

**Acknowledgment.**—We are indebted to Mr. S. M. Nagy for all analyses.

### Summary

The syntheses of three  $\alpha$ -(dialkylaminomethyl)-8-amino-6-methoxy-4-quinolinemethanols (IIa, b, c) and three  $\alpha$ -(dialkylaminomethyl)-8-hydroxy-4-quinolinemethanols (IIa, b, c) are described. These compounds have been tested for avian antimalarial activity.

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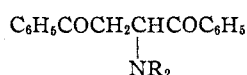
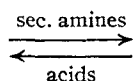
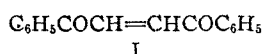
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

## Some $\alpha$ -*t*-Amino-*s*-dibenzoylethanes and 3-*t*-Amino-2,5-diphenylfurans. The Preparation and Reactions of Dibenzoyl-*N*-morpholinoethylene<sup>1</sup>

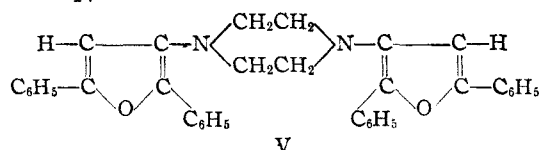
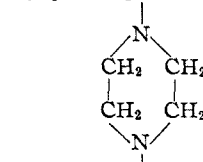
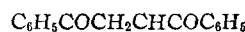
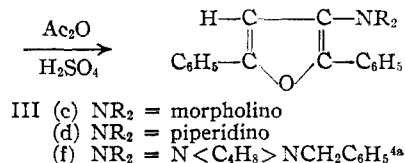
BY ROBERT E. LUTZ, PHILIP S. BAILEY<sup>2a</sup> AND NEWTON H. SHEARER, JR.<sup>2</sup>

In an earlier paper the unexpected results obtained in the reaction between amines and dibenzoylmethylene were described.<sup>3</sup> The present communication deals with the straightforward addition of amines to *trans*-dibenzoylethylene (I) to give  $\alpha$ -aminodibenzoylethanes (II) and with the reactions of the products. A number of these compounds were made in connection with the search for new types of antimalarials.

In 1900 Paal and Schulze<sup>4</sup> added aniline to both *cis*- and *trans*-dibenzoylethylene by warming a mixture of the reactants. In the present work the analogous additions of a number of aliphatic amines were carried out at room temperature either in ether or in ethanol solution. The amines used were dimethylamine, diethylamine, morpholine; piperidine, piperazine, 1-ampylpiperazine and 1-benzylpiperazine.



- II (a) NR<sub>2</sub> = N(CH<sub>3</sub>)<sub>2</sub>  
 (b) NR<sub>2</sub> = N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>  
 (c) NR<sub>2</sub> = morpholino  
 (d) NR<sub>2</sub> = piperidino  
 (e) NR<sub>2</sub> = H<C<sub>4</sub>H<sub>8</sub>>NC<sub>6</sub>H<sub>11</sub><sup>4a</sup>  
 (f) NR<sub>2</sub> = N<C<sub>4</sub>H<sub>8</sub>>NCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub><sup>4a</sup>



The hypothetical monoaddition compound, dibenzoyl-*N*-piperazinoethane, could not be isolated, even when a three molar excess of piperazine

Only one of these products had been made before, namely, dibenzoyldimethylaminoethane (IIa) by rearrangement of diphenacyldimethylammonium bromide by means of alkali.<sup>5</sup>

In the case of the piperazine addition the *bis*-compound (IV) was formed, as would be expected, by the reaction of two molecules of dibenzoylethylene (I) with one of piperazine.

(1) Part of the work described in this paper was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and the University of Virginia. The Survey Number, designated SN, identifies a drug in the records of the Survey of Antimalarial Drugs. The antimalarial activities of these compounds to which Survey Numbers have been assigned will be tabulated in a forthcoming monograph.

