Reaction of 5-Phenyl-4-keto-2-thiazolidinethione (III) with Ammonia.—A mixture of 2.5 g. of 5-phenyl-4-keto-2-thiazolidinethione (III), 40 ml. of absolute ethanol and 3 ml. of ammonia was sealed in a glass bomb tube and heated at 100° for 12 hours. After cooling, the bomb contents were filtered and the resulting solid recrystallized from aqueous dimethylformamide. The yield of α-mercapto-α-phenylacetamide was 0.88 g. (37%), m.p. 246.5–247° dec.

Anal. Calcd. for C_8H_9NOS: C, 57.5; H, 5.4; N, 8.4. Found: C, 57.9; H, 5.2; N, 8.7.

2-Anilino-5-phenyl-4(5)-thiazolone (IV). (a).—A mixture of 1.2 g. of 5-phenyl-4-keto-2-thiazolidinethione (III), 4 ml. of aniline and 25 ml. of glacial acetic acid was heated under reflux for 12 hours. Cooling and adding a few pieces of ice caused separation of a solid mass which was filtered and added to 100 ml. of boiling water. Decantation of the hot water removed the large amount of acetanilide formed during the reaction. The residual oil was dissolved in 5 ml. of ethanol, from which 0.8 g. (48%) of colorless crystals separated, m.p. 191–191.5°.

(b).—A mixture of 1.5 g. (0.078 mole) of 2-amino-5-phenyl-4(5)-thiazolone (VI),[10b] 0.73 g. (0.078 mole) of aniline and 15 ml. of glacial acetic acid was heated under reflux for two hours. Addition of hot water and cooling caused the separation of 1.4 g. (72%) of white crystals which were recrystallized from ethanol, m.p. 191–191.5°.

Anal. Calcd. for $C_{15}H_{12}N_2OS$: C, 67.1; H, 4.5; N, 10.4. Found: C, 67.4; H, 4.6; N, 10.6.

No depression of melting point was observed upon admixture of the products obtained from (a) and (b) above.

2-Benzylamino-5-phenyl-4(5)-thiazolone (V). (a).—A mixture of 0.5 g. of 5-phenyl-4-keto-2-thiazolidinethione (III), 0.4 ml. of benzylamine and 25 ml. of glacial acetic acid was heated under reflux for 16 hours, 6 ml. of benzylamine added, and the resulting solution allowed to reflux for an additional four hours. Dilution of the reaction mixture with hot water caused the separation of 0.57 g. (77%) of solid which was recrystallized from ethanol, m.p. 185–185.5°.

(b).—A mixture of 1.6 g. of 2-amino-5-phenyl-4(5)-thiazolone (VI),[10b] 2 ml. of benzylamine and 15 ml. of glacial acetic acid was heated under reflux for two hours. Hydrogen sulfide was evolved during the reaction. Addition of hot water to the reaction mixture and cooling caused the crystallization of 0.78 g. (36%) of white crystals which were recrystallized from ethanol, m.p. 185–185.5°.

Anal. Calcd. for $C_{16}H_{14}N_2OS$: C, 68.1; H, 5.0; N, 9.9. Found: C, 68.4; H, 5.0; N, 10.1.

No depression in melting point was observed upon admixture of the products formed by methods (a) and (b) above.

Reaction of 3,5-Diphenyl-4-keto-2-thiazolidinethione (IX) with Ammonia.—A mixture of 5.0 g. of 3,5-diphenyl-4-keto-2-thiazolidinethione, 3 ml. of ammonia and 40 ml. of absolute ethanol was heated in a sealed glass bomb tube at 100° for 12 hours. Filtration of the hot bomb contents gave 1.4 g. of unchanged starting material, m.p. 229–230°, while the filtrate on cooling deposited 0.12 g. of monoclinic sulfur, m.p. 116–117°. Evaporation of this filtrate to near dryness under reduced pressure gave a gummy residue which was suspended in hot cyclohexane and filtered to give 1.7 g. of a white solid, m.p. 120–132°. This solid was extracted several times with boiling chloroform, the chloroform extracts concentrated and cyclohexane added to give 0.9 g., of colorless platelets, m.p. 157–158°. The compound was purified by sublimation at 154° (0.5 mm.), m.p. 160–161°. Analysis and a mixed melting point determination showed the compound to be phenylacetamide.

