2,5-Diphenyl-3-morpholinofuran and its 2-Hydro, 2-Bromo and 2-Hydroxymorpholinofurylium Salts (1).

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2,5-Diphenyl-3-morpholinofuran (**1**) reacts with bromine and trifluoroacetic acid, giving respectively 2-bromo and 2-hydro furylium salts (**2,3**). The 2-hydroxy furylium bromide (**4**) was obtained by reaction of *cis*-morpholino-1,2-dibenzoylethylene (**5**) with hydrogen bromide. The nmr spectra of these salts show differences between the two morpholino dimethylene moieties of each caused by restricted rotation at the 3-immonium group. Chemical relationships studied include reductions to the morpholinofuran, conversions to 3-furanones, and the slow reaction of morpholinodibenzoylethylene with phenylmagnesium bromide to give *cis*-dibenzoylstyrene (**13**).

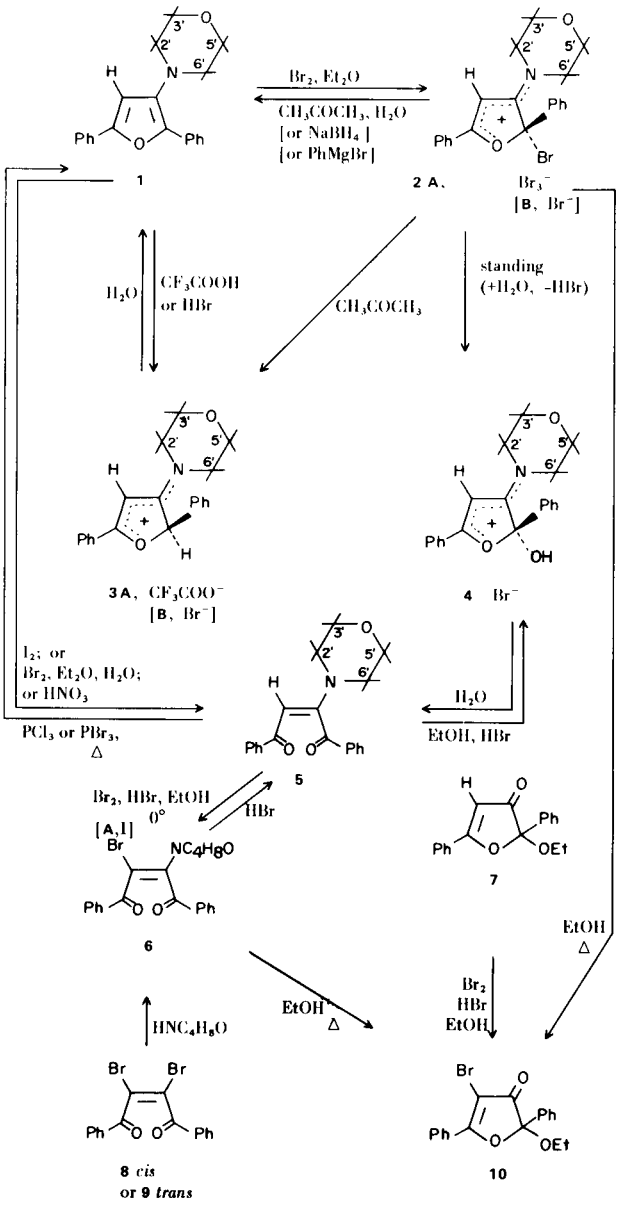
Interest in the facile bromine and phosphorus pentachloride oxidations of tetraphenylfuran and the mechanisms of these and comparable reactions of pyrroles (3) led us to investigate the action of bromine on furans carrying the strong electron donating tertiary amino group in position-3 which would highly activate the 2-position and promote reaction there rather than at the normally active open position-4 (4).