(2) (a) Holder of Philip Francis du Pont Fellowship, 1942-1944; present address: University of Texas, Austin, Texas. (b) Present address: Tennessee Eastman Corporation, Kingsport, Tennessee.

(3) Lutz and Bailey, THIS JOURNAL, **67**, 2229 (1945).

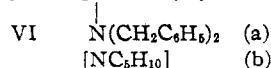
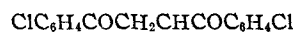
(4) Paal and Schulze, *Ber.*, **33**, 3795 (1900).

(4a) [—N<C<sub>4</sub>H<sub>8</sub>>N—] is the piperazine nucleus.

(5) Thomson and Stevens, *J. Chem. Soc.*, 1932 (1932).

was used. A likely explanation for the failure to obtain it is found in the general instability of these addition compounds and in the comparatively high insolubility of the piperazino-*bis*-dibenzoylethane (IV). Probably the mono additive is formed in equilibrium with the components, with the *bis* compound the only product isolated because of its insolubility.

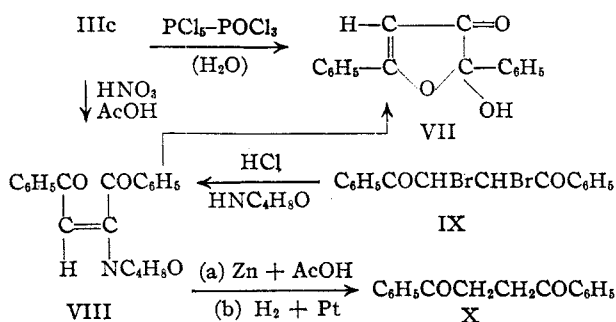
Along with the compounds described above *N,N*-dibenzylamino and *N*-piperidino-di-(*p*-chlorobenzoyl)-ethane (VIa and b) were obtained by the addition of the appropriate amines to di-(*p*-chlorobenzoyl)-ethylene. These compounds were made for antimalarial testing with a view toward the possible activating influence of the two para chlorines.



The structures of the addition compounds (II) were demonstrated by two reactions. The added amines were eliminated and dibenzoyl ethylene regenerated by treatment with hot acetic or hydrochloric acid or by allowing a water solution of the hydrochloride to stand for several hours; this same type of determination has been carried out by Paal and Schulze<sup>4</sup> on anilindibenzoyl ethane. And the addition compounds were cyclized to the corresponding furans (III) by means of acetic anhydride and sulfuric acid; the piperazino-*bis*-addition compound (IV) yielded a *bis*-furan (V) in this reaction.

One addition compound, namely, dibenzoyldimethylaminoethane (IIa) was largely deaminated to dibenzoyl ethylene under the standard furanizing conditions and no furan was obtained in this case.

Diphenylmorpholinofuran (IIIc) was studied further. Treatment with phosphorus pentachloride and oxychloride at 100° followed by hydrolysis, yielded 2,5-diphenyl-2-hydroxyfuranone-3 (VII); this reaction parallels that of 3-acetoxy-2,5-diphenylfuran which is converted into 2-chloro-2,5-diphenylfuranone-3<sup>6</sup> under the same conditions (the obtaining of the chloro rather than the hydroxyfuranone was due to the care taken to avoid hydrolysis during the isolation of the product).

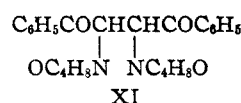


Oxidation of the morpholinofuran (IIIc) by means of nitric acid in acetic acid solution yielded a compound which is formulated as *cis*-dibenzoylmorpholinoethylene (VIII) on the basis of analogy to the oxidation of other typical 2,5-diphenylfurans.<sup>7</sup> The structure of this unsaturated diketone was confirmed by the following facts: It was also obtained by the treatment of dibenzoyldibromomethane (IX) with morpholine; it yielded dibenzoyl ethane with loss of the morpholino group upon reduction; and it gave 2,5-diphenyl-2-hydroxyfuranone-3 (VII) upon hydrolysis.

