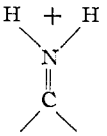
tetrazole. In the sodium salt these appear at 3400 and 3333 cm.$^{-1}$ and at 3450 and 3370 in the light green and 3395 and 3333 in the hemihydrate. Since no lowering of frequency, compared to the sodium salt, is observed, bonding to the 5-amino group is not suggested.

Considerably more details than have been previously described are found in the 2940–2500 cm.$^{-1}$ region and presumably represent the ring N–H group. These bands are not present in salt or complexes.

In the 1680–1440 cm.$^{-1}$ region are a number of sharp bands including the one previously unknown, at 1450–1440 cm.$^{-1}$. The 1675 and 1640 and 1610 absorptions have been discussed[8–10] and are attributed variously to exo-amino bending (1675–1640) and to —N=N— or



If the latter is the correct assignment for 1610 cm.$^{-1}$, it should not appear in any of the salts. The 1450 cm.$^{-1}$ band may be the missing C=N (endo) and the 1300–1250 cm.$^{-1}$ band may be the exo C–N stretch.

In the 1160–900 cm.$^{-1}$ region are a number of bands, which have been attributed to ring vibrations.[8–10] Basic differences are shown between the simple sodium salt and the complexes which suggest ring involvement. Coördination involving the ring would probably not be between two adjacent nitrogen atoms and so it is probable that the copper atom is not in the plane of the ring.

Ring participation is also indicated by its rupture on treatment of the complexes with dilute acids.

Acknowledgment.—The author wishes to thank the Fulbright Commission and the U. S. Atomic Energy Commission which supported this work in Chile and the U. S., respectively. Thanks are also due R. M. Herbst, who supplied the various tetrazoles and gave considerable helpful advice, and Eduardo Schalscha for his invaluable ass.stance in obtained hard-to-find materials in Chile.

EAST LANSING, MICHIGAN
SANTIAGO, CHILE

(10) D. Percival, Ph.D. Thesis, Michigan State College, 1955.

[CONTRIBUTION FROM THE EASTERN RESEARCH LABORATORY OF THE DOW CHEMICAL COMPANY]

Some Reactions of the Bis-[Salicylaldimine]-Cu(II) Chelates

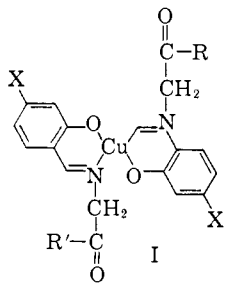
BY HERBERT S. VERTER[1] AND ALBERT E. FROST[2]

RECEIVED NOVEMBER 4, 1958

Several new Schiff bases having the bis-[salicylaldimine]-Cu(II) structure were prepared. Transesterification and amidation reactions were performed on bis-[salicylaldimine]-Cu(II) chelates derived from amino acid esters and a mechanism is proposed to explain rapid ester exchange of the bidentate chelates and absence of ester exchange under comparable conditions in the tridentate chelates. A reaction involving ligand exchange is reported.

It is of considerable interest to study the reactions of simple metal chelate systems in order to gain an insight into the more complex systems in which metals are involved.

This project was modelled after some experiments of Pfeiffer which seemed capable of further extension.[3] Pfeiffer's experiments involved transesterifications on the amino acid ester portion of bis-[N-(carboxymethyl methyl ester)-salicylaldimine]-Cu(II), Ia (R = OMe, X = H). For example, refluxing Ia in *n*-butyl alcohol for ten minutes gives Ib (R = OBu, X = H).



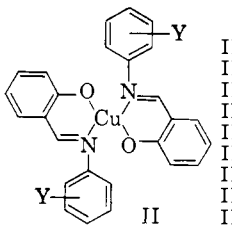
Ia, R = OMe	X = H	
Ib, R = OBu	X = H	
Ic, R = NHBu	X = H	
Id, R = $NHCH_2COOMe$	X = H	
Ie, R = OMe	X = Cl	
If, R = OMe	X = OH	
Ig, R = NHBu	X = OH	
Ih, R = NHBu	X = Cl	
Ii R = OBu	X = Cl	

I

(1) Department of Chemistry, Harvard University, Cambridge, Mass.

(2) Chas. Pfizer and Co., Inc., Brooklyn 6, N. Y.

