

*Anal.* Found: C, 84.34; H, 8.04.

The distillates were redistilled. The first portion boiled at 80–85° and was an azeotrope of water and methyl isopropenyl ketone. The second fraction was water, boiling at 98–100°. A very small third fraction boiling at 55–60° (3 mm.) was evidently the dimer, 2,6-dimethylocten-1-dione-3,7, which forms when methyl isopropenyl ketone is heated to 100°. <sup>5d</sup>

#### Reduction of the Polymer of Methyl Isopropenyl Ketone.

—To a solution of 25 g. of polymer (mol. wt. 11,200 by viscosity determination) in 600 cc. of dioxane was added 90 g. of Raney nickel. The mixture was shaken in a hydrogen atmosphere at 175° and 2000 pounds pressure for about seventeen hours until there was no further absorption of hydrogen. After cooling the mixture, the bomb was opened, the catalyst filtered, and the clear solution was poured slowly into a large volume of water. The reduction product separated and was collected on a filter. It was further purified by solution in methyl ethyl ketone and reprecipitated by pouring this solution into twice the volume of water. The product was then dried. The yield was 19 g. of a white powdery material melting over a range of 195–205°.

*Anal.* Calcd. for Formula VI or VII (86.47% ring closure): C, 76.71; H, 11.68. Found: C, 76.02, 75.84; H, 11.39, 11.39.

One attempt to reduce the polymer in dioxane at 200° caused a violent decomposition of the dioxane and the safety plug of the bomb blew out.

**Chloroacetylation of Reduction Product.**—Three and one-half grams of the reduction product was treated with 28 cc. of chloroacetyl chloride and 5 cc. of pyridine at room temperature for twenty-four hours. The mixture was poured into water, the polymer filtered, dissolved in methyl

ethyl ketone and reprecipitated by pouring the solution into water. This was repeated three times, and then the polymer was washed with water until the washings gave no test for chlorine. The product was dried at 70° and then weighed 2.6 g. It was a white powdery material melting at 195–205°.

*Anal.* Calcd. for chloroacetyl derivative of VI: C, 71.41; H, 10.47; Cl, 5.42. Calcd. for chloroacetyl derivative of VII: C, 60.48; H, 8.04; Cl, 16.57. Found: C, 72.38, 72.70; H, 10.98, 10.68; Cl, 3.67, 3.47.

**Acetylation of Reduction Product.**—Two grams of the reduction product was treated with 20 cc. of acetic anhydride and 20 cc. of dry pyridine at room temperature for thirty-six hours. The mixture was diluted to 200 cc. with methyl ethyl ketone and poured into water. The polymer was filtered and purified by reprecipitating twice from methyl ethyl ketone solution and finally washing with water. The product was dried at 70° and then weighed 1.4 g. It was a white powdery material melting at 190–200°.

*Anal.* Calcd. for acetyl derivative of VI: C, 72.08; H, 10.14; CH<sub>3</sub>CO-, 23.90. Calcd. for acetyl derivative of VII: C, 75.33; H, 11.28; CH<sub>3</sub>CO-, 6.93. Found: C, 75.47; H, 11.35; CH<sub>3</sub>CO-, 6.84.

The analysis for acetyl groups was carried out by the method of Matchett and Levine.<sup>9</sup>

### Summary

The polymer of methyl isopropenyl ketone has been shown to have a "head to tail" type of structure.

(9) Matchett and Levine, *Ind. Eng. Chem., Anal. Ed.*, **13**, 98 (1941).

URBANA, ILLINOIS

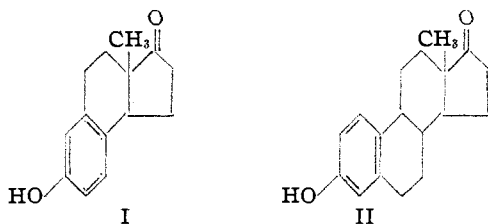
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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

## The Synthesis of an Analog of the Sex Hormones

BY W. E. BACHMANN AND DONALD G. THOMAS

In connection with our investigations on the synthesis of sex hormones and related compounds<sup>1</sup> we have prepared 6-hydroxy-2-methyl-3'-keto-1-, 2,3,4-tetrahydro-1,2-cyclopentenonaphthalene (I). We were interested in determining the estrogenic activity of this compound in view of similarity in structure with estrone (II).