These reactions are in line with corresponding reactions of other aminodibenzoyl ethylenes.<sup>8</sup> It is interesting to note, however, that dibenzoylmorpholinoethylene (VIII) is much more resistant to

hydrolysis than aminodibenzoyl ethylene itself which is converted to the hydroxyfuranone (VII) by the action of very dilute ethanolic hydrogen chloride at room temperature.<sup>8b</sup>

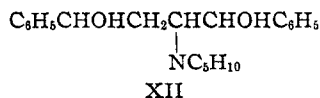
In the reaction between dibenzoyldibromomethane and morpholine to produce dibenzoylmorpholinoethylene, a second and minor product was also found which was extremely difficult to separate by fractional crystallization and it was not isolated in a pure condition. Analysis of the superficially purified mixture indicated that the second compound was not an isomer but was dibenzoyldimorpholinoethane (XI), and was present to the extent of about 32%. If this hypothesis is



correct, the compound constitutes the only one of its class in the 1,4-diketone field, in contrast to the benzalacetophenone series where this type of compound is readily obtained.<sup>9</sup> Further study of this will be undertaken in the near future.

The unsaturated morpholino diketone (VIII), obtained as the chief product of the reaction between the dibromide (IX) and morpholine, was expected to be the more stable of the two possible geometric isomers of this structure in view of the mode of formation of the double bond during the reaction. The compound obtained presumably has the *cis* configuration because it was also obtained by the oxidation of the corresponding furan, a reaction which usually gives the *cis* form.<sup>7</sup> In an earlier paper<sup>3</sup> where it was shown that, unexpectedly, the *cis*-dibenzoylmethylethylene is more stable than the *trans* isomer, a cyclic resonance structure was proposed in order to account for its greater stability. Perhaps the case of the dibenzoylmorpholinoethylene is analogous and affords another example of this phenomenon. It is unfortunate that both stereoisomers have not been obtained so that the relationship between the two could be studied.

One of the amine addition compounds of dibenzoyl ethylene, the piperidino compound (VIb), has been hydrogenated successfully without loss of the piperidino group to give a mixture of stereoisomers of 1,4-diphenyl-2-piperidinobutanediol-1,4 (XII). From this mixture one of the isomers



has been isolated apparently in a pure condition.

None of the compounds made in this investigation and tested to date has shown significant antimalarial activity.

(6) Lutz, Stuart, Wilder and Connor, *THIS JOURNAL*, **59**, 2314 (1937).

(7) Lutz and Wilder, *THIS JOURNAL*, **56**, 978 (1934).

(8) (a) Conant and Lutz, *THIS JOURNAL*, **47**, 881 (1925); (b) Lutz and Amacker, results to be published shortly.

(9) Cromwell, *Chem. Rev.*, **38**, 83 (1946). Some additional analogs made for antimalarial screening tests, will be described in a forthcoming publication from this Laboratory.

### Experimental<sup>10</sup>

**Dibenzoyl-N-morpholinoethane (IIc)** (SN-2594).—In a typical procedure a solution of 75 g. of dibenzoylethylene (I), 60 ml. of morpholine and 150 ml. of ether was allowed to stand for two hours. Crystals separated, were filtered and washed with cold di-isopropyl ether, 90 g. (87%), m. p. 101–103°. Several recrystallizations from ethanol raised the melting point to 105–106°.

*Anal.* Calcd. for  $C_{20}H_{21}NO_2$ : N, 4.33. Found: N, 4.23.

The hydrochloride was made from acetone by means of ethereal hydrogen chloride and recrystallized from methanol; m. p. 169–171°.

*Anal.* Calcd. for  $C_{20}H_{21}NO_2 \cdot HCl$ : C, 66.75; H, 6.16. Found: C, 66.68; H, 6.21.

Reaction of 0.5 g. of the base in 20 ml. of glacial acetic acid with 1.5 g. of zinc dust (refluxing for two minutes) and recrystallization of the product from ethanol yielded 0.2 g. of dibenzoylethane. In a similar experiment the zinc was omitted and dibenzoylethylene (I) was obtained.

