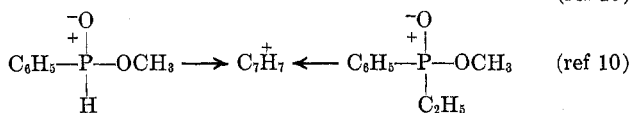
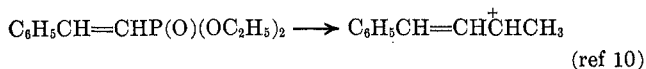
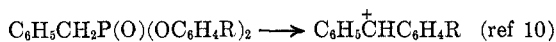
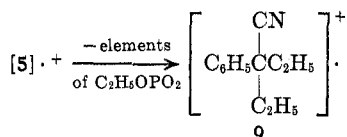


The ir spectrum of the phosphonate **5** shows strong $\overset{+}{\text{P}}-\overset{-}{\text{O}}$ and $\text{C}\equiv\text{N}$ absorptions at 1255 and 2240 cm^{-1} , respectively. The nmr spectrum shows one quintet centered at δ 2.35, a second at 3.74, and a third at 4.20. Each quintet integrates for two protons. The two downfield absorptions are assigned to methylene groups attached to oxygen in agreement with reported nmr nonequivalence between methoxy^{9a} and ethoxy^{9b} groups attached to phosphorus. The upfield absorption at δ 2.35 is assigned to the protons of the methylene unit flanked by two carbon atoms. All six methylene protons exhibit long-range coupling with ^{31}P . By integration nine protons in methyl groups and five aromatic protons are observed.

A mass spectrometric analysis of the phosphonate **5** reveals a molecular ion (also the base peak) at m/e 281. An electron impact induced rearrangement accounts for the peak at m/e 173 assigned to the fragment molecular cation for phenyldiethylacetonitrile **9**. A similar electron impact induced 1,3 migration from oxygen to carbon has been reported for several other phosphonates.¹⁰



Experimental Section

A mixture of benzoyl cyanide (2.62 g, 20 mmol) and excess triethyl phosphite (13.2 g, 80 mmol) in anhydrous benzene (50 ml) was refluxed under nitrogen for 72 hr. From the reaction mixture the solvent was removed under vacuum; the residual liquid was distilled under vacuum giving a mixture of triethyl phosphite and triethyl phosphate, 9.6 g, bp 65–70° (1.25 mm). The pot residue was chromatographed over a column of silica (12 in. \times 1 in.). The elutions with a 4:1 hexane–benzene mixture afforded colorless crystals of *cis*- α,β -dicyanostilbene oxide: 0.64 g, 26%; mp 166–166.5°; ir (CHCl_3) 2240 (w, CN), 1590 (w, aromatic), and 790 and 870 cm^{-1} (epoxide ring); λ_{max} (methanol) 222 $\text{m}\mu$ (ϵ 269.2) 278 (588.8) and 324 (933.3); nmr (CCl_4) multiplet centered at δ 7.58 (phenyl).

The elutions with hexane–benzene (3:1) gave colorless crystals of *trans*- α,β -dicyanostilbene: 0.53 g, 23%; mp 161.5–162° (benzene–hexane); ir (CHCl_3) 2230 (s, CN) and 1600 cm^{-1} (m, aromatic); λ_{max} (CHCl_3) 280 $\text{m}\mu$ (ϵ 3467) and 324 (15,490); nmr (CCl_4) multiplet centered at δ 7.65 (phenyl).

The elutions with benzene–ether (3:1) gave α -cyano- α -phenyl propyl phosphonate (1.0 g, 17.8%), a colorless viscous liquid which was further purified by distillation under vacuum (short path): bp 148–148.5° (0.75 mm); $n_D^{27.5}$ 1.4955; ir (film) 2240 (m, CN), 1590 (w, aromatic), and 1255 cm^{-1} (vs, $\text{P}=\text{O}$); λ_{max} (CHCl_3) 312 $\text{m}\mu$ (ϵ 169.8); nmr (CCl_4) δ 0.92 (t, 3 H, CCH_3), 1.02 (t, 3 H, CCH_2), 1.40 (t, 3 H, CCH_2), 2.35 (quintet, 2 H, PCCH_2CH_2), 3.74 (quintet, 2 H, POCH_2CH_2), 4.20 (quintet, 2 H, POCH_2CH_2), and a multiplet centered at 7.50 (5 H, phenyl);

(9) (a) F. Ramirez, A. V. Patwardhan, N. B. Desai, and S. R. Heller, *J. Amer. Chem. Soc.*, **87**, 549 (1965); (b) T. H. Siddall, III, and C. A. Prohaska, *ibid.*, **84**, 3467 (1962).