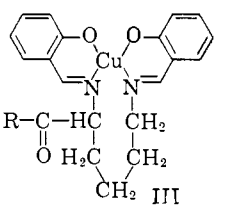
(3) P. Pfeiffer, W. Offerman and H. Werner, *J. prakt. Chem.*, **159**, 313 (1942).



II

IIa, Y = *o*-Cl	IIm, Y = *m*-COOMe
IIb, Y = *m*-Cl	IIn, Y = *p*-COOMe
IIc, Y = *p*-Cl	IIo, Y = *o*-COOMe
IId, Y = *o*-NO_2	
IIe, Y = *m*-NO_2	
IIf, Y = *p*-NO_2	
IIg, Y = *o*-NO_2, *p*-OMe	
IIh, Y = H	
IIi, Y = *o*-OC_2H_5	
IIj, Y = *m*-OC_2H_5	
IIk, Y = *p*-OC_2H_5	
IIl Y = *o*-OMe	

Several of Pfeiffer's experiments on bis-[N-(carboxymethyl methyl ester)-salicylaldimine]-Cu-(II) (Ia) were repeated successfully. In addition, a successful transesterification was run on Ie (R = OMe, X = Cl) with butyl alcohol to produce Ii (R = OBu, X = Cl).



III

IIIa, R = OMe
IIIb, R = NHBu
IIIc, R = OBu
IIId, R = OEt

In an attempt to extend the transesterification reaction to mercaptans, and formation of thiol

TABLE I

CHARACTERIZATION OF BIS-[SALICYLALDIMINE]-Cu(II) CHELATES

No.	M.p., °C.	Color	Preparative method	Recryst. solvent	Solubility[a] Lig-roin	Ether	Ace-tone	Chloro-form	Ben-zene	Water	Pyri-din	Metha-nol	Di-oxan	Ele-ment	Anal. data, % Calcd.	Found
IIa	270	Light brown	Ref. 3	Benzene–ligroin	i	sls	sls	s	sls	i	s	sls	sls	Cu	12.1	11.7
														N	5.35	5.1
IIb	206	Burnt umber	Ref. 3	Benzene–ligroin	i	sls	s	s	s	i	s	sls	sls	Cu	12.1	11.9
														N	5.35	5.4
IIc	237	Golden brown	Ref. 3	Benzene–ligroin	sls	sls	s	s	s	i	s	sls	s	Cu	12.1	11.9
														N	5.35	5.3
IId	265	Brown	Ref. 5	Xylene–ligroin	i	sls	s	sls	sls	i	s	sls		C	57.3	57.0
														H	3.3	3.5
IIe	276	Golden brown	Ref. 3	2-Nitropropane	i	i	sls	s	sls	i	s	i	sls	Cu	11.7	11.8
														N	10.3	9.7
IIf	300	Olive green	Ref. 3	Nitrobenzene	i	sls	sls	s	sls	i	s	sls	s	Cu	11.7	11.8
														N	10.3	9.7
IIg	270	Brown green	Ref. 5	Nitrobenzene	i	i	sls	sls	sls	i	s	sls		Cu	10.5	10.2
														N	9.25	8.9
IIh	140	Brown	Ref. 3	Benzene–ligroin	sls	s	s	s	s	i	s	s	s	Cu	13.9	13.2
														N	6.15	6.2
IIi	100	Brown	Ref. 3	Methanol	sls	sls	s	s	s	i	s	sls	s	Cu	11.7	10.8
														N	5.15	5.3
IIj	127	Brown	Ref. 3	Methanol–water	sls	s	s	s	s	i	s	s	s	Cu	11.7	11.7
														N	5.15	5.2
IIk	166	Purple brown	Ref. 3	Methanol–water	sls	s	s	s	s	i	s	s	s	Cu	11.7	11.7
														N	5.15	5.2
III	222	Brown	Ref. 3	Benzene–ligroin	i	sls	sls	s	s	i	s	s	sls	Cu	12.5	12.0
														N	5.45	5.5
IIm	178	Brown	Ref. 5	Xylene–ligroin	i	sls	s	s	sls	i	s	sls	s	Cu	11.1	10.8
														N	4.9	4.9
IIn	216	Black	Ref. 5	Xylene	i	i	sls	s	sls	i	s	i		Cu	11.1	10.8
														N	4.9	4.9
V	275	Apple green	Ref. 5	Nitrobenzene	i	i	sls	s	sls	sls	s	sls		Cu	18.8	19.2
														N	4.14	4.3
Ic	228	Tan green	Amidation	Dimethyl formamide	i	i	sls	sls	sls	i	s	sls		Cu	12.0	11.7
														N	10.6	10.5
Ig	193	Black with coppery luster	Amidation	Dimethyl formamide	i	i	sls	sls	sls	i	s	sls		N	9.95	9.1
Ih	205	Tan green	Amidation	Xylene–ligroin	i	i	sls	sls	i	i	i	i		Cu	10.6	10.4
														H	5.35	5.4
Salicylaldehyde Cu(II)	260	Olive green	Ref. 5	Not recrystallized	i	i	i	i	i	i	s	i		Cu	18.8	19.1
														C	49.7	49.4