**Dibenzoyl-N-piperidinoethane (IId) Hydrochloride** (SN-399).—Crystallized from ethanol and dry ether; m. p. 162–163°.

*Anal.* Calcd. for  $C_{21}H_{23}NO_2 \cdot HCl$ : C, 70.48; H, 6.76. Found: C, 70.22; H, 6.56.

The free base melted at 92–93°. It decomposed on standing.

*Anal.* Calcd. for  $C_{21}H_{23}NO_2$ : C, 78.47; H, 7.21. Found: C, 78.29; H, 7.34.

**1,4-Diphenyl-2-piperidinobutanediol-1,4 (XII) Hydrochloride** (SN-1962).—A solution of dibenzoyl-N-piperidinoethane (IId) in methanol was hydrogenated using platinum oxide. The reduction proceeded at a fairly constant rate until nearly two moles of hydrogen was absorbed after which the rate slowly decreased; the reduction was interrupted after 3.4 moles had been absorbed. The product was isolated, dissolved in acetone and treated with ethereal hydrogen chloride. Two batches of crystals were obtained. The first crop of crystals after several recrystallizations from a methanol-dry ether mixture melted at 230–231°.

*Anal.* Calcd. for  $C_{21}H_{27}NO_2 \cdot HCl$ : C, 69.69; H, 7.80. Found: C, 69.70; H, 7.79.

The second crop of crystals was a mixture which melted at 160–163° after several recrystallizations from methanol.

*Anal.* Calcd. for  $C_{21}H_{27}NO_2 \cdot HCl$ : C, 69.69; H, 7.80. Found: C, 69.12; H, 8.17.

**Dibenzoyl-N-dimethylaminoethane (IIa)** (SN-13,408).—Twenty-five grams of a 25% aqueous dimethylamine solution was added to a suspension of 16.5 g. of dibenzoylethylene in 100 ml. of methanol with cooling. After standing for six hours at room temperature and overnight in the refrigerator the crystallized product was filtered, 16 g. (80%), m. p. 64–65°. Repeated recrystallization from 70% methanol did not change the melting point. The compound turned yellow when exposed to light.

*Anal.* Calcd. for  $C_{15}H_{19}NO_2$ : N, 4.98. Found: N, 5.03.

**Dibenzoyl-N-diethylaminoethane (I Ib) Hydrochloride**—(SN-2631).—The free base, made as I Ic above, did not precipitate from the reaction mixture even after two days, and was obtained as an oil upon washing the mixture with water and evaporating the ether under reduced pressure. Acidification of an acetone solution of the base with ethereal hydrogen chloride, gave the hydrochloride (83%, m. p. 127–130°) which after several recrystallizations from ethanol and dry ether melted at 135–136°.

*Anal.* Calcd. for  $C_{20}H_{23}NO_2 \cdot HCl$ : C, 69.45; H, 6.99. Found: C, 69.70; H, 7.30.

**1-(4-Benzylpiperazino)-dibenzoylethane (II f)** was prepared in 93% yield in a manner similar to I Ic except that no excess benzylpiperazine was used; recrystallized from a 3–7 mixture of dioxane and ethanol; m. p. 127–127.5°.

*Anal.* Calcd. for  $C_{27}H_{28}N_2O_2$ : N, 6.79. Found: N, 6.59.

The dihydrochloride (SN-12,946) was prepared by adding ethereal hydrogen chloride to a solution of the base in a 1–9 mixture of dioxane and absolute ether. It crystallized as fine white needles from absolute ethanol; m. p. (sintering) 225–240°.

*Anal.* Calcd. for  $C_{27}H_{28}N_2O_2 \cdot 2HCl$ :  $Cl^-$ , 14.61. Found:  $Cl^-$ , 14.57.

