catalyst. The lecture bottles were agitated for the reaction time listed and heated externally by infrared lamps. [b] The conversion of the starting material and the yields were determined by g.c. ratios of the crude product before distillation.

for example, no *p*-methoxyfluorobenzene was obtained, only phenyl fluoroformate.

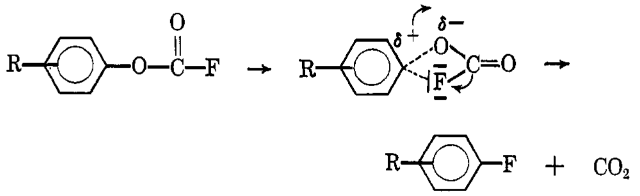
The reaction mechanism for the introduction of a fluorine atom into a nucleus by the gas phase decarboxylation of an aromatic fluoroformate was not primarily investigated; however, from the experimental results and previous reports, certain conclusions concerning the mechanism can be made. Analogous to the Schiemann reaction[2] the reaction could proceed through either (i) a carbonium cation, (ii) a free radical, or (iii) a polar structure.

(i) The ionic reaction mechanism was investigated in the case of the decarboxylation of aromatic and aliphatic chloroformates. It was found that aryl chloroformates react with aromatic hydrocarbons in the presence of Lewis acids, such as $AlCl_3$, to give phenyl benzoate or its derivatives.[3] Under similar reaction conditions alkyl chloroformates decompose readily to alkyl chlorides, which in turn alkylate the aromatic hydrocarbon.[4,5] This indicates, that an aryl-O-CO$^+$ cation is more stable than an alkyl-O-CO$^+$ cation. The aryl-O-CO$^+$ cation undergoes a Friedel-Crafts reaction rather than decomposing to a phenyl cation.

A similar behavior was found in the case of the fluoroformates. It was shown that alkyl fluoroformates can be readily decarboxylated to alkyl fluorides in the presence of Lewis acids or bases as catalysts,[6] while under similar conditions phenyl fluoroformate undergoes only polymerization and carbonate formation.[1] Therefore, the decarboxylation of aryl haloformates can be expected to result in the formation of higher condensed aromatic compounds and not in aryl halides, provided it follows an ionic reaction mechanism. In addition, the formation of free ions in a gas phase reaction at 700° is not very likely. On this basis an ionic reaction mechanism can be excluded.

(ii) A free-radical mechanism, assuming completely free radicals of appreciable lifetime outside the van der Waals interaction sphere, can also be rejected. In this case isomer formation should be found in the decarboxylation of the substituted phenyl fluoroformates. This was never observed. The fluorine atom always entered the nucleus at the site of the fluoroformate group.[7] In addition, one could expect along with the isomerization some biphenyl formation and fluorine addition across an aromatic double bond.[8] This, however, was not the case.

(iii) The most likely mechanism is an internal nucleophilic substitution (SNi),[9] assuming the following internal return reaction. The activated intermediate is an ion pair with a partial positive charge on the α-carbon atom. This mechanism was investigated for alkyl chlorosulfites and alkyl chloroformates,[10] confirming the SNi mechanism. In our case, the steric and electronic configuration (overlapping of the fluorine atom orbitals with the π cloud of the aromatic system) strongly favor an ion-pair intermediate. The intermediate could decompose either by a radical mechanism (elimination of CO_2, formation of a phenyl and fluorine radical and their immediate combination) or a polar mechanism. We tend to prefer the polar mechanism due to the pronounced electronegativity differences between the α-carbon atom and the fluorine atom. In addition, the C-O-C bond is thermally less stable than the C-F bond. Therefore, the C-O-C bond should cleave first, followed by a nucleophilic attack of the fluorine atom on the electron-deficient α-carbon atom. Kinetic investigations of the influence of different substituents and of concentration effects upon yields and conversion would be a further proof of the correctness of the suggested mechanism.



Experimental Section

Starting Materials.—Carbonyl chloride fluoride was prepared from $COCl_2$ and AsF_3.[11] No purification of the crude COFCl

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[2] A. Roe, *Org. Reactions*, **5**, 196 (1949).

[3] W. H. Coppock, *J. Org. Chem.*, **22**, 325 (1957).

[4] E. H. Renne, *J. Chem. Soc.*, **41**, 33 (1882).

[5] N. P. Buu-Hoï and J. Janicaud, *Bull. soc. chim. France*, **12**, 640 (1945).

