# Isoimidium Salts derived from Diphenylmethylenesuccinic Acid and their Conjugate Bases. Ene-type Reactions involving Transfer of Acyl Groups

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The amic acids (2a—d), obtained from diphenylmethylenesuccinic anhydride and amines, were converted into the isoimidium perchlorates (4a—d). Deprotonation of the ternary salts yielded the isolable butenolides (5a—c), which formed ene-type adducts (8) and (9) with aromatic aldehydes and carbon disulphide, respectively. The action of arenediazonium salts led to novel 1-aryl-4-diphenylmethylene-4H-pyrazolin-5-ones (11). A different type of diphenylmethylenesuccinisoimidium salt, compound (12), was prepared and attempts to convert it into the cross-conjugated 1,3-dipole (13) are described. The action of acetic anhydride on the 1-monomorpholide (3a) of diphenylmethylenesuccinic acid results in the formation of 1-acetoxy-3-morpholinocarbonyl-4-phenylnaphthalene (20a) *via* a mixed anhydride.

THE synthesis of succinisoimidium and homophthaliso-imidium salts and the properties of the corresponding bases are described in the preceding papers. This article concerns isoimidium salts derived from diphenyl-methylenesuccinamic acids and the chemistry of their conjugate bases.

Diphenylmethylenesuccinic anhydride (1) reacted with morpholine, piperidine, pyrrolidine, and aniline to give in each case a single product, which is assigned the 4-amic acid structure (2) rather than the alternative (3) in accordance with the greater electrophilic character of C-4 over that of C-1, the electron deficiency of the latter being reduced by conjugation with the phenyl groups. This mode of ring-opening leads to the formation of the corresponding 4-ester when the anhydride is treated with ethanol.[1] The structure of the anilic acid (2d) was confirmed as follows: the derived isoimidium salt (4d) was treated with ethanol to give the ester (6; X = NHPh); this ester was also obtained by the action of aniline and dicyclohexylcarbodi-imide on 1-monoethyl diphenylmethylenesuccinate (6; X = OH), the product[2] of the Stobbe condensation of benzophenone with diethyl succinate.

The amic acids (2a—d) were converted into the pale

yellow isoimidium perchlorates (4a—d) by means of acetic anhydride and perchloric acid. The salts are somewhat hygroscopic; their i.r. spectra exhibit carbonyl absorptions at the typically high frequencies of 1 860—1 840 and C=N⁺ bands near 1 700 cm⁻¹. Deprotonation of the ternary salts (4a—c) with triethylamine gave the orange crystalline butenolides (5a—c), which were isolated without difficulty, in contrast to the correspond-ing compounds in the succinic acid series, whose existence could only be demonstrated by trapping experiments (see preceding papers). However, the butenolides de-composed at room temperature, the diethylamino-derivative (5c) most rapidly, and they could not be re-crystallised. Their structures are in accord with their spectroscopic properties, in particular γ-lactone carbonyl absorptions at 1 780—1 770 cm⁻¹ and the appearance of singlets due to olefinic protons at δ *ca.* 5, and, in the case of (5a), by its reaction with perchloric acid, which regenerated the isoimidium salt (4a). The morpholino-derivative (5a) disproportionated on heating to a mixture of the anhydride (1) and dimorpholide (7) of diphenyl-methylenesuccinic acid; the dimorpholide was also obtained by the action of morpholine on the isoimidium perchlorate (4a).

The diphenylmethylenebutenolides (5), like the 2-benzopyran-1-ones and 2,3-dihydrofuran-2-ones, dis-

[1] H. Stobbe, *Ber.*, 1911, **44**, 1297.
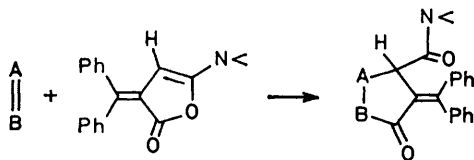[2] H. Stobbe, *Annalen*, 1894, **282**, 280.