The instability of the dihydrochloride was demonstrated by dissolving a small portion of it in water and allowing the solution to stand overnight. A yellow solid separated which was identified by mixture melting point as dibenzoylethylene.

**1-Amylpiperazine** was made by a variation of the general method of Baltzly.<sup>11</sup> To a solution of 431 g. (5 moles) of piperazine in 1.2 liters of methanol was added 396 g. (2 moles) of amyl iodide over a period of ten minutes with cooling as required to prevent boiling. After standing for four days the precipitated piperazine hydroiodide was filtered and the methanol was distilled under reduced pressure. The residual oil was dissolved in ether and washed twice with 3 N sodium hydroxide solution. Evaporation under reduced pressure yielded 343 g. of red hygroscopic oil which was fractionally distilled; yield 161 g. (51%); b. p. 105–110° at 9 mm.;  $n_D^{20}$  1.4650–1.4659.

The dihydrochloride was precipitated from absolute ether; m. p. 261–265° (dec.); yield 86%. After recrystallization from isopropanol and ethanol the melting point was 267–269°.

*Anal.* Calcd. for  $C_9H_{20}N_2 \cdot 2HCl$ :  $Cl^-$ , 30.94. Found:  $Cl^-$ , 30.90.

**1-(4-Amylpiperazino)-dibenzoylethane (II e) dihydrochloride** (SN-12,708) was prepared like I Ib and recrystallized from a 2–8 mixture of ethanol and dioxane; m. p. 245–246° (vac.).

*Anal.* Calcd. for  $C_{25}H_{32}N_2O_2 \cdot 2HCl$ : N, 6.02. Found: N, 5.96.

**1,4-Piperazino-bis-dibenzoylethane (IV)** (SN-4674).—A suspension of 71 g. (0.3 mole) of dibenzoylethylene in 300 ml. of absolute ethanol at 50° was treated with 14 g. (0.16 mole) of piperazine. The mixture was stirred for four hours at room temperature during which time the dibenzoylethylene dissolved and IV precipitated. After cooling to 15° the product was filtered and washed with cold methanol; yield 78 g. (93%); m. p., 182–184° (dec.). After several recrystallizations from toluene the pale yellow rods melted at 185–186° (dec.).

*Anal.* Calcd. for  $C_{36}H_{34}N_2O_4$ : C, 77.40; H, 6.13; N, 5.02. Found: C, 77.44; H, 6.29; N, 5.10.

In an attempt to prepare a mono rather than a bis compound the reaction was carried out using the ratio of four moles of piperazine to one of dibenzoylethylene. However, only the bis compound was obtained.

**N-Dibenzylamino-di-(p-chlorobenzoyl)-ethane (VI a)<sup>12</sup>** was prepared like I Ic but the product did not precipitate from the reaction mixture and was isolated by evaporation under a stream of air and crystallized from ethanol; m. p. 116–118°.

*Anal.* Calcd. for  $C_{30}H_{23}Cl_2NO_2$ : C, 71.71; H, 5.01. Found: C, 71.46; H, 5.43.

**Di-(p-chlorobenzoyl)-N-piperidinoethane (VI b)<sup>12</sup>**.—This compound could not be obtained by the usual procedure. Fifteen grams (0.049 mole) of di-p-chlorobenzoylethylene was added with stirring to 6.6 g. (0.078 mole) of piperidine. The mixture was heated at 95° for three minutes, allowed to stand at room temperature for one

(10) All melting points reported in this paper are corrected. The authors are indebted to Misses Clara Vondra, Joyce Blume, Geraldine Alley and Mr. C. S. Floyd for many of the micro analyses reported here.

(11) Baltzly, Buck, Lorz and Schön, *THIS JOURNAL*, **66**, 263 (1944).

(12) Submitted for screening test against avian malaria.

hour, then shaken with 50 ml. of methanol and filtered. The yield of tan solid melting at 113–115° was 17 g. (88%). It was recrystallized twice from a benzene-hexane mixture; white rhombic prisms; m. p. 114–115°.

