

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

2-Diphenylacetyl-1,3-indandione 1-Hydrazone—A New Reagent for Carbonyl Compounds¹

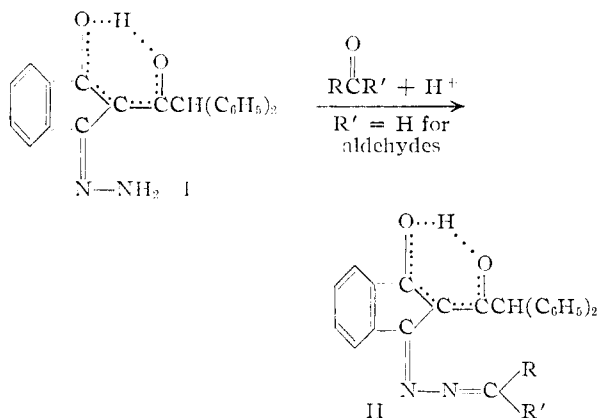
BY ROBERT A. BRAUN AND WILLIAM A. MOSHER

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2-Diphenylacetyl-1,3-indandione 1-hydrazone² has been found to be a potentially valuable reagent for identifying and characterizing carbonyl compounds, and is superior in several instances to the common carbonyl reagents. 2-Diphenylacetyl-1,3-indandione 1-hydrazone is shown to react with aldehydes and ketones in the presence of acid catalyst to give mixed azines. Over fifty derivatives of carbonyl compounds containing a great variety of functional groups have been prepared. All the derivatives are fluorescent in ultraviolet light and represent a new class of fluorescent compounds.

In a previous paper³ we described the preparation of 2-diphenylacetyl-1,3-indandione 1-hydrazone by the reaction of excess hydrazine with 2-diphenylacetyl-1,3-indandione in aqueous methanol. Further study showed this material to be an excellent reagent for carbonyl compounds. We wish to report the preparation of a large number of derivatives of aldehydes and ketones with this reagent and consider its advantages over presently used reagents.

The reaction of I with aldehydes or ketones is catalyzed by acid and proceeds very rapidly upon warming to the reflux temperature of the solvent used. The reaction is generally complete in less than five minutes. Any of the mineral acids, acetic acid, *p*-toluenesulfonic acid or boron trifluoride



etherate can be used successfully as catalysts. Solvents such as ethanol, ether, dioxane or chloroform may be used. The preferred reaction conditions are chloroform as solvent and a small quantity of concentrated hydrochloric acid as catalyst. The derivatives are highly crystalline, yellow to red solids and may be recrystallized easily from a mixture of chloroform and methanol.

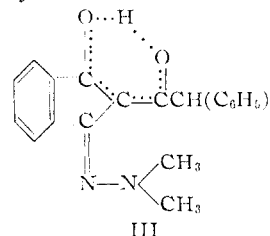
2-Diphenylacetyl-1,3-indandione 1-hydrazone has been used to characterize over sixty carbonyl compounds and it appears to be superior in some instances to the common carbonyl reagents, even the most widely used reagent, 2,4-dinitrophenylhydrazine. All of the derivatives here reported melt without decomposition and in the useful

melting point range. There is a sufficiently good spread of melting points so that even closely related carbonyl compounds may be identified satisfactorily. The yields of derivatives have been well over 95% when particular care was taken in the isolation of the product. Due to the high molecular weight of this reagent compared with the commonly used reagents, small amounts of carbonyl compounds can be identified easily. 2-Diphenylacetyl-1,3-indandione 1-hydrazone is particularly useful in identifying long chain alkyl carbonyl compounds which give either oils or difficultly isolable, low melting solids with other reagents. With the new reagent there is no difficulty in obtaining derivatives of 2-octanone, 2-undecanone and 5-nonanone. A derivative of diacetone alcohol was obtained as well as one for mesityl oxide. With other reagents diacetone alcohol undergoes dehydration so that actually the derivative of mesityl oxide is obtained. Hindered ketones such as *p*-fluorophenyl *t*-butyl ketone and triphenylsilyl phenyl ketone formed derivatives without difficulty, although several attempts to prepare a derivative of benzopinacolone were unsuccessful.

