N-Phenyl-N-benzylbenzamide.—A solution of 5.83 g. (0.032 mole) of N-benzylideneaniline and 7.85 g. (0.064 mole) of benzoic acid in 40 ml. of xylene was placed in a 100-ml. three-necked flask equipped with a magnetic stirrer, reflux condenser, dropping funnel, and thermometer. To this mixture was added a solution of 3.20 g. (0.043 mole) of trimethylamine borane in 20 ml. of xylene. The reaction mixture was heated under reflux (140°) for 12 hr. The color of the solution was a dark yellow-brown. The reaction mixture was allowed to cool and then poured into a separatory funnel. This solution was washed twice with 50-ml. portions of a 10% sodium carbonate solution and once with 50 ml. of a 10% sodium hydroxide solution. The xylene solution was then washed with two 50-ml. portions of 15% hydrochloric acid and dried for several hours over anhydrous magnesium sulfate. The drying agent was removed by filtration and the xylene taken off under diminished pressure. The oil which remained solidified upon standing. This crude product melted at 90–97°. Upon recrystallization twice from ethanol the product melted at 106.0–106.5°. The infrared spectrum and melting point of this product were identical with those for an authentic specimen of N-phenyl-N-benzylbenzamide. The yield was 2.40 g. or 26.2% of the theoretical amount.

A second crop of crystals was obtained from the filtrates of the recrystallizations. This product melted at 60–64° and after recrystallization twice from ethanol melted at 66.5–67.0°.

Anal. Calcd.: C, 87.91; H, 6.96. Found: C, 87.98; H, 7.05.

The melting point, (lit., m.p. 67°[6]) infrared spectrum, and elemental analysis all indicated that this material was the tertiary amine, N,N-dibenzylaniline. The preparation of the picrate derivative, which melted at 133.5–134.0° dec. as compared to 131–132° dec. reported in literature,[6] confirmed this fact.

N-*p*-Nitrophenyl-N-*p*-nitrobenzylacetamide.—The typical procedure was employed for the preparation of this compound except that the reaction was allowed to reflux for 18 hr. A yield of 4.16 g. of a yellow solid formed upon cooling the reaction mixture. This product was recrystallized from absolute ethanol and three different fractions obtained.

The first fraction was shown to be the secondary amine, N-*p*-nitrobenzyl-*p*-nitroaniline, by means of the infrared spectrum and mixed melting point (188–189°).

The second fraction was a mixture of the secondary amine and the acetamide, which was separated by means of extracting out the acetamide with a benzene–cyclohexane solvent mixture.

The third fraction was also a mixture and was separated by means of chromatography over Merck acid-washed alumina. Using petroleum ether (b.p. 30–60°), a mixture of equal parts of petroleum ether and benzene, and benzene successively as eluents, two principal compounds were obtained. The first compound was shown to be the tertiary amine, N-*p*-nitrobenzyl-N-ethyl-*p*-nitroaniline, by means of its infrared spectrum and the elemental analyses.

Anal. Calcd.: C, 59.70; H, 4.99; N, 13.95. Found: C, 59.60; H, 5.04; N, 14.25.

The yield of this amine was 2.76 % of the theoretical amount of yellow crystals melting at 133.5–134.0°. The second product isolated from this fraction was more of the secondary amine.

N^1-Acetyl-N^4-acetyl-N^4-benzylsulfanilamide.—The typical procedure was used in the preparation of this compound. However, the product obtained from the reaction mixture yielded two fractions upon recrystallization from ethanol.

The first fraction consisted of two compounds which were separated by means of a fractional crystallization. The first compound, melting at 191–192°, was shown to be the monoacetylated derivative, N-^{4}acetyl-N^4-benzylsulfanilamide, from its infrared spectrum (single carbonyl peak at 6.16 μ) and elemental analyses (Calcd.: N, 9.21. Found: N, 9.17). The other compound was thought to be the tertiary amino derivative. This material melted at 187–188° and its infrared spectrum (single carbonyl peak at 5.85 μ) and elemental analyses (Calcd.: N, 8.44; S, 9.65. Found: N, 8.49; S, 9.63) were consistent with the structure for N^1-acetyl-N^4-benzyl-N^4-ethylsulfanilamide.

The second fraction also appeared to be a mixture and was chromatographed over Merck acid-washed alumina using ethyl ether and ethyl acetate for elution. The first compound isolated was identical to the one from the first fraction which was assigned the structure for N^1-acetyl-N^4-benzyl-N^4-ethylsulfanilamide. The second and third compounds obtained were the monoacetylated derivative identical with the one from the first fraction and some of the diacetyl derivative as shown by a mixed melting point and infrared spectrum.[1]

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[6] C. Matzudaira, *Ber.*, **20**, 1611 (1887).