[6] S. Nakanishi, T. C. Myers, and E. V. Jensen, *J. Am. Chem. Soc.*, **77**, 3099, 5033 (1955).

[7] During the decarboxylation of bromophenyl fluoroformates bromine-free or dibromo derivatives were obtained in small quantities. This can be explained by the fact that bromobenzene itself starts to decompose at 757° at a contact time of 0.6 sec. at a rate of 1.86%: M. Szwarc and D. Williams, *J. Chem. Phys.*, **20**, 1171 (1952). The rate of decomposition was found to be independent of the substituent in the ring: M. Szwarc and D. Williams, *Proc. Roy. Soc.* (London), **A219**, 341 (1953).

[8] L. A. Bigelow, *et al.*, *Ind. Eng. Chem.*, **39**, 360 (1947).

[9] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1959, p. 294.

[10] E. S. Lewis and W. C. Herndon, *J. Am. Chem. Soc.*, **83**, 1955 (1961).

[11] K. O. Christe and A. E. Pavlath, *J. Org. Chem.*, **30**, 1639 (1965).

TABLE II

PHYSICAL AND SPECTRAL PROPERTIES OF THE SUBSTITUTED PHENYL FLUOROFORMATES[a]

Substituent	B.p., °C. (mm.)	n_D (°C.)	Density, g./cm.^{3} (°C.)	Calcd., % C	H	Br	F	Found, % C	H	Br	F	N.m.r.[b] F^{19}	Proton
2-Bromo	66 (4.5)	1.5110 (22)	1.610 (23.5)	38.36	1.83	36.53	8.68	38.62	1.92	36.96	8.7	18.9 (s, -OCOF)	450 (m)
4-Bromo[c]	72.5 (6)	1.5170 (23.8)	1.657 (24)	38.36	1.83	36.53	8.68	38.47	1.97	36.80	8.8	16.6 (s, -OCOF)	
2-Fluoro	33 (6.5)	1.4434 (23)	1.275 (24)	53.17	2.55		24.04	53.15	2.66		23.8	19.5 (s, -OCOF), 130 (s, phenyl F)	445 (m)
4-Fluoro	52 (15)	1.4490 (23.5)	1.304 (24.8)	53.17	2.55		24.04	53.00	2.47		23.8	16.8 (s, -OCOF), 115 (s, phenyl F)	425 (m)
4-Trifluoromethyl	68 (25)	1.4151 (25.5)	1.390 (24)	46.16	1.92		36.55	46.21	1.96		36.6	16.8 (s, -OCOF), 63.7 (s, $-CF_3$)	435 (m)
4-Methyl	70 (17)	1.4663 (24)	1.143 (24.8)	62.34	4.55		12.34	62.32	4.51		11.8	16.6 (s, -OCOF)	400 (m), 115 (s, $-CH_3$)
4-Methoxy	51 (1)	1.4843 (23)	1.252 (24.8)	56.47	4.12		11.18	56.34	4.14		11.3	17.4 (s, -OCOF)	405 (m), 217 (s, $-OCH_3$)
α-Naphthyl fluoroformate	80 (1)	1.5662 (24)	1.251 (24.5)	69.47	3.68		10.00	69.36	3.67		9.7	16.6 (s, -OCOF)	Complicated m in aromatic region

[a] The infrared spectra of all compounds were taken and showed the characteristic fluoroformate absorptions: $\nu_{C=O}$ 1840–1850 cm.$^{-1}$, ν_{COC} 1220–1260 cm.$^{-1}$, ν_{CF} 990–1000 cm.$^{-1}$, and the characteristic patterns for the corresponding substituted aromatics. [b] All spectra were recorded on a Varian HR-60 spectrometer using 5% solutions in CCl_4 containing $CFCl_3$ as an internal reference Chemical shifts are quoted as parts per million upfield from $CFCl_3$ and as cycles per second downfield from tetramethylsilane. [c] This compound was reported in the literature to have b.p. 65° (1.5 mm.) and $n^{25}D$ 1.5166: W. A. Sheppard, *J. Org. Chem.*, **29**, 1 (1964).

