the two compounds were obtained pure. They are both very soluble in alcohol and ether, slightly soluble in benzene, and soluble in water only on boiling for considerable time. They then crystallize from the water very slowly. The higher melting form is a white powder or small, hard spheres. The lower melting form is distinctly crystalline.

Anal. Calcd. for $C_{12}H_{14}O_4$ (222.1): C, 64.8; H, 6.35. (*Mixture of two forms*) Found: C, 64.4, 64.7, 64.8; H, 6.4, 6.4, 6.7. *Eq. wt.* Subs., 0.3017; NaOH (0.1013 *N*) 26.8 cc. = 0.1086 g. NaOH. Eq. wt., 111.1. Silver salt: 0.4099 g. gave 0.2002 g. Ag. Eq. wt., 113. (*Lower melting form*, m. p. 159–160°.) Found: C, 64.5, 64.7; H, 6.4, 6.5. Silver salt: 0.5001 g. gave 0.2436 g. Ag. Eq. wt., 113.6. (*Higher melting form*, m. p. 170–172°.) Found: C, 64.3, 64.3; H, 6.4, 6.3. Silver salt: 0.3333 g. gave 0.1628 g. Ag. Eq. wt., 113. *Eq. wt.* Subs., 0.2011; NaOH (0.1031 *N*) 18.1 cc. = 0.0746 g. NaOH. Eq. wt., 107.8.

Acid from the oxidation[1] of 2,3,5,6-tetramethyl-3-phenylcyclohexene-5-dione-1,4, m. p. 170–172°; synthetic acid, m. p. 170–172°; mixed melting point, m. p. 170–171°.

The author wishes to thank Dr. W. L. Evans and the Department of Chemistry of the Ohio State University for the use of their laboratory during the last week of experimental work on this problem.

Summary

The identity of the acid obtained by the oxidation of 2,3,5,6-tetramethyl-3-phenylcyclohexene-5-dione-1,4 has been established.

The two racemic forms of α,α′-dimethyl-α-phenylsuccinic acid have been prepared and characterized.

Two other new compounds, 1-phenylpropane-1,2,2-tricarboxylic acid, triethyl ester and α-methyl-β-phenyl-β-cyanobutyric acid, ethyl ester, have been prepared and described.

POUGHKEEPSIE, N. Y. RECEIVED AUGUST 2, 1933

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

Diarsyls. VI. 3,3′,3′′,3′′′-Tetranitro-, 3,3′,3′′,3′′′-Tetra-amino- and 3,3′,3′′,3′′′-Tetra-(acetylamino)-tetraphenyldiarsyl

BY F. F. BLICKE, U. O. OAKDALE[1] AND J. F. ONETO

A number of years ago Michaelis[2] heated 3,3′-dinitrodiphenylarsinic acid with phosphorous acid for a short time and stated that he obtained 3,3′,3′′,3′′′-tetranitrotetraphenyldiarsyl; a longer period of interaction, according to him, yielded the corresponding tetraamino diarsyl which he then acetylated to the tetraacetyl derivative.

While Michaelis undoubtedly obtained the tetranitrodiarsyl, although his method is an unsatisfactory one since at elevated temperatures the nitro groups also are reduced, it is certain in view of our experiments that he was mistaken in his claims regarding the isolation of the other two diarsyls.

3,3′-Dinitrodiphenylarsinic acid was converted into the dinitrodiphenylchloroarsine and the latter into the corresponding hydroxy arsine. This substance, dissolved in acetic acid, is transformed rapidly into the diarsyl when treated with hypophosphorous acid at ordinary temperature.

3,3′,3′′,3′′′-Tetraaminotetraphenyldiarsyl was prepared by four methods: (a) reaction between 3,3′,3′′,3′′′-tetraaminotetraphenylarsyl oxide and 3,3′-diaminodiphenylarsine; (b) interaction between the above mentioned oxide and diphenylarsine; (c) reaction of tetraphenylarsyl oxide and 3,3′-diaminodiphenylarsine; (d) reduction of 3,3′-diaminodiphenylarsinic acid with hypophosphorous acid.