(10) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p 649.

mass spectrum m/e 281 (M^+) base peak, 266 ($\text{M} - \text{CH}_3$)⁺, 253 ($\text{M} - \text{C}_2\text{H}_4$)⁺, 238 ($\text{M} - \text{CH}_3 - \text{C}_2\text{H}_4$)⁺, 255 ($\text{M} - 2\text{C}_2\text{H}_4$)⁺, 210 ($\text{M} - \text{CH}_3 - 2\text{C}_2\text{H}_4$)⁺, 197 ($\text{M} - 3\text{C}_2\text{H}_4$)⁺, 173 [$\text{C}_6\text{H}_5(\text{CN})-\text{C}(\text{C}_2\text{H}_5)_2$]⁺, 158 [$\text{C}_6\text{H}_5(\text{CN})\text{C}(\text{C}_2\text{H}_5)\text{CH}_2$]⁺, 145 [$\text{C}_6\text{H}_5\text{HC}(\text{CN})-\text{C}_2\text{H}_5$]⁺, 144 [$\text{C}_6\text{H}_5\text{C}(\text{CN})\text{C}_2\text{H}_5$]⁺, 130 [$\text{C}_6\text{H}_5(\text{CN})\text{CHCH}_2$]⁺, 129 [$\text{C}_6\text{H}_5(\text{CN})\text{C}=\text{CH}_2$], 117 ($\text{C}_6\text{H}_5\text{CH}_2\text{CN}$)⁺, 116 ($\text{C}_6\text{H}_5\text{CH}(\text{CN})$)⁺, 102 ($\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$)⁺, 91 (C_7H_7)⁺, and 51 ($\text{NCC}\equiv\text{CH}$)⁺.

Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_2\text{P}$: C, 59.78; H, 7.11; N, 4.98; P, 11.03. Found: C, 60.03; H, 7.14; N, 4.71; P, 10.69.

Registry No.—**1**, 613-90-1; **3**, 23214-43-9; **4**, 2450-55-7; **5**, 23230-35-5.

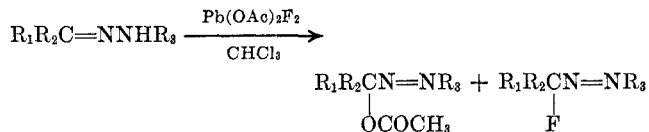
Lead(IV) Diacetate Difluoride. I. Reaction with Ketone Arylhydrazones¹

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Recently, we reported the isolation of lead(IV) diacetate difluoride from the reaction of lead tetraacetate with liquid hydrogen fluoride in chloroform solution.² As part of a general study of the chemistry of this compound and because of a specific interest in its potential as a fluorinating agent, we have examined its action on a series of ketone arylhydrazones. It has been found that the reaction of lead(IV) diacetate difluoride with this class of compounds affords mixtures of azo acetates³ and azo fluorides.⁴ The former substances are well known and have been prepared by treatment of ketohydrazones³ and ketazines⁵ with lead tetraacetate; the azo fluorides, as far as we are aware, have not been prepared previously.



The yields and properties of five azo fluorides and their accompanying azo acetates are summarized in Table I. Although the yields of the azo fluorides are smaller than those of the companion azo acetates, the mild conditions and ease of carrying out the reaction make this fluorination useful. Generally, the reaction was conducted under reflux in chloroform; at lower temperatures the yields of the azo fluorides were unchanged, but those of the azo acetates were substantially decreased in some cases. Resolution of the mixtures of azo compounds was trouble free and was readily effected either by column chromatography or by fractional distillation.

