(0.018 mole) of α-phenylsulfonylphenylacetic acid (obtained from the metalation of phenyl benzyl sulfone) in 100 ml. of ether was treated with an excess of an ethereal solution of diazomethane at ice-bath temperature. After the addition of the ethereal solution of diazomethane, the reaction mixture was allowed to stand at room temperature for 1 hr. After the ether and excess diazomethane had been removed by evaporation, the residue was extracted with dilute aqueous sodium carbonate and recrystallized from aqueous methanol. The recrystallized material weighed 4.7 g. (90%) and melted at 109–110°.

Anal. Calcd. for $C_{15}H_{14}O_4S$: C, 62.07; H, 4.83. Found: C, 61.88; H, 5.10.

Metalation of phenyl benzyl sulfide. Ten grams (0.05 mole) of phenyl benzyl sulfide was dissolved in 150 ml. of dry ether and filtered into the reaction flask which had been previously flushed with nitrogen. To this solution was added slowly with stirring an equimolar amount of *n*-butyllithium in ether. The addition caused an immediate color change and reflux of the ether. After the reflux had somewhat subsided, the reaction mixture was heated at reflux temperature for 5 hr. The reaction mixture was then carbonated by pouring over a slurry of ether and crushed solid carbon dioxide. After the removal of the carbon dioxide, water was added and the aqueous layer was separated, filtered, and acidified with dilute hydrochloric acid. This gave 9.2 g. of solid material melting at 100–102°. After treatment of this solid with dilute aqueous sodium carbonate, filtration, and acidification of the aqueous filtrate, there was obtained 8.8 g. (75%) of solid melting at 102–103°, neutralization equivalent 249. The melting point of this compound corresponds to that reported by Fuchs and Breuer[6] for α-phenylmercaptophenylacetic acid, prepared from α-chlorophenylacetic acid and sodium thiophenolate. The ether layer was dried over anhydrous calcium chloride, filtered, and the ether removed. A yellow oil remained, which on cooling solidified. After recrystallization from methanol, the crystalline solid weighed 1.3 g. (13%) and melted at 41–42°. A mixed melting point with a sample of phenyl benzyl sulfide, melting point 42–43°, was 41–42°.

To 1.6 g. (0.007 mole) of α-phenylmercaptophenylacetic acid in 50 ml. of dry ether was added an excess of an ethereal solution of diazomethane. After the ether and excess diazomethane had been removed, the residue was taken up in 60 ml. of glacial acetic acid and treated with 10 ml. of 35% hydrogen peroxide. The reaction mixture was heated on the steam bath for 1 hr. After the addition of a further 10 ml. of hydrogen peroxide, the reaction mixture was heated to reflux for 0.5 hr. and was then poured into an excess of cold water. The precipitated solid was collected by filtration and recrystallized from aqueous methanol. The recrystallized material weighed 1.3 g. (67%) and melted at 109–110°. A mixture melting point with the methyl ester prepared from α-phenylsulfonylphenylacetic acid, m.p. 109–110°, was 109–110°.

α-Phenylmercaptophenylacetamide. One gram (0.004 mole) of α-phenylmercaptophenylacetic acid was heated on the steam bath with 5 ml. of thionyl chloride for 20 min. The reaction mixture was then poured into 20 ml. of ice-cold concentrated ammonia. The precipitated solid was collected by filtration and recrystallized from dilute aqueous ethanol. This gave 0.8 g. (82%) of crystalline solid melting at 174–175°.

Anal. Calcd. for $C_{14}H_{13}NOS$: N, 5.76. Found: N, 5.87.

α-Phenylsulfonylphenylacetamide. A solution composed of 0.3 g. (0.001 mole) of α-phenylmercaptophenylacetamide, 50 ml. of acetone and 10 ml. of 35% hydrogen peroxide was heated to reflux on the steam bath for 1 hr., after which an additional 10 ml. of 35% hydrogen peroxide was added and the solution was again heated at reflux temperature for 3 hr. The reaction mixture was then poured over an excess of ice and the acetone was removed by evaporation on the steam bath. The colorless solid which precipitated was collected by filtration. It weighed 0.2 g. (65%) and melted at 195–197°. Recrystallization from dilute aqueous ethanol brought the melting point up to 203–204°.

