

masses of fine filaments. After seed crystals have been obtained, fructose hemihydrate free from both anhydrous fructose and fructose dihydrate can be crystallized at 20 to 21° from a slowly stirred, seeded solution containing about 81% fructose.

Composition.—Material crystallized as described above was filtered by suction and stored over anhydrous fructose seeded with fructose hemihydrate at 0°. This desiccant was selected because, at this temperature, it should take up the excess water by forming additional hemihydrate without danger of overdrying the sample. After six days, during which lumps were crushed occasionally, the water content was reduced from over 10 to 5.2%,⁴ and the sample changed from a pasty mass to a dry crystalline powder. The water content of the sample was further reduced to 4.93% by fresh anhydrous fructose desiccant over which the sample was stored at 0° for 5 months. Consideration of the agreement of this value with the theoretical value for fructose hemihydrate (4.73%), and of the method of drying, leads to the conclusion that this material is fructose hemihydrate. This conclusion was confirmed by drying the sample at 0° for an additional month over anhydrous calcium chloride. During the first two weeks the water content decreased to 4.68%, at which it remained, in excellent agreement with the theoretical value. At no time in the history of this product was any anhydrous fructose observed in it, either microscopically or by X-ray diffraction.

Discussion

The agreement of our X-ray powder data with those reported by Wolfrom and Thompson² indicates that the sample which gave their X-ray data was L-fructose hemihydrate and not an anhydrous dimorph as they suggested. Since it is very improbable that stable and metastable forms of a pure substance would show identical melting points, the agreement they found between the melting points of their L-fructose and anhydrous D-fructose suggests further that the material used for that determination had also been dehydrated during their purification treatment.⁵ Their purification step of soaking the crystals overnight in ethanol at 25° appears to be the most likely place for dehydration to occur. Our observations show that such dehydration occurs readily at 25° in 95% ethanol. It will occur slowly, even at 0°, in more concentrated ethanol.

The initial specific rotation (−129°) and mutarotation constant (0.074) of fructose hemihydrate are in sufficiently good agreement with accepted values⁶ to indicate that D-fructose has the β-pyranose configuration in the hemihydrate.

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(4) Calculated from refractive indices of solutions containing weighed amounts of the hemihydrate and water. The tables of R. F. Jackson and J. A. Mathews, *J. Research Natl. Bur. Standards*, **8**, 412 (1932) (RP 426), were used to convert refractive indices to fructose percentages.

(5) In a private communication, Professor Wolfrom and Dr. Thompson agree that their original material must have been L-fructose hemihydrate and that dehydration had occurred in the samples they used for analysis and melting point determinations.

(6) H. S. Isbell and W. W. Pigman, *J. Research Natl. Bur. Standards*, **20**, 778 (1938), (RP 1104.)

NEW COMPOUNDS

Some Thiazole, Benzenesulfonamide and *n*-Hexylresorcinol Derivatives

2-Acetamido-5(?)-thiazolesulfinic Acid.—When 2-acetamido-5(?)-thiazolesulfonyl chloride^{1,2,3} was reduced with sodium bisulfite solution similar to the procedure used in preparing *p*-acetamidobenzenesulfinic acid,⁴ the corresponding sulfinic acid was obtained (62% yield). After it was freshly precipitated from a neutral solution of its sodium salt by acidification, or after rapid crystallization from water, it decomposed at 203° when heated from 195°. However, the decomposition point was no criterion of purity inasmuch as analytical results of it and its barium salt were erratic. The first analyses of such a sample³ indicated incorrectly that the compound was 2-acetamido-5-mercaptothiazole, which has subsequently been made by Hurd and Wehrmeister.³ The sulfinic acid lost sulfur dioxide upon standing at room temperature or when boiled with water. It decolorized iodine in aqueous solution.

*Anal.*⁵ Calcd. for C₈H₈N₂O₃S₂: C, 29.12; H, 2.93. Found: C, 29.30; H, 2.85.