$$\text{(a)}\quad (H_2NC_6H_4)_2As{-}O{-}As(C_6H_4NH_2)_2 + 2\,(H_2NC_6H_4)_2AsH \longrightarrow 2\,(H_2NC_6H_4)_2As{-}As(C_6H_4NH_2)_2 + H_2O$$

$$\left.\begin{array}{l}\text{(b)}\quad (H_2NC_6H_4)_2As{-}O{-}As(C_6H_4NH_2)_2 + 2\,(C_6H_5)_2AsH \\ \text{(c)}\quad (C_6H_5)_2As{-}O{-}As(C_6H_5)_2 + 2\,(H_2NC_6H_4)_2AsH\end{array}\right\} \longrightarrow \begin{array}{l}(H_2NC_6H_4)_2As{-}As(C_6H_4NH_2)_2 + \\ (C_6H_5)_2As{-}As(C_6H_5)_2 + H_2O\end{array}$$

In methods b and c a mixture of 3,3′,3′′,3′′′-tetraaminotetraphenyldiarsyl and tetraphenyldiarsyl was obtained. However, separation of the two compounds was easily carried out by extraction of the mixture in the presence of benzene with dilute hydrochloric acid; the amino compound dissolved in the aqueous acidic layer in the form of a water-soluble hydrochloride while the tetraphenyldiarsyl entered into the benzene layer. The isolation of the two diarsyls in yields as high as 85% proves that the unsymmetrical diarsyl, 3,3′-diaminotetraphenyldiarsyl, which might be

---

(1) Parke, Davis and Company Fellow.

(2) Michaelis, *Ann.*, **321**, 149 (1902).

produced in reactions b and c, is not formed at all or only to a slight extent.

When the tetraaminodiarsyl, dissolved in acetone, was treated with acetic anhydride, it was converted into the corresponding tetraacetyl derivative, a compound characterized by its great insolubility and its high melting point. Suspended in ethylene bromide the diarsyl absorbed oxygen but the rate of absorption was very slow.

Experimental Part

Apparatus.—In many of the experiments the ordinary free radical apparatus, without the lower stopcock,[3] was used. However, in instances in which it was necessary to prepare a suspension of an insoluble diarsyl the modified radical apparatus (Fig. 1) was found to be very serviceable. It can also be used to advantage in other experiments since it is not necessary to break the tip of the apparatus in order to remove the product. The ground glass joint is 14 mm. in diameter. When an aminotetraphenyldiarsyl is precipitated from an acid solution by alkali, or a hydroxytetraphenyldiarsyl is precipitated from an alkaline solution by acid, the diarsyl is obtained in the form of a flocculent precipitate which remains suspended in the liquid; consequently, it can only be separated from the mother liquor by filtration. In order to carry out this process the precipitation is effected in the bulb of the apparatus shown in Fig. 2 and the apparatus then turned in such a manner that the liquid and precipitated material settle on the filter plate. With the aid of a stream of nitrogen the liquid is forced through the filter and out of the apparatus through the lower stopcock. The filter plate, A, consists of two perforated nickel disks held together by two small bolts. A piece of filter paper is placed between the disks and the latter are held in place by a nickel-plated split band of spring bronze.

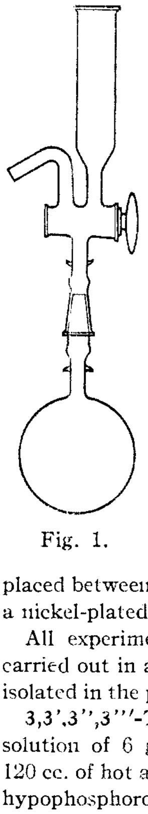
Fig. 1.

All experiments in which diarsyls were formed were carried out in an atmosphere of nitrogen and the products isolated in the presence of carbon dioxide.

3,3',3'',3'''-Tetranitrotetraphenyldiarsyl.—To a cold solution of 6 g. of 3,3'-dinitrodiphenylhydroxyarsine[4] in 120 cc. of hot acetic acid in a "radical" bulb, 22 cc. of 50% hypophosphorous acid containing 2 drops of hydriodic acid was added. The solid diarsyl which immediately precipitated was, after two hours, separated from the liquid by decantation, washed thrice with 40 cc. of acetic acid, twice each with absolute alcohol and absolute ether, dried *in vacuo*, recrystallized from hot, pure pyridine and the above washings repeated. The pale yellow crystals melted in nitrogen in a sealed tube at 203-204°;[5] yield, 3.3 g.