cussed in the preceding paper, contain the structural unit $>C=C(NR_2)-O-CO-$ and were therefore expected to undergo ene-type additions to electrophilic partners (see

ations were made in the case of the $p$-nitrophenyl analogue (8b): the n.m.r. spectrum of the crude reaction product indicated the presence of the *trans*-compound



a; N< = morpholino      c; N< = NEt₂
b; N< = piperidino      d; N< = NHPh
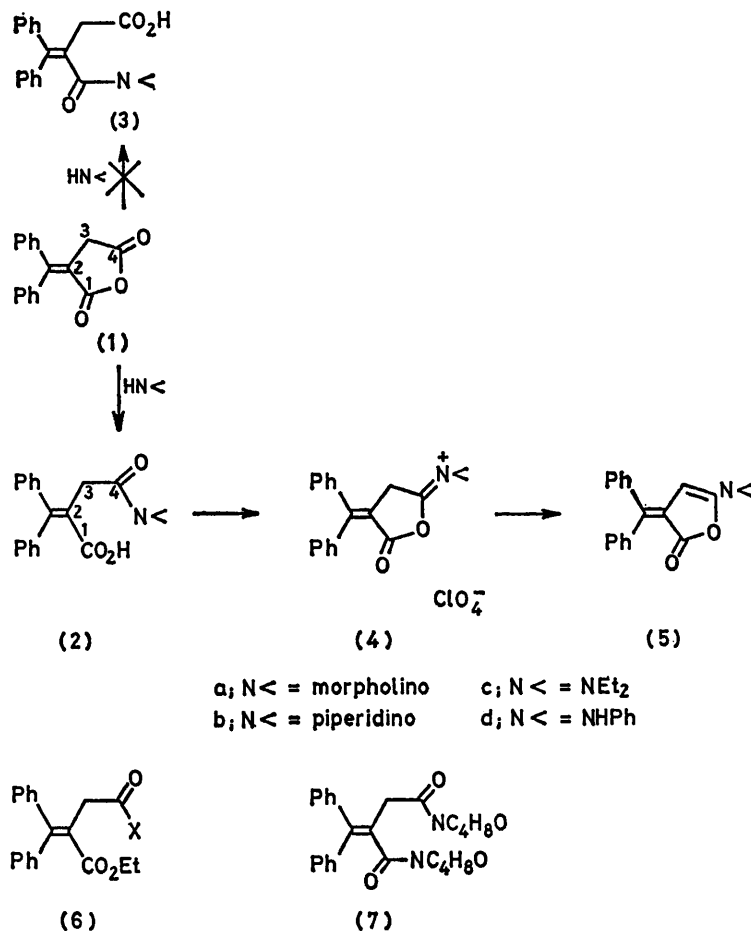
Scheme).[3] The morpholinobutenolide (5a) did react in this fashion with benzaldehyde and $p$-nitrobenzaldehyde to yield the adducts (8a and b) as mixtures of geometrical



SCHEME

isomers, in which the *cis*-forms predominated to the extent of 3 : 1 for (8a) and 7 : 1 for (8b). The *trans*-benzaldehyde adduct (8a) showed $J_{AB}$ 2.4 Hz, but the *cis*-compound, which was isolated after fractional crystallisation, appeared to contain two conformational isomers, since its n.m.r. spectrum exhibited doublets at $\delta$ 5.54 and 4.22, and at 5.38 and 4.31, due to two pairs of adjacent methine protons; the doublets were split by 6.5 and 6.0 Hz in the two conformers. Similar observ-

[3] A. E. Baydar, G. V. Boyd, R. L. Monteil, P. F. Lindley, and M. M. Mahmoud, *J.C.S. Chem. Comm.*, 1976, 650.

($J$ 1.2 Hz); the spectrum of the isolated *cis*-isomer contained two pairs of doublets with coupling constants of 7.0 and 6.3 Hz. The exact geometry of the *cis*-furanones is under investigation.

The morpholino-derivative (5a) did not react with cyclopentanone or cyclohexanone nor with the carbon enophiles dimethyl acetylenedicarboxylate, dimethyl fumarate, or $N$-phenylmaleimide; treatment with carbon disulphide, however, gave a quantitative yield of the orange adduct (9a); the piperidino-analogue (9b) was obtained from compound (5b). The action of arene-diazonium fluoroborates on the butenolides (5a—c) in the presence of triethylamine led to the pyrazolinones (11a—h), presumably *via* the adducts (10). The products are noteworthy because they are the first pyrazolinones possessing diarylmethylene substituents.