The acid was characterized further by a derivative, 2-acetamido-5(?)-thiazolyl 2,4-dinitrophenyl sulfone, prepared as follows: to a solution of 2.06 g. (0.01 mole) of the sulfinic acid in 23 ml. of ethanol, 5 ml. of water and 4 ml. of 2.5 *N* sodium hydroxide solution, was added 2.02 g. (0.01 mole) of 2,4-dinitrochlorobenzene. After 15 minutes of refluxing, the precipitate was filtered off and recrystallized from glacial acetic acid. The product weighed 1.85 g. (50%), m.p. 291–292.5°. No success was had in treating the sulfinic acid with *p*-nitrobromobenzene for the purpose of obtaining a known derivative.

Anal. Calcd. for C₁₁H₈N₄O₇S₂: C, 35.48; H, 2.17; S, 17.22. Found: C, 35.63; H, 2.09; S, 16.94.

Methyl 2-Amino-5-thiazolecarboxylate.—Methyl formylchloroacetate was made by condensing 208 g. of methyl chloroacetate in 450 ml. of toluene with dry methyl formate (121 g.) in the presence of sodium methoxide (109 g.) which was added over 1.5 hours at 0°. The mixture was stirred for four hours at 0° and was then stirred with 600 ml. of cold water to dissolve the sodium methyl formylacetate. The aqueous solution was neutralized with 128 ml. of concd. hydrochloric acid; 190 g. of thiourea was added and the mixture was refluxed for one hour and 45 minutes. Next, the solution was stirred with 15 g. of activated carbon and filtered. By neutralizing with sodium hydroxide solution, 156 g. of the ester was obtained, m.p. 187–188°. When recrystallized from water, it melted at 192–193.5°. The yields, based on the methyl chloroacetate employed, varied from 40 to 50%.

Anal. Calcd. for C₈H₈N₂O₃S: C, 37.96; H, 3.82. Found: C, 37.91; H, 3.45.

2-Amino-5-thiazolecarboxamide.—Methyl 2-amino-5-thiazolecarboxylate (200 g.) was stirred for 10 hours at 50° in 2.5 l. of concd. ammonium hydroxide solution. The mixture was cooled, filtered, and the filtrate was concentrated under reduced pressure. Then it was chilled to precipitate the product (m.p. 230°, dec.), which was washed with water. An analytical sample, washed with benzene, acetone and then recrystallized from water melted at 231–232° (dec.); yield 121 g. (54%).

Anal. Calcd. for C₄H₆N₃OS: N, 29.36. Found: N, 29.13.

2-Sulfanilamido-5-thiazolecarboxamide.⁷—2-Amino-5-

(1) H. J. Backer and J. A. K. Buisman, *Rec. trav. chim.*, **63**, 228 (1944).

(2) H. E. Faith, *This Journal*, **69**, 2063 (1947).

(3) C. D. Hurd and H. L. Wehrmeister suggest the possibility of the sulfonyl group being attached to the amino nitrogen, *ibid.*, **71**, 4008 (1949).

(4) H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 7.

(5) All melting points are uncorrected.

(6) Microanalyses by Dr. Carl Tiedcke, Laboratory of Microchemistry, Teaneck, N. J.

(7) For biological data see H. J. Florstene and M. E. Rohrer, *J. Pharmacol.*, **99**, 198 (1948).

thiazolecarboxamide (122 g., 0.85 mole) was suspended in 400 ml. of dry pyridine and 216 g. (0.97 mole) of *p*-nitrobenzenesulfonyl chloride was added within 90 minutes. After the addition, the mixture was kept at 60° for two hours. Then it was diluted with water and the precipitate filtered off. It was added to dilute sodium hydroxide solution and filtered free of an insoluble portion (26 g.) which was evidently 2-amino-5-thiazolecarbonitrile (see below). The alkaline filtrate, when acidified, yielded 86 g. (31%) of the nitro compound. A portion of it, when crystallized twice from aqueous ethanol, decomposed at temperatures between 300–325°. It was stirred over a one-hour period into a suspension of 90 g. of iron powder and 350 ml. of 5% acetic acid. The mixture was kept below 50° during the addition and afterwards was heated with steam for 90 minutes. After cooling, it was made alkaline with sodium hydroxide and filtered. This process was repeated twice. Acidification of the filtrates to about pH 5 to 6 gave a precipitate which was crystallized from aqueous ethanol; m.p. 276° (dec.), yield 60 g. (77%). It was soluble in dilute hydrochloric acid. When hydrolyzed in 5% sodium hydroxide solution, it gave an acid product (m.p. 214° dec.) which did not depress the melting point of 2-sulfanilamido-5-thiazolecarboxylic acid.⁸

Anal. Calcd. for C₁₀H₁₀N₄O₃S₂: C, 40.26; H, 3.38; N, 18.78. Found: C, 40.31; H, 3.47; N, 18.59.