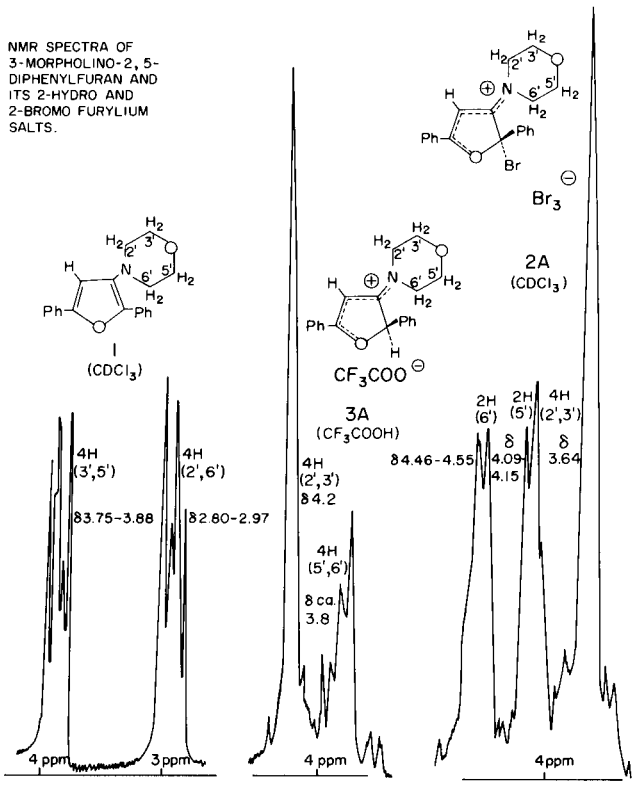
2,5-Diphenyl-3-morpholinofuran (**1**) reacted rapidly with two molecules of bromine in ether to give a stable salt-like adduct which on the basis of analysis, properties and reactions was formulated as 2,5-diphenyl-2-bromo-3-morpholinofurylium perbromide (**2A**). This reaction was obviously initiated by preferred and typical electrophilic attack of bromonium ion at the active 2-position of the cross-conjugated 2,3-enamine and 2,5-dienoxy system. The resulting perbromide **2A** is a σ-complex which is unique in its stability relative to the inherently unstable intermediate σ-complexes assumed in ordinary furan and pyrrole oxidation and substitution reactions (3).

The structure **2A** is supported by the bathochromic shift in infrared frequency from 1600 cm^{-1} for the morpholinofuran enamine double bond of **1** to 1640 cm^{-1}, which is attributable to the formation of the conjugated 3-immonium group. This is in analogy with the infrared shift observed in the formation of comparable salts of enamines (5). Consistent with this evidence there was observed a marked 23 nm bathochromic shift in the principal ultraviolet absorption band in going from the morpholinofuran **1** to the perbromide **2A**, which also is attributable to formation of the immonium group.

The nucleophile **1** would be expected to react as an enamine toward strong acid (6) and to undergo protonation at C-2 to give the immonium cation **3**, an analog of **2**. This was shown to occur by adding two equivalents of trifluoroacetic acid to a chloroform solution of **1**; this resulted in 13-18 nm bathochromic shifts in the ultraviolet absorptions. The nmr spectrum of **1** observed in deuteriochloroform showed the expected signals (see figure). In trifluoroacetic acid it showed two one-proton singlets, δ 6.87 and 7.03, which indicated that protonation had occurred at C-2. Assignment of the resonance signal at δ 6.87 to the benzylic 2-proton is based on the absence of this signal in the spectrum of **1** observed in deuteriotrifluoroacetic acid. Had **1** behaved as a typical aromatic amine and undergone protonation at the nitrogen atom rather than at C-2, one would have expected this signal to appear farther downfield (5,6). The signal at δ 7.03 must represent the vinyl proton at position-4.