Anal. Calcd. for $C_{24}H_{16}O_8N_4As_2$: As, 23.49. Found: As, 23.37.

From the diarsyl and iodine 3,3'-dinitrodiphenyliodoarsine was obtained, m. p. 94-95°. A sample of the iodide, prepared by mixing 3,3'-dinitrodiphenylhydroxyarsine with acetic acid and hydriodic acid, melted at 94-95° after recrystallization from acetic acid.

Anal. Calcd. for $C_{12}H_8O_4N_2AsI$: I, 28.46. Found: I, 28.24.

Suspended in 25 cc. of ethylene bromide 1.1079 g. of the diarsyl absorbed 52 cc. (N. T. P.) of oxygen in twenty-five minutes; calcd., 38 cc.

3,3'-Diaminodiphenylarsinic Acid.—A mixture of 850 g. of ferrous sulfate and 2500 cc. of water was stirred vigorously and 365 g. of flake sodium hydroxide, dissolved in 1400 cc. of water, added. A solution of 75 g. of crude 3,3'-dinitrodiphenylarsinic acid,[6] 60 g. of sodium hydroxide and 750 cc. of water was added, the mixture stirred for one hour and treated in the manner described by Wieland and Rheinheimer.[6] By extraction of adhering amino acid from the copious precipitate of sodium chloride and sodium sulfate with small quantities of dilute hydrochloric acid a total yield of 85-90% can be obtained; m. p. 235° with decomposition.[6,7]

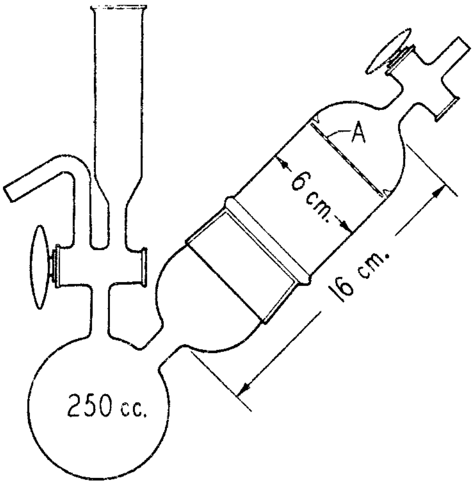

Fig. 2.

3,3',3'',3'''-Tetraamino- and 3,3',3'',3'''-Tetra-(acetylamino)-tetraphenylarsyl Oxide.—Sulfur dioxide was passed into a solution prepared from 20 g. of the 3,3'-diamino acid, 85 cc. of concd. hydrochloric acid and a few drops of hydriodic acid. The crystalline dihydrochloride of 3,3'-diaminodiphenylchloroarsine precipitated in quantitative yield. For analysis the hydrochloride was dissolved in the least possible amount of water and precipitated by the addition of fuming hydrochloric acid.[6,8]

Anal. Calcd. for $C_{12}H_{14}N_2AsCl_3$: As, 20.40; Cl, 28.49. Found: As, 20.52; Cl, 28.43.

---

(3) See Blicke and Powers, This Journal, **54**, 3356 (1932).

(4) Michaelis, *Ann.*, **321**, 145 (1902).

(5) Michaelis was unable to recrystallize this substance because of its insolubility and found a melting point of 200°.

(6) Wieland and Rheinheimer, *Ann.*, **423**, 36 (1921).

(7) Wieland and Rheinheimer obtained yields of 50-58% by their method but reported no melting point for the acid.

(8) The hydrochloride has been obtained by Wieland and Rheinheimer by another method. The dry material, as well as the oxide obtained from it, irritates strongly the mucous membrane of the nose and throat.

In order to obtain the oxide a solution of the hydrochloride was stirred with ether and ammonia water. From the ether the oxide was obtained as a colorless gum.

To obtain the tetraacetyl derivative the oxide was dissolved in hot acetic anhydride and after twelve hours most of the excess anhydride was removed, water added, the crystalline product filtered and recrystallized from 50% alcohol; m. p. 236–237°.

Anal. Calcd. for $C_{32}H_{32}O_5N_4As_2$: As, 21.34. Found: As, 21.35.