(1) For the most recent article in this series see Bachmann and Holmes, *THIS JOURNAL*, **63**, 2592 (1941).

The compound was synthesized in *cis*- and *trans*-forms from 6-methoxy-1-tetralone by the procedure employed for the preparation of the desoxy derivative.<sup>2</sup> Since the actual configurations have not been determined the two forms have been designated by the prefixes  $\alpha$  and  $\beta$ . The  $\alpha$ -form was inactive in 5 mg. doses but the  $\beta$ -form induced the estrus response when injected into ovariectomized rats in 5 mg. doses.

We are grateful to Miss Helen C. McRae of the Department of Gynecology and Obstetrics of this University for these tests and to the Horace H. Rackham School of Graduate Studies for a generous grant which made possible this investigation.

(2) Bachmann and Thomas, *ibid.*, **63**, 598 (1941).

### Experimental

**$\gamma$ -*m*-Anisylbutyric Acid.**—A solution of 46.8 g. of *m*-iodoanisole and 21.8 g. of ethyl bromide in 75 cc. of ether was added in portions to 10.7 g. of ground magnesium and 125 cc. of ether in a three-necked flask equipped with condenser, dropping funnel and mercury seal stirrer. When the addition was complete (about forty-five minutes), 100 cc. of benzene was added and the mixture was refluxed for an hour. Another 100 cc. of benzene was then added and refluxing was continued for four or five hours. The mixture was cooled to 5° and ethylene oxide gas, after being passed first over soda lime and then potassium hydroxide pellets, was led to within an inch of the surface of the stirred mixture. When 30 g. of ethylene oxide had been added, the entire contents of the flask set to a gelatinous solid. After standing for two hours (or overnight), the mixture was refluxed for three or four hours during which time most of the solid disappeared. The mixture was cooled to 5° and after addition of 6 g. more of ethylene oxide gelation again occurred. After standing an hour, the mixture was refluxed for an hour and a half, then cooled, hydrolyzed and worked up in the usual manner. The product was fractionated under reduced pressure. A fore-run up to 110° was discarded and the main fraction was collected from 110–150° at 12 mm.; most of it boiled within the range 143–150°. The yield of  $\beta$ -*m*-anisylethyl alcohol suitable for conversion to the bromide was 25.8 g. (85%). In runs in which the ethyl bromide was omitted the yields were considerably lower. In one run in which the second addition of ethylene oxide was omitted the yield was about 10% lower. This alcohol has been prepared previously from *m*-anisylmagnesium bromide and ethylene chlorohydrin,<sup>3</sup> by the reduction of ethyl *m*-anisylacetate,<sup>4</sup> and from *m*-anisylmagnesium bromide and ethylene oxide.<sup>5,6,7</sup> In the latter three cases no ethyl bromide was used, only one addition of ethylene oxide was made and the yields were lower than those obtained by our procedure.

To 15.2 g. of the alcohol in 20 cc. of benzene cooled in an ice-bath was added dropwise 10.2 g. of phosphorus tribromide in 15 cc. of benzene. The solution was kept cold for an hour and then warmed at 60° for three hours in a water-bath before cooling and pouring onto ice. The benzene solution was washed successively with dilute sodium hydroxide solution, dilute hydrochloric acid and water, dried and fractionated; the yield of  $\beta$ -*m*-anisylethyl bromide boiling at 130–142° at 9 mm. was 14.2 g. (66%). This compound has been prepared previously in about the same yield by Hewett<sup>5</sup> who rapidly added phosphorus tribromide to a warm (60°) solution of the alcohol in carbon tetrachloride.

To a cooled solution of sodio-malonic ester prepared from 3.45 g. of sodium, 40 cc. of absolute alcohol and 32 g. of malonic ester was added 21.5 g. of the above bromide in 20 cc. of absolute alcohol. The mixture, which very shortly began to precipitate sodium bromide, was refluxed for seven hours. Sixty cc. of 45% potassium hydroxide solution was added and refluxing was continued for two to

three hours more. After removal of some of the alcohol in a current of air, water was added and the turbid solution was heated for two hours on a steam-bath. The solution was cooled, extracted with benzene and the aqueous solution was filtered into an excess of hydrochloric acid; the crystalline  $\beta$ -*m*-anisylethylmalonic acid which precipitated weighed 17.6 g. Another 4 g. obtained by ether extraction of the filtrate brought the total yield to 90%.