Anal. Calcd. for C_8H_9NO: C, 71.1; H, 6.7; N, 10.4. Found: C, 71.0; H, 6.9; N, 10.4.

The chloroform-insoluble fraction above (0.6 g., m.p. 150–151°) was shown to be ammonium thiocyanate by analysis and a mixed melting point determination.

Anal. Calcd. for NH_4SCN: C, 15.8; H, 5.3; N, 36.8. Found: C, 16.1; H, 5.5; N, 36.9.

Reaction of 3,5-Diphenyl-4-keto-2-thiazolidinethione (IX) with Aniline.—A mixture of 3.0 g. of 3,5-diphenyl-4-keto-2-thiazolidinethione (IX) and 10 ml. of freshly-distilled aniline was heated under reflux for 20 hours. Hydrogen sulfide was evolved slowly during this period. The cooled reaction mixture was diluted with 100 ml. of ether, the resulting solution extracted with dilute hydrochloric acid, and the ethereal layer washed with water, dried and evaporated to give a residual oil which solidified on standing. Recrystallization from dilute ethanol gave 1.3 g. of *sym*-diphenylthiourea, m.p. 150–151°, unchanged upon admixture with an authentic sample. Unchanged starting material and *sym*-diphenylthiourea were obtained when IX and aniline were heated together in ethanol solution.

sym-Diphenylthiourea also was formed when 4-amino-3,5-diphenyl-2(3)-thiazolinethione (VIII) and aniline were heated together for 15 minutes and the reaction mixture worked up as described above.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Preparation and Identity of Phenylmaleic Acid and Phenylfumaric Acid

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Evidence is presented to show that the compound previously reported to be phenylmaleic acid[2] is a half-hydrate of phenylmaleic acid, and that the compound previously reported to be phenylfumaric acid[3] is actually phenylmaleic acid. The properties of authentic phenylfumaric acid are described for the first time. A convenient preparation for both phenylmaleic acid and phenylfumaric acid is described which involves the reaction of benzenediazonium chloride with dimethyl maleate.

A compound which was formed by the mild aqueous hydrolysis of phenylmaleic anhydride and which melted at 100° was described by Alexander[2] in 1890 as phenylmaleic acid. The compound was characterized by elemental analysis and by the fact that on heating at its melting point it was readily reconverted to the anhydride. In 1915, Almstrom[3] reported a compound, m.p. 128–129°, prepared by the alkaline hydrolysis of phenylmaleic anhydride, which was designated as phenylfumaric acid on the basis of elemental analysis, mode of formation and non-identity with the previously described phenylmaleic acid.

The present paper presents evidence to show that the alleged phenylmaleic acid of Alexander is a half-hydrate of phenylmaleic acid and that the alleged phenylfumaric acid described by Almstrom is actually phenylmaleic acid. In addition, the preparation and properties of authentic phenylfumaric acid are described for the first time.

Phenylmaleic anhydride[4] was hydrolyzed with dilute sodium hydroxide to give a compound, m.p. 129–131°, which was described by Alm-

(1) Parke, Davis and Company Fellow, 1952–1954.

(2) H. Alexander, *Ann.*, **258**, 67 (1890).

(3) G. K. Almstrom, *Ber.*, **48**, 2009 (1915).