3,3′,3″,3‴-Tetraaminotetraphenyldiarsyl. (a) **From 3,3′,3″,3‴-Tetraaminotetraphenylarsyl Oxide and 3,3′-Diaminodiphenylarsine.**—A solution of 1.4 g. of 3,3′-diaminodiphenylarsine[9] in 35 cc. of absolute alcohol (apparatus Fig. 1) was mixed with 1.5 g. of the arsyl oxide, dissolved in 10 cc. of the same solvent. After twelve hours the alcohol was decanted, the crystalline product washed with alcohol, with absolute ether and then dried; yield 2.1 g.; m. p. 168–169° in a sealed tube filled with nitrogen.

Anal. Calcd. for $C_{24}H_{24}N_4As_2$: As, 28.93. Found: As, 28.78.

Dissolved in 20 cc. of acetophenone[10] 1.3782 g. of the diarsyl absorbed 61 cc. (N. T. P.) of oxygen in one minute; calcd., 59 cc.

To prepare the tetrahydrochloride, 1.3 g. of the diarsyl was mixed with 1.7 cc. of concd. hydrochloric acid in a radical bulb, 35 cc. of water added and the solution filtered into a second bulb; 13 cc. of fuming hydrochloric acid was added whereupon 1.4 g. of the crystalline tetrahydrochloride precipitated; m. p. about 283° with decomposition.

Anal. Calcd. for $C_{24}H_{28}N_4As_2Cl_4$: As, 22.57; Cl, 21.35. Found: As, 22.53; Cl, 21.32.

Dissolved in 37 cc. of water 1.620 g. of the tetrahydrochloride absorbed 33 cc. (N. T. P.) of oxygen in one minute; calcd., 54 cc. When the oxidized solution was treated with fuming hydrochloric acid, 1.2 g. of the dihydrochloride of 3,3′-diaminodiphenylchloroarsine precipitated which shows that upon oxidation of the diarsyl tetrachloride the corresponding arsyl oxide is formed to a very large extent.

Anal. Calcd. for $C_{12}H_{14}N_2AsCl_3$: Cl, 28.94. Found: Cl, 28.63.

Sodium hydroxide solution was added to 4.0 g. of the tetrahydrochloride of the diarsyl; 2.4 g. of the diarsyl precipitated; m. p. 168–169°.

(b) From 3,3′,3″,3‴-Tetraaminotetraphenylarsyl Oxide and Diphenylarsine.—To a solution of 3.4 cc. of diphenyl arsine in 15 cc. of absolute alcohol there was added 5.3 g. of the tetraamino oxide, dissolved in 25 cc. of alcohol. After thirty-six hours the alcohol layer was decanted from the crystalline precipitate and the latter treated with 3.4 cc. of concd. hydrochloric acid, 70 cc. of water and 35 cc. of benzene. The acid layer was decanted into a second radical bulb and extracted with 20 cc. of benzene. The combined benzene layers were treated with 50 cc. of dilute hydrochloric acid, the benzene solution filtered into another bulb, concentrated, and the tetraphenyldiarsyl dried; yield 3.9 g.; calcd. yield 4.5 g.; m. p. 130–131° in a sealed tube filled with nitrogen. From 1.4 g. of the material, dissolved in benzene, and 0.77 g. of iodine, 2 g. of diphenyliodoarsine was obtained; mixed m. p. 42–43°. When 1.9 g. of the diarsyl was oxidized in benzene solution there was formed 1.2 g. of tetraphenylarsyl oxide, mixed m. p. 92–93°, and about 0.4 g. of diphenylarsinic acid.

The filtered hydrochloric acid solution was treated with 20 cc. of fuming hydrochloric acid whereupon 5.6 g. of the crystalline tetrahydrochloride of tetraaminotetraphenyldiarsyl separated immediately. It was identified by conversion into the free diarsyl with alkali; m. p. 167–169° in a sealed tube filled with nitrogen.

(c) **From Tetraphenylarsyl Oxide and 3,3′-Diaminodiphenylarsine.**—To 5.2 g. of 3,3′-diaminodiphenylarsine, dissolved in 15 cc. of benzene, there was added 4.7 g. of tetraphenylarsyl oxide, dissolved in 15 cc. of the same solvent. The tetraaminodiarsyl separated slowly and after eighteen hours the benzene layer, which contained the tetraphenyldiarsyl, was decanted into a second bulb. The precipitate was heated with 40 cc. of benzene to remove traces of tetraphenyldiarsyl and the benzene decanted. The residue of the tetraaminodiarsyl weighed 3.7 g.; m. p. 163–165°.