Conversion of 2-Duroylresorcinol into a Fluorenone Derivative[1]

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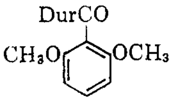
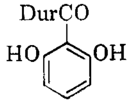
Received November 10, 1961

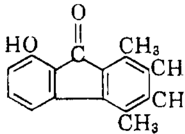
When the dimethyl ether of 2-duroylresorcinol (I) is demethylated with hydrobromic acid or aluminum chloride the phenol II may undergo further reaction. With hydrobromic acid in fact it suffers cleavage to resorcinol and duroic acid. Production of phenol II has been accomplished with aluminum chloride, but long heating with this reagent brings about change to 1,2,3,4-tetramethyl-8-hydroxyfluorenone (III).



I



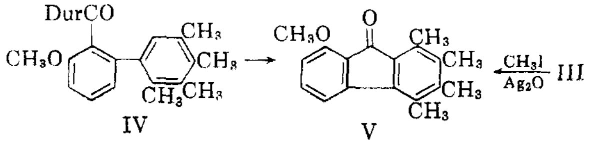
II



III

Isomerization of the duryl radical to the corresponding prehnityl group had been observed earlier[3]; the ring closure thus made possible is remarkable in that it is an arylation of an aromatic ring by a phenol.

The structure of the new fluorenone was established by an independent synthesis of its methyl ether; ether I reacted with prehnitylmagnesium bromide to give 2-duroyl-3-prehnitylanisole (IV).



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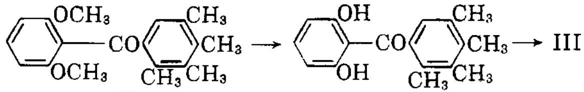
[1] This research was supported in part by a grant from the Office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

[2] Chas. Pfizer Co. Fellow, 1961–1962.

[3] G. Baddely, G. Holt, and S. M. Makar, *J. Chem. Soc.*, 2415 (1952).

This ketone, when heated with polyphosphoric acid, formed the corresponding fluorenone V.

Confirmatory evidence for the postulated sequence of changes was obtained by subjecting the dimethyl ether of 2-prehnitoylresorcinol (VI) to the action of aluminum chloride. Demethylation occurred first to give the phenol VII which could be isolated and underwent ring closure to form the fluorenone III.


VI VII

Experimental[4]

Cleavage of the Dimethyl Ether of 2-Duroylresorcinol.—A solution of 12 g. of ether I,[5] 150 ml. of glacial acetic acid, and 45.6 ml. of 48% hydrobromic acid was heated under reflux, with stirring, for 20 hr. and poured into ice water. Recrystallization of the colorless precipitate from benzene gave 5.6 g. (78.9%) of duroic acid, m.p. 177–178°, which was identified by a mixed melting point and comparison of infrared spectra. From the filtrate was obtained 4.6 g. of crude resorcinol.

2-Duroylresorcinol.—In a procedure similar to that of Mauthner[6] a mixture of 4.6 g. of ether I, 46 ml. of dry chlorobenzene, and 4.6 g. of aluminum chloride was heated under reflux for 0.5 hr. with stirring, cooled to room temperature, and poured into a cold solution of 46 ml. of concd. hydrochloric acid in 460 ml. of water. Chlorobenzene was removed by steam distillation. The red-brown, solid product was recrystallized from 95% ethanol to give 3.22 g. (77.2%) of 2-duroylresorcinol, m p. 157–158°.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.35; H, 6.74.

2-Prehnitoylresorcinol.—A mixture of 2.12 g. of ether VI, 2.2 g. of aluminum chloride, and 15 ml. of chlorobenzene was heated under reflux and with stirring for 0.5 hr. The product was a yellow oil, which eventually solidified; recrystallized from benzene it formed yellow crystals, yield 1.19 g. (59.7%), m.p. 98–99°. The infrared spectrum has a sharp, strong band at 3440 cm.$^{-1}$ (nonchelated hydroxyl group), a broad, weak band between 3300 and 3100 cm.$^{-1}$ (chelated hydroxyl group), and a broad, strong band between 1630 and 1580 cm.$^{-1}$ (chelated carbonyl group).

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.21; H, 6.51.

1,2,3,4-Tetramethyl-8-hydroxyfluorenone.—A mixture of 2 g. of phenol II, 20 ml. of chlorobenzene, and 4.5 g. aluminum chloride was heated under reflux for 2.5 hr., stirred at room temperature overnight, and poured with stirring into a solution of 20 ml. of concd. hydrochloric acid in 200 ml. of water. The resulting slurry was steam distilled to remove chlorobenzene, and the crude fluorenone was recrystallized from benzene, yield 0.56 g. (30.3%), m.p. 170–171°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.73; H, 6.69.