As shown in Table II, and in accordance with expectations, the ultraviolet spectra of the azo fluorides are

(1) This research has been supported by National Science Foundation Grant GP-3672.

(2) J. Bornstein and L. Skarlos, *J. Amer. Chem. Soc.*, **90**, 5044 (1968).

(3) D. C. Iffland, L. Salisbury, and W. R. Schafer, *ibid.*, **83**, 749 (1961).

(4) For convenience and consistency, the term "azo fluoride" has been adopted for the general structure shown. See ref 3, footnote 3. The systematic fluoroarylozo alkane name is used throughout the text and Experimental Section.

(5) B. T. Gillis and M. P. La Montagne, *J. Org. Chem.*, **32**, 3318 (1967); **33**, 1294 (1968).

TABLE I
 AZO FLUORIDES AND AZO ACETATES, $R_1R_2C(R)N=NR_3$

Compd ^a	R	R ₁	R ₂	R ₃	Yield, %	Mp or bp, °C (mm)	Calcd, %				Found, %			
							C	H	F	N	C	H	F	N
1	F	CH ₃	CH ₃	2,4-(NO ₂) ₂ C ₆ H ₃	16	51-52	42.19	3.52	7.42	21.88	41.99	3.56	7.22	21.70
1a	OAc	CH ₃	CH ₃	2,4-(NO ₂) ₂ C ₆ H ₃	53	87-88 ^b								
2	F	CH ₃	CH ₃	C ₆ H ₅	10 ^c	56 (1.50)	65.06	6.63	11.44	16.87	65.05	6.79	11.21	17.04
2a	OAc	CH ₃	CH ₃	C ₆ H ₅	41	95 (1.50) ^b								
3	F	CH ₃	C ₂ H ₅	C ₆ H ₅	17 ^{d,e}	65 (1.25)	66.67	7.22	10.56	15.56	66.49	7.05	10.33	15.73
3a	OAc	CH ₃	C ₂ H ₅	C ₆ H ₅	42 ^e	102 (1.25) ^b								
4	F	(CH ₂) ₅	(CH ₂) ₅	2,4-(NO ₂) ₂ C ₆ H ₃	16	79-80	48.64	4.39	6.42	18.92	48.86	4.52	6.20	18.94
4a	OAc	(CH ₂) ₅	(CH ₂) ₅	2,4-(NO ₂) ₂ C ₆ H ₃	52	111-112 ^f								
5	F	C ₆ H ₅	C ₆ H ₅	<i>p</i> -NO ₂ C ₆ H ₄	5	123-123.5	68.08	4.18	5.67	12.54	68.20	4.23	5.43	12.46
5a	OAc	C ₆ H ₅	C ₆ H ₅	<i>p</i> -NO ₂ C ₆ H ₄	39	134-134.5	67.20	4.53		11.20	67.11	4.53		11.24

^a All compounds are from reactions carried out under reflux in chloroform unless otherwise noted. Column chromatography, as described in the Experimental Section, was used to isolate all products except those for which a boiling point is recorded; these were isolated by distillation. ^b Reference 3. ^c *n*³¹D 1.5055. ^d *n*²⁵D 1.5060. ^e From reaction carried out at 0°. ^f Reference 3 gives a melting point of 102-103°.

 TABLE II
 SPECTROPHOTOMETRIC PROPERTIES OF AZO
 FLUORIDES AND COMPANION AZO ACETATES

Compd	Uv, nm (log ε) ^a	Nmr, δ ^b
1	220 (5.14)	8.58 (m, 2, ArH), 7.44 (d, 1, <i>J</i> = 9 Hz, ArH), 1.58 [d, 6, <i>J</i> = 19 Hz, C(CH ₃) ₂]
	268 (5.13)	
1a	222 (5.15)	
	270 (5.16)	
2	269 (3.87)	7.53 (m, 5, ArH), 1.48 [d, 6, <i>J</i> = 19 Hz, C(CH ₃) ₂]
2a	267 (3.86)	
3	269 (4.13)	7.53 (m, 5, ArH), 1.88 (m, 2, CH ₂ -CH ₃), 1.45 [d, 3, <i>J</i> = 19 Hz, C(F)CH ₃], 0.95 (t, 3, <i>J</i> = 7.5 Hz, CH ₂ CH ₃)
3a	268 (4.13)	
4	222 (5.15)	8.53 (m, 2, ArH), 7.45 (d, 1, <i>J</i> = 9 Hz, ArH), 1.82 [m, 10, (CH ₂) ₅]
	270 (5.17)	
4a	221 (5.14)	
	272 (5.19)	
5	282 (4.15)	7.81 (m, ArH) (in CDCl ₃)
5a	283 (4.16)	7.90 (m, 14, ArH), 2.38 (s, 3, CH ₃) (in CDCl ₃)

