N, 12.17; F, 16.51. Found: C, 52.10; H, 5.28; N, 12.23; F, 16.57).

1,4-Diazaspiro[4.5]decane (IV).—To 9.8 g (0.1 mole) of redistilled cyclohexanone dissolved in 100 ml of refluxing benzene in a flask with a Dean–Stark trap was added dropwise 6.0 g (0.1 mole) of ethylenediamine. After the separation of water was completed, the benzene was removed under reduced pressure and the residue distilled in a short-path distillation apparatus. The material boiling above 65° (0.1 mm) was collected. The distillate was rapidly redistilled on a spinning-band column and the fraction boiling at 71–72° (0.05 mm) collected. The yield of IV was 37%: $n^{30}D$ 1.4978; mp 30–31° (lit.[10] bp 61–61.5° (0.01 mm); mp 28.5–30°; $n^{30}D$ 1.4962). This product is stable for several weeks if kept in a refrigerator, but it turns into a yellow liquid in 2–3 days at room temperature. It is rapidly decomposed by water. *Anal.* Calcd for $C_8H_{16}N_2$: C, 68.52; H, 11.50; N, 19.98; mol wt, 140. Found: C, 68.50; H, 11.57; N, 19.96; mol wt, 142 (osmotic), 140 (mass spectral).

Registry No.—II, 14120-51-5; III, 14120-52-6; phenylurea derivative of III, 14120-53-7; IV, 177-03-7.

Synthesis of 2-Methyl-4H-pyran-4-one

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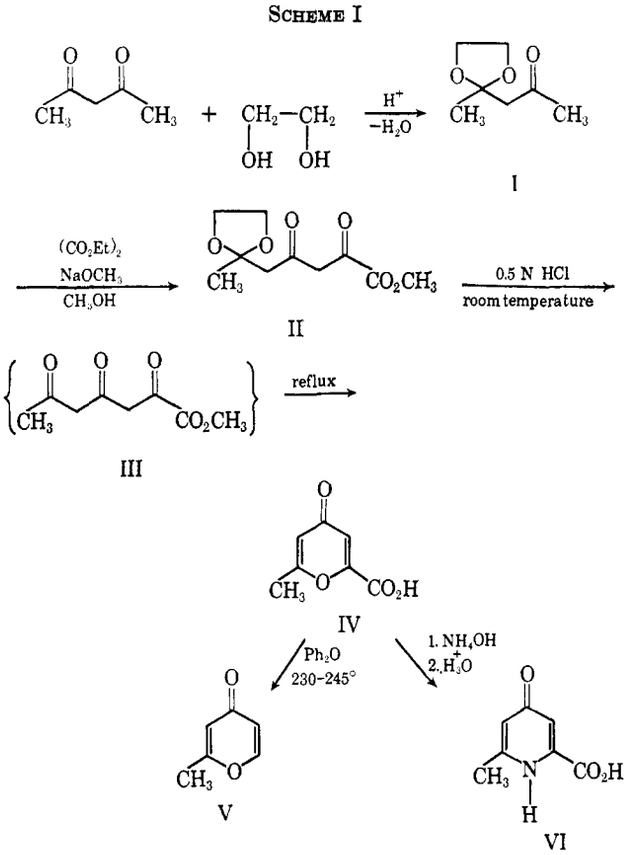
Received May 3, 1967

Although 2-methyl-4H-pyran-4-one has been cited in the literature,[1] a synthesis of this compound apparently has never been reported. We now wish to present a convenient total synthesis of 2-methyl-4H-pyran-4-one in four steps starting from acetylacetone. The synthesis is outlined in Scheme I.

In the first step, one of the keto functions of acetylacetone was rendered inactive by ketal formation[2] with ethylene glycol to form I.[3]

2-Methyl-2-acetonyl-1,3-dioxolane (I) was acylated with diethyl oxalate and sodium methoxide in methanol to form methyl 2,4-diketo-6-ethylenedioxyheptanoate (II) in a crude yield of 89%. This intermediate was characterized by its infrared spectrum [$\lambda_{max}^{CCl_4}$ = 5.72 ($-C(=O)OCH_3$), 6.1 and 6.8 μ (β-diketone carbonyls, and 9.55 (ethylenedioxy ether linkages)] and by analysis of its copper chelate. Crude II was treated with 0.5 *N* hydrochloric acid at room temperature to effect hydrolysis of the ketal group. The intermediate triketone (III) was not isolated; instead, the reaction mixture was refluxed to complete ring closure and subsequent ester hydrolysis, forming 6-methyl-4H-pyran-4-one-2-carboxylic acid (IV) in 45–50% yield from crude II. The structure of IV was established by its spectral properties, analytical data, and its conversion to 6-methyl-4-pyridone-2-carboxylic acid (VI).