Decarboxylation of 17.6 g. of the malonic acid at 180° gave 13.7 g. (95%) of  $\gamma$ -*m*-anisylbutyric acid which distilled at 165–170° at 0.8 mm. and solidified on cooling; m. p. 42–46° (unrecrystallized) (reported, 49–50°). This acid has been prepared previously by other investigators employing different procedures.<sup>8,9,10,11</sup>

#### 6-Methoxy-1-keto-1,2,3,4-tetrahydronaphthalene.

Finely powdered phosphorus pentachloride (27.7 g.) was added to a cold solution of 21.5 g. of  $\gamma$ -*m*-anisylbutyric acid in 100 cc. of benzene and the mixture was allowed to stand at room temperature for one to two hours. After cooling in an ice-bath the acid chloride was cyclized by treating it with a chilled solution of 19 cc. of stannic chloride in 50 cc. of benzene. A cream colored complex precipitated immediately. After standing in an ice-bath for ten minutes the product was poured onto ice and worked up by the procedure used in an analogous case.<sup>12</sup> The 6-methoxytetralone which was distilled at 130–135° at 0.7 mm. rapidly solidified on cooling; yield, 18.7 g. (96%). A sample after recrystallization from 60–75° petroleum ether-acetone melted at 78–79.5° (reported, 77.5 to 82°). This compound has been prepared previously by cyclization of  $\gamma$ -*m*-anisylbutyric acid with sulfuric acid<sup>8,13</sup> with stannic chloride,<sup>14</sup> and by oxidation of 6-methoxytetralin with chromic acid.<sup>15</sup>

**Methyl 6-Methoxy-1-keto-1,2,3,4-tetrahydronaphthalene-2-glyoxalate.**—Condensation of 18.7 g. of 6-methoxytetralone with dimethyl oxalate for five hours at 5–15° as previously described<sup>12</sup> gave 25.5 g. (92%) of the glyoxalate which melted at 75–77°. A sample recrystallized twice from methanol formed yellow rectangular plates; m. p. 76.5–77.5°. With a 2% alcoholic solution of ferric chloride it gave a deep red color.

*Anal.* Calcd. for C<sub>14</sub>H<sub>14</sub>O<sub>6</sub>: C, 64.1; H, 5.4. Found: C, 64.2; H, 5.5.

**Methyl Ester of 6-Methoxy-1-keto-1,2,3,4-tetrahydro-2-naphthoic Acid.**—Decarbonylation of 23.9 g. of the above crude glyoxalate with 12 g. of finely powdered soft glass at 175–185° in the manner previously described<sup>2</sup> gave 20.5 g. (96%) of crystalline product suitable for methylation. A sample after evaporative distillation at 150–190° and 1 mm. and two recrystallizations from 60–75° petroleum ether containing a small amount of acetone formed colorless crystals; m. p. 88–89.5° with previous softening (Pyrex tube in a preheated bath), the value depending on the rate of heating. With alcoholic ferric chloride it gave a blue-green color.

(8) Thompson, *J. Chem. Soc.*, 2310 (1932).

(9) Robinson and co-workers, *ibid.*, 1288 (1935); 192 (1936); 747 (1936).

(10) Chuang and Huang, *Ber.*, **69**, 1505 (1936).

(11) Martin, *THIS JOURNAL*, **58**, 1438 (1936).

(12) Bachmann, Cole and Wilds, *ibid.*, **62**, 824 (1940).

(13) Rapson and Robinson, *J. Chem. Soc.*, 1285 (1935).

(14) Peak and Robinson, *ibid.*, 1581 (1937).

(15) Burnop, Elliott and Linstead, *ibid.*, 727 (1940).

(3) Shoesmith and Connor, *J. Chem. Soc.*, 2230 (1927).

(4) Rapson and Robinson, *ibid.*, 1533 (1935).

(5) Hewett, *ibid.*, 50 (1936).

(6) Natelson and Gottfried, *THIS JOURNAL*, **61**, 1001 (1939).

(7) Bergmann and Weizmann, *J. Org. Chem.*, **4**, 266 (1939).

*Anal.* Calcd. for  $C_{18}H_{14}O_4$ : C, 66.7; H, 6.0. Found: C, 66.5; H, 6.2.