p-Chloro salicylaldehyde Cu(II)	240	Apple green	Ref. 5	Nitrobenzene	i	i	sls	sls	i	i	s	sls	Cu 17.0 16.5 Cl 18.4 18.4
If	300	Olive green	Ref. 3	Dimethyl formamide–water	i	i	i	i	i	i	s	i	Cu 13.8 12.9 N 5.85 5.9
Ie	192	Olive green	Ref. 3	Xylene–ligroin	i	i	sls	sls	sls	i	s	i	Cu 13.7 13.6 N 5.4 5.4
Ii	169	Olive green	Transesterification	Butyl alcohol	i	sls	s	sls	sls	i	s	i	Cu 11.9 12.6 N 4.7 5.1
IV	145	Khaki	Ref. 3	Benzene–ligroin	i	i	s	s	s	i	s	sls	Cu 14.8 15.0 N 6.52 6.6

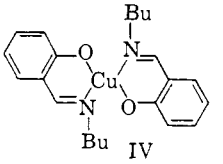
[a] i = insoluble; sls = slightly soluble; s = soluble.

esters, Ia (R = OMe, X = H) was heated with butyl mercaptan. An ash-white product, identified as the copper salt of butyl mercaptan was isolated. This is a solubility product phenomenon analogous to the decomposition of bis-[salicylaldimine]-Cu(II) chelates by hydrogen sulfide. The copper salt of butyl mercaptan is so insoluble that decomposition of the chelate occurs.

Upon refluxing Ia (R = OMe, X = H) in *n*-butylamine for ten minutes, the amide Ic (R = NHBu, X = H) was obtained. Evidence includes analyses and infrared spectra (3.05, 6.03, 6.45 μ).

Extension to other compounds of type I was successful. Bis-[N-(carboxymethyl methyl ester)-*p*-chlorosalicylaldimine]-Cu(II), Ie (R = OMe, X = Cl), behaved in the same manner as Ia. With (R = OMe, X = OH), the amidation reaction seemed to take place; but results were not conclusive. A side reaction in basic solvents may have caused anomalous results.

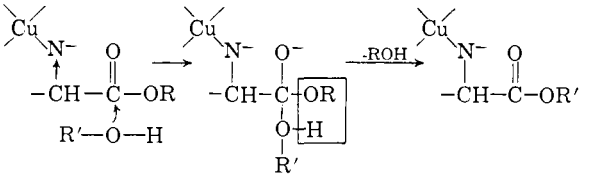
An attempt to amidate the Schiff base chelate derived from lysine, (1-carbomethoxy)-pentamethylene bis-[salicylaldimine-1,5]-Cu(II) (IIIa), R = OMe, gave not the expected amide IIIb, but *trans* - bis - [N - (*n* - butyl) - salicylaldimine]-Cu(II), formula IV. In this case amine exchange in the Schiff base is more rapid than the amidation reaction.



IV

An unsuccessful attempt was made to extend the amidation reaction to peptide formation. A solution of Ia (R = OMe, X = H) in dimethylformamide was refluxed with a tenfold excess of glycine methyl ester and sodium acetate in water, but only water-soluble tar was obtained.