(4) L. E. Miller, H. B. Staley and D. J. Mann, THIS JOURNAL, **71**, 374 (1949).

strom[3] as phenylfumaric acid and which has now been found to be reconverted by short heating at a temperature above its melting point to phenylmaleic anhydride. Although it was unaffected by boiling dilute hydrobromic acid, boiling 4 *N* sodium hydroxide or boiling water containing iodine, it was converted in 96% yield by the action of ultraviolet light into an isomeric dibasic acid, m.p. 206.5–207.5°, which was reconverted into phenylmaleic anhydride only under strenuous conditions (heating at 250–270° for 40 minutes, followed by sublimation). It would thus appear that the lower melting isomer was phenylmaleic acid while the higher melting isomer was the hithertofore unknown phenylfumaric acid.

This conclusion is confirmed by an examination of the ultraviolet absorption spectra of the two acids. The spectrum of the acid, m.p. 129–131° ($\lambda_{\max}$ 277 mμ, log ϵ 4.18) is markedly similar to the spectrum of *trans*-cinnamic acid ($\lambda_{\max}$ 273 mμ, log ϵ 4.30). The spectrum of the acid, m.p. 206.5–207.5° (shoulder at 230–250 mμ, log ϵ 3.74–3.72), is intermediate between the composite curve for benzene + fumaric acid (shoulder at 230–250 mμ, log ϵ 3.8–3.2) and *cis*-cinnamic acid ($\lambda_{\max}$ 264 mμ, log ϵ 3.98). The lower and less intense absorption given by the higher melting isomer (phenylfumaric acid) as contrasted with the lower melting isomer (phenylmaleic acid) is in accord with the considerable increase in steric inhibition of coplanarity expected for the *trans* acid, although the increase in both intensity and wave length of maximum absorption over the composite curve of benzene + fumaric acid indicates that complete inhibition has not been achieved.

Mild aqueous hydrolysis of phenylmaleic anhydride gave a compound, m.p. 105–107°, which was converted to phenylmaleic anhydride on melting and whose properties thus correspond to those given for the compound, m.p. 100°, prepared by Alexander[2] in an identical manner and designated by him as phenylmaleic acid. Elemental analysis, contrary to the results reported by Alexander,[2] indicated that the compound was a half-hydrate of phenylmaleic acid. This conclusion is confirmed by an examination of its infrared absorption spectrum, which shows the absence of the anhydride double peak in the 1750–1860 cm.$^{-1}$ region and the presence of two peaks at 3350 and 3590 cm.$^{-1}$, both absent in the spectrum of phenylmaleic acid.

A convenient preparation of both of the isomeric acids was found to be the reaction of benzenediazonium chloride with dimethyl maleate in the presence of cupric chloride, sodium acetate and acetone[5] to give phenylmaleic acid (isolated as the anhydride) in 6% yield and phenylfumaric acid in 12% yield.

Experimental[6]

Phenylmaleic Anhydride and Phenylfumaric Acid by the Meerwein Reaction.—A solution of benzenediazonium chloride was prepared by slowly adding 17.3 g. (0.25 mole) of sodium nitrite dissolved in 40 ml. of water to a stirred, cooled (0–5°) solution containing 23.3 g. (0.25 mole) of freshly-distilled aniline, 52 ml. of concentrated hydrochloric acid and 30 ml. of water. After stirring until a total reaction time of 45 minutes had elapsed, the solution was filtered. This filtered diazonium solution was then added in one portion to a solution containing 24 g. (0.167 mole) of dimethyl maleate, 250 ml. of acetone, 8 g. of cupric chloride dihydrate, 34 g. of sodium acetate trihydrate and 55 ml. of water. The reaction mixture was stirred at 30–35° for 11 hours; the acetone was removed by evaporation under diminished pressure and the residue was extracted with three 200-ml. portions of benzene and two 200-ml. portions of ether. The benzene extracts were washed twice with saturated sodium bicarbonate solution followed by water. The combined benzene–ether extracts were evaporated to dryness under reduced pressure. The residue was dissolved in a solution containing 100 ml. of water, 10 ml. of 95% ethanol and 20 g. of sodium hydroxide and was then heated under reflux for four hours, cooled and extracted with ether. The basic solution was acidified with 50% sulfuric acid to *p*H 1 and extracted with four 250-ml. portions of ether. Evaporation of the ether extracts gave a solid residue which was heated at 120° for 20 minutes and then extracted with 100 ml. of methylene chloride. Evaporation of the methylene chloride gave 14 g. of a black solid which was sublimed at 100° (0.05 mm.) to give in addition to about 2 ml. of a light colored liquid of unknown composition, a colorless crystalline solid. Recrystallization of the solid from acetone–petroleum ether gave 1.8 g. (6%) of pure phenylmaleic anhydride, m.p. 119°. No depression in melting point was obtained upon admixture with an authentic sample of phenylmaleic anhydride.[4]