The solvent was removed completely from the benzene solution, the residue boiled with 50 cc. of benzene, the solution filtered into another bulb and the solvent removed; the tetraphenyldiarsyl obtained melted at 127–128°.

(d) **From 3,3′-Diaminodiphenylarsinic Acid and Hypophosphorous Acid.**—To 5.8 g. of the diamino acid (apparatus Fig. 2) there was added 30 cc. of 50% hypophosphorous acid and a few drops of hydriodic acid. The solution was heated in a bath at 70° for four hours, cooled and 100 cc. of 10% sodium hydroxide solution added slowly while the mixture was shaken continuously. The precipitated diarsyl was filtered, washed with water, with absolute alcohol, dissolved in 20 cc. of hot acetone, the solution transferred to an ordinary radical bulb and concentrated. The diarsyl which separated was washed with 80% acetone and dried; yield 2.5 g.; m. p. 163–165°.

Anal. Calcd. for $C_{24}H_{24}N_4As_2$: As, 28.93. Found: As, 28.31.

3,3′,3″,3‴-Tetra-(acetylamino)-tetraphenyldiarsyl.—An acetone solution of 0.6 g. of the tetraamino diarsyl, (apparatus, Fig. 1), was heated with 6 cc. of acetic anhydride at 65° for one hour, the crystalline product washed with acetone and hot alcohol; yield 0.6 g.; m. p. above 300°.[11]

Anal. Calcd. for $C_{32}H_{32}O_4N_4As_2$: As, 21.85. Found: As, 21.11.[12]

Suspended in ethylene bromide the diarsyl absorbed oxygen very slowly. The compound was suspended in acetic acid and iodine added. The yellow, crystalline solid obtained, 3,3′-di-(acetylamino)-diphenyliodoarsine, m. p. 189–190°, when treated with sodium hydroxide solution was hydrolyzed to the tetra-(acetylamino)-tetraphenylarsyl oxide; mixed m. p. 235–237°.

---

(9) The preparation of this compound will be described later.

(10) This substance was used as a solvent since the diarsyl is insoluble in bromobenzene, the solvent usually employed in the absorption apparatus.

(11) Michaelis, *Ann.*, **321**, 150 (1902), stated that he could only obtain tetraaminotetraphenyldiarsyl in the form of an amorphous compound but that upon acetylation the crystalline tetraacetyl derivative was formed which melted at 162°.

(12) Since we were unable to purify the diarsyl by recrystallization, due to its insolubility, the crude product was used for analysis.

Summary

The preparation of 3,3′,3″,3‴-tetranitro-, 3,3′,3″,3‴-tetraamino- and 3,3′,3″,3‴-tetra(acetylamino)-tetraphenyldiarsyl has been described.

ANN ARBOR, MICH. RECEIVED AUGUST 3, 1933

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

The Action of Amines on the Esters of Carboxy Substituted Ureas, Thioureas and Guanidines. III

BY J. ALDEN MURRAY AND F. B. DAINS

This is a continuation of the study of the action of amines on carbonyldiurethan and allophanic ester[1] together with their sulfur analogs and on the ethyl esters of guanidinecarboxylic acids. These latter can be regarded as derivatives of allophanic ester or carbonyldiurethan in which the carbonyl oxygen is replaced by S, CH_3S, NH or NH_2.

The experimental results have shown that with the sulfur derivatives the S or CH_3S was the first point of attack, while with the guanidinecarboxylic esters, as in carbonyldiurethan, the carbethoxy groups were first affected. In some cases ring closure occurred to form heterocyclic compounds.

Experimental

1. Urea Derivatives

Methyl and Ethyl Amines and Allophanic Ester.—On long standing the ester went into solution in the amines (33%) and from the residues, on evaporation, were isolated 1-methylbiuret (m. p. 175°) and 1-ethylbiuret (m. p. 159°) in 60% yields.[2]

Benzylamine and Allophanic Ester.—γ-Benzylallophanic ester[3] (I), $C_6H_5CH_2NHCONHCOOC_2H_5$, was the main product when the components were heated at 135° for three hours.