The previously proposed mechanism for the transesterification reaction has been interpreted as an electron withdrawal from the carbonyl carbon through the conjugate ketimine system toward the copper atom which makes possible reaction with the donor oxygen of the solvent (R'OH) molecules.[4]

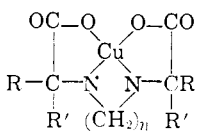


The following information raised doubts as to the validity of this mechanism. It is reported[4] that (1-carbomethoxy)-pentamethylene bis-[salicylaldimine-1,5]-Cu(II) (IIIa) (R = OMe) undergoes a transesterification reaction analogous to that of the glycine derivative Ia. However, a check of Pfeiffer's original work showed this experiment was never performed. Actually, Pfeiffer had carried out transesterifications on Ia only. Our attempts to transesterify IIIa (R = OMe)

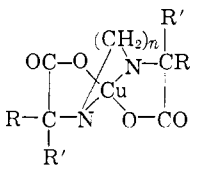
(4) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 400.

proved unsuccessful. Only starting material and decomposition products were obtained. If the mechanism of equation 1 is correct, IIIa should also undergo a transesterification reaction in view of its structural similarity to Ia. No such reaction was observed.

In searching for a new transesterification mechanism, it was realized that the glycine derivatives I exist in the *trans* configuration,[5,6] whereas the lysine derivative IIIa is held in the *cis* configuration by the pentamethylene bridge. Schlessinger[7-11] has demonstrated for a series of polymethylene bis-[α-imino acid]-copper chelates of the general formula (VA, VB) that when $n = 2$ or 3 a single form, *cis* configuration of the copper chelate exists. When $n = 10$, a single form, *trans* configuration exists. For values of $n = 5$ and $n = 7$, both *cis* and *trans* modifications were detected.

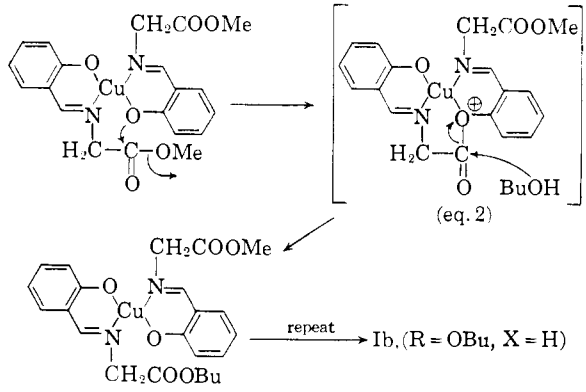


VA *cis* configuration



VB *trans* configuration

Molecular models of the Fischer–Hirshfelder type suggest that in IIIa only a *cis* configuration is possible. The square planar bonding of copper precludes the existence of rotational isomers midway between *cis* and *trans*. Column chromatograms (alumina) showed the presence of only one material which bears this out. The actual mechanism may be

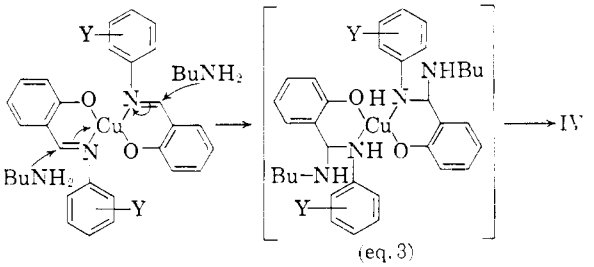


(eq. 2)

The mechanism involves an attack on the ester carbonyl linkage by the oxygen of the salicylaldehyde portion of the molecule to form an intermediate lactone type structure. This reaction would be expected to be reversible and reaction with the alcohol in excess, *e.g.*, the alcohol used as solvent opens the intermediate to give the new ester.

An attempt to replace the chlorine atom of bis-[N-(*o*-chlorophenyl)-salicylaldimine]-Cu(II) (IIa) by the butylamine moiety gave a beautifully crystalline, brown-green product of lower melting point (79°) than expected for the desired compound. The infrared spectrum showed no NH band. Moreover, no chloride ion could be detected in the reaction mixture. This indicated the chloride ion was still bound to the aromatic nucleus. What actually had been produced was bis - [N - (*n* - butyl) - salicylaldimine] - Cu(II), compound IV, *via* an exchange of the aniline moiety by the butylamine.