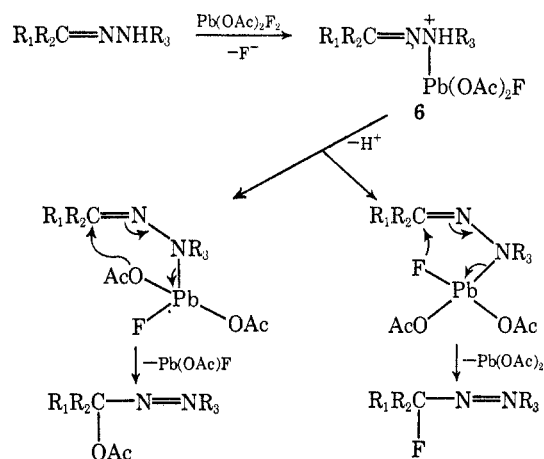
^a λ_{max} determined in 95% ethanol with a Beckman Model DU spectrometer. ^b Spectra obtained at 60 Mcps with a Varian Associates Model HA-60 spectrometer in CCl₄ with tetramethylsilane as internal standard, except where noted: s, singlet; d, doublet; t, triplet; m, multiplet.

practically identical with those of the corresponding azo acetates. The nmr spectra of the azo fluorides are fully consistent with the proposed structures, for which additional evidence was obtained by synthesis. Thus stirring of a suspension of 2-acetoxy-2-(2,4-dinitrophenylazo)propane (1a) with liquid hydrogen fluoride⁶ at -78° for 2-5 min afforded 2-fluoro-2-(2,4-dinitrophenylazo)propane (1) in 60% yield. In similar fashion, azo acetate 4a was converted into 1-fluoro-1-(2,4-dinitrophenylazo)cyclohexane (4) in 66% yield. Presumably, this method can be extended to the preparation of other azo fluorides.

There is evidence, albeit of limited scope, to suggest that the reaction of lead(IV) diacetate difluoride with ketone arylhydrazones proceeds by an ionic mechanism. Thus the yields of azo compounds produced on treatment of acetone 2,4-dinitrophenylhydrazone with lead(IV) diacetate difluoride are essentially unchanged when

(6) For a related reaction see J. Bornstein, M. R. Borden, F. Nunes, and H. I. Tarlin, *J. Amer. Chem. Soc.*, **85**, 1609 (1963).

the reaction is run in the presence of oxygen or nitrobenzene. On the basis of this observation and the mechanism proposed recently by Harrison, Norman, and Gladstone⁷ to explain the oxidation of ketone arylhydrazones by lead tetraacetate, we wish to suggest that both the fluorination and acetoxylation occur *via* a pathway involving the common intermediate 6. In this connection it should be noted that chelation² of the acetoxy groups to the lead atom in lead(IV) diacetate difluoride probably makes them less susceptible to displacement by the NH nitrogen of the hydrazone than the fluorine atoms.



Experimental Section⁸

The ketone arylhydrazones used in this study were prepared by standard procedures.⁹ Chloroform, freshly purified by washing with concentrated sulfuric acid according to the method of Vogel,¹⁰ was used as reaction medium.

The following typical examples illustrate the general procedures used to prepare the azo compounds.

Reaction of Lead(IV) Diacetate Difluoride with Acetone 2,4-Dinitrophenylhydrazone. A. 2-Fluoro-2-(2,4-dinitrophenylazo)propane (1).—This reaction was carried out in an atmosphere of dry nitrogen. To a stirred, refluxing slurry of 7.96 g (0.022 mol) of lead(IV) diacetate difluoride² in 50 ml of chloroform was added

(7) M. J. Harrison, R. O. C. Norman, and W. A. F. Gladstone, *J. Chem. Soc.*, 735 (1967).