The structures of salts **3A** and **2A** receive strong support from the nmr absorptions in deuteriochloroform of the morpholino groups which in each case show magnetic non-equivalence of their dimethylene moieties (see figure). The positive charge localized largely on nitrogen evidently deshields the *N*,2′-methylene protons and shifts their signals downfield into near coincidence with those of the respective *O*,3′-methylene protons, making them magnetically nearly equivalent, and giving rise to 4-proton singlets assignable to the respective 2′,3′-dimethylene moieties nearer the furyl C-4 (7). The 3-furyl exocyclic immonium double bond in preventing rotation of the morpholino group in the two cases, forces the 5′,6′-dimethylenes





toward the furyl C-2 into the shielding and deshielding regions of the 2-substituents, causing them to become magnetically different from the respective 2',3'-dimethylene moieties and giving rise to the respective pairs of 4-proton multiplets (7). The relatively upfield position of the 4-proton multiplet for the 5,6-dimethylene of **3A** is attributed to a shielding effect by the noncoplanar 2-phenyl group, and the relatively downfield positions of the two 2-proton multiplets of **2A** are ascribed to a net deshielding by the combination of phenyl and bromine (8) at the furyl C-2.

The 2-hydro and 2-bromo bromides **3B** and **2B** were obtained from **1** by the action in ether solutions of hydrogen bromide, and of one molecule of bromine, respectively. They were only moderately stable. Two equivalents of trifluoroacetic acid in deuteriochloroform were required to maintain the proton at C-2 of **3A** and to observe the nmr spectrum free from interference by the presence and absorption of free furan **1**. The second 2-substituent in the salts **3A** and **2A** is held by the accommodation of the positive charge by the nitrogen. Without this 3-nitrogen, stable furylium salts have been isolated only where there are 5,5-diphenyl groups which can neither leave the molecule carrying the positive charge nor migrate and allow furanization [*e.g.* the stable 2,3,4,5,5-pentaphenylfurylium salts (4e,9)].

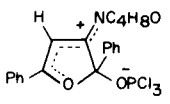
The perbromide **2A** has the brominating and oxidizing power corresponding to two bromine molecules, one stemming from the perbromide ion and the other from the 2-bromine which is very "positive". It is reduced to the furan **1** by sodium borohydride, through reductive displacement of the 2-bromine, or possibly by hydride attack at C-3 or C-5 with subsequent loss of hydrogen bromide. It is nearly quantitatively reduced to the hydrofurylium bromide **3B** by acetone with evident formation of bromoacetone. In refluxing ethanol, utilizing all of its oxidizing power with self bromination at C-4, and also undergoing hydrolytic steps, it gave 2,5-diphenyl-2-ethoxy-4-bromo-3-furanone (**10**) (10) which was produced also by the action of alcoholic hydrogen bromide on morpho-

linobromodibenzoylethylene (**6**), and by bromination of 2,5-diphenyl-2-ethoxy-3-furanone (**7**) in ethanol containing hydrogen bromide.

Upon standing for several weeks **2A** lost a molecule of bromine and at the same time became hydrolyzed by atmospheric moisture, with formation of 2,5-diphenyl-3-morpholino-2-hydrofurylium bromide (**4**) which retained the furan ring skeleton and is an analog of the salts **2** and **3**. The salt character of **4** is shown by the ready liberation of *cis*-morpholinodibenzoylethylene (**5**) from which the salt **4** could be remade by the action of ethereal hydrogen bromide. Infrared, ultraviolet and nuclear magnetic resonance spectra support the acyclic structure for the base **5**, and they support the cyclic structure for the salt **4** by their close analogies with the spectra of the salts **2A** and **3A** (11).

The formation of morpholinodibenzoylethylene (**5**) rather than the furan **1** from **2A** may be understood in terms either of hydrolysis of the 2-bromo group or of slow liberation of the furan **1** and its subsequent oxidation to **5** by the released bromine in the presence of atmospheric moisture. Empirically the overall reaction from **1** through **2A** to **5** constitutes a furan oxidation which can be brought about in a one-step process, either by nitric acid, by iodine in moist ether (2), or by the action of bromine in ethanol (**4** crystallizing). Compound **2A** is a relatively stable σ-complex which, although able to lose bromine, does not itself readily undergo self-bromination at its enamine β-carbon because of the diminution of its nucleophilicity by the positive charge. Bromination at position-4 can occur, of course, when the enamine system is liberated from the salt; in a separate experiment *cis*-morpholinodibenzoylethylene (**5**) was easily brominated, giving its bromo derivative **6**.