2-Amino-5-thiazolecarbonitrile.—This compound was obtained from the amide as a by-product from the above reaction; yield 24%. It was soluble in dilute hydrochloric acid and insoluble in cold sodium hydroxide solution. When a portion was refluxed for four minutes in 2 *N* sodium hydroxide solution, ammonia was given off. Upon cooling and acidifying this solution, an acid precipitate was obtained. It melted with decomposition at 213–214° after being crystallized from water. A mixed melting point of the sample with 2-amino-5-thiazolecarboxylic acid,⁹ prepared from its ester, was not depressed. The nitrile was acetylated with acetic anhydride to form a product which melted at 295–296°, corresponding to that of 2-acetamido-5-thiazolecarbonitrile, reported by Backer and Buisman.⁹ The 2-amino-5-thiazolecarbonitrile melted at 208–210° after crystallization from aqueous ethanol.

Anal. Calcd. for C₄H₅N₃S: C, 38.39; H, 2.42; N, 33.58. Found: C, 38.42; H, 2.40; N, 33.89.

***p*-(1,3,4-Thiadiazol-2-ylsulfamyl)-succinilic Acid.**⁷—2-Amino-1,3,4-thiadiazole hydrochloride¹⁰ was heated with *p*-acetamidobenzenesulfonyl chloride in pyridine for one hour at 90° to give a 58% yield of the corresponding sulfonamide. This was deacetylated by refluxing in 10% hydrochloric acid for four minutes to give 2-sulfanilamido-1,3,4-thiadiazole¹¹ (55–75% yield). The succinyl derivative was prepared by refluxing for one hour a solution of 12.55 g. of 2-sulfanilamido-1,3,4-thiadiazole and 5.64 g. of succinic anhydride in 110 ml. of absolute ethanol. While hot, the solution was stirred with decolorizing carbon and filtered. The filtrate was concentrated under reduced pressure, diluted with water, and the product separated by filtration. It was dissolved in cold sodium bicarbonate solution, filtered, and reprecipitated by the addition of acid. After crystallization from aqueous ethanol solution and drying at room temperature, the product melted partially at 135–140° as if hydrated. When dried at 110°, it melted at 221–223° (dec.); yield 10.3 g.

Anal. Calcd. for C₁₂H₁₂N₄O₅S₂: C, 40.44; H, 3.39; N, 15.72. Found: C, 39.68; H, 3.40; N, 15.67.

***N*-(*p*-2-Thiazolylsulfamylphenyl)-succinamide.**⁷—A mixture of anhydrous *p*-(2-thiazolylsulfamyl)-succinilic acid¹² (64.4 g.) and 180 ml. of thionyl chloride was kept at 30° for 25 minutes until gas evolution ceased, then was diluted with ligroin, filtered, and the solid washed with ligroin. It was added to 60 ml. of concd. ammonium hydroxide solution and kept at 0° for 20 minutes. Excess ammonia was removed *in vacuo* and the cold solution was neutralized with 20% hydrochloric acid. The precipitate was filtered from the liquid, stirred with activated carbon in ammonium hy-

droxide solution, and precipitated by acidification. When crystallized from 40% ethanol, it melted at 215° (dec.); yield 39.8 g. (58%). The compound is insoluble in sodium bicarbonate solution, but soluble in dilute sodium hydroxide solution from which it precipitated unchanged, when acidified. Alkaline or acid hydrolysis yielded sulfathiazole. The analytical sample, dried over phosphorus pentoxide at room temperature, contained one mole of water.

Anal. Calcd. for C₁₃H₁₄N₄O₄S₂·H₂O: C, 41.92; H, 4.33; N, 15.05. Found: C, 41.83; H, 4.25; N, 15.29.