(8) Melting points are corrected and boiling points are uncorrected. Infrared spectra were recorded on a Beckman Model IR-10 spectrometer. Calcium chloride was used as drying agent. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(9) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," Order I, John Wiley & Sons, Inc., New York, N. Y., 1941, pp 354-397.

(10) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, John Wiley & Sons, Inc., New York, N. Y., 1966, p 176.

over a period of 5 min a solution of 5.22 g (0.022 mol) of acetone 2,4-dinitrophenylhydrazone in 60 ml of chloroform. The resulting orange mixture was stirred and heated under reflux for an additional 30 min prior to being cooled and poured into water. The suspension was filtered by suction and the chloroform solution was separated from the filtrate. The aqueous phase was extracted with a 100-ml portion of chloroform and the combined chloroform extracts were washed once with 5% sodium bicarbonate and then twice with water. The dried extract was concentrated under reduced pressure to yield an orange oil which was chromatographed on a column (25 × 2.5 cm diameter) of silica gel. Elution with 4:1 hexane-benzene gave an orange solid which, on recrystallization from methanol, afforded 0.88 g (16%) of azo fluoride 1, having the properties recorded in Tables I and II.

B. 2-Acetoxy-2-(2,4-dinitrophenylazo)propane (1a).—Continued elution with pure benzene of the column from which azo fluoride 1 was obtained, as described above, gave a yellow solid which, on recrystallization from methanol, afforded 3.48 g (53%) of azo acetate 1a, displaying strong peaks in the ir (CCl₄) at 1745, 1600, 1365, 1345, 1245, 1190, and 1155 cm⁻¹. Additional data are given in Tables I and II. A mixture melting point determination and ir spectral comparison showed 1a to be identical with an authentic specimen.³

Reaction of Lead(IV) Diacetate Difluoride with 2-Butanone Phenylhydrazone. Formation of 2-Fluoro-2-phenylazobutane (3) and 2-Acetoxy-2-phenylazobutane (3a).—In a 300-ml, heavy-walled polyethylene jar sealed with a cap holding a drying tube filled with calcium chloride, a stainless steel dial thermometer, and an addition tube of polyethylene connected to a dropping funnel were placed 26.04 g (0.072 mol) of lead(IV) diacetate difluoride and 50 ml of chloroform. After the magnetically stirred suspension had been cooled to 0° in an ice bath, a solution of 11.60 g (0.072 mol) of 2-butanone phenylhydrazone in 15 ml of chloroform was added over a period of 30 min in order to maintain the temperature as close as possible to 0°. The mixture was stirred in the ice bath for an additional 30 min and the resulting amber suspension was then poured into water. The white solid was removed by suction filtration and the chloroform layer was separated from the filtrate. The aqueous layer was extracted with a 100-ml portion of chloroform and the combined chloroform extracts were washed once with 5% sodium bicarbonate and then twice with water. The dried extract was concentrated under reduced pressure to give a red oil which, on distillation under reduced pressure through a semimicro column, gave two main fractions.

Fraction 1, a yellow oil, was identified as azo fluoride 3, yield 2.23 g (17%), bp 65–66° (1.25 mm). Some additional properties are indicated in Tables I and II.

Fraction 2, an orange oil, was identified as azo acetate 3a, yield 6.70 g (42%), bp 102–103° (1.25 mm), *n*_D²⁰ 1.5142 (lit.³ *n*_D²⁰ 1.5141). Its ir spectrum (neat) was indistinguishable from that of an authentic sample.³