SCHEME I



In the final step IV was decarboxylated by heating in diphenyl ether at 230–245° followed by partial distillation of the reaction mixture under slight vacuum. 2-Methyl-4H-pyran-4-one (V) was obtained in the distillate as a 10–15% diphenyl ether solution. After separation from diphenyl ether, crude V was obtained in an approximate quantitative conversion and 93% purity. Analytical material[4] was readily obtained by glpc fractionation. Unlike 4H-pyran-4-one and 2,6-dimethyl-4H-pyran-4-one the 2-methyl derivative is a liquid at room temperature. The nmr spectrum of V has a rather simple appearance, though somewhat more complex when examined in detail since the 3-H appears to be involved in spin coupling with the remaining protons in the molecule. The 5-, 3-, and 6-hydrogens exhibit an ABX-type spectrum with further splitting of the 3-hydrogen by the 2-methyl hydrogens. The apparent coupling constants (in cycles per second) are $|J_{2,3}| \leqslant 0.7$, $|J_{3,5}| = 2.5$, $|J_{3,6}| \leqslant 0.6$, and $|J_{5,6}| = 5.7$.

In retrospect, going from acetylacetone to methyl 2,4,6-triketoheptonoate (III) was, in essence, an acylation of acetylacetone at the terminal methyl position, though indirect. Since Hauser and co-workers[5] have shown that acetylacetone dicarbanion can be acylated at the methyl position, it might appear preferable to obtain III directly from acetylacetone by acylation of its dicarbanion with dimethyl oxalate. This reaction, however, does not appear feasible since the dicarbanion product VII would be expected to undergo facile

(1) Use of 2-methyl-4H-pyran-4-one as a reactant was described by L. L. Woods (*J. Org. Chem.*, **27**, 696 (1962)); in a private communication Woods informed us that he had obtained a sample from Monsanto Chemical Co. of Texas City, Texas. We subsequently obtained a sample of 2-methyl-4H-pyran-4-one from Dr. R. J. Evans of Monsanto. We wish to thank Dr. Woods for his correspondence and Dr. Evans for the sample.

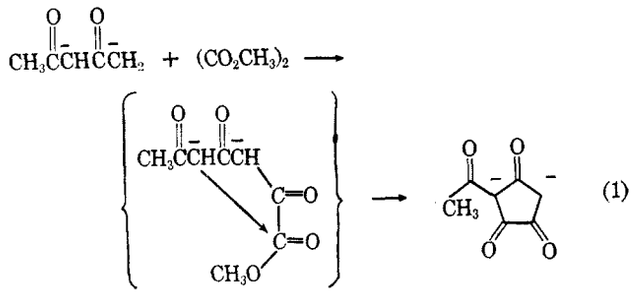
(2) H. Stetter and S. Vestner, *Ber.*, **97**, 169 (1964).

(3) In our initial procedure (see Experimental Section), glycol monoacetate, which is also formed in the reaction, *i.e.*, by alcoholic cleavage of acetylacetone (H. Adkins, W. Kutz, and D. C. Coffman, *J. Am. Chem. Soc.*, **52**, 4391 (1930)), proved rather difficult to separate from I by fractional distillation. Subsequent use of a procedure similar to one described by P. C. Dutta, P. K. Dutta, and K. N. S. Sastry [*J. Ind. Chem. Soc.*, **31**, 881 (1954)] led to a substantial reduction of glycol monoacetate in the crude reaction mixtures.

(4) This material was identical with the 2-methyl-4H-pyran-4-one obtained from Monsanto.[1]

(5) (a) C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958); (b) S. D. Work and C. R. Hauser, *J. Org. Chem.*, **28**, 725 (1963).

intramolecular acylation to a 1,2,4-cyclopentanetrione[6] (eq 1).