***p*-(2-Thiazolylsulfamyl)-succinilic acid.**—*p*-(2-Thiazolylsulfamyl)-succinilic acid (1.43 g.) was treated with thionyl chloride as described in the above preparation of the succinamide derivative. The chlorination product (1.32 g.) was added to 6 ml. of aniline at 30°. After warming for 30 minutes at 50°, the mixture was chilled and stirred into dilute hydrochloric acid. The insoluble portion was filtered from solution and decolorized with charcoal in dilute ammonium hydroxide solution. It was insoluble in dilute sodium bicarbonate solution. For analysis it was dried over phosphorus pentoxide at 100° for 2.5 hours *in vacuo*; yield 0.8 g., m.p. 249–250°.

Anal. Calcd. for C₁₉H₁₈N₄O₄S₂: C, 53.13; H, 4.21; N, 13.02. Found: C, 52.93; H, 4.00; N, 13.35.

2(or 4)-Methylenebis-4(or 2)-aminobenzenesulfonamide.—*m*-Methylenediacetanilide¹³ (5.6 g., 0.02 mole) was added in portions to cold chlorosulfonic acid (24 g.). The mixture was warmed slowly to 60° and kept at that temperature for two hours. Then it was poured onto 80 g. of crushed ice. The precipitate was removed by filtration and washed with water. Without further purification, the disulfonyl chloride¹⁴ was added in portions to 35 ml. of cold concd. ammonium hydroxide solution and was kept at 0° for one hour. Excess ammonia was removed under reduced pressure and the solution was acidified with hydrochloric acid. The product was dissolved in dilute sodium hydroxide solution and reprecipitated by acidification, after filtration. The methylenebisacetamidobenzenesulfonamide weighed 2.64 g. (30%), m.p. 265–268° (dec.). It was deacetylated by refluxing a 4.51-g. (0.0102 mole) portion with 61 ml. of 10% hydrochloric acid for 25 minutes. After stirring with decolorizing carbon, the solution was filtered and neutralized with dilute sodium hydroxide solution. The product was dissolved in alkali, filtered and reprecipitated. When crystallized from dilute ethanol, it melted at 265° (dec.) and weighed 1.55 g. (46.5%).

Anal. Calcd. for C₁₈H₁₆N₄O₄S₂: C, 43.81; H, 4.53; N, 15.72. Found: C, 43.53; H, 4.68; N, 15.53.

Decomposition Product from *N*-2-Pyrimidyl-*p*-nitrobenzenesulfonamide.—*N*-2-Pyrimidyl-*p*-nitrobenzenesulfonamide¹⁵ was obtained from *p*-nitrobenzenesulfonyl chloride and 2-aminopyrimidine in anhydrous pyridine in good yield (80%). It melted at 278–280°¹⁶ when heated from 270°, reported 273°.¹⁷ When it stood in sodium hydroxide solution at 25° or was heated in the alkaline solution, a yellow precipitate formed. The filtrate from this produced sulfur dioxide when acidified with dilute sulfuric acid. The precipitate, washed with water and crystallized twice from ethanol-acetic acid solution melted at 273–274°. A sodium fusion of the compound was negative for sulfur. It is soluble in concd. hydrochloric acid and insoluble in dilute alkaline solution. The elemental analyses indicated that there was a loss of the sulfone group from the molecule.¹⁸

Anal. Calcd. for C₁₀H₈N₂O₂: C, 55.55; H, 3.73; N, 25.92. Found: C, 55.75; H, 3.84; N, 26.00.

4-*n*-Hexyl-1,3-phenylenebis-(oxyacetic Acid).—A solution of 19.4 g. (0.1 mole) of 4-*n*-hexylresorcinol in 125 ml.

(13) L. Thorp and E. A. Wildman, *ibid.*, **37**, 372 (1915).

(14) It is likely that the chlorosulfonation occurred in the positions para to the acetamido groups.

(15) P. S. Winnek and R. O. Roblin, Jr., U. S. Patent 2,430,439.

(16) *Anal.* Calcd. for C₁₀H₈N₂O₂: C, 42.85; H, 2.88. Found: C, 42.58; H, 2.78.

(17) R. G. Shepherd and C. E. Fellows, *THIS JOURNAL*, **70**, 157 (1948).

(18) For stability studies of other sulfones and sulfonamides under alkaline conditions see (a) H. J. Backer and S. K. Wadman, *Rec. trav. chim.*, **68**, 595 (1949); (b) T. B. Johnson and I. B. Douglass, *THIS JOURNAL*, **63**, 1571 (1941); (c) F. G. Bordwell and G. D. Cooper, *ibid.*, **73**, 5187 (1951).