Reaction of 2-Acetoxy-2-(2,4-dinitrophenylazo)propane (1a) with Hydrogen Fluoride. Formation of 2-Fluoro-2-(2,4-dinitrophenylazo)propane (1).—To 0.50 g (1.69 mmol) of azo acetate 1a in a polyethylene test tube cooled in a Dry Ice-acetone bath was added 1.0 ml of liquid hydrogen fluoride. The brown suspension was stirred with a nickel spatula for 2 min and then a large excess of potassium fluoride was added. The reaction vessel was removed from the cooling bath and after standing at room temperature for 15 min the mixture was eluted with ether. The ether extract was washed once with 5% sodium bicarbonate and then twice with water. Evaporation at reduced pressure of the dried ether solution gave an orange oil which was chromatographed on a column (20 × 1.2 cm diameter) of silica gel with 6:1 benzene-hexane as eluent. An orange solid was thus obtained which was recrystallized from methanol to give 0.26 g (60%) of azo fluoride 1, mp 51–52°. Compound 1 was shown by mixture melting point determination and ir spectral comparison to be identical with an authentic sample prepared above by reaction of lead(IV) diacetate difluoride with acetone 2,4-dinitrophenylhydrazone.

1-Fluoro-1-(2,4-dinitrophenylazo)cyclohexane (4).—Treatment of 0.50 g (1.49 mmol) of 1-acetoxy-1-(2,4-dinitrophenylazo)cyclohexane (4a) with liquid hydrogen fluoride for 5 min by the procedure used above to convert azo acetate 1a into azo fluoride 1 afforded an orange solid which was recrystallized from methanol, yield 0.29 g (66%), mp 79–80°. It was identical in all respects with a sample of 4 prepared by fluorination of cyclohexanone

2,4-dinitrophenylhydrazone with lead(IV) diacetate difluoride (Table I).

Registry No.—Lead(IV) diacetate difluoride, 20706-24-5; 1, 23386-00-7; 1a, 23386-01-8; 2, 23386-02-9; 2a, 23386-03-0; 3, 23383-04-1; 3a, 23386-05-2; 4, 23386-06-3; 4a, 23386-07-4; 5, 23386-08-5; 5a, 14803-32-8.

Selective Electrochemical Reduction of Polyfunctional Molecules

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It has been recognized for a number of years that controlled-potential electrolysis, employing as it does constant electrode potential in order to discriminate between two or more electrode processes,¹ provides a considerably more selective method of effecting electrochemical reaction than does the method of constant-current electrolysis used in the older literature.² Controlled-potential electrolysis is in fact now widely used both in coulometric analysis of mixtures of reducible species³ and in preparative-scale electrochemical synthesis. In most cases the latter application involves preparation of an electrolysis product in sufficient quantities for characterization by the usual chemical and spectroscopic methods, in order to test or confirm an electrode mechanism proposed, *e.g.*, from voltammetric data.⁴ Despite the common use of controlled-potential electrolysis for the latter purpose, there are surprisingly few reports of its use for the specific purpose of carrying out oxidations or reductions not possible by the usual chemical means. This is unfortunate, for even a cursory examination of the organic polarographic literature⁵ will reveal the possibility of many selective electrochemical reductions which would be either impossible or very difficult using the conventional reducing agents of organic chemistry. The principal criterion for the successful application of the electrochemical method is simply that, when a molecule contains two or more reducible functions, the electrode process of interest must be easier than any others by at least 0.2 V; if so, electrolysis at a potential corresponding to the first process will permit clean conversion into the product of this reduction process and no other.⁶ The first instance (and still one of the best examples) where this principle was taken advantage of for explicitly synthetic purposes was reported by Lingane, Swain, and Fields.⁷

(1) J. J. Lingane, "Electroanalytical Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1958.

(2) S. Swann, Jr., in "Technique of Organic Chemistry," Vol. 2, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p 385.

(3) G. W. C. Milner and G. Phillips, "Coulometry in Analytical Chemistry," Pergamon Press, London, 1967.

(4) L. Meites, "Polarographic Techniques," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1965, Chapter 10.

(5) (a) D. J. Pietrzyk, *Anal. Chem.*, **40**, 194R (1968); **38**, 278R (1966).

(b) P. Zuman, "Organic Polarographic Analysis," Pergamon Press, London, 1964.

(6) L. Meites in "Technique of Organic Chemistry," 3rd ed, Vol. 1, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., p 3281 ff.

(7) J. J. Lingane, C. G. Swain, and M. Fields, *J. Amer. Chem. Soc.*, **65**, 1348 (1943).