The derivatives of aldehydes and ketones are generally yellow. However, when there is extensive conjugation in the carbonyl compound used the color is shifted to orange or red. This is illustrated by comparing the derivatives of the several ketones: acetophenone (yellow), *p*-phenylacetophenone (yellow-orange), *p*-phenylbenzophenone (orange-red).

All of the derivatives are strongly fluorescent in ultraviolet light, in the solid state as well as in solution. This fluorescence may be of value in identifying small amounts of carbonyl compounds by paper or column chromatography.

The carbonyl derivatives have a very characteristic band in the infrared absorption spectrum at 5.95–6.01 μ which is due to the two C=N bonds of the azine structure. This assignment was confirmed by the synthesis of III. This compound has



a band at 5.97 μ but the band is just one-half as intense as the corresponding band in the azines.

(1) From the dissertation submitted by Robert A. Braun in partial fulfillment of the requirements for the Ph.D. degree, University of Delaware. Presented in part at the New York Meeting of the American Chemical Society, September, 1957.

(2) 2-Diphenylacetyl-1,3-indandione 1-hydrazone is available from the Nease Chemical Company, State College, Pennsylvania.

(3) R. A. Braun and W. A. Mosher, *THIS JOURNAL*, **80**, 2749 (1958)

This decrease in intensity must be due to the fact that this compound has only one C=N bond.

Experimental⁴

2-Diphenylacetyl-1,3-indandione 1-Hydrazone.—The 2-diphenyl-1,3-indandione 1-hydrazone used was prepared by the method described previously.³

2-Diphenylacetyl-1,3-indandione 1-Azine with Acetone (Derivative of Acetone).—A mixture of 1.91 g. (0.0054 mole) of 2-diphenylacetyl-1,3-indandione 1-hydrazone, 0.29 g. (0.005 mole) of acetone, 2 drops of concentrated hydrochloric acid and 20 ml. of chloroform was warmed for five minutes on a hot water-bath. The bright yellow solution was filtered to remove unreacted reagent and upon the addition of 30 ml. of ether the derivative crystallized as yellow needles. The product was filtered, washed with ether and dried at 100°; yield 1.87 g. (95.0%), m.p. 226–227°. An analytical sample recrystallized from methanol-chloroform mixture had the same melting point.

Anal. Calcd. for C₂₆H₂₂N₂O₂: C, 79.40; H, 5.35; N, 7.14; mol. wt., 393. Found: C, 79.42; H, 5.49; N, 7.15; mol. wt. (modified Rast⁵), 403.

Its **2,4-dinitrophenylhydrazone** was prepared using a large excess of 2,4-dinitrophenylhydrazone. The mono-2,4-DNP was isolated as orange needles, m.p. 274–275°. The infrared spectrum (in KBr) showed bands at 3.01 μ (N–H stretching) and 3.10 μ (OH). There were no bands in the carbonyl region (5.7–6.1 μ). This is further proof of the enol structure of II.

Anal. Calcd. for C₃₂H₂₆N₆O₅: C, 66.88; H, 4.53; N, 14.62. Found: C, 66.73; H, 4.31; N, 14.70.

2-Diphenylacetyl-1,3-indandione, 1-azine with acetone fluoresces brightly with a yellow color in ultraviolet light, in both the crystalline form and in solution. It is soluble in cold chloroform, carbon tetrachloride and pyridine, in hot acetone and hot methanol, and insoluble in water. In concentrated sulfuric acid a clear red solution is obtained, and upon dilution with water the azine is recovered quantitatively.

Preparation of Derivatives of Carbonyl Compounds Using 2-Diphenylacetyl-1,3-indandione 1-Hydrazone as Reagent (Table I).—A mixture of 0.005 mole of carbonyl compound, 1.58 g., 0.0045 mole of 2-diphenylacetyl-1,3-indandione 1-