From the foregoing it seemed certain that *cis*-morpholinodibenzoylethylene (**5**) would be reducible by phosphorus trichloride through *cis*-group participation in a reductive-furanization, presumably *via* the reversibly formed intermediate complex **11** where the positive charge would be localized largely on nitrogen and where the phosphorus atom on oxygen would carry a negative charge. Such an unstable complex upon heating should break down irreversibly into the stable entities, phosphoryl trichloride and the aromatic morpholinofuran **1**. Such a reductive furanization to **1** did indeed occur, albeit slowly, and phosphorus tribromide reacted similarly (12).



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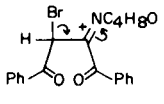

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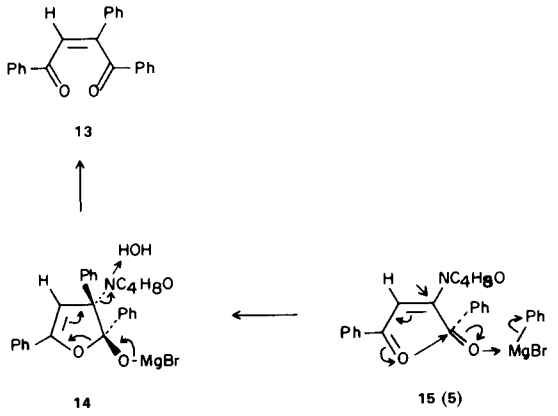
The noteworthy brominating reactivity of morpholinobromodibenzoylethylene (**6**) which seems to involve hydrogen bromide, is illustrated by its bromination of acetone and reduction thereby to morpholinodibenzoylethylene (**5**). The brominating action of **6** can be rationalized in terms of an equilibrium species such as **12** where the bromine would be "positive" and very reactive in an oxidative sense.

Treatment of the perbromide **2A** with phenylmagnesium bromide followed by ice-water quench gave two products in comparable yield: the furan **1**, the product of reduction, and morpholinodibenzoylethylene (**5**), the result of hydrolysis. The latter compound **5** was shown in a separate experiment to be relatively unreactive toward phenylmagnesium bromide. This is understandable in terms of complex formation and of steric and electronic effects which would stabilize the molecule and interfere with the several normal types of additions by this nucleophilic reagent. However, **5** does react *very slowly* with phenylmagnesium bromide. In a typical experiment 50% of **5** was recovered, and *cis*-dibenzoylstyrene (**13**) was isolated in 2.6% yield. Had the latter been produced free in the reaction mixture it would have reacted further (2d); therefore its formation from **15** (**5**) must be explained in terms of a stable intermediate cyclic enolate complex such as **14** which would release **13** only upon hydrolytic quenching with ketonization and elimination of morpholine.



EXPERIMENTAL (13)

NMR Spectra of 2,5-Diphenyl-3-morpholinofuran (**1**) (4).

These data are as follows: δ (deuteriochloroform); 6.67 (s, 1, vinyl), 2.8-3.0 and 3.7-3.9 (coupled 4 proton multiplets, CH_2CH_2); 7.2-7.6 (m, 6); 7.6-7.8 (m, 2) and 7.9-8.1 (m, 2, aromatic); δ in trifluoroacetic acid (**3A**, not isolated); 7.03 (s, 1, vinyl); 6.87 (s, 1, benzylic proton, disappearing on addition of deuterium oxide); 4.20 (s, 4, $C^2{}'H_2C^3{}'H_2$) overlapped by *ca.* 3.8 (m, 4, $C^5{}'H_2C^6{}'H_2$) (see figure); 7.6-8.3 (m, 10, aromatic).

2,5-Diphenyl-2-hydro-3-morpholinofurylium Bromide (**3B**).