Heated at 150° for five hours, 1,5-dibenzylbiuret (II), $HN(CONHCH_2C_6H_5)_2$, (m. p. 169°) resulted, while at 200° the biuret dissociated to give cyanuric acid and *s*-dibenzylurea (m. p. 169°).[4]

Phenyl Isocyanate and Allophanic Ester.—The ester and isocyanate were heated at 125° for five hours.[5] The residue consisted of unchanged ester, carbanilide, and the addition product 1-phenyl-5-carbethoxybiuret (m. p. 175°).[6]

Phenylhydrazine and γ-Phenylallophanic Ester.—This mixture, when heated at 130° for five hours, gave aniline and 1-phenylurazole (m. p. 263°).[7]

Methyl and Ethyl Amines and Carbonyldiurethan.—The diurethan dissolved immediately in an excess of 33% ethylamine solution, but in a few minutes a deposit of allophanic ester appeared.[8] On two weeks standing this dissolved and the solution was found to contain 1-ethylbiuret and traces of an oil, the ethyl ester of ethylcarbamic acid.[9]

With methylamine, the diurethan gave, in thirty-six hours, 1-methylbiuret.

Benzylamine and Carbonyldiurethan.—In water solution on standing, and at 115° without water, the reactants formed allophanic ester and ethyl benzylcarbamate (m. p. 49°),[10] results due to simple aminolysis. At 135°, the products were ammonia, allophanic ester and ethyl γ-benzylallophanate (I); at 160°, 1,5-dibenzylbiuret (II); and at 200° *s*-dibenzylurea.

Hydrazine and Carbonyldiurethan.—On standing in alcoholic solution, allophanic ester alone was isolated.

Phenylhydrazine and Carbonyldiurethan.—When molar quantities were heated at 115 or 140°, 1-phenylurazole was the main product,[7] but at 160° iminodicarboxylic acid diphenylhydrazide (III), $HN(CONHNHC_6H_5)_2$, was formed. It is soluble in sodium hydroxide.

2. Thiourea Derivatives

Thioallophanic Ester, $H_2NCSNHCOOC_2H_5$.[11]—The ester was hydrolyzed to thiourea by aqueous ammonia and alkyl amines, and by alcoholic potassium hydroxide. Heated at 160° for an hour with aniline or *o*-toluidine, it yielded the *s*-diaryl oxygen ureas. Efforts to methylate the ester were fruitless.

Amines and the Methyl Ether of Thiocarbonyldiurethan, $CH_3SC(NCOOC_2H_5)NHCOOC_2H_5$.[12]—The primary amines react with the methyl thioether in alcoholic solution with the loss of mercaptan and the formation of substituted guanidines. The yields were very satisfactory. Thus, methylamine gave γ-methyl-β-dicarbethoxyguanidine (IV), $CH_3NHC(NCOOC_2H_5)NHCOOC_2H_5$. Analogous results were obtained with ethylamine (V), ethanolamine (VI), benzylamine (VII), aniline (VIII), *o*-toluidine (IX), phenylhydrazine (X), *o*-aminophenol (XI), *p*-aminobenzoic acid (XII), anthranilic acid (XIII), and methyl anthranilate (XIV).

---

(1) (a) Dains, Greider, and Kidwell, THIS JOURNAL, **41**, 1004 (1919); (b) Dains and Wertheim, *ibid.*, **42**, 2303 (1920).

(2) Hofmann, *Ber.*, **4**, 265 (1871); Biltz and Jeltsch, *ibid.*, **56**, 1919 (1923).

(3) Prepared, for comparison, in 70% yield by heating benzylurea and ethyl chloroformate on the steam-bath for an hour.

(4) A mixture of the biuret and urea melted about 150°.

(5) Lakra and Dains, THIS JOURNAL, **51**, 2221 (1929).

(6) Ref. 1a, p. 1007.

(7) Ref. 1b, p. 2308.

(8) Ref. 1a, p. 1007.

(9) Basterfield, Woods and Whelen, THIS JOURNAL, **49**, 2848 (1927).

(10) Hantzsch, *Ber.*, **31**, 180 (1898).

(11) Doran, *J. Chem. Soc.*, **69**, 325, 331, 336 (1896); Dixon and Taylor, *ibid.*, **93**, 696 (1903); Dixon and Kennedy, *ibid.*, **117**, 80 (1920).

(12) Olin and Dains, THIS JOURNAL, **52**, 3326 (1930).