*An Isomeric Diphenylmethylenesuccinisoimidium Salt.* —We prepared an isoimidium perchlorate of the 1-amic acid series (3). The required monomorpholide (3a) was obtained by alkaline hydrolysis of the dimorpholide (7); attack at the more electrophilic and less hindered 4-carbonyl group of (7) was expected and is in line with

the alkaline hydrolysis of the diethyl ester (6; X = OEt) to yield 4-monoethyl diphenylmethylenesuccinate (6; X = OH).[1] Treatment of the amic acid (3a) with acetic anhydride and perchloric acid gave the yellow morpholino-isoimidium perchlorate (12) in excellent yield, whose structure follows from its analysis, its spectroscopic properties, and from its reaction with morpholine, which regenerated the dimorpholide (7).
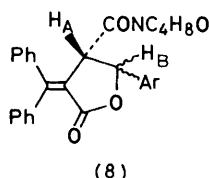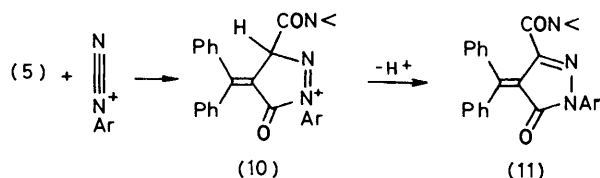


(8)

a; Ar = Ph
b; Ar = p-NO$_2$·C$_6$H$_4$
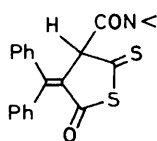
(9)

a; N< = morpholino
b; N< = piperidino

(5) +



(10)                                (11)

a; Ar = Ph, N< = morpholino
b; Ar = p-ClC$_6$H$_4$; N< = morpholino
c; Ar = p-NO$_2$·C$_6$H$_4$, N< = morpholino
d; Ar = m-NO$_2$·C$_6$H$_4$, N< = morpholino
e; Ar = p-MeOC$_6$H$_4$, N< = morpholino
f; Ar = Ph, N< = piperidino
g; Ar = p-ClC$_6$H$_4$, N< = piperidino
h; Ar = p-ClC$_6$H$_4$, N< = NEt$_2$

The isomeric acids (2a) and (3a) and the derived iso-imidium salts (4a) and (12) were similar; for instance, the latter show carbonyl absorption at 1 840 and 1 870 cm$^{-1}$, respectively, and their methylene protons resonate at δ 4.31 and 3.97.

We investigated the deprotonation of the isoimidium salt (12) with the aim of producing the base (13), which incorporates the trimethylenemethane structure (14). Trimethylenemethanes are of continuing interest [4] and a number of hetero-analogues, which may be represented as cross-conjugated dipoles, are known. These include the transient allyl oxides (15),[5] the stable imidazolidines (16; X = S, NPh, or NCOR; Y = O or S),[6] and the stable betaines (17; n = 1 or 2).[7] Certain mesoionic systems also belong to this class.[8] The anhydro-base (13) would be the first cross-conjugated 1,3-carbon dipole. We hoped that the compound might be stabilised sterically by the phenyl substituents and

electronically by the push–pull of the morpholino and carbonyl groups.

When the perchlorate (12) was treated with triethylamine in benzene or acetonitrile red solutions resulted which became colourless within seconds. Their i.r. spectra exhibited a band at 1 820 cm$^{-1}$, attributed to a cyclic carbonyl group, which likewise decayed in a few seconds. Work-up of these solutions gave only the amic acid (3a). We thought that the red colour might be due to the fleeting existence of the dipolar base (13) and we attempted to trap it as a cycloadduct with 4-phenyl-1,2,4-triazoline-3,5-dione, N-phenylmaleimide, dimethyl acetylenedicarboxylate, and 1-diethylamino-propyne. However, when the deprotonation was carried out in the presence of any one of these reagents no adduct was obtained and the amic acid (3a) was isolated. With the object of providing additional stabilisation of the dipolar molecule by the introduction of an acetyl group [to give (18)], we treated the red solution, obtained from the perchlorate (12) and triethylamine in benzene, with acetyl chloride. The resulting red mixture yielded an intractable gum, whose i.r. spectrum showed no carbonyl absorptions beyond 1 630 cm$^{-1}$ and which therefore did not contain any of the desired acetyl derivative.