This salt crystallized from a dry acetone solution of perbromide **2A** after it had been refluxed for 30 seconds and cooled; m.p. *ca.* 220° dec. The ir spectra of this and of a sample made from **1** by precipitation from ethereal hydrogen bromide were identical.

Anal. Calcd. for $C_{20}H_{20}BrNO_2$: C, 62.18; H, 5.18; N, 3.62. Found: C, 62.05; H, 5.12; N, 3.45.

2,5-Diphenyl-3-morpholino-2-bromofurylium Perbromide (**2A**).

To a stirred solution of 3 g. (0.01 mole) of **1** in 300 ml. of dry ether, was added dropwise a 3.6 g. (0.022 mole) of bromine. The orange precipitate was filtered and washed with dry ether: light yellow, m.p. 154-156° dec.; ir (potassium bromide pellet) 1640 cm^{-1}; uv (chloroform), 275, 360 nm (ϵ^{-3} 16.9, 15.2); nmr (deuteriochloroform) see figure; δ 7.4-7.87 (m, 6) and 8.1-8.3 (m, 4, aromatic), 7.25 (s, 1, vinyl), 4.4-4.65 (m, 2, $NC^{6'}H_2$), 4.0-4.2 (m, 2, $OC^{5'}H_2$), 3.4-3.9 (s, unsymmetrical, 4, $C^{2'}H_2C^{3'}H_2$).

Anal. Calcd. for $C_{20}H_{19}BrNO_2 \cdot Br_3$: C, 38.43; H, 3.06. Found: C, 38.38; H, 3.07.

Reactions of Perbromide **2A**.

(A) A solution of 4 g. of **2A** in 100 ml. of dry acetone after refluxing for 30 seconds was diluted with water and cooled; yield of **1**, 1.75 g. (89%), m.p. 111-114°. The formation of a lachrimator (bromoacetone) was noted. (B) To a suspension of 0.5 g. of **2A** in 6 ml. of diglyme was added 0.5 g. of sodium borohydride with stirring for one hour; quenching in ice water gave **1**, 0.2 g. (75%). (C) Reaction of **2A** with phenylmagnesium bromide (6 equivalents in ether) gave **1** (40%) and **5** (43%).

2,5-Diphenyl-3-morpholino-2-bromofurylium Bromide (**2B**).

This was prepared like **2A** but using *one* equivalent of bromine, m.p. 148-151° (dried *in vacuo;* C-analysis was 2% high, evidently due to partial decomposition). An ethanol solution after 1 hour at 0° and quenching in aqueous sodium carbonate gave **5** (82%). Treatment of **2B** with bromine by dropwise addition to an ethanol solution containing a small quantity of hydrogen bromide, and heating for 5 minutes, gave **10** (50%). Ir and uv spectra were very similar to, but not identical with, those of **2A**.

3,4-Dibromo-2,5-diphenylfuran (**14**).

This was made in 88% yield from 2,5-diphenylfuran by dropwise addition of bromine in acetic acid over 13 hours; m.p. 88.5-89°.

cis-Morpholino-1,2-dibenzoylethylene (**5**) (4a).

Preparations: (A) Treatment of 8 g. of dibenzoylacetylene (4c) in 200 ml. of acetone with 8 ml. of morpholine (10 minutes at 40°), cooling and concentrating, gave 10 g. of **5**; yellow, m.p. 174-176°. (B) Addition of 1 equivalent of bromine to the furan **1** in ethanol, quenching with water, ether extractions, and crystallization from ethanol, yielded **5** (73%). (C) Dropwise addition of 2.61 g. of bromine to a solution of **1**, 5 g., in 500 ml. of water and 75 ml. of concentrated hydrochloric acid, allowing the mixture to stand for 30 minutes, quenching in aqueous sodium carbonate, and crystallization of the precipitate from ethanol, yielded 2.1 g. of **5** (40%). Using twice as much bromine, only the 2-ethoxyfuranone **10** was obtained. (D) The action of iodine in moist ether on **1** gave **5** and a second product which analyzed for the iodo analog of **6[A]**, m.p. 154-156° (12).