*Anal.* Calcd. for  $C_{21}H_{21}Cl_2NO_2$ : N, 3.59. Found: N, 3.49.

**2,5-Diphenyl-3-morpholinofuran (IIIc).**—A solution of 25 g. of dibenzoylmorpholinoethane (IIc) in 125 ml. of acetic anhydride was treated with 8 ml. of concd. sulfuric acid. The mixture was kept at 45° for seven hours, and was then hydrolyzed in ice and sodium carbonate. The resulting mixture was extracted with ether, leaving 8 g. of insoluble material of m. p. 202–204° (the sulfate, later converted to free base). The ether solution was evaporated and the residue crystallized from ethanol; yield 14 g.; m. p. 112–114°. The total yield of base was 19.5 g. (83%). After several recrystallizations from ethanol the melting point was 113–114°. It was soluble in 10% hydrochloric acid.

*Anal.* Calcd. for  $C_{20}H_{19}NO_2$ : C, 78.66; H, 6.27. Found: C, 78.71; H, 6.16.

**2,5-Diphenyl-3-N-piperidinofuran (IIId)** was prepared in 70% yield from IIId in the same manner as IIIc except that the reaction mixture was not heated but was kept at room temperature for forty-eight hours. After several recrystallizations from ethanol it melted at 102.5–103.5°.

*Anal.* Calcd. for  $C_{21}H_{21}NO$ : C, 83.13; H, 6.98. Found: C, 82.97; H, 7.19.

**1-(4-Benzylpiperazino)-2,5-diphenylfuran Hydrochloride (IIIe).**—The base (m. p. 70–72°) was obtained in 46% yield in the same way as IIIc. It was converted to the monohydrochloride by dissolving it in a 1–2 mixture of hexane, acetone and absolute ether and acidifying with ethereal hydrogen chloride. The melting point after recrystallization from a methanol-ether solution was 246–247° (in vac.).

*Anal.* Calcd. for  $C_{27}H_{26}N_2O \cdot HCl$ : C, 75.24; H, 6.08. Found: C, 75.06; H, 6.30.

**3,3'-(1,4-Piperazino)-bis-2,5-diphenylfuran (V)** was prepared like IIIc; crystallized from 95% dioxane; m. p. 266–267°.

*Anal.* Calcd. for  $C_{30}H_{26}N_2O_2$ : C, 82.74; H, 5.79; N, 5.36. Found: C, 83.01; H, 5.80; N, 5.55.

The attempts to furanize dibenzoyl-N-dimethylaminoethane (IIa) in a manner similar to (IIc) gave chiefly dibenzoylethylene along with a small amount of a colorless white nitrogen-free material of m. p. 191–192°.

**Treatment of 2,5-Diphenyl-3-morpholinofuran (IIIc) with Phosphorus Pentachloride.**—A mixture of 1 g. of IIIc, 2 g. of phosphorus pentachloride and 0.2 ml. of phosphorus oxychloride was heated at 100° for two minutes during which time the mixture softened but did not melt completely. The oil obtained upon hydrolysis was washed with water and dissolved in 10 ml. of ethanol. Cooling, adding 90 ml. of water and allowing to stand for several days gave a crystalline product which was recrystallized from 80% ethanol; yield of VII, 0.3 g. of m. p. 82–83° (identified by mixture melting point with authentic sample).

**Dibenzoyl-N-morpholinoethylene (SN-1630) (VIII).** (a) **From 2,5-Diphenyl-3-morpholinofuran (IIIc).**—To a suspension of 5 g. of IIIc in 25 ml. of acetic acid was added a solution of 10 ml. of nitric acid in 15 ml. of acetic acid. The solid dissolved and after ten minutes the solution was poured into excess sodium bicarbonate solution and the resulting suspension was extracted with ether. An insoluble residue remained, 1.3 g.; m. p., 169–171°. (Evaporation of the ether extract and recrystallization of the residue from ethanol yielded 1.2 g. of starting material.) Following several recrystallizations of the product from ethanol the melting point was 176–177°.