**6-Methoxy-2-methyl-2-carbomethoxy-1-keto-1,2,3,4-tetrahydronaphthalene.**—Methylation of 8.28 g. of the crude aforementioned compound as previously described<sup>2</sup> gave 8.05 g. of product boiling at 165–175° at 2 mm. It crystallized from 60–75° petroleum ether–acetone in colorless rectangular prisms; yield, 7.34 g. (84%); m. p. 91–92.5°. The melting point of a sample was not raised after another recrystallization. By redistillation of the combined residues from the filtrates of several runs and recrystallization an additional amount of the product was obtained.

*Anal.* Calcd. for  $C_{14}H_{10}O_4$ : C, 67.7; H, 6.5. Found: C, 67.8; H, 6.4.

**Dimethyl Ester of 6-Methoxy-2-methyl-2-carboxy-1,2,3,4-tetrahydronaphthalene-1-acetic Acid.**—The Reformatsky reaction was carried out on 7.44 g. of the aforementioned keto-ester as previously described.<sup>2</sup> A mixture of 60 cc. of ether and 30 cc. of benzene was used as solvent and the temperature kept between 55–65°. The product, an oil which did not crystallize, was dehydrated as previously described<sup>12</sup> to a mixture of the *syn*- and *anti*-forms of 6-methoxy-2-methyl-2-carboxy-1,2,3,4-tetrahydronaphthylidene-1-acetic acid. This mixture was reduced with 2% sodium amalgam as previously described<sup>12</sup> to give a mixture of the potassium salts of the *cis*- and *trans*-forms of 6-methoxy-2-methyl-2-carboxy-1,2,3,4-tetrahydronaphthalene-1-acetic acid. Acidification of this mixture gave 6.5 g. (78%) of the two forms and from the filtrate there was obtained 1.2 g. of impure product by ether–benzene extraction.

Esterification of 6.5 g. of the mixture of acetic acids by means of diazomethane and crystallization from 60–75° petroleum ether–ether gave 4.3 g. (60%) of impure  $\alpha$ -form of the dimethyl ester; m. p. 64–76°. A sample recrystallized twice for analysis formed colorless needles; m. p. 77.5–79°.

*Anal.* Calcd. for  $C_{17}H_{22}O_5$ : C, 66.6; H, 7.2. Found: C, 66.8; H, 7.2.

The  $\beta$ -form of the dimethyl ester was obtained as an oil by evaporation of the filtrate from the  $\alpha$ -form; yield, 2.76 g. (39%).

**6-Methoxy-2-methyl-2-carbomethoxy-1,2,3,4-tetrahydronaphthalene-1-acetic Acid.**—The  $\alpha$ -form of the acid ester was prepared from the  $\alpha$ -dimethyl ester in the manner previously described.<sup>2</sup> From 4.02 g. of the dimethyl ester (m. p. 64–76°) there was obtained after recrystallization from 60–75° petroleum ether–ether 3.05 g., m. p. 116–119.5° and 0.40 g., m. p. 110–117°; total yield, 90%. A sample evaporatively distilled at 180–220° and 1.5 mm. crystallized from petroleum ether–acetone in colorless hexagonal plates; m. p. 118.5–120.5°.

*Anal.* Calcd. for  $C_{18}H_{20}O_5$ : C, 65.7; H, 6.9. Found: C, 65.6; H, 6.9.

The  $\beta$ -form prepared similarly from 2.76 g. of crude  $\beta$ -dimethyl ester crystallized when an ether solution of the product was allowed to evaporate slowly. The product (1.9 g.; m. p. 95–120°) was recrystallized from 60–75° petroleum ether–ether; yield, 1.21 g. (46%); m. p. 127–129°. A sample after evaporative distillation at 180–210°

and 1.5 mm. crystallized from petroleum ether–acetone in colorless triangular prisms; m. p. 128–130°.

*Anal.* Calcd. for  $C_{16}H_{20}O_5$ : C, 65.7; H, 6.9. Found: C, 65.5; H, 6.8.