NMR Spectra of *cis*-Morpholinodibenzoylethylene (**5**) and its Perfluoroacetate.

These data are as follows: δ of **5** in deuteriochloroform, 6.2 (s, 1, vinyl), 3.35 and 3.70 (m, 8, equivalent CH_2CH_2 groups), 7.25-7.65 (m, 6) and 7.8-8.2 (m, 4, aromatic); the trifluoroacetate analog of **4** (not isolated); δ of **5** in deuteriochloroform plus 2 equivalents of trifluoroacetic acid; 6.77 (s, 1, vinyl), 3.93 (s, 4, $C^{2'}H_2C^{3'}H_2$) overlapped by 3.64 (broad multiplet, 4, $C^{5'}H_2C^{6'}H_2$), 7.5-7.8 (m, 6) and 7.9-8.2 (m, 4, aromatic); the hydroxyl proton of the trifluoroacetate appears only as a part of the trifluoroacetic acid proton peak, indicating rapid proton exchange; δ of **5** in trifluoroacetic acid; 6.83 (s, 1, vinyl) 4.17 (s, 4, $C^{2'}H_2C^{3'}H_2$), 7.45-7.86 (m, 6) and 7.97-8.20 (m, 4, aromatic).

Reactions of *cis*-Morpholinodibenzoylethylene (**5**).

(A) Treatment with 3 equivalents of phenylmagnesium bromide in ether for 2 hours at 30° followed by quenching in ice water gave 50% of unchanged **5** and 1.4% (corrected yield 2.6%) of *cis*-dibenzoylstyrene (**13**). (B) A solution of **5** in phosphorus trichloride was refluxed for 1.5 hours and quenched in ice and sodium carbonate. Extraction of the product with ether and fractional crystallization gave unchanged **5** and furan **1**; however, (C) using phosphorus tribromide (10 ml., 100°, 2 hours) only **1** was obtained (83%) (12).

2-Hydroxy-2,5-diphenyl-3-morpholinofurylium Bromide (**4**).

This salt was obtained (A) from **5** by the action of ethereal hydrogen bromide, and (B) from perbromide **2A** by reaction spontaneously in the solid state upon standing for several weeks while exposed to the atmosphere. It was purified by washing with dry ether and recrystallization from acetone; m.p. 243-245°. Conversion of **4** to base **5** was effected by treatment with 5% aqueous sodium hydroxide or carbonate.

Anal. Calcd. for $C_{20}H_{20}BrNO_2$: C, 59.71; H, 5.01. Found: C, 59.61; H, 5.24.

3-Bromo-2-morpholino-1,4-diphenyl-2-butene-1,4-dione (morpholinobromo-1,2-dibenzoylethylene) (**6**).

(A) A solution of 1 g. of **8** (or **9**) in 50 ml. of dry ether and 1 g. of morpholine was allowed to stand (18 hours for **8** and 1 week for **9**). After evaporation the orange residue was washed with water and crystallized from methanol; 0.9 g. (89%). (B) Addition of bromine to a methanolic sodium methoxide solution of **5** gave **6** (77%). (C) A solution of 1 g. of **5** in absolute ethanol containing 0.5 g. of hydrogen bromide and 0.5 g. of bromine (0°, 45 minutes) gave 0.9 g. of **6** (72%); m.p. 120-121°; ir, 1670 cm^{-1} (carbonyl).

Anal. Calcd. for $C_{20}H_{18}BrNO_3$: C, 60.01; H, 4.53. Found: C, 60.10; H, 4.82.

The Hydrobromide of **6**.

This was obtained by the action of ethereal hydrogen bromide on **6** or by the action of bromine in ether on **5**, m.p. 145-147° (not analyzed).

The Action of Acetone on **6** with or without Added Hydrogen Bromide.

Refluxing for 10 minutes, cooling and treatment with sodium carbonate gave **5** (88%), m.p. 174-176°. Under different conditions in ethanol or ethanol-acetone mixture, containing hydrogen bromide, the products included the bromoethoxyfuranone **10** (10), the corresponding hydroxy analog **10B** (10), and **5**.