The methylene chloride insoluble residue above (7.0 g.) was recrystallized from water containing decolorizing charcoal to give 3.8 g. (12%) of phenylfumaric acid, m.p. 206.5–207.5°.

Anal. Calcd. for $C_{10}H_8O_4$: C, 62.5; H, 4.2. Found: C, 62.6; H, 4.4.

Phenylmaleic Acid.—Three grams of phenylmaleic anhydride was dissolved in 100 ml. of 0.4 *N* sodium hydroxide by heating at 75–80° for 20 minutes. The solution was filtered, acidified to *p*H 1 with 50% sulfuric acid and extracted with four 50-ml. portions of ether. Evaporation of the ether and crystallization of the residue from benzene gave pure phenylmaleic acid, m.p. 129–131°. Short heating at a temperature above its melting point converted phenylmaleic acid quantitatively to the anhydride, m.p. 119°.

Isomerization of Phenylmaleic Acid to Phenylfumaric Acid.—A solution of three grams of phenylmaleic anhydride was dissolved in 900 ml. of boiling water and was irradiated with high-intensity ultraviolet light (hydrogen arc) for 20 hours at 65°. After cooling, the solution was extracted with three 250-ml. portions of ether. Evaporation of the ether solution and recrystallization of the residue from water gave 3.1 g. (96%) of phenylfumaric acid, m.p. 206.5–207.5°.

Conversion of Phenylfumaric Acid to Phenylmaleic Anhydride.—Pure phenylfumaric acid was heated at 250–270° for 40 minutes and then sublimed twice at 250° (1 mm.). Crystallization of the sublimate from methylene chloride–petroleum ether gave phenylmaleic anhydride, m.p. 117–119°. No depression in melting point was observed upon admixture with an authentic sample of phenylmaleic anhydride and the infrared spectra were identical.

Phenylmaleic Acid Half-hydrate (Alexander's Phenylmaleic Acid[2]).—One gram of phenylmaleic anhydride was allowed to dissolve in 100 ml. of water at room temperature over a period of seven days. Extraction of the solution with ether followed by evaporation of the ether gave pale yellow crystals, m.p. 105–107° (with effervescence).

Anal. Calcd. for $C_{10}H_8O_4 \cdot {}^1/_2H_2O$: C, 59.7; H, 4.5. Found: C, 60.0; H, 4.7.

When the solid was melted and then held at 110–114°, bubbling occurred during the first 15 minutes followed by crystallization from the melt of colorless crystals, m.p. 119°, identical with authentic phenylmaleic anhydride.

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[5] H. Meerwein, E. Buchner and K. Van Emster, *J. prakt. Chem.*, **152**, 237 (1939).

[6] All melting points are corrected. The microanalyses were performed by Mrs. Esther Fett, Mrs. Lucy Chang and Mr. Joseph Nemeth. The infrared spectra (Nujol mull) were determined by Miss Helen Miklas and the ultraviolet spectra (measured in aqueous solution) by Mrs. Barbara B. Burnett.