VII

(1)

An even shorter route to 2-methyl-4H-pyran-4-one (V) can be envisioned by an acylation at the methyl position of acetoacetaldehyde dicarbanion[7] to form diketo aldehyde VIII which, hypothetically, could be cyclized to V (eq 2).

VIII

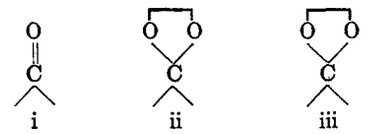
(2)

Acylation of aliphatic esters by such dicarbanions have not been reported. Indeed, a number of problems have been associated with dicarbanion acylations of aliphatic esters.[5b,8] Furthermore, the tendency of some diketoaldehydes to trimerize to 1,3,5-tris(acylacetyl)benzenes[7] adds to the improbable feasibility of this route to V.

Experimental Section

Melting points and boiling points are uncorrected. Nmr spectra were obtained with a Varian A-60 instrument at 60 Mc. Analytical glpc was accomplished with an F & M instrument, Model 300. Preparative glpc was accomplished with an F & M instrument, Model 810.

2-Methyl-2-acetonyl-1,3-dioxolane (I).—A stirred mixture of 74 g (0.74 mole) of acetylacetone, 41.5 g (0.67 mole) of ethylene glycol, and 220 ml of benzene was refluxed for 15 min to remove residual water, a Dean–Stark trap being used for this purpose. *p*-Toluenesulfonic acid monohydrate (0.3 g) was added and the mixture was refluxed until no further removal of water was observed (*ca.* 5.5 hr). The room-temperature mixture was treated with 3 g of potassium carbonate, shaken, filtered, and the filtrate was combined with that from another identical run and concentrated at atmospheric pressure to remove the bulk of benzene. The concentrate was filtered to remove some residual inorganic material and the filtrate (252 g) was vacuum distilled using a 4-ft Vigreux column at a reflux ratio of 20:1. After distilling a forerun of 92 g below 136° (156 mm), five subsequent fractions were collected and analyzed by glpc on a 0.25 in. × 10 ft 20% Carbowax 20M on Chromosorb W column: 1, bp 136–138° (157 mm), yield 14.8 g; 2, bp 139–140° (157–159 mm), yield 12.2 g; 3, bp 140–142 (157 mm), yield 23 g; 4, bp 142° (157 mm), yield 28.5 g; 5, bp 141–143° (159 mm), yield 14.9 g. The approximate weight per cent of unchanged acetylacetone–unknown–glycol monoacetate–monoketal (I)–diketal for the five fractions collected is given, respectively, by 1:3:39:57:0, 0:4:40:56:trace, 0:5:27:67:1, 0:1:8:90:1, and 0:0:4:90:6. A glpc sample of glycol monoacetate was characterized by its infrared spectrum ($\lambda_{max}^{CCl_4}$ 2.85, 5.72, 8.0, and 9.2 μ) and its glpc retention time, both of which were identical with that of an authentic sample. Glpc samples of I and the diketal, methylenebis[2-methyl-2-(1,3-dioxolanyl)], had respective infrared spectra: $\lambda_{max}^{CCl_4}$ 5.82 μ (i), 9.44 μ (ii), and 9.18 and 9.5 μ (iii).



i ii iii

Methyl 2,4-Diketo-6-ethylenedioxyheptanoate (II).—The acylation procedure of Royals[9] was used with slight modifications. To a rapidly stirred solution of 1.65 g (0.072 g-atom) of sodium in 35 ml of absolute methanol was added dropwise a solution of 9.5 g (0.06 mole) of 2-methyl-2-acetonyl-1,3-dioxolane (90% pure), 10.2 g (0.07 mole) of redistilled diethyl oxalate, and 10 ml of absolute methanol during 30 min, the reaction temperature being maintained between 15 and 18° by external cooling. Stirring was continued at 15° for 2 hr, at room temperature for 4 hr (in one run, the product's sodium salt precipitated preventing further stirring), and allowed to stand overnight. The reaction mixture was cooled in ice water and while stirring a cold solution of 2.5 ml of concentrated sulfuric acid in 15 ml of water was run in. The resulting mixture was poured into 40 ml of water and extracted with three 60-ml portions of chloroform and once with benzene. The combined extracts were washed with water, shaken with a little anhydrous potassium carbonate, and filtered. Removal of the solvents *in vacuo* left 12.3 g (89%) of crude II as a dark viscous oil: $\lambda_{max}^{CCl_4}$ 5.72 (-*C*(=O)OCH$_3$), 6.1 and 6.28 (β-diketone carbonyls), and 9.55 μ (iv). A copper