2-Ethoxy-4-bromo-2,5-diphenyl-3-furanone (**10**) (10).

Preparations: (A) Upon refluxing an ethanol solution of **2A**

for 5 minutes and cooling, a mixture of morpholine hydrobromide and **10** precipitated; this was separated by fractional crystallization from ethanol, m.p. 104-106° (32%). (B) A solution of 0.3 g. of 2-ethoxy-2,5-diphenyl-3-furanone (**7**) in 50 ml. of absolute ethanol containing 0.2 g. of hydrogen bromide and 0.17 g. of bromine, was refluxed for 5 minutes. Evaporation gave **10**, 0.33 g., m.p. 105-107° (86%) (bromine in ethanol without hydrogen bromide did not react with **7**). (C) The action of ethanolic hydrogen chloride on 2-benzoyloxy-4-bromo-2,5-diphenylfuran (10) (heated for 15 minutes) gave **10**. (D) Treatment of **5** with one equivalent of bromine in chloroform (long standing) followed by evaporation and fractional crystallizations of the residue from ethanol, gave **10** (15%), m.p. 105-107° (lit.(10b) 95°); ir, 1720 cm^{-1} (furanone C=O). It was stable toward refluxing acetone-alcohol mixture containing hydrogen bromide (refluxing for 5 minutes).

Anal. Calcd. for $C_{18}H_{15}BrO_2$: C, 60.18; H, 4.21. Found: C, 59.99; H, 4.18.

Unsuccessful Attempts to Obtain 2,5-Diphenyl-3-bromo-4-morpholinofuran.

(A) Acetic anhydride and a trace of sulfuric acid did not react with 2-bromo-1,4-diphenyl-3-morpholino-1,4-butanedione (4c) at 50°. At temperatures above this **5** was obtained which is the product of dehydrobromination. (B) The action of 33% hydrogen bromide in acetic acid gave *trans*-dibenzoylethylene (11%) presumably the result of reduction of the α-bromine (15) followed by elimination of morpholine.

Unsuccessful Attempts to Obtain 3,4-Dimorpholino-2,5-diphenylfuran.

Reactions did not occur between (A) 1,4-diphenyl-2,3-dimorpholino-1,4-butanedione (4c) and acetic anhydride and sulfuric acid, or (B) between 3,4-dibromo-2,5-diphenylfuran, morpholine and cuprous oxide at 250° for 48 hours.

1,3,4-Triphenyl-2-morpholino-1,4-butanedione, (**16**).

A mixture of 6 g. of morpholine and 10 g. of *cis*-dibenzoylstyrene (**13**) crystallized upon standing for 30 minutes. Recrystallization from ethanol gave 5.4 g. of **16** (75%). Using *trans*-dibenzoylstyrene the yield of **16** was 93%, m.p. 223.5-225°.

Anal. Calcd. for $C_{26}H_{25}NO_3$: C, 78.17; H, 6.30. Found: C, 78.12; H, 6.17.

3-Morpholino-2,4,5-triphenylfuran (**17**).

A solution of 10 g. of **15** in 50 ml. of acetic anhydride and 1 ml. of concentrated sulfuric acid was heated at 110-115° for 15 minutes and hydrolyzed. Work-up and crystallizations from ethanol gave 0.53 g. (6%), m.p. 211-212°; UV max (ethanol), 234, 279, 308 nm (ϵ^{-3} 22.9, 13.4, 22.8).

Anal. Calcd. for $C_{26}H_{23}NO_2$: C, 81.86; H, 6.08. Found: C, 81.65; H, 6.02.

REFERENCES

(1) Supported by grants from the Office of Ordnance Research, U. S. Army, and the National Science Foundation (G9494, CP8631).

(2) Ph.D. Dissertations, University of Virginia: (a) W. M. Hankins, 1969; (b) W. J. Welstead, 1961; (c) C. L. Dickerson, 1953; (d) J. I. Dale, 1962.