TABLE I
DERIVATIVES OF CARBONYL COMPOUNDS USING I AS REAGENT

	M.p., °C.	Formula	Nitrogen, %	
			Calcd.	Found
Acetaldehyde	180.5–181.5	C ₂₅ N ₂ O ₂	7.37	7.33
Chloroacetaldehyde	169.5–170	C ₂₅ H ₂₁ ClN ₂ O ₂	6.75	6.71
<i>n</i> -Butyraldehyde	167.5–168	C ₂₇ H ₂₄ N ₂ O ₂	6.86	6.86
α -Phenylpropionaldehyde	194.5–195.5	C ₂₂ H ₂₆ N ₂ O ₂	5.96	5.86
Benzaldehyde	239–240	C ₃₀ H ₂₂ N ₂ O ₂ ^a	6.33	6.62
<i>p</i> -Nitrobenzaldehyde	278–279	C ₃₀ H ₂₁ N ₃ O ₄ ^b	8.62	8.51
<i>p</i> -Tolualdehyde	255–255.5	C ₃₁ H ₂₄ N ₂ O ₂	6.14	6.09
<i>p</i> -Dimethylaminobenzaldehyde	271–271.5	C ₃₂ H ₂₇ N ₃ O ₂	8.65	8.54
Salicylaldehyde	245–246	C ₃₀ H ₂₂ N ₂ O ₃	6.11	5.77
Cinnamaldehyde	225–226	C ₃₁ H ₂₄ N ₂ O ₂	5.98	5.81
Acrolein	85.5–86.5	C ₂₆ H ₂₀ N ₂ O ₂	7.14	6.84
Crotonaldehyde	184.5–185.5	C ₂₇ H ₂₂ N ₂ O ₂	6.89	6.54
Citral	165–166	C ₃₃ H ₃₂ N ₂ O ₂	5.74	5.63
2-Furaldehyde	209.5–210.5	C ₂₈ H ₂₀ N ₂ O ₃	6.47	6.44
Pyruvic aldehyde ^c	220–221	C ₂₅ H ₂₀ N ₂ O ₃	6.86	6.71
2-Hydroxy-1-naphthaldehyde	274–275	C ₃₄ H ₂₄ N ₂ O ₃	5.51	5.55
Terephthalaldehyde ^d	342–342.5	C ₃₄ H ₂₆ N ₄ O ₄	6.95	7.01
Acetone	226–227	C ₂₆ H ₂₂ N ₂ O ₂ ^e	7.10	7.15
2-Butanone	197.5–198	C ₂₇ H ₂₄ N ₂ O ₂ ^f	6.86	6.75
2-Pentanone	166–167	C ₂₈ H ₂₆ N ₂ O ₂	6.62	6.52
2-Heptanone	147.5–148.5	C ₃₀ H ₃₀ N ₂ O ₂	6.22	6.04
2-Octanone	128.5–130.5	C ₃₁ H ₃₂ N ₂ O ₂	6.03	6.05
2-Nonanone	126.5–127.5	C ₃₂ H ₃₄ N ₂ O ₂	5.93	5.81

(4) All melting points are corrected. Microanalyses are by the Geller Microanalytical Laboratories, West Englewood, N. J.

(5) R. P. Linstead, J. A. Elvidge and M. W. Halley, "A Course in Modern Techniques of Organic Chemistry," Butterworths Publications, Ltd., London, 1955, p. 145.