In a final attempt to prepare the acetyl compound we heated the amic acid (3a) with acetic anhydride and obtained a stable crystalline product C$_{23}$H$_{21}$NO$_4$, whose i.r. spectrum (1 772 and 1 640 cm$^{-1}$) and n.m.r. spectrum, which showed the presence of 10 aromatic protons and of the morpholino and acetyl groups, were compatible with formula (18). However, the lack of colour of the compound and its behaviour on hydrolysis indicated that it had a different structure. Treatment with cold hydrochloric acid or hot aqueous sodium hydrogen carbonate gave an acidic compound, C$_{21}$H$_{19}$NO$_3$, $v_{max.}$ 1 600 cm$^{-1}$, which gave a positive phenol reaction when coupled with p-methoxybenzenediazonium fluoroborate, and which reformed the original compound by the action of acetic anhydride. We considered that the phenol might be the naphthol (20b) and its precursor the corresponding acetate (20a). The formation of naphthalene derivatives is remarkably easy in the diphenylmethylenesuccinic acid series: thus Johnson and Goldman [9] obtained the ester (20c) by heating the half-ester (19) with a mixture of acetic anhydride, sodium acetate, and acetic acid. Attempts to degrade our morpholino-compound C$_{21}$H$_{19}$NO$_3$ to the known [9] phenolic acid (20d) failed because of the resistance of the morpholide to hydrolysis. The structure of the acetyl derivative was eventually shown to be (20a) by its unambiguous synthesis from the acid (20e) [9] and morpholine in the presence of dicyclohexylcarbodi-imide.

When the amic acid (3a) was briefly warmed with

[4] J. H. Davis and W. A. Goddard, III, J. Amer. Chem. Soc., 1977, 99, 4242, and references cited therein.

[5] H. M. R. Hoffmann, Angew. Chem. Internat. Edn., 1973, 12, 819.

[6] (a) A. E. Winberg and D. D. Coffmann, J. Amer. Chem. Soc., 1965, 87, 2776; (b) W. Schössler and M. Regitz, Chem. Ber., 1974, 107, 1931.
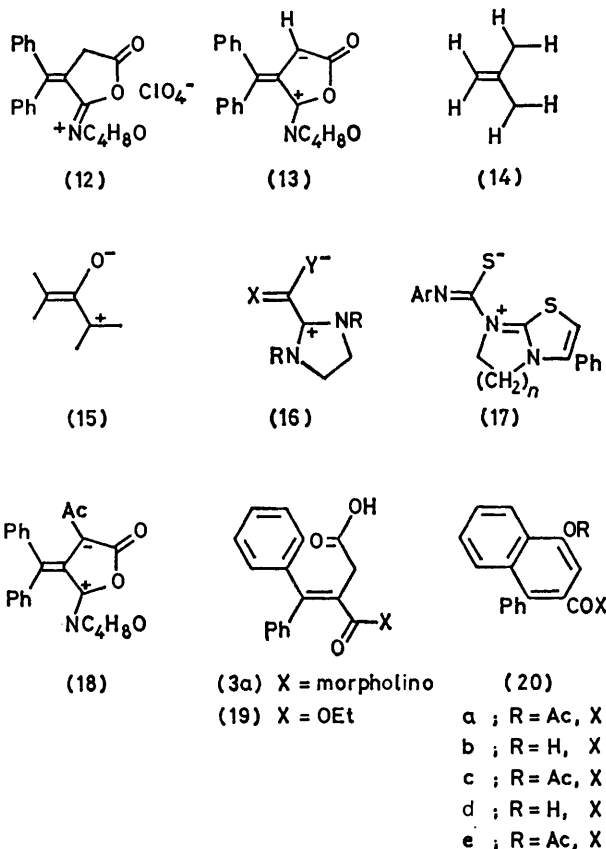
[7] W. Ried, W. Merkel, S.-W. Park, and M. Dräger, Annalen, 1978, 79.

