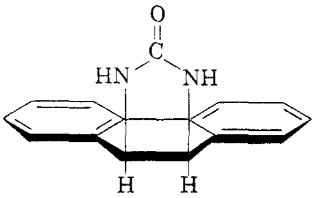
analogous condensation products spiro(fluorene-9,4′-imidazolidine-)2′,5′-dione (I) and 3a,6a-(2,2′-diphenylene) glycoluril (II) might be obtained in the same manner.

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

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Received February 15, 1957

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).

TABLE I

DATA CONCERNING *N*-PHENYLPIPERAZINIUM SALTS DERIVED FROM VARIOUS ORGANIC ACIDS

Acids	Yield (%)	Melting Point (°C. corr.)	Nitrogen, % Calcd.	Nitrogen, % Found	Acids	Yield (%)	Melting Point (°C. corr.)	Nitrogen, % Calcd.	Nitrogen, % Found
p-Anisic	91.0	158.3–159.3	8.91	8.88	Isovaleric	70.0	78.9–80.4	10.59	10.25
Cyclohexanebutyric	92.0	87.7–88.6	8.42	8.29	Caprylic	40.0	58.4–60.6	9.13	8.87
Cyclohexaneacetic	93.0	79.4–80.9	10.85	10.82	Valeric	85.5	50.5–52.5	10.59	10.27
Cyclohexanecaproic	91.0	91.6–93.4	12.85	12.80	Phenoxyacetic	97.7	117.9–119.0	8.92	8.84
Cyclohexanevaleric	90.0	67.8–68.9	8.12	7.95	Propanoic	33.0	58.9–59.8	12.35	12.00
Cyclohexanepropionic	96.0	85.2–87.2	8.80	8.77	Salicylic	96.0	184.8–185.8	9.34	9.36
Acetic	91.0	82.0–83.0	12.61	12.50	Hendecanoic	50.0	50.5–52.5	8.04	8.38
Enanthic	40.0	56.1–57.5	9.56	9.43	Malonic	93.5	111.8–113.8	13.10	13.12
Caproic	35.5	65.2–67.3	10.05	9.85	Oxalic	95.0	226.7–227.2	12.45	12.47
Lauric	89.0	60.6–61.5	7.74	7.74	Isophthalic	97.0	184.4–185.8	11.41	11.26
Levulinic	65.5	82.8–84.2	10.12	10.32	Phthalic	98.0	188.3–189.9	11.41	11.25
Formic	75.5	112.6–113.6	13.71	13.68					

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Substituted α,α,α-Trifluoroacetophenones, α-Trifluoromethylbenzyl Alcohols, and α-Chloro-α-trifluoromethyltoluenes

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Received February 25, 1957

As part of a study of substituent effects in nucleophilic displacement reactions at electron-deficient, saturated carbon atoms, a series of five *meta* and *para* substituted α-chloro-α-trifluorotoluenes have been prepared. Three new substituted α,α,α-trifluoroacetophenones were obtained by the reaction of arylmagnesium bromides with trifluoroacetic acid.[1] The ketones were reduced by hydrogen or sodium borohydride to α-trifluoromethylbenzyl alcohols, which were converted to the corresponding chlorides by reaction with thionyl chloride. Preliminary studies indicate a very low reactivity of the chlorides toward the strong nucleophilic reagents iodide, thiosulfate, phenoxide, and butoxide ions, and towards alcoholic silver nitrate. In all cases *p*-methoxy-α-chloro-α-trifluoromethyltoluene was more reactive than the *p*-chloro, *m*-trifluoromethyl, or unsubstituted analogs.

TABLE I

α,α,α-TRIFLUOROACETOPHENONES, $YC_6H_4COCF_3$

Y	B.p., °C/Mm.	Yield, %	n_D^{30}	Formula	Calcd. C	Calcd. H	Found C	Found H
H[a]	66–67/33	67	1.4528					
p-CH_3[b]	81–82.5/22	66	1.4645					
p-CH_3O	70–70.5/2	56	1.4944	$C_9H_7O_2F_3$	52.9	3.5	53.2	3.6
p-Cl[c]	84/24	56	1.4852	$C_8H_4OClF_3$	46.1	1.9	48.9	2.3
m-CF_3	65–67.5/24	68	1.4100	$C_9H_4OF_6$	44.6	1.7	44.5	1.7
			α-Trifluoromethylbenzyl Alcohols, $YC_6H_4CHOHCF_3$					
H[d]	53–54.5/2	87	1.4550					
p-CH_3	74.5–75/2.5	72	1.4626[e]	$C_9H_9OF_3$	56.8	4.8	57.3	5.0
p-CH_3O	87–88/1	91	1.4743	$C_9H_9O_2F_3$	52.4	4.4	52.6	4.5
p-Cl	71–73/1.9	82	1.4785	$C_8H_6OClF_3$	45.6	2.9	45.7	3.1
m-CF_3	95–97/24	80	1.4133	$C_9H_6OF_6$	44.3	2.5	44.9	3.1
			α-Chloro-α-trifluoromethyltoluenes, $YC_6H_4CHClCF_3$					
H	70–71/27	73	1.4540	$C_8H_6F_3Cl$	49.4	3.1	49.2	3.3
p-CH_3	89–90/27	66	1.4590	$C_9H_8F_3Cl$	51.8	3.9	52.0	4.2
p-CH_3O	57.5–59.5/1	73	1.4746	$C_9H_8OClF_3$	48.1	3.6	47.9	3.9
p-Cl	95–95.5/24	67	1.4778	$C_8H_5Cl_2F_3$	41.9	2.2	41.6	2.4
m-CF_3	75.5–76.5/25	54	1.4128	$C_9H_5ClF_6$	41.1	1.9	40.9	2.2

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