Anal. Calcd. for $C_{14}H_{13}NO_2S$: N, 5.41. Found: N, 5.56.

Hydrazide of α-phenylmercaptophenylacetic acid. An ethereal solution of 3 g. (0.012 mole) of α-phenylmercaptophenylacetic acid was converted to the methyl ester with diazomethane. The crude ester was converted to the hydrazide, m.p. 85–86°. The yield was 1.1 g. and crystallization was from water.

Anal. Calcd. for $C_{14}H_{14}N_2OS$: N, 10.85. Found: N, 10.88.

Hydrazide of α-phenylsulfonylphenylacetic acid. A mixture of 0.6 g. (0.002 mole) of methyl α-phenylsulfonylphenylacetate, 100 ml. of absolute ethanol, and 5 ml. of 85% hydrazine hydrate was allowed to stand at room temperature in a stoppered flask for one week. The ethanol was removed by evaporation on the steam bath and the residue was recrystallized from aqueous ethanol. The yield of solid material melting at 182–183° was 0.5 g. (83%).

Anal. Calcd. for $C_{14}H_{14}N_2O_3S$: N, 9.66. Found: N, 9.48.

α-Phenylsulfonylphenylacetamide. One gram (0.0036 mole) of the acid was converted to the amide, m.p. 278°, with thionyl chloride and ammonia. The yield was 40% and crystallization was from aqueous ethanol.

Anal. Calcd. for $C_{14}H_{13}NO_3S$: N, 5.09. Found: N, 5.19.

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Alkaline Condensation of Phenanthraquinone with Urea

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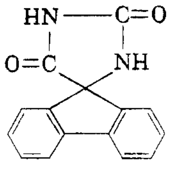
In a previous publication[2] the results of a study of the alkaline condensation of benzil with urea was reported. The products of this reaction were 3a,6a-diphenyl glycoluril, and the rearrangement product 5,5-diphenylhydantoin. The results from a series of 4,4′-disubstituted benzils used in this reaction gave relative migratory aptitudes of *p*-substituted phenyl groups which indicated that the rearrangement involved in the hydantoin formation is closely allied with the benzilic acid rearrangement.

Since phenanthraquinone undergoes the benzilic acid rearrangement,[3] it was supposed that the



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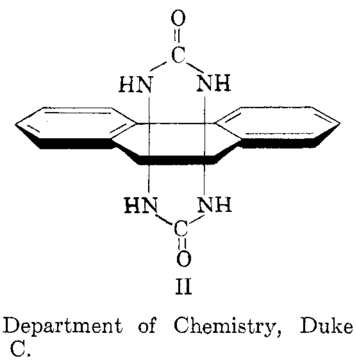

II

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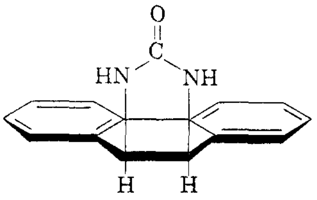
[1] Present address Department of Chemistry, Duke University, Durham, N. C.

[2] W. R. Dunnavant and F. L. James, *J. Am. Chem. Soc.*, **78,** 2740 (1956).

[3] A. von Baeyer and P. Friedländer, *Ber.*, **10,** 126 (1877).

analogous condensation products spiro(fluorene-9,4′-imidazolidine-)2′,5′-dione (I) and 3a,6a-(2,2′-diphenylene) glycoluril (II) might be obtained in the same manner.

It was found, however, that when phenanthraquinone was refluxed for 5 hr. with urea in ethanolic potassium hydroxide, followed by the addition of water, 4,5-diphenylene-4,5-dihydro-2-imidazolone (III) was obtained in 69% yield, but no II.