The infrared spectrum shows bands assignable to a chelated, phenolic hydroxyl group (3300 cm.$^{-1}$) and to a conjugated, chelated carbonyl group in a five-membered ring (1660 cm.$^{-1}$).

Fluorenone III was produced also when a mixture of 2.6 g. of ketone VI, 20 ml of chlorobenzene, and 3 g. of aluminum chloride was heated with stirring for 3 5 hr. under reflux and then stirred overnight at room temperature. The product was recrystallized from benzene, m.p. 171–172°, yield 42.3%. A mixture melting point determination and comparison of infrared spectra showed this compound to be identical to that prepared from 2-duroylresorcinol. The fluorenone was formed also when a mixture of 0.52 g. of phenol VII, 1.2 g. of anhydrous aluminum chloride, and 15 ml. of chlorobenzene was heated under reflux, with stirring, for 3.5 hr., m.p. 170–171°, yield 23.4%.

1,2,3,4-Tetramethyl-8-methoxyfluorenone.—Methylation of phenol III by a procedure modeled after that of Lander[7] gave ketone V as yellow crystals, m.p. 169–170°, yield 93.8%.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.90; H, 7.07.

The infrared spectrum shows bands attributed to a conjugated carbonyl group in a five-membered ring (1690 cm.$^{-1}$) and an ether linkage (1275 cm.$^{-1}$).

2-Duroyl-3-prehnitylanisole.—A solution of 13.2 g. of ethylene bromide in 25 ml. of anhydrous ether was added under nitrogen to a suspension of 3.0 g. of bromoprehnitene, 2.06 g. of magnesium turnings, and 25 ml. of anhydrous ether. The reaction mixture was heated under reflux for 3 hr. and added slowly at reflux temperature, over a period of 30 min., to a solution of 4.2 g. of ether I in 50 ml. of dry benzene. The mixture was heated under reflux for 17.5 hr., with stirring, cooled to room temperature, and stirred for 20 min. with 50 ml. of concd. ammonium chloride solution. The orange-brown, oily product crystallized when stirred with absolute ethanol. Recrystallization from 95% ethanol gave 1.12 g. (19.8%) of ketone IV, m.p. 157–158°.

Anal. Calcd. for $C_{28}H_{32}O_2$: C, 83.96; H, 8.05. Found: C, 84.08; H, 7.78.

A mixture of 0.5 g. of the ketone and 25 ml. of polyphosphoric acid was heated at 60–70°, with stirring, for 4 hr. The yellow product was submitted to chromatographic separation; ketone V, 0.15 g. (45.1%), was eluted at 20:1 benzene–ether and identified by a mixed melting point and comparison of infrared spectra.

Dimethyl Ether of 2-Prehnitoylresorcinol.—A solution of 8.8 g. of prehnitoyl chloride in 20 ml. of ether was added dropwise to a solution of 2,6-dimethoxyphenyllithium made from 9.66 g. of 1,3-dimethoxybenzene.[8] The reaction mixture was heated for 3 hr. under reflux, cooled, and poured into a slurry of ice and hydrochloric acid. The product, isolated by conventional procedures, was a purple solid, yield 12.7 g.; it was placed on a column of 250 g. of acid-washed alumina and eluted with cyclohexane–ether. With pure cyclohexane 2.9 g. of 1,3-dimethoxybenzene was isolated. Ketone VI (7.3 g.) was obtained with cyclohexane containing 8% of ether, m.p. 124–125°, yield 54.5%.

Anal. Calcd. for $C_{19}H_{22}O_3$: C, 76.5; H, 7.43. Found: C, 76.7; H, 7.26

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(4) All melting points are uncorrected.

(5) R. C. Fuson, G. W. Parshall, and E. H. Hess, *J. Am. Chem. Soc.*, **77**, 3776 (1955).

(6) F. Mauthner, *J. prakt. Chem.*, **139**, 290 (1934).

(7) G. D. Lander, *J. Chem. Soc.*, 729 (1900).

(8) G. Wittig and U. Pockels, *Ber.*, **72B**, 89 (1939).

Reaction of 2-Hydroxy-3-nitro-5,6-diphenylpyrazine with Pyridine

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Received February 9, 1962

The action of either thionyl chloride or phosphorus oxychloride upon 2-hydroxy-3-nitro-5,6-diphenylpyrazine (I)[1] has previously been shown

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(1) G. Karmas and P. Spoerri, *J. Am. Chem. Soc.*, **75**, 5517 (1953)