(3a) R. E. Lutz and W. J. Welstead, *J. Am. Chem. Soc.*, **85**, 755 (1963); (b) R. E. Lutz and D. W. Boykin, *J. Org. Chem.*, **32**, 1179 (1967); (c) R. E. Lutz, W. J. Welstead, R. G. Bass and J. I. Dale, *ibid.*, **27**, 1111 (1962).

(4a) R. E. Lutz, P. S. Bailey and N. H. Shearer, *J. Am. Chem. Soc.*, **68**, 2224 (1946); (b) R. E. Lutz, T. Amacker, S. M. King and N. H. Shearer, *J. Org. Chem.*, **15**, 181 (1950); (c) R. E. Lutz and W. R. Smithey, *ibid.*, **16**, 51 (1951); (d) S. M. King, C. R. Bauer and R. E. Lutz, *J. Am. Chem. Soc.*, **73**, 2253 (1951); (e) For stable furylium salts, see L. P. Tenney, W. M. Hankins, R. E. Lutz and D. W. Boykin, *J. Heterocyclic Chem.*, **5**, 435 (1968), and references cited therein. (f) *cf.* Phosphorus pentachloride conversion of 3-acetoxy-2,5-diphenylfuran, at 25-40° to 2-chloro-2,5-diphenyl-3-furanone, and at 100° to 3,4-dichloro-2,5-diphenylfuran; R. E. Lutz, A. H. Stuart, F. N. Wilder and W. C. Connor, *J. Am. Chem. Soc.*, **59**, 2312 (1937).

(5a) B. Witkop and J. B. Patrick, *ibid.*, **75**, 4474 (1953); (b) D. E. Edwards, F. N. Clarke and B. Douglas, *Can. J. Chem.*, **32**, 235 (1954); (c) N. J. Nelson and V. W. Gash, *J. Am. Chem. Soc.*, **76**, 2781 (1954).

(6) A variety of 2-amino substituted furans have been shown by nmr spectroscopy to behave toward acids, not like typical aromatic amines with formation of simple ammonium salts, but rather as enamines or dienamines with formation of immonium salts: *e.g.*, 2-amino-3-cyano-4,5-dimethylfuran in trifluoracetic acid adds the proton at carbon-5. C. T. Wie, S. Sunder, and C. D. Blanton, Jr., *Tetrahedron Letters*, **44**, 4605 (1968).

(7) *cf.* The interpretation of the nmr spectrum of *N*-thioacetylmorpholine, $CH_3C(=\bar{S})=\overset{+}{N}C_4H_8O$ by R. H. Bible, "Guide to the NMR Empirical Method," Plenum Press, New York, 144, 1967.

(8) *cf.* Long range deshielding effect of halogen: R. C. Fort, Jr., J. W. H. Cheeseman and E. C. Taylor, *J. Org. Chem.*, **29**, 2440 (1964).

(9) It will be interesting to see whether or not 3-methoxy analogs of **1** would form salts sufficiently stable for isolation or detection under conditions comparable with those described above.

(10) R. E. Lutz and A. H. Stuart, *J. Am. Chem. Soc.*, (a) **59**, 2322 (1937); (b) **58**, 1885 (1936).

(11) An acyclic formulation had been suggested earlier for **4** involving protonation at the 4-carbonyl oxygen of **5**. R. E. Lutz and S. M. King, *J. Org. Chem.*, **17**, 1524 (1952).

(12) Reactions carried out by Dr. C. J. Ohnmacht, Postdoctoral Research Assistant; to be reported later.

(13) NMR: Perkin-Elmer R-20 (60 Mcps). Known compounds obtained in reactions were identified by ir spectra or/and mixture melting points with authentic samples.

(14) R. E. Lutz, *J. Am. Chem. Soc.*, **48**, 2916 (1926).

(15) M. Couper and R. E. Lutz, *J. Org. Chem.*, **7**, 79 (1942).

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