5-Nonanone	128–138.5	C ₃₂ H ₃₄ N ₂ O ₂	5.85	5.76
3-Methyl-2-butanone	169–170	C ₂₈ H ₂₆ N ₂ O ₂	6.72	6.53
1-Phenyl-2-propanone	191.5–192.5	C ₃₂ H ₂₆ N ₂ O ₂	5.95	5.81
3-Phenyl-2-butanone	180.5–181.5	C ₃₂ H ₂₈ N ₂ O ₂	5.78	5.78
Methyl cyclopropyl ketone	177.5–178.5	C ₂₉ H ₂₄ N ₂ O ₂ ^g	6.66	6.50
Methyl cyclopentyl ketone	238–239	C ₃₀ H ₂₆ N ₂ O ₂ ^h	6.25	6.27
Cyclohexanone	248.5–249	C ₂₉ H ₂₆ N ₂ O ₂	6.21	6.36
1,1-Diphenyl-2-propanone	232–233.5	C ₃₄ H ₃₀ N ₂ O ₂	4.93	5.14
Acetophenone	239.5–240	C ₂₇ H ₂₄ N ₂ O ₂	6.13	6.02
Methyl <i>p</i> -tolyl ketone	237.5–238.5	C ₃₂ H ₂₆ N ₂ O ₂	5.73	5.83
Phenyl isopropyl ketone	204–205	C ₃₁ H ₂₈ N ₂ O ₂	5.72	5.62
<i>p</i> -Nitroacetophenone	297.5–298	C ₃₁ H ₂₃ N ₃ O ₄	8.38	8.25
<i>p</i> -Phenylacetophenone	255.5–256	C ₂₇ H ₂₂ N ₂ O ₂	5.26	5.09
<i>p</i> -Phenylbenzophenone	210–211	C ₃₂ H ₃₀ N ₂ O ₂	4.71	4.48
Fluorenone	282–283	C ₃₆ H ₂₄ N ₂ O ₂	5.42	5.21
<i>n</i> -Butyrophenone	229.5–230.5	C ₃₃ H ₂₈ N ₂ O ₂	5.78	5.69
1-Acetylnaphthalene	251.5–252.5	C ₂₈ H ₂₆ N ₂ O ₂	5.53	5.50
4-Phenyl-3-buten-2-one	228–229	C ₃₁ H ₂₆ N ₂ O ₂	5.79	5.68
Mesityl oxide	165–166	C ₂₉ H ₂₆ N ₂ O ₂	6.21	6.39
4-Hydroxy-4-methyl-2-pentanone ⁱ	210–211	C ₂₉ H ₂₈ N ₂ O ₂	6.18	6.09
4-(<i>o</i> -Hydroxyphenyl)-3-buten-2-one	252–253	C ₃₃ H ₂₆ N ₂ O ₃	5.76	5.40
Chloro-2-propanone	179.5–180	C ₂₈ H ₂₁ ClN ₂ O ₂	6.53	6.65
α -Chloroacetophenone	214.5–215.5	C ₃₁ H ₂₃ ClN ₂ O ₂	5.71	5.61
α -Bromo- <i>p</i> -nitroacetophenone	224–225	C ₃₁ H ₂₂ BrN ₃ O ₄	7.25	7.14
<i>o</i> -Hydroxyacetophenone	270–271	C ₃₀ H ₂₄ N ₂ O ₃	5.92	5.65
4-(2-Furyl)-3-buten-2-one	233–233.5	C ₃₁ H ₂₄ N ₂ O ₃	5.92	5.88
Methyl 2-thienyl ketone	268.5–269	C ₃₀ H ₂₆ N ₂ O ₂ S	6.06	5.88
Phenoxy-2-propanone	193.5–194.4	C ₃₂ H ₂₈ N ₂ O ₃	5.76	5.67
2-Benzoylpyridine	231.5–232	C ₃₁ H ₂₅ N ₃ O ₂	8.09	7.96
<i>p</i> -Fluorophenyl <i>t</i> -butyl ketone	236.5–237.5	C ₃₄ H ₂₉ FN ₂ O ₂	5.51	5.48
2-(<i>p</i> -Acetylphenyl)-4-methylpentane	200–200.5	C ₃₇ H ₃₈ N ₂ O ₂	5.18	5.00
Pyruvic acid	251–252	C ₂₆ H ₂₀ N ₂ O ₄	6.60	6.29
Ethyl acetoacetate	179–180	C ₂₉ H ₂₆ N ₂ O ₄	6.02	6.17
2,3-Butanedione ^j	260.5–261	C ₂₇ H ₂₂ N ₂ O ₃	6.63	6.60
<i>p</i> -Dimethylaminobenzalacetone	234–235	C ₃₁ H ₂₉ N ₃ O ₂	8.21	8.15
2-Hexanone	135–136	C ₂₉ H ₂₈ N ₂ O ₂	6.42	6.30
2-Undecanone	104–105	C ₃₁ H ₃₈ N ₂ O ₂	5.53	5.54
Triphenylsilyl phenyl ketone ^k	209–210	C ₄₈ H ₃₆ N ₂ O ₂ Si	4.00	3.81

^a *Anal.* Calcd.: C, 81.43; H, 5.01. Found: C, 81.24; H, 5.38. ^b *Anal.* Calcd.: C, 73.91; H, 4.34. Found: C, 74.08; H, 4.25. ^c 48% aqueous solution; 1:1 molar ratio of aldehyde to reagent; reagent attacked only aldehyde group. ^d Excess reagent used; reaction at both aldehyde groups. ^e *Anal.* Calcd.: C, 79.12; H, 5.62. Found: C, 79.20; H, 5.61. ^f *Anal.* Calcd.: C, 79.38; H, 5.92. Found: C, 79.10; H, 6.01. ^g *Anal.* Calcd.: C, 79.97; H, 5.75. Found: C, 80.31; H, 5.81. ^h *Anal.* Calcd.: C, 80.33; H, 6.29. Found: C, 80.31; H, 6.25. ⁱ Diacetone alcohol. Infrared spectrum of derivative shows free –OH band at 2.88 μ. ^j 1:1 molar ratio of 2,3-butanedione to reagent; reagent attacks only one carbonyl group. ^k A. G. Brook, THIS JOURNAL, 79, 4373 (1957).