(8) H. J. Backer and J. de Jonge, *Rec. trav. chim.*, **61**, 463 (1942).

(9) H. J. Backer and J. A. K. Buisman, *ibid.*, **63**, 226 (1944).

(10) M. Freund and C. Meinecke, *Ber.*, **29**, 2514 (1896).

(11) R. O. Roblin, Jr., J. W. Williams and P. S. Winnek, *THIS JOURNAL*, **63**, 2062 (1940).

(12) M. L. Morse and E. S. Miller, *ibid.*, **64**, 1572 (1942).

of water containing 20 g. of sodium hydroxide was refluxed with 24.2 g. (0.256 mole) of chloroacetic acid for three hours. The solution was acidified with hydrochloric acid, and the precipitate was stirred with sodium bicarbonate solution. The insoluble sodium salt of the monoacetic acid derivative was filtered from the solution. Acidification of the filtrate and the subsequent crystallization of the precipitate from dilute ethanol yielded 12.3 g. (33%) of the bis-(oxyacetic acid) monohydrate, m.p. 143–144°.

Anal. Calcd. for $C_{16}H_{22}O_6 \cdot H_2O$: C, 58.52; H, 7.37. Found: C, 58.35; H, 7.60.

3-Hydroxy-4(or 6)-*n*-hexylphenoxyacetic Acid.—This compound occurred as a by-product in the synthesis of the above bis-(oxyacetic acid). With equal moles of chloroacetic acid and hexylresorcinol in alkaline solution, poor yields of the monoacetic acid derivative were obtained. Accordingly, the following method was developed.¹⁹ Sodium granules (11.5 g.) in 500 ml. of xylene, 5 g. of activated charcoal and 105 g. of 4-*n*-hexylresorcinol were mixed, allowed to stand at room temperature for two hours, and finally refluxed for one hour. Then 62.5 g. of ethyl chloroacetate was added and the mixture refluxed for one hour. Sodium hydroxide solution (500 ml. of 2.5 *N*) was added and the xylene was removed by distillation, the volume of the aqueous layer being kept constant by the addition of water. The solution was diluted with water, filtered, and poured into cold hydrochloric acid. The precipitate was stirred with sodium bicarbonate solution and the insoluble sodium salt was filtered off. After the solution was acidified to precipitate the free acid, the sodium bicarbonate treatment and acidification was repeated again. The product was crys-

5-Nitroisatin Thiosemicarbazone.—Nine grams (0.047 mole) of 5-nitroisatin³ dissolved in 200 ml. of absolute ethanol was added to a warm solution of 4.3 g. (0.047 mole) of thiosemicarbazide in 125 ml. of water and 10 ml. of glacial acetic acid and the mixture refluxed for one hour. The aqueous ethanol solution upon cooling gave 11.5 g. (92%) of yellow crystals which did not melt below 350° despite considerable darkening at approximately 300°. An analytical sample was obtained by recrystallization from a water-pyridine solvent pair.

Anal. Calcd. for $C_9H_7N_5O_3S$: N, 26.32. Found: N, 26.15.

(3) 5-Nitroisatin, m.p. 253–255°, was prepared by the method of Baeyer, *ibid.*, **12**, 1312 (1879).

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2-Alkyl-naphthalimides

2-Alkyl-(or *N*-alkyl)-naphthalimides have been prepared by refluxing naphthalic anhydride in an excess of the amine for one hour; with dodecylamine the temperature employed was 110–120°. A stirred suspension of 5 g. of the anhydride in 35 ml. of the amine became clear on 10 minutes heating. After an hour, the excess solvent was removed by distillation *in vacuo* and the solid residue recrystallized. The five new imides are listed in Table I.