TABLE III

DECARBOXYLATION OF SUBSTITUTED AROMATIC FLUOROFORMATES TO THE CORRESPONDING FLUORIDES[a,b]

Fluoroformate	Reaction temp.,[e] °C.	Contact time, sec.	% conversion of the starting material[c]	Products, % yield[c,d] Substituted fluorobenzene	Substituted phenol	Phenyl fluoroformate	Benzene	Fluorobenzene	Substituted benzene	Tar + decompn. products
o-Bromophenyl	780	1.5	68.4	*o*-Bromo, 29.4	*o*-Bromo, 5.5	2.1	0.2	1.9	1,2-Dibromo, 1.3	59.6
p-Bromophenyl	700	3	42.4	*p*-Bromo, 55.9		Trace	Trace	Trace	1,4-Dibromo, trace	43.8
	790	1.5	90.9	*p*-Bromo, 57.2		Trace	Trace	2.8	1,4-Dibromo, 8.6	31.4
	750	2.5	76.0	*p*-Bromo, 50.9		3.5	0.4	2.3	1,4-Dibromo, 4.3	38.6
o-Fluorophenyl	730	3	34.8	*o*-Fluoro, 15.7	*o*-Fluoro, 32.9			3.9		47.5
	690	7	2.5	*o*-Fluoro, 38.2	*o*-Fluoro, 34.6			3.2		24.0
	790	1.5	77.9	*o*-Fluoro, 35.1	*o*-Fluoro, 29.9			5.0		30.0
p-Fluorophenyl	730	3	88.3	*p*-Fluoro, 37.7	*p*-Fluoro, 18.9					44.4
p-Trifluoromethylphenyl	720	1.5	29.5	*p*-Trifluoromethyl, 36.4					Trifluoromethyl, 6.3	57.3
	660	7	12.3	*p*-Trifluoromethyl, 42.6					Trifluoromethyl, 3.4	54.0
p-Methylphenyl	750	3	96.1	*p*-Methyl, 33.8	*p*-Methyl, 21.2		15.6	3.2	Methyl, 0.5	25.7
p-Methoxyphenyl	700	2	100	*p*-Methoxy, . . .		21.4	7.2	3.4		69.0
	660	2	89	*p*-Methoxy, . . .		21.2	5.2	0.7		72.9
1-Naphthyl	750	3	100	1-Fluoronaphthalene, 14.2					Naphthalene, 2.3	83.5
	680	7	100	1-Fluoronaphthalene, 25.0					Naphthalene, trace	74.8

[a] All reactions were carried out at atmospheric pressure using dry nitrogen as a carrier gas and a tubular quartz reactor (diameter 1 cm., length of heated zone 33 cm.) with Pt gauze as a filling. [b] The vapor pressure of the fluoroformate was maintained at 100 mm. in every case. [c] The conversion of the starting material and the yields were determined by g.c. ratios of the crude product before separation. [d] The compounds were separated on a preparative g.c. column and identified by their retention times and infrared and n.m.r. spectra. [e] The reaction temperature was measured by a thermocouple on the outside wall of the tubular reactor.

(containing 90 to 95% COFCl) was required, since the presence of $COCl_2$ and COF_2 as impurities did not result in the formation of undesired products provided COFCl was used in excess. All the other chemicals were purchased from supply houses.

Preparation of Substituted Phenyl Fluoroformates.—All reactions were carried out in the same way, except for slight variations in reaction time, temperature, solvent, and amount of reactants (listed in Table I). In a typical experiment, *p*-fluorophenol (0.1 mole), COFCl (0.3 mole), toluene (50 m.) as a solvent, and tributylamine (0.5 ml.) as a catalyst were placed into a 150-ml. stainless steel lecture bottle equipped with a pressure gauge and a Whitey valve. The lecture bottle was agitated 16 hr. at 60° (external heating by two infrared lamps). The volatile products, mostly HCl and excess carbonyl halides, were bled off. The product was degassed at room temperature in a vacuum. The resulting solution was filtered and vacuum distilled. The conversion of the starting material and yield of *p*-fluorophenyl fluoroformate were determined by the g.c. ratios of the crude product before distillation and are listed in Table I. The yields after distillation were usually somewhat lower due to mechanical losses during the distillation. Physical and spectral properties of the substituted phenyl fluoroformates are listed in Table II.