**Dimethyl Ester of 6-Methoxy-2-methyl-2-carboxy-1,2,3,4-tetrahydronaphthalene-1-propionic Acid.**—The Arndt–Eistert–Wolff reaction was carried out on 2.92 g. of the  $\alpha$ -acid ester as previously described.<sup>2,12</sup> The product after evaporative distillation at 175–195° and 0.4 mm. was a light yellow oil (2.79 g.) which crystallized when cooled and scratched with petroleum ether–ether. It was recrystallized from 60–75° petroleum ether–ether; yield, 2.26 g. (70%); m. p. 51.5–53° to a cloudy liquid. A sample of the  $\alpha$ -form after two more recrystallizations from petroleum ether containing a small amount of acetone formed heavy colorless plates; m. p. 52–53.5° to a somewhat cloudy liquid clearing at about 64°.

*Anal.* Calcd. for  $C_{18}H_{24}O_5$ : C, 67.5; H, 7.5. Found: C, 67.4; H, 7.5.

The  $\beta$ -form was obtained in 78% yield as a slightly yellowish oil after evaporative distillation at 155–170° and 0.1 mm.

**2'-Carbomethoxy-3'-keto-6-methoxy-2-methyl-1,2,3,4-tetrahydro-1,2-cyclopentenaphthalene.**—Cyclization of 2.24 g. of the aforementioned  $\alpha$ -propionic ester as previously described<sup>12</sup> gave 1.9 g. of cyclic keto-ester which readily crystallized when scratched with petroleum ether–ether. It was recrystallized from 60–75° petroleum ether–ether; yield, 1.61 g. (80%). A sample of the  $\alpha$ -form after another recrystallization from petroleum ether containing a small amount of acetone formed colorless plates, m. p. 94–96.5° with previous softening (Pyrex tube in a preheated bath), the value depending on the rate of heating. With 2% alcoholic ferric chloride a violet color was obtained.

*Anal.* Calcd. for  $C_{17}H_{20}O_4$ : C, 70.8; H, 7.0. Found: C, 70.6; H, 7.0.

Cyclization of 2.36 g. of the  $\beta$ -isomer gave 1.77 g. of an oil which crystallized when scratched with petroleum ether–acetone. Recrystallization from 60–75° petroleum ether–ether gave 0.86 g. (40%) of the  $\beta$ -form; m. p. 108–114° with previous softening. (This cyclization was run on propionic ester obtained by the Arndt–Eistert–Wolff reaction on oily  $\beta$ -acid ester and was undoubtedly contaminated by some of the  $\alpha$ -form of the propionic ester.) A sample after recrystallization from petroleum ether containing a small amount of acetone formed irregular colorless plates; m. p. 117–119° with previous softening (Pyrex tube in a preheated bath), the value depending on the rate of heating. With 2% alcoholic ferric chloride a violet color was obtained.

*Anal.* Calcd. for  $C_{17}H_{20}O_4$ : C, 70.8; H, 7.0. Found: C, 70.5; H, 6.8.

**3'-Keto-6-methoxy-2-methyl-1,2,3,4-tetrahydro-1,2-cyclopentenaphthalene.**—The cyclic keto-esters obtained above were hydrolyzed for two hours in an atmosphere of nitrogen as previously described.<sup>2,12</sup> From 1.15 g. of the  $\alpha$ -compound there was obtained 0.90 g. of the  $\alpha$ -form as an almost colorless oil. After evaporative distillation at 120–160° and 0.4 mm. and cooling at about –10° in 60–75° petroleum ether containing a few drops of ether the product crystallized; yield, 0.64 g. (70%); m. p. 38.5–40.5°. A

sample crystallized from the same solvents in broad colorless needles, m. p. 39–40.5°.

*Anal.* Calcd. for  $C_{18}H_{38}O_2$ : C, 78.2; H, 7.9. Found: C, 78.1; H, 7.9.

The  $\beta$ -form obtained from 400 mg. of  $\beta$ -cyclic keto-ester crystallized immediately after evaporative distillation at 120–150° and 0.01 mm.; yield, 275 mg. (86%); m. p. 104–112°. A sample crystallized from 60–75° petroleum ether containing a drop or two of acetone in colorless plates; m. p. 112–113.5°.

*Anal.* Calcd. for  $C_{18}H_{38}O_2$ : C, 78.2; H, 7.9. Found: C, 78.2; H, 7.8.

