Barnett's[5] method was employed to synthesize the *lin*-phthaloylfluorenone. *o*-(Fluorenone-2-carbonyl)benzoic acid was formed by oxidation of *o*-(fluorene-2-carbonyl)benzoic acid and was esterified in ethanol.

Experimental[6]

2-(9′-Fluorenyl)fluorene (I).—9-Bromofluorene (2.44 g.) and fluorene (1.66 g.) were dissolved in carbon disulfide (30 ml.). Anhydrous aluminum chloride (1.35 g.) was added in small portions with stirring at the boiling point. The reaction color immediately turned greenish blue and hydrogen chloride gas was evolved. After warming for 0.5 hr. on the water bath, the mixture was cooled and poured into water. The carbon disulfide layer was separated, washed with water, and evaporated to dryness to give colorless needles 1.5 g., m.p. 225–226° (from benzene), soluble in hot benzene, acetic acid, and ethyl acetate, and stable at the melting point. Ultraviolet absorption spectra: $\lambda_{max}^{CHCl_3}$ mμ (log ε); 272.5 (4.52), 296 (4.15), 307 (4.22), 323 (3.27).

Anal. Calcd. for $C_{26}H_{18}$: C, 94.51; H, 5.49; mol. wt., 330. Found: C, 94.15; H, 5.68; mol. wt., 325.

Clemmensen Reduction of 9-Fluorenol.—A mixture of amalgamated zinc (10 g.), water (10 ml.), toluene (40 ml.), concd. hydrochloric acid (35 ml.), and 9-fluorenol (10 g.) was refluxed briskly for 24 hr. Hydrochloric acid was added every 6 hr. After the reaction, fluorene (8 g., m.p. 113–114°) was obtained by steam distillation. A residual product was filtered and recrystallized from ethyl acetate to yield I, 0.8 g., m.p. 224–227°.

Reaction of Fluorene and 9-Fluorenol.—9-Fluorenol (0.8 g.) and fluorene (0.73 g.) in acetic acid (7 ml.) and two drops of concd. sulfuric acid were refluxed for 5 hr. After pouring into cold water, the white amorphous product was filtered off giving 0.8 g. of I, m.p. 224–226° (from benzene).

Oxidation of I.—A solution of I (1.0 g.) in glacial acetic acid (10 ml.) was refluxed with sodium dichromate (3 g.) and concd. sulfuric acid (1 drop) for 3 hr. After cooling and diluting the solution with cold water, the yellow amorphous precipitate was filtered and treated with dilute sodium hydroxide (10%). Acidification of the alkali soluble part gave a precipitate which was recrystallized from acetic acid to yield yellow prisms of *o*-(fluorenone-2-carbonyl)benzoic acid (0.2 g.), m.p. 257–258°, identical with that obtained by oxidation of *o*(fluorene-2-carbonyl)benzoic acid.

Anal. Calcd. for $C_{21}H_{12}O_4$: C, 76.82; H, 3.68. Found: C, 76.67; H, 3.77.

The alkali-insoluble part was recrystallized from acetic acid to afford small orange-red needles, m.p. 367°, 0.5 g., which gave a blue color test with concd. sulfuric acid. This was identical with the *lin*-phthaloylfluorenone which was prepared by Barnett's method.[5]

Anal. Calcd. for $C_{21}H_{10}O_3$: C, 81.28; H, 3.25. Found: C, 81.17; H, 3.47.

Ethyl *o*-(Fluorenone-2-carbonyl)benzoate.—The acid was esterified in the usual manner to give yellow crystals, m.p. 108–110° (from alcohol).

Anal. Calcd. for $C_{23}H_{16}O_4$: C, 77.51, H, 4.53. Found: C, 77.15; H, 4.61.

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Fries Rearrangement of 3-Nitrophenyl Butyrate

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Few examples of the Fries isomerization of nitrophenyl esters are reported in the literature.[1–10] The reduced tendency of these esters to undergo Fries rearrangement must be associated with the retarding effect of the nitro substituent in the phenyl ring.[11–16]

The Fries reaction of 3-nitrophenyl acetate,[2,3] propionate,[6] phenylacetate, and benzoate[10] has already been realized. In the present work 3-nitrophenyl butyrate has been subjected to the Fries rearrangement by heating it for 2.5 hr. in the absence of a solvent in the presence of aluminum chloride at 140°. The isomerization yielded 3.5–5% of the so far unknown 4-nitro-2-hydroxybutyrophenone, which was characterized by its phenylhydrazone. The structure of this new ketone was proved by oxidation which gave 4-nitro-2-hydroxybenzoic acid.