TABLE I
PROPERTIES OF 2-ALKYLNAPHTHALIMIDES

Substituent	M.p., °C.	Yield, %	Solvent	Analyses, %					
				Calcd.			Found		
				C	H	N	C	H	N
<i>n</i> -Amyl	84–85	78	90–120° ligroin and ethanol	76.3	6.4	5.2	76.1	6.5	4.9
<i>n</i> -Hexyl	74–75	74	90–120° ligroin	76.9	6.8	5.0	76.9	6.8	5.0
γ -Methoxypropyl	95–96	85	90–120° ligroin and ethanol	71.3	5.5	5.2	71.5	5.5	5.3
Cyclohexyl	224–225	85	Ethanol	77.5	6.1	5.0	78.0	6.1	5.2
<i>n</i> -Dodecyl	57–58	68	Methanol	78.9	8.5	3.8	79.2	8.3	4.1

tallized from benzene. Concentration of the benzene mother liquor yielded additional product, which received the treatment just described; yield 49.0 g. (36%), m.p. 178–180°. It gave a positive test for a phenol with 2% phosphomolybdic acid and ammonium hydroxide.²⁰

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.40; H, 7.89.

(19) By Donald L. Wright of Pitman-Moore Company.

(20) G. H. Stillson, D. W. Sawyer and C. K. Hunt, *THIS JOURNAL*, **67**, 306 (1945).

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Thiosemicarbazones of 5-Substituted Isatins¹

5-Bromoisatin Thiosemicarbazone.—Addition of 10.5 g. (0.0465 mole) of 5-bromoisatin² dissolved in 150 ml. of glacial acetic acid to a warm solution of 4.25 g. (0.0465 mole) of thiosemicarbazide in 175 ml. of water and 10 ml. of glacial acetic acid gave an immediate precipitate. The mixture was heated under reflux for 30 minutes, cooled, and the yellow crystals recrystallized from ethyl acetate to give 10.0 g. (75%) of 5-bromoisatin thiosemicarbazone which decomposes at 273–275° (considerable darkening before decomposition).

Anal. Calcd. for $C_9H_7N_4OSBr$: N, 18.72. Found: N, 18.43.

(1) Contribution No. 554 from the Chemistry Laboratory of Indiana University. This work was supported by a contract between the Office of Naval Research, Department of the Navy, and Indiana University.

(2) 5-Bromoisatin, m.p. 255–256°, was prepared by the method of Borsche and Jacobs, *Ber.*, **47**, 360 (1914).

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Some Derivatives of 2-Carbomethoxycyclohexanone¹

2-Carbomethoxymethyl-2-carbomethoxycyclohexanone and 2- β -carbomethoxyethyl-2-carbomethoxycyclohexanone were prepared by the action of methyl bromoacetate and methyl β -bromopropionate, respectively, on the sodio derivative of 2-carbomethoxycyclohexanone² according to procedures analogous to those used previously for the preparation of the corresponding diethyl esters.³ The keto-diester, b.p. 126–130° at 12 mm. and 150–155° at 15 mm., gave negative ferric and permanganate tests and were characterized as their semicarbazones, m.p. 222–225° and 162–165°, respectively.

Anal. Calcd. for $C_{12}H_{19}N_3O_5$: C, 50.5; H, 6.7; N, 14.7. Found: C, 50.6, 50.5; H, 7.1, 7.1; N, 15.1, 14.7.

Anal. Calcd. for $C_{13}H_{21}N_3O_5$: C, 52.2; H, 7.1; N, 14.0. Found: C, 52.4, 52.0; H, 7.4, 7.0; N, 14.3, 14.0.

2-Cyanomethyl-2-carbomethoxycyclohexanone.—The sodio derivative of 2-carbomethoxycyclohexanone was prepared by stirring and refluxing (three hours) a solution of 7.88 g. of the keto ester in 75 ml. of dry benzene, with 1.15 g. of sodium. A solution of 9.15 g. of chloroacetonitrile

(1) This work was supported in part by a Research Corporation Grant-in-aid.

(2) W. E. Bachmann and A. S. Dreiding, *J. Org. Chem.*, **13**, 317 (1948); pyrazolone derivative, m.p. 180.5–182.5° [reported: 177° (R. Levine and C. R. Hauser, *THIS JOURNAL*, **66**, 1768 (1944)), 180° (H. Ruhkopf, *Ber.*, **70**, 941 (1937))].

(3) E. H. Charlesworth, J. A. McRae and H. M. MacFarlane, *Can. J. Research*, **21B**, 37 (1943); H. T. Openshaw and R. Robinson, *J. Chem. Soc.*, 941 (1937).