[8] C. A. Ramsden, J.C.S. Chem. Comm., 1977, 109.

[9] W. S. Johnson and A. Goldman, J. Amer. Chem. Soc., 1945, 67, 430.

acetic anhydride an impure solid was isolated, whose i.r. spectrum (1 820, 1 750, and 1 616 cm$^{-1}$) and n.m.r. spectrum indicated that it was the mixed anhydride of

1 570 cm$^{-1}$, $\delta$([$^2$H$_6$]DMSO) 7.4—7.1 (m, 2 Ph) and 3.8—3.1 (12 H, m, CH$_2$ and piperidino) (Found: C, 75.4; H, 6.6; N, 3.75. C$_{22}$H$_{23}$NO$_3$ requires C, 75.6; H, 6.65; N, 4.0%);



(12)　(13)　(14)

(15)　(16)　(17)

(18)

(3a) X = morpholino
(19) X = OEt

(20)

a ; R = Ac, X = morpholino
b ; R = H, X = morpholino
c ; R = Ac, X = OEt
d ; R = H, X = OH
e ; R = Ac, X = OH

the amic acid with acetic acid. Hydrolysis or treatment with ethanol yielded the amic acid; attempted recrystallisation from boiling ethyl acetate resulted in the formation of the naphthalene (20a). It thus appears that the mixed anhydride is an intermediate in the cyclisation.

EXPERIMENTAL

I.r. spectra refer to Nujol mulls, light petroleum to the fraction boiling at 40—60°. Perchloric acid was of 70% strength.

*Diphenylmethylenesuccin-4-amic Acids* (2).—A solution of diphenylmethylenesuccinic anhydride (1) (2.64 g, 0.01M) in warm chloroform (10 ml) was treated dropwise with the appropriate amine (1 mol. equiv.) and then cooled; the product was precipitated by adding ether or light petroleum. The following were obtained: N-(3-*carboxy*-4,4-*diphenylbut-3-enoyl)morpholine* (2a) (3.18 g, 90%), m.p. 182.5—184.5° (from ethanol), $\nu_{max.}$ 2 700—2 300, 1 725, 1 600, 1 575, and 1 100 (morpholine ether) cm$^{-1}$, $\delta$([$^2$H$_6$]DMSO) 7.5—6.95 (m, 2 Ph), 3.38 (s, CH$_2$), and 3.85—3.08 (8 H, m, morpholino), *m/e* 351 ($M^+$), 334 ($M^+$ − OH), and 225 ($M^+$ − morpholino) (Found: C, 71.4; H, 6.15; N, 3.85. C$_{21}$H$_{21}$NO$_4$ requires C, 71.75; H, 6.0; N, 4.0%); N-(3-*carboxy*-4,4-*diphenylbut-3-enoyl)piperidine* (2b) (3.19 g, 91%), m.p. 226—228° (from ethanol), $\nu_{max.}$ 2 700—2 400, 1 725, and

N-(3-*carboxy*-4,4-*diphenylbut-3-enoyl)diethylamine* (2c) (2.94 g, 87%) (isolated by extraction of the reaction mixture with 0.5M-sodium hydrogencarbonate and subsequent acidification), m.p. 136—137° (from aqueous ethanol), $\nu_{max.}$ 3 060, 1 735, 1 710, and 1 590 cm$^{-1}$, $\delta$(CDCl$_3$) 12.55br (disappears on adding D$_2$O, OH), 7.32—7.1 (m, 2Ph), 3.32 (s, CH$_2$), 3.28 (2 H, q), 2.75 (2 H, q), 1.05 (3 H, t), and 0.72 (3 H, t, (2Et), *m/e* 337 ($M^+$), 320 ($M^+$ − OH), and 265 ($M^+$ − NEt$_2$) (Found: C, 74.7; H, 6.9; N, 4.0. C$_{21}$H$_{23}$NO$_3$ requires C, 74.75; H, 6.85; N, 4.15%); and N-(3-*carboxy*-4,4-*diphenylbut-3-enoyl)aniline* (2d) (3.49 g, 98%), m.p. 158.5—159° (from ethanol), $\nu_{max.}$ 3 290, 1 700, and 1 660 cm$^{-1}$ (Found: C, 77.0; H, 5.1; N, 3.8. C$_{23}$H$_{19}$NO$_3$ requires C, 77.3; H, 5.35; N, 3.9%).