An authentic sample of this compound, previously reported by Charles,[5] was prepared and compared with IV. The two compounds were in every way identical (melting point, mixed m.p., infrared spectra). The same reaction occurred with IIb (Y = *m*-Cl), IIc (Y = *p*-*d*) and with IIn (Y = *p*-COOMe). The amine exchange reaction appears to be a general reaction with essentially quantitative yields.[12] A possible mechanism follows



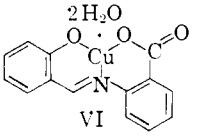
(eq. 3)

The aliphatic base attacks the electron deficient carbon at the polarized azomethine link. The driving force of the reaction may be attributed to the large excess of butylamine over the substituted aniline displaced, or to the greater basicity of the aliphatic amine.

The above mechanism also permits prediction of the amine exchange reaction as observed on attempted amidation of the Schiff Base chelate derived from lysine, (1-carbomethoxy)-pentamethylene bis-[salicylaldimine-1,5-Cu(II) (IIIa, R = OMe).

An attempt to replace the chlorine atom of IIa with methoxyl was unsuccessful. Refluxing IIa with sodium methoxide in methanol gave in small yield a dark product, presumably impure copper oxide. None of the methoxyl derivative IIL was produced.

With the exception of bis-[N-(*o*-carbomethoxyphenyl)-salicylaldimine]-Cu(II) (IIo) compounds of groups I, II, and III, were readily prepared. An attempt to prepare the methyl anthranilate derived chelate, IIo (X = *o*-COOMe) by the method of Charles[5] gave an apple-green compound, identified *via* infrared and analytical data as VI, a "tridentate" chelate.



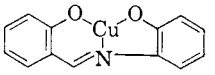
VI

Of the several chelates prepared, this was the only one to exhibit solubility in water. An anal-

(5) R. G. Charles, *J. Org. Chem.*, **72**, 677 (1957).
(6) G. Svatos, C. Curran and J. Quagliano, THIS JOURNAL, **77**, 6159 (1955).
(7) W. Schlessinger, *Ber.*, **44**, 1135 (1911).
(8) W. Schlessinger, *ibid.*, **45**, 1486 (1912).
(9) W. Schlessinger, *ibid.*, **47**, 2406 (1914).
(10) W. Schlessinger, *ibid.*, **58**, 1877 (1925).
(11) Reference 4, Chapter VIII.

(12) While this paper was in preparation, a similar amine exchange reaction involving Schiff Bases and their copper chelates was reported by Y. Muto, *Nippon Kagaku Zasshi*, **76**, 252 (1955); *C. A.*, **51**, 17559f (1957); "The Ligand Exchange Reaction of Organic Cupric Inner Complex Salts."

ogous compound was prepared by Pfeiffer.[13] Using *o*-aminophenol in place of methyl anthranilate he obtained VII



VII

As a final check, anthranilic acid, salicylaldehyde and Cu(II) acetate gave a product in every way identical with VI.

No mention was made by Pfeiffer[3] of the preparation of the tridentate chelate derived from the methyl ester of cystine. An attempt to prepare the cystine chelate by the method of Pfeiffer failed and extensive decomposition seemed to occur. It was not possible to prepare the Schiff base derived from salicylaldehyde and cystine methyl ester. Refluxing the forementioned compounds in ethanol for two hours yielded elemental sulfur and a small amount of an impure product which was not further identified.

Experimental

A. Preparation of Bis-(salicylaldimine]-Cu(II) Chelates. 1. Method of Pfeiffer.[3]—This method consists in refluxing in methanol solution 1:1:1 ratio by weight of bis-[salicylaldehyde]-Cu(II), sodium acetate and the aniline, amine or amino ester.

2. Method of Charles.[5]—To a methanolic solution of salicylaldehyde, a methanolic or aqueous solution of the amine or aniline is added to preform the Schiff Base ligand. Aqueous sodium acetate and copper acetate are then added and the mixture heated to reflux.

The aniline derived Schiff Bases are best made by the method of Charles. Only bis-[salicylaldehyde]-Cu(II) was recovered in attempting the method of Pfeiffer on *o*-nitroaniline, *o*-nitro-*p*-methoxyaniline and *o*-carbomethoxyaniline. The amino acid ester derived Schiff Bases are easily made by the method of Pfeiffer.