iv

chelate of II was precipitated from aqueous solution with copper acetate and a little ammonia. Recrystallization from chloroform–hexane afforded a green crystalline solid: mp 147–152° dec; $\lambda_{max}^{CCl_4}$ 5.76, 6.3, 6.58, and 9.5 μ.

Anal. Calcd for $C_{20}H_{26}O_{12}Cu$: C, 46.02; H, 5.02. Found: C, 45.76; H, 5.06.

6-Methyl-4H-pyran-4-one-2-carboxylic Acid (IV).—Crude methyl 2,4-diketo-6-ethylenedioxyheptanoate (II) (5 g) was stirred with 125 ml of 0.5 *N* HCl for 20 hr and the resulting solution was filtered to remove a little oily insoluble material. The filtrate was slowly heated to reflux and after refluxing for 1.5 hr the solution was cooled. The resulting brown crystals were collected, washed, and dried: yield, 0.47 g; mp 247–250° dec with gas evolution. Concentration of the mother liquor afforded a second crop of 1.2 g (total yield 50%), mp 247–252° dec. Recrystallization from a mixture of acetone–methyl ethyl ketone (1:1) and sufficient water to effect solution (Darco treated) gave short yellow needles, mp 256–256.7° dec sharply. The infrared spectrum (Fluorolube–Nujol) displayed a broad adsorption band between ~3.8 and 4.7 μ (max at 4.2 μ) presumed to be associated with complex formation between carboxyl OH and ring ether oxygen; other maxima include 5.8 (acid C=O), 6.08 (ring C=O),[10] and 6.26 and 6.4 μ (ring double bonds).[10] The nmr[11] spectrum (DMSO) showed bonds at −2.32 (doublet, 6-CH$_3$, $|J_{5,6}| \approx 0.6$ cps), −6.31 (multiplet, 5-H), −6.76 (doublet, 3-H, $|J_{3,5}| \approx 2.7$ cps), and −7.0 ppm (broad singlet, -COO*H*) (TMS).

Anal. Calcd for $C_7H_6O_4$: C, 54.6; H, 3.92; neut equiv, 154. Found: C, 54.8; H, 4.19; neut equiv, 158.

A stoppered solution of 0.50 g of 6-methyl-4H-pyran-4-one-2-carboxylic acid and 13 ml of concentrated ammonia was allowed to stand for 24 hr with occasional warming. Adjustment of the pH to *ca.* 4 with acetic acid precipitated 0.30 g of 6-methyl-4-pyridone-2-carboxylic acid (VI), mp 281–281.5° dec. A second crop of 0.06 g (total yield 62%), mp 280–281.5° dec, was obtained by further lowering of the pH of the mother liquor to 3.5. The analytical sample was obtained by two recrystallizations from dilute ethanol, mp 282–282.5° (lit.[12] mp 295°) after drying *in vacuo* at 80° for 7 hr.

Anal. Calcd for $C_7H_7NO_3$: C, 54.9; H, 4.61; N, 9.14. Found: C, 54.9; H, 4.47; N, 9.04.

2-Methyl-4H-pyran-4-one (V).—The decarboxylation procedure is an adaptation of a procedure described by Hennis and

(6) C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **8**, 84 (1954).

(7) T. M. Harris, S. Boatman, and C. R. Hauser, *J. Am. Chem. Soc.*, **87**, 3186 (1965).

(8) R. J. Light and C. R. Hauser, *J. Org. Chem.*, **25**, 538 (1960).

(9) E. E. Royals, *J. Am. Chem. Soc.*, **67**, 1508 (1945).

(10) K. Yamada, *Bull. Chem. Soc. Japan*, **35**, 1323 (1962).

(11) Chemical shift (ppm from TMS) designate center of peak(s).