hydrazone, 20 to 30 ml. of chloroform and two drops of concentrated hydrochloric acid is warmed at reflux until a deeply colored, nearly clear solution is obtained. The time for reaction will vary from a few minutes to about ten minutes depending upon the structure of the carbonyl compound. The solution is filtered hot to remove any unreacted reagent. About 20 ml. of methanol is added to the filtrate. Usually the derivative will crystallize immediately. If there is no crystallization the solvent is removed *in vacuo* to a volume of about 2 ml. and the methanol or anhydrous ether is added. The crystalline product is filtered and recrystallized from chloroform-methanol mixture using as little chloroform as possible, then oven-dried at 70–100°. Usually one recrystallization is sufficient to give an analytically pure derivative. The derivatives are fluorescent and intensely colored crystalline solids. For quantitative preparation of derivatives a 5 to 10% excess of 2-diphenylacetyl-1,3-indandione 1-hydrazone is used. Sufficient derivative for melting

point, analysis and spectra usually can be obtained by using one-half to one-quarter of the amounts specified.

The infrared spectra of the derivatives of the following carbonyl compounds were determined (in KBr): acetaldehyde, acetone, chloroacetone, 1-phenyl-2-propanone, 1,1-diphenyl-2-propanone, acetophenone, *p*-nitroacetophenone, methyl thienyl ketone, fluorenone, methyl cyclopropyl ketone, methyl cyclopentyl ketone, diacetone alcohol and citral. These spectra support the proposed structure (II) for the mixed azines. None show any bands in the N-H stretching region or any bands in the free (non-hydrogen bonded) carbonyl region. All of the derivatives have a broad band of very high intensity in the 6.2-6.4 μ region that can be assigned to the hydrogen bonded enolic β -diketone structure stabilized by resonance.⁶ All of these mixed azines have a strong, needle sharp band at 5.95-6.01 μ which is due to the C=N bonds of the azine structure. The derivatives also have the following bands in common: 6.88-6.92, 7.15-7.30, 8.05-8.17, 9.20-9.27, 9.43-9.70, 11.08-11.24, 12.52-12.84, 13.14-13.34, 13.60-13.94 and 14.22-14.32 μ . In addition to these there are bands that are characteristic for each derivative in the 9 to 13 μ region.

(6) (a) L. J. Bellamy and L. Beecher, *J. Chem. Soc.*, 4487 (1954); (b) *THIS JOURNAL*, **75**, 479 (1953).

2-Diphenylacetyl-1,3-indandione 1-dimethylhydrazone could not be prepared directly from the reaction of 2-diphenylacetyl-1,3-indandione and *unsym*-dimethylhydrazine but was successfully made in the following way. A mixture of 2-diphenylacetyl-1,3-indandione 1-azine with acetone (3.88 g., 0.02 mole) and 50 ml. of anhydrous ethanol was heated at reflux for five hours. The solution changed color from bright yellow to dark orange-red. The insoluble material was filtered, washed with small portions of ethanol and dried, yielding 1.93 g. of unreacted 2-diphenylacetyl-1,3-indandione 1-azine with acetone, m.p. 226-227°. The filtrate was evaporated to one-half its volume and cooled in Dry Ice. The orange crystals were collected and washed with ether; yielding 1.60 g. of III. After recrystallization from ethanol it melted at 221.5-222.5°. The orange crystals were fluorescent. The infrared spectrum was identical with that of 2-diphenylacetyl-1,3-indandione 1-azine with acetone with the exception of the intensity of the C=N band at 5.97 μ which is about one-half as intense as the corresponding band of 2-diphenylacetyl-1,3-indandione 1-azine with acetone. This would be expected since III has only one C=N bond while the azine has two.