**3'-Keto-6-hydroxy-2-methyl-1,2,3,4-tetrahydro-1,2-cyclopentenonaphthalene (I).**—The  $\alpha$ -form was obtained by refluxing 400 mg. of pure recrystallized methyl ether in a nitrogen atmosphere with 4 cc. of 48% hydrobromic acid and 4 cc. of glacial acetic acid for forty-five minutes during which time an orange-red color developed. The product which precipitated on dilution with water redissolved completely when excess 10% sodium hydroxide solution was added. The alkaline solution was treated briefly with Norit and filtered into an excess of hydrochloric acid. The hydroxy ketone which precipitated (225 mg.) was filtered off; by extraction of the filtrate with ether–benzene an additional 60 mg. of product was obtained; total yield, 75%; m. p. 154–155.5° with slight previous softening. After sublimation at 135–155° and 0.01 mm. and recrystallization from alcohol–water it formed clusters of colorless needles; m. p. 155–156°.

*Anal.* Calcd. for  $C_{18}H_{38}O_2$ : C, 77.7; H, 7.5. Found: C, 77.5; H, 7.4.

The  $\beta$ -form was obtained by refluxing 200 mg. of methyl ether (evaporatively distilled but not recrystallized) in a nitrogen atmosphere with 2 cc. of 48% hydrobromic acid and 2 cc. of glacial acetic acid for forty-five minutes. A green color developed on heating. The product was worked up as described for the  $\alpha$ -isomer and sublimed at 130–180° and 0.01 mm.; yield, 100 mg. (53%); m. p. 209–213° (vac.). From benzene it crystallized in almost colorless irregular plates; yield, 70 mg. (37%); m. p. 212–214° (vac.).

*Anal.* Calcd. for  $C_{18}H_{38}O_2$ : C, 77.7; H, 7.5. Found: C, 77.6; H, 7.6.

### Summary

The *cis* and *trans* forms of 3'-keto-2-methyl-6-hydroxy-1,2,3,4-tetrahydro-1,2-cyclopentenonaphthalene have been synthesized from 6-methoxy-1-tetralone by the method employed for the synthesis of the sex hormone equilenin. These hormone analogs possess the B, C, and D ring structure of equilenin, but lack the A ring. In addition a hydroxyl group is situated in the aromatic ring. One of the forms is weakly estrogenic when injected into ovariectomized rats.

ANN ARBOR, MICH.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

## Studies on High Molecular Weight Aliphatic Amines and their Salts. IV. Electrical Conductivities of Aqueous Solutions of the Hydrochlorides and Acetates of Dodecyl- and Octadecylamines<sup>1</sup>

BY A. W. RALSTON, CHARLES W. HOERR AND EVERETT J. HOFFMAN

Our knowledge of the electrical conductivities of solutions of colloidal electrolytes is based chiefly upon studies made with compounds in which the paraffin chain is in the anionic portion of the molecule. In this type of colloidal electrolyte, it has been recently shown by studies upon sodium alkyl sulfates and sodium alkyl sulfonates that when the equivalent conductivity is plotted against concentration the curves show three characteristic slopes.<sup>2</sup> In the first range the equivalent conductivity falls as a linear function of the square root of the concentration similar to the behavior observed in strong electrolytes. An

extremely rapid fall of equivalent conductivity with increased concentration characterizes the second range. In the third range this rapid fall is halted, and the curve shows a definite rise before falling again. These latter two ranges have been explained upon the basis of micelles, the existence of which was first postulated by McBain.<sup>3</sup> In their work upon the conductivity of cetylpyridinium chloride solutions in fields of varying strengths, Malsch and Hartley<sup>4</sup> concluded that their results could only be explained upon the existence of micelles. The present paper reports the electrical conductivities of aqueous solutions of dodecyl- and octadecylamine acetates and the corresponding hydrochlorides, and compares their behavior with that of anionic colloidal electrolytes.

(1) For previous paper see Ralston, Hoerr and Hoffman, *THIS JOURNAL*, **63**, 2576 (1941).

(2) McBain and Betz, *ibid.*, **57**, 1905 (1935); Howell and Robinson, *Trans. Roy. Soc. (London)*, **A156**, 386 (1936); McBain, Dye and Johnston, *THIS JOURNAL*, **61**, 3210 (1939); Wright, Abbott, Sivertz and Tartar, *ibid.*, **61**, 549 (1939); Ward, *J. Chem. Soc.*, 522 (1939).

(3) McBain, *Trans. Faraday Soc.*, **9**, 99 (1913).

(4) Malsch and Hartley, *Z. Physik. Chem.*, **170A**, 321 (1934).