(12) J. N. Collie and G. Bishop, *J. Chem. Soc.*, **127**, 963 (1925).

Easterly.[13] 6-Methyl-4H-pyran-4-one-2-carboxylic acid (1.50 g) and 10 ml of diphenyl ether were placed in a 25-ml distillation flask to which was attached a small Vigreux column (70 mm), condenser, and receiver. The flask was immersed in an oil bath preheated to 223°. The bath temperature was raised to 230° whereupon ebullition of the mixture began. The bath temperature was maintained between 230 and 245° until the ebullition slackened; about 17 min were required. The bath was lowered and the system was carefully subjected to a vacuum of 220 mm for distillation. Heating of the mixture was resumed and a distillate of 7.63 g was collected at 192–204° (210 mm). The distillate was partitioned between 15 ml of 5 *N* HCl and 50 ml of hexane. The organic layer was extracted with two 15-ml portions of 5 *N* HCl. The acid layers were combined and carefully treated with solid potassium carbonate until the mixture became cloudy. This was extracted with four 40-ml portions of methylene chloride. The dried ($MgSO_4$) and combined extracts were evaporated *in vacuo* leaving a clear oil as residue (1.14 g). Glpc analysis of the residue on a 0.25 in. × 10 ft 410 gum rubber (20% on Chromosorb WAW, 60–80 mesh) column at 150° showed it consists of *ca.* 93% 2-methyl-4H-pyran-4-one, corresponding approximately to a quantitative conversion. Analytical material was obtained by glpc fractionation on a $^3/_8$ in. × 20 ft gum rubber (20% on Chromosorb W HMDS, 30–60 mesh) column at 150°: $n^{25}D$ 1.5280; λ_{max}^{hexane} 239 (ϵ 3410); λ_{max}^{EtOH} 247 (ϵ 1340); $\lambda_{max}^{CCl_4-CS_2}$ 5.99 (vs, C=O),[10] 6.15 and 6.29 (s, ring double bonds),[10] 7.04, 7.20, 7.32, 7.96, 11.2 and 12.2 (s), 8.20, 8.50, 9.43 and 9.91 (m), 10.7, and 11.6 μ (vs); nmr ($CDCl_3$), −2.28 (doublet, 2-CH_3, $|J_{2,3}| \leq 0.7$ cps), −6.14 (multiplet, 3-H), −6.26 (quartet, 5-H, $|J_{3,5}| = 2.5$, $|J_{5,6}| = 5.7$ cps), and 7.77 ppm (quartet, 6-H), $|J_{3,6}| \leq 0.6$ cps) (TMS).

Anal. Calcd for $C_6H_6O_2$: C, 65.4; H, 5.49. Found: C, 65.1; H, 5.46.

Registry No.—I, 14255-36-8; methylenebis(2-methyl-2-[1,3-dioxolanyl]), 14255-37-9; II, 14255-38-0; copper chelate of II, 14495-16-0; IV, 14255-39-1; V, 5848-33-9; VI, 14255-41-5.

Acknowledgment.—Thanks are due Dr. J. P. Heechen and Mr. R. A. Nyquist for determination and interpretation of nmr and infrared spectra, respectively. Appreciation is extended to Professor J. W. Crump of Albion College for helpful discussions and encouragement during the course of this work.

(13) J. P. Easterly and H. E. Hennis, U. S. Patent 3,152,148 (1964); *Chem. Abstr.*, **62**, 530 (1965).

Heterocyclic Compounds. VIII.[1] The Reaction of Ethoxyacetylene with 2- and 4-Pyridone

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Received June, 6, 1967

Treatment of pyridones with dienophiles leads to variable results. For example, fusion of N-methyl-2-pyridone and maleic anhydride gave a rather unusual derivative,[2] whereas in an autoclave hexafluoro-2-butyne added normally to 2-pyridone.[3] Benzyne and N-methyl-2-pyridone, in contrast, afforded either a Diels–Alder product or a phenylpyridone depending on the exact generation procedure.[4,5] With 2-pyridone the benzyne reagent produced small amounts of 2-phenoxypyridine, 1-phenyl-2-pyridone, and acridone.[4] No related study exists for ethoxyacetylene, although amines do react with the ethynyl function to yield alkoxyvinylamines.[6] Since 2- and 4-pyridone have tautomeric forms, it was felt that a brief investigation into this area would be useful and might provide some interesting N- and O-substitution compounds.[7]