*Anal.* Calcd. for  $C_{20}H_{19}NO_2$ : C, 74.74; H, 5.96; N, 4.36. Found: C, 74.65; H, 5.85; N, 4.20.

(b) **From Dibenzoyldibromoethane (IX).**—A mixture of 20 g. of morpholine, 20 g. of IX and 150 ml. of absolute ethanol was refluxed with stirring for seventy minutes during which time most of the solid dissolved. The insoluble material was filtered (3.5 g., m. p. 165–166°). The filtrate was cooled and filtered, and the product was digested with warm water to remove morpholine hydrobromide. The residual material (11.4 g.), evidently a mixture, melted at 154–164°, and showed no depression in a mixture melting point with the first 3.5-g. batch. Attempts to separate this mixture by fractional crystallization from either ethanol or ethyl acetate failed. Slow evaporation of an ethyl acetate solution of the material yielded two types of crystals, rods and cubes. The rods which were predominant melted without decomposition at 169–175° and showed no depression in a mixture melting point with material (VIII) obtained by the nitric acid oxidation of 2,5-diphenyl-3-morpholinofuran (IIIc). The cubes melted at 168–173° with decomposition and gave a mixture melting point depression (159–165°) with the rods and also with the unsaturated morpholino diketone (VIII) obtained by the oxidation of the furan (IIIc).

The material (m. p. 156–160°) from which the rods and cubes were obtained must therefore be a mixture of the expected dibenzoylmorpholinoethylene and some foreign material which, from the analysis of the mixture, must have a lower carbon, a higher hydrogen and a higher nitrogen content than the unsaturated morpholinodiketone (VIII). It is believed to be dibenzoyldimorpholinoethane (XI). If this is the case, the analysis indicates that the mixture was approximately 68% dibenzoylmorpholinoethylene.

*Anal.* of the mixture. Calcd. for  $C_{20}H_{19}NO_2$ : C, 74.74; H, 5.96; N, 4.36. Calcd. for  $C_{24}H_{23}N_2O_4$ : C, 70.57; H, 6.91; N, 6.86. Found: C, 73.41; H, 6.36; N, 5.12.

**Reduction of dibenzoylmorpholinoethylene (VIII)** by glacial acetic acid and zinc dust at 100° (for two minutes) gave dibenzoylethane (X) which was identified by mixture melting point. Catalytic reduction in ethanol solution using palladium-barium sulfate gave a mixture of products which appeared to contain chiefly dibenzoylethane.

**Hydrolysis of Dibenzoylmorpholinoethylene (VIII)** by concentrated ethanolic hydrogen chloride (at room temperature for five days and refluxing for three hours) gave an oil which was washed with water, dissolved in ethanol and cooled. Upon dilution with twice the volume of water and allowing to stand for one week, a small amount of white crystals formed on the side of the vessel and an oil precipitated. The white crystals melted at 85–87° and showed no depression in a mixture melting point with 2,5-diphenyl-2-hydroxyfuranone-3 (VII).

### Summary

Secondary amines have been added to dibenzoylethylene and to di-(*p*-chlorobenzoyl)-ethylene to give a series of  $\alpha$ -l-amino saturated 1,4-diketones. The addition compounds are easily broken up by the action of dilute acids. Some have been furanized.

2,5-Diphenyl-3-morpholinofuran has been converted by phosphorus pentachloride into 2,5-diphenyl-2-hydroxyfuranone-3 and by nitric acid oxidation into *cis*-dibenzoylmorpholinoethylene. The latter is also obtained in the reaction between morpholine and dibenzoyldibromoethane. It is reduced to dibenzoylethane and hydrolyzed to 2,5-diphenyl-2-hydroxyfuranone-3.

Dibenzoylpiperidinoethane has been hydrogenated to the piperidino-1,4-glycol.

CHARLOTTESVILLE, VIRGINIA RECEIVED JUNE 28, 1946