Anal. Calcd. for $C_{25}H_{22}N_2O_2$: N, 7.33. Found: N, 7.29.
NEWARK, DELAWARE

[CONTRIBUTION FROM UNIVERSITY OF MICHIGAN, ROHM & HAAS CO., AND THE PENNSYLVANIA STATE UNIVERSITY]

Effect of Structure on the Stereochemistry of Electrode Reactions. Unsaturated C_4 -Dibasic Acids and Esters. Stereospecific Reduction of the Double Bond

BY ISADORE ROSENTHAL, JOHN R. HAYES, AARON J. MARTIN AND PHILIP J. ELVING

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Acetylenedicarboxylic acid (ADCA), dibromomaleic acid, and dibromofumaric acid have been coulometrically and polarographically reduced over a range of pH; the reduction products were identified polarographically, and, in the case of the macroscale electrolyses, by isolation and chemical and physical examination. Dibromomaleic and dibromofumaric acids are quantitatively reduced to ADCA in a two-electron process; their diesters behave similarly. Between pH 0.4 and 3.0 ADCA is reduced in a three-electron process to form *rac*- α,α' -dimethylsuccinic acid; its monoester yields diethyl *rac*- α,α' -dimethylsuccinate. However, the diethyl ester of ADCA is reduced to dimethyl fumarate. The stereospecificity of the reduction of ADCA and its esters is explained as being due to steric factors inherent in the compounds rather than to interaction between the reducible compounds and the electrode. Dimethylmaleic acid (anhydride) and dimethylfumaric acid are reduced by *trans* addition of hydrogens with single 2-electron waves to yield *rac*- and *meso*-dimethylsuccinic acids, respectively. The latter apparently represent the first clearly substantiated case of a stereospecific reduction of a double bond at the dropping mercury electrode.

A previous study¹ on vicinal dibromo acids and esters showed that such compounds could undergo two-electron reduction to form the corresponding olefinic compounds and that under some conditions one geometrical isomer was produced preferentially. The present study is a continuation of this work and presents another system in which over-all stereospecific reductions occur.

Polarographic data for the acids studied—acetylenedicarboxylic (ADCA), dibromofumaric, dibromomaleic, dimethylfumaric and dimethylmaleic—and their ethyl esters have not been previously reported, except for a decomposition potential for ADCA^{2a} and mention of the use of the polarographic determination of ADCA^{2b} to follow its catalytic hydrogenation. Polarography of phenyl-substituted acetylenes and ethylenes³ in neu-

tral or basic solution showed the triple bonds to be more difficult to reduce than the corresponding double bonds. Since the acetylene derivatives yield a single polarographic wave involving 4 electrons, it was assumed that as soon as the double bond was formed on the reduction of the triple bond, it too was reduced.

Summary of Experimental Behavior

Acetylenedicarboxylic acid and a number of related dicarboxylic acids and their monoethyl and diethyl esters have been reduced over a range of pH at a micro mercury dropping electrode, using polarographic technique, and at a massive stirred mercury cathode; coulometric measurements were also made using the massive electrode. The reduction products were identified polarographically, and by isolation and chemical and physical examination. The experimental data are summarized in Tables I and II. The polarographic currents were diffusion-controlled.

Dimethylmaleic Acid (Anhydride)⁴ and Dimethylfumaric Acid.—These acids undergo two-electron reduction at more negative potentials than maleic or fumaric acids. Melting points of the residues

(4) See subsequent discussion.

(1) P. J. Elving, I. Rosenthal and A. J. Martin, *THIS JOURNAL*, **77**, 5218 (1955).

(2) (a) L. Schwaer, *Collection Czechoslov. Chem. Commun.*, **7**, 326 (1935); *Chem. Listy*, **26**, 485 (1932); (b) A. L. Markman, *J. Gen. Chem. U.S.S.R.*, **24**, 67 (1954); *Zhur. Obshchei Khim.*, **24**, 65 (1954); *C. A.*, **49**, 8001 (1955).

(3) (a) H. A. Laitinen and S. Wawzonek, *THIS JOURNAL*, **64**, 1765 (1942); (b) S. Wawzonek, E. W. Blaha, R. Berkey and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235 (1955); (c) G. J. Hoijtink, J. van Schooten, E. de Boer and W. I. Aalbersberg, *Rec. trav. chim.*, **73**, 355 (1954); G. J. Hoijtink, *ibid.*, **73**, 895 (1954); **74**, 1525 (1955).