Experimental[17]

3-Nitrophenyl butyrate was prepared in 80% yield from sodium 3-nitrophenoxide (obtained from 3-nitrophenol and sodium ethoxide in benzene) and butyryl chloride in benzene. After the removal of the solvent the residual ester[18] was used without further purification, as it decomposed on distilling. The ester (10.5 g., 0.05 mole) was mixed with aluminum chloride (6.55 g., 0.05 mole,) in a flask protected against moisture and heated in an oil bath at 135–140° for 150 minutes. At the beginning of the reaction hydrogen chloride was evolved. The solidified product was dissolved

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in 20 cc. of ethanol, and poured into a mixture of 10 cc. of concd. hydrochloric acid and 150 cc. of water. The aqueous layer was extracted with four 40- cc. portions of tetrachloromethane and two 15-cc. portions of benzene. The combined extracts were used to dissolve the organic layer. The solution was washed with eight 50-cc. portions of water. It was then dried over sodium sulfate and filtered through cotton. Removal of the solvent gave a brown oily residue. A part of this was dissolved in 70% ethanol, mixed with phenylhydrazine, and boiled for 2–3 min. On allowing to stand it overnight in a refrigerator, red needles melting at 179–180° separated.

Anal. Calcd. for $C_{13}H_{17}O_3N_3$: N, 14.04; mol. wt. 299.3. Found: N, 14.30.

Another part of the residual oil was washed with water again and extracted with petroleum ether. On concentrating the extract yellowish oily crystals separated. They were collected and recrystallized from ethanol to give a solid melting at 63.5–64°.

Anal. Calcd. for $C_{10}H_{11}O_4N$: N, 6.73; mol. wt. 209.2. Found: N, 6.81.

The method of oxidation of 4-nitro-2-hydroxybutyrophenone to 4-nitro-2-hydroxybenzoic acid was the same (potassium permanganate in potassium hydroxide solution) as used for the oxidation of 4-nitro-2-hydroxypropiophenone.[6]

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Mannich Bases Derived from Acetylated Hydantoins

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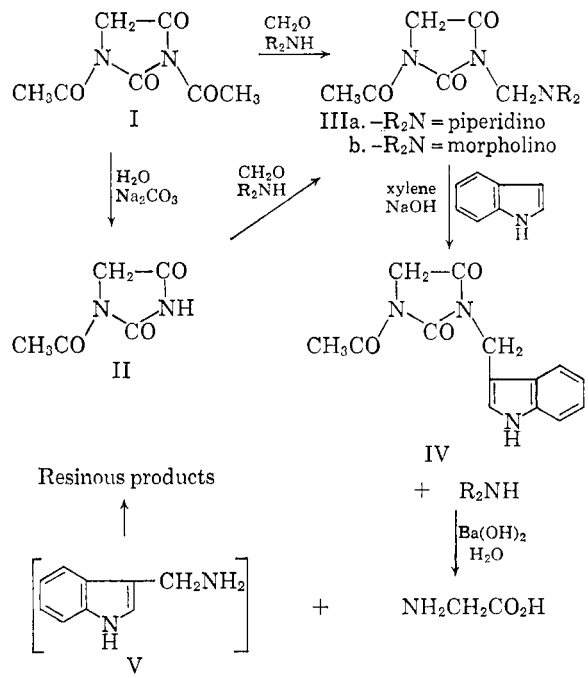
1,3-Diacetylhydantoin (I), prepared by the reaction of hydantoin with acetic anhydride in the presence of fused sodium acetate,[1] has been investigated as a precursor of the tryptophan side chain. Treatment of this compound with aqueous formaldehyde and either piperidine or morpholine was found to yield crystalline Mannich bases in excellent yield. Elemental analysis of these derivatives indicated that one of the acetyl groups had been replaced by an aminomethyl group.

Mannich base formation has also been observed with 1-acetylhydantoin (II), a compound readily prepared by the partial hydrolysis of 1,3-diacetylhydantoin.[1] Treatment of this material with aqueous formaldehyde and either piperidine or morpholine yielded the same Mannich bases obtained with 1,3-diacetylhydantoin.

Reaction of either Mannich base with indole under conditions similar to those described by Butenandt and Hellmann[2] gave a single condensation product in 20–32% yield. The latter compound had an elemental analysis which indicated the dialkylamino group had been replaced by an indolyl group. Upon alkaline hydrolysis[3] the compound yielded glycine along with an insoluble resinous product but no tryptophan.

On the basis of these results the Mannich bases have been identified as 1-acetyl-3-*N*-piperidinomethylhydantoin (IIIa) and 1-acetyl-3-*N*-morpholinomethylhydantoin (IIIb), respectively. The condensation product is indicated as being 1-acetyl-3-(3′-indolylmethyl)hydantoin (IV) since this compound on hydrolysis should be converted into glycine and 3-indolylmethylamine (V). The latter compound, which is relatively unstable, might be expected to form the resin isolated in its place under the conditions used to accomplish the hydrolysis.



The exact course of the reaction forming the Mannich bases from 1,3-diacetylhydantoin has not been determined. A possible intermediate is 1-acetylhydantoin, since this material could be produced by the alkaline conditions employed in the aminomethylation reaction.

Efforts to prepare Mannich bases by the reaction of either piperidine or morpholine and formaldehyde with various other glycine derivatives were unsuccessful. Compounds of the latter type examined include hydantoin, 3-methylhydantoin, aceturic acid, hippuric acid, acetaminoacetonitrile, *N*-phthaliminoacetonitrile, and 2-phenyl-5-oxazolone.

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