Decarboxylation of the Substituted Phenyl Fluoroformates.—The same setup was used for all reactions. A stream of dry N_2, monitored by a flowmeter, was passed through a 10-ml. flask, containing the fluoroformate starting material. A fluoroformate vapor pressure of 100 mm. was maintained by external heating of the flask with an oil bath. The fluoroformate–nitrogen mixture was passed through an electrically heated quartz tube with Pt gauze used as filling. The products were quenched at the exit of the tube by two cold traps, one at −78 and the other at −196°. The second trap was connected to a mercury blowoff. The heating of the reaction tube was automatically controlled and its temperature was measured with a thermocouple on its outside wall. The inlet part of the setup between the fluoroformate container and the reaction tube was heated by three infrared lamps to prevent condensation of the starting material. The conversion of the starting material and the yields were determined by weighing of the recovered starting material and of the collected products. The composition of the products was analyzed by g.c. The compounds themselves were identified after g.c. separation by infrared measurements and by n.m.r. measurements. The results of all these reactions are summarized in Table III.

Thermochromic Compounds. II

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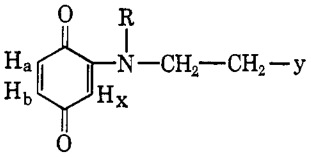
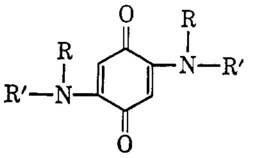
Received June 9, 1965

β-Hydroxyl secondary amines react with quinones to form monosubstituted compounds which are thermochromic. N.m.r. spectra show that the structure of the "colorless" thermochromic compound is not I, but a product formed from I by intramolecular reaction between the hydroxyl group and the quinone moiety.

Konig and co-workers[2-4] have reported that certain compounds of type I (Y = OH) are thermochromic,[5] piezochromic, solvatochromic, fluorescent, soluble in base as well as in acid, and have an unusual double polarographic reduction curve.



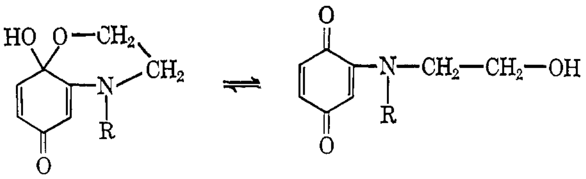
Ia, R = CH_2CH_2OH; Y = OH
b, R = CH_3; Y = OH
c, R = CH_3; Y = Cl



IIa, R = H;
R′ = CH_2CH_2OH
b, NRR′ = morpholinyl

These properties are related to specific structural details: the hydroxyl group must be on the carbon β to the nitrogen, the R group may not be a hydrogen, the hydrogen α to the nitrogen may not be substituted, and the quinone ring may be substituted at H_a and H_b with methyl groups or a fused ring. Similar compounds lacking any one of these structural details show none of the above listed properties. The 2,5-disubstituted β-ethanolaminoquinones are not thermochromic.

The nonthermochromic aminoquinones are deeply colored, while the thermochromic quinones are light in color but become deeply colored when their solutions are heated. A temperature-dependent equilibrium has been suggested for the thermochromic mechanism.[4]



cold form
III

hot form
IV

There are several reasonable structures and equilibria which might be proposed. For this reason the n.m.r. spectra of three of these compounds and several model compounds were run at temperatures from 37 to 120° to determine the structure and equilibrium responsible for the thermochromism and other unusual properties.

Results

The spectrum of Ic is relatively simple, as seen in Table I. The spectrum showed no temperature dependence.

TABLE I

ABSORPTION PEAKS OF COMPOUND Ic AT 37°

In $CDCl_3$		In DMSO-d_6		No. of protons	Assignment	Ref.[a]
P.p.m.	Shape	P.p.m.	Shape			
6.66	2 peaks	6.76	2 peaks	2	Ring	314
5.71	Singlet	5.70	Singlet	1	Ring	
3.81	Quartet	3.95	Triplet	4	Methylenes	12, 29, 31, 199
3.10	Sharp	3.10	Sharp	3	Methyl	91, 610

[a] The numbers given are the spectra numbers from "NMR Spectra Catalog," N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, Ed., Varian Associates, Inc., Palo Alto, Calif., 1962.

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[1] Summer N.S.F. Teacher Research Participation Program, Dominican College, Racine, Wis.

[2] K.-H. Konig, *Chem. Ber.*, **92**, 257 (1959).

[3] K.-H. Konig and G. Letsch, *ibid.*, **92**, 1789 (1959).

[4] H. Berg, K.-H. Konig, D. Tresselt, and H. Wagner, "Contributi Teorici e Sperimentali di Polarografia," Vol. 5, Consiglio Nazionale Delle Ricerche, Spoleto, Italy, 1960.

[5] J. H. Day, *Chem. Rev.*, **63**, 65 (1963).