B. Amidation Reaction.—1.5 g. of ester was refluxed for 10 minutes in 30 ml. of *n*-butylamine. The excess amine was then removed by steam distillation. During removal of the amine, the black oil, which separated, gradually solidified becoming a grey-green, finally a light green powder. The product was filtered, washed, dried and purified by recrystallizing from a minimum quantity of hot dimethylformamide. The product precipitated out as a brown-green powder.

C. Amine Exchange Reaction.—1.5 g. of chelate (types II or III) was refluxed with 30 ml. of *n*-butylamine for 10 minutes. An equal volume of water was added to the hot reaction mixture followed by cooling in an ice-bath. The brown-green crystals that formed were filtered off and recrystallized from ethanol.

D. Transesterification Reaction.—The procedure of Pfeiffer[2] was followed.

E.—*p*-Chlorosalicylaldehyde was prepared by the method of Hodgson and Jenkinson.[14]

F.—Infrared spectra were run in Nujol mulls on a Baird Model 4-55 double beam recording spectrophotometer equipped with sodium chloride optics.

Acknowledgment.—A grateful acknowledgment must be given to Mr. Peter Andrellos whose advice and encouragement greatly aided this work.

(13) P. Pfeiffer, Th. Hesse, H. Pfitzner, W. Schill and H. Thielert, *J. prakt. Chem.*, **149**, 219 (1937).

(14) H. H. Hodgson and J. A. Jenkinson, *J. Chem. Soc.*, 1740 (1927)

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO AND FROM THE DEPARTMENT OF CHEMISTRY, ST. LOUIS UNIVERSITY]

Preparation of N-Trisubstituted Borazines by Reduction of B-Trichloroborazines[1]

BY LEO F. HOHNSTEDT[2] AND DANIEL T. HAWORTH

RECEIVED FEBRUARY 26, 1959

The reduction of B-trichloro-N-trisubstituted borazines with $NaBH_4$ in polyethyleneglycol-dimethyl ethers leads to good yields of the corresponding N-trisubstituted borazine, $B_3N_3R_3H_3$. The reaction of a primary amine and trichloroborane in chlorobenzene provides a convenient route for preparation of the B-trichloroborazines. The new compounds N-tri-*p*-tolylborazine, N-tri-*p*-anisylborazine and B-trichloro-N-tricyclohexylborazine are reported.

Over a period of years considerable effort has been devoted to the development of improved methods for the synthesis of borazine,[3] $B_3N_3H_6$, and various of its derivatives. As reported in an earlier communication,[4] borazine may be prepared in a reasonably satisfactory procedure based on the reduction of B-trichloroborazine, $B_3N_3H_3Cl_3$, with $LiBH_4$. As suggested at that time, it would be advantageous to use $NaBH_4$ as the reducing agent, since the diborane generated in the reduction can be allowed to interact with $NaBH(OCH_3)_3$ to regenerate $NaBH_4$ (eq. 1, 2). B-trichloroborazine and

$$3LiBH_4 + B_3N_3H_3Cl_3 \longrightarrow B_3N_3H_6 + 1.5B_2H_6 + 3LiCl \quad (1)$$

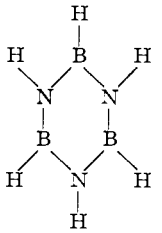
$$B_2H_6 + 2NaBH(OCH_3)_3 \longrightarrow 2NaBH_4 + 2B(OCH_3)_3 \quad (2)$$

$NaBH_4$ failed to react in a variety of solvents in which B-trichloroborazine is soluble but in which $NaBH_4$ is insoluble. However, the desired reaction proceeds smoothly when the solvent is diethylene glycol–dimethyl ether, in which $NaBH_4$ and B-trichloroborazine are soluble. Borazine can be

(1) Presented in part at the 132nd National Meeting of the American Chemical Society, New York, Sept., 1957.

(2) Department of Chemistry, St. Louis University, St. Louis, Missouri.

(3) Borazine has been recommended as the name for



which previously has been referred to as borazole. George W. Schaeffer, Abstracts of Papers presented at the April Meeting of the American Chemical Society, p. 2L (1958).

(4) R. Schaeffer, M. Steindler, L. Hohnstedt, H. S. Smith, Jr., L. B. Eddy and H. I. Schlesinger, THIS JOURNAL, **76**, 3303 (1954).