III

Acidification of the filtrate after the removal of III gave a brown resinous material from which a small amount of I was isolated, which was identified by its melting point, mixed melting point, and infrared spectrum as being identical with an authentic sample of the spiro hydantoin.[4]

The infrared spectrum[5] of I shows a broad band in the NH region at 3200 cm.$^{-1}$ The carbonyl absorptions are characteristic of compounds containing the CONHCO group. These appear as two widely separated bands at 1780 and 1710 cm.$^{-1}$ Compound III shows NH absorption in the 3100 cm.$^{-1}$ region and bands at 1650, 1695, and 1715 cm.$^{-1}$ The 1650 cm.$^{-1}$ band appears in disubstituted ureas and can be assigned to CO absorption.[6] Information is not available to allow full interpretation of the NH absorption in compounds containing the NHCONH group.[6]

In observing the deviation from the expected course of this reaction it is of interest to note that, unlike the benzils with carbonyls in skew positions (not coplanar) previously used in this reaction, the carbonyls of phenanthraquinone must necessarily have *cis*-coplanarity.

EXPERIMENTAL[7]

4,5-Diphenylene-4,5-dihydro-2-imidazolone. A mixture of 6 g. of phenanthraquinone, 4.86 g. of urea, and 3.02 g. of potassium hydroxide in 100 ml. of 95% ethanol was refluxed for 5 hr. The deep brown solution was allowed to cool and was then poured into 300 ml. of ice water. A tan amorphous precipitate was obtained which, after filtering and drying, weighed 4.7 g. (69%). Four recrystallizations from glacial acetic acid (Norit) yielded tiny white needles of III which failed to melt at 400°.

Anal. Calcd. for $C_{15}H_{12}ON_2$: C, 76.24; H, 5.12; N, 11.85. Found: C, 76.59; H, 5.23; N, 11.73.

Spiro(fluorene-9,4′-imidazolidine)-2′,5′-dione. The filtrate from above was acidified with hydrochloric acid and stirred rapidly for 30 min. A brown resinous material was obtained which, after several recrystallizations from glacial acetic acid (Norit) afforded 50 mg. of hard white crystals of I, melting point 350–354° dec. No mixed melting point depression with an authentic sample[4] was observed. The literature reports 352–356° dec.[8]

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[4] The authentic sample of spiro(fluorene-9,4,-imidazolidine)-2,,5,-dione was obtained through the courtesy of Prof. M. S. Newman of The Ohio State University, Columbus, Ohio.

[5] The infrared spectra were obtained as Nujol mulls on a Perkin-Elmer Model 21 Spectrophotometer.

[6] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 191.

[7] The microanalysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[8] M. S. Newman and W. B. Lutz, *J. Am. Chem. Soc.* **78**, 2471 (1956).

Derivatives of Piperazine. XXIX. Salts of *N*-Phenylpiperazine for Utilization in Identification of Organic Acids

C. B. POLLARD AND NARAIN S. GIDWANI

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In previous papers[1–3] from this laboratory, certain piperazinium salts were reported for utilization in identification of organic acids. The present paper describes the method of preparation and data concerning 23 new salts of *N*-phenylpiperazine which may be employed for the identification of organic acids. Data for these compounds are shown in Table I.

By the methods employed, the following acids failed to give derivatives which are of practical value in qualitative organic analysis: butyric, iodoacetic, α-bromopropionic, α-bromobutyric, succinic, tartaric, and 4-nitrophthalic. These derivatives showed reasonably sharp melting points which did not change on continued crystallization. However, all analytical determinations gave inconsistent results which did not agree with any reasonable structures.

EXPERIMENTAL

Salts of the unsubstituted liquid monobasic acids were prepared by mixing equal molar quantities of *N*-phenylpiperazine and the individual acid.

The dibasic acids react in the ratio of two moles of *N*-phenylpiperazine to one of the acid.

Acetone solutions of the solid acids were mixed with *N*-phenylpiperazine to produce the salts.

All of the salts were purified by recrystallization from hot acetone or by washing with hot acetone. In all cases the salts form almost immediately.

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[1] C. B. Pollard and D. E. Adelson, *J. Am. Chem. Soc.* **56**, 150 (1934).

[2] C. B. Pollard, D. E. Adelson, and J. P. Bain, *J. Am. Chem. Soc.*, **56**, 1759 (1934).

[3] M. Prigot and C. B. Pollard, *J. Am. Chem. Soc.*, **70**, 2758 (1948).