The condensation of 2-pyridone with ethoxyacetylene in refluxing chloroform proceeded sluggishly; the black solution on distillation was readily separated into two liquid fractions. The major, low-boiling material was identified as 2-acetoxypyridine (I), previously formed with difficulty from sodium 2-pyridinolate and acetyl chloride[8,9] or by heating pyridine 1-oxide with acetic anhydride.[10,11] The infrared, nuclear magnetic resonance, and ultraviolet spectral data confirmed this assignment of structure. The minor, high-boiling material analyzed for $C_9H_{11}NO_2$ and was formulated as N-(1-ethoxyvinyl)-2-pyridone (II). The ultraviolet spectrum held two maxima at 227 and 303 mμ that was suggestive of an unchanged chromophoric system, for a similar pair of bands is found in the parent 2-pyridone at 227 and 297 mμ.[12] In the infrared the lack of a strong absorption between 3700–3300 cm^{-1} indicated the masking of the amide hydrogen function; additional correlations were made at 1670 (conjugated ketone) and 1286 cm^{-1} (vinyl ether).[13] The nuclear magnetic resonance spectrum exhibited the expected resonances at δ 1.32 (methyl), 4.00 (aliphatic methylene), 4.40 and 4.47 (vinyl methylene), and 6.27, 6.55, 7.50, and 7.55 (ring hydrogens).[14–16] Such a consequence is interesting, as only a few N-acylpyridones are known at present.[17] It has been mentioned that the rarity of N-acylpyridones may be caused by a rapid rearrangement of these compounds to the corresponding O-acylpyridines.[18] Employing this suggestion, the reaction course here would proceed from II through an unstable N-acetylpyridone to I. The direct formation of I can alternatively occur by formation

(1) For the previous paper in this series, see B. Weinstein and D. N. Brattesani, *J. Heterocyclic Chem.*, **4**, 151 (1967).

(2) B S. Thagarajan and K. Rajagopalan, *Tetrahedron*, **19**, 1483 (1963).

(3) L. A. Paquette, *J. Org. Chem.*, **30**, 3107 (1965).

(4) L. Bauer, C. L. Bell, and G. E. Wright, *J. Heterocyclic Chem.*, **3**, 393 (1966).

(5) These results should be considered with caution in view of a recent disclosure concerning the effect of the silver ion on the reactions of benzyne; see L. Friedman, *J. Am. Chem. Soc.*, **89**, 3071 (1967).

(6) For a review on the chemistry of ethynyl ethers, see J. F. Ahrens, "Advances in Organic Chemistry," Vol. 2, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 117.

(7) For a brief discussion of N-acetylpyridones and acetoxypyridines, see H. Meislich, "The Chemistry of Heterocyclic Compounds," Vol. 14, E. Klingsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, pp 509 and 643–646.

(8) A. E. Chichibabin and P. G. Szokow, *Ber.*, **58**, 2650 (1925).

(9) Y. Yeno, T. Takaya, and E. Imoto, *Bull. Chem. Soc. Japan*, **37**, 864 (1964)

(10) J. H. Markgraf, H. B. Brown, Jr., S. C. Mohr, and R. G. Peterson, *J. Am. Chem. Soc.*, **85**, 958 (1963).

(11) T. Cohen, I. H. Song, and J. H. Fager, *Tetrahedron Letters*, 237 (1965).

(12) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorpon Spectroscopy in Organic Chemistry," Edward Arnold Ltd., London, 1957, p 157.

(13) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 207.

(14) C. L. Bell, R. S. Egan, and L. Bauer, *J. Heterocyclic Chem.*, **2**, 420 (1965).

(15) W. Brügel, *Z. Elektrochem.*, **66**, 159 (1962).

(16) H.-H. Perkampus and U. Krüger, *Chem. Ber.*, **100**, 1165 (1967).

(17) M. Dohrn and P. Diedrich, *Ann.*, **494**, 284 (1932).

(18) D. Y. Curtin and L. L. Miller, *J. Am. Chem. Soc.*, **89**, 637 (1967), footnote 23.