*Diphenylmethylenesuccinisoimidium Salts* (4).—A suspension of the appropriate amic acid (2) (0.01M) in acetic anhydride (15 ml) was slowly treated with perchloric acid (1.5 ml); the resulting solution deposited the pale yellow isoimidium salt, which was collected, washed with ether, and stored in a vacuum desiccator. The following *tetrahydro-3-diphenylmethylenefuran-2-one perchlorates* were prepared: 5-*morpholinio-* (4a) (3.85 g, 88%), hygroscopic, m.p. 189—191° (decomp.), $\nu_{max.}$ 1 840, 1 710, and 1 080br cm$^{-1}$, $\delta$(CD$_3$CN) 7.55—7.0 (m, 2Ph), 4.31 (s, CH$_2$), and 4.05—3.4 (8 H, m, morpholino) (Found: C, 57.4; H, 4.8; Cl, 8.0; N, 3.15. C$_{21}$H$_{20}$ClNO$_7$,0.5H$_2$O requires C, 56.95; H, 4.8; Cl, 8.0; N, 3.15%); 5-*piperidinio-* (4b) (3.94 g,

91%), hygroscopic, m.p. 195—197° (decomp.), $\nu_{max.}$ 1 862, 1 838, 1 720, and 1 090br cm$^{-1}$, $\delta(CF_3CO_2H)$ 7.55—7.2 (m, 2Ph), 4.38 (s, CH$_2$), and 4.1—3.8 (4 H, m) and 1.85 (6 H, m) (piperidino) (Found: C, 60.3; H, 5.3; Cl, 8.5; N, 3.2. $C_{22}H_{22}ClNO_6,0.5H_2O$ requires C, 59.9; H, 5.3; Cl, 8.05; N, 3.2%); 5-*diethylammonio*- (4c) (3.51 g, 84%), hygroscopic, m.p. 190—192° (decomp.), $\nu_{max.}$ 1 855, 1 702, and 1 090br cm$^{-1}$, $\delta(CD_3CN)$ 7.5—7.2 (m, 2Ph), 4.27 (s, CH$_2$), and 3.87, 3.5 (4 H, two overlapping q) and 1.3 (6 H, t) (2Et) (Found: C, 59.0; H, 5.3; Cl, 8.3; N, 3.25. $C_{21}H_{22}$-$ClNO_6,0.5H_2O$ requires C, 58.8; H, 5.4; Cl, 8.45; N, 3.35%); and 5-*anilinio*- (4d) (3.30 g, 75%), m.p. 127.5—128.5° (decomp.), $\nu_{max.}$ 1 850, 1 680, and 1 110br cm$^{-1}$ (Found: C, 62.6; H, 4.35; N, 3.0. $C_{23}H_{18}ClNO_6$ requires C, 62.8; H, 4.15; N, 3.2%).

N-(3-*Ethoxycarbonyl*-4,4-*diphenylbut*-3-*enoyl)aniline* (6; X = NHPh).—(a) The solution obtained from the anilinio perchlorate (4d) (1.0 g) and ethanol (10 ml) was poured into water, giving the *ester* (0.52 g, 60%), m.p. 114.5—115.5° (from aqueous ethanol), $\nu_{max.}$ 3 350, 1 708, and 1 665 cm$^{-1}$ (Found: C, 77.6; H, 6.2; N, 3.4. $C_{25}H_{23}NO_3$ requires C, 77.9; H, 6.05; N, 3.65%).

(b) A solution of 3-ethoxycarbonyl-4,4-diphenylbut-3-enoic acid (6; X = OH) [2] (3.1 g), aniline (0.93 g, 1 mol. equiv.), and dicyclohexylcarbodi-imide (2.06 g, 1 mol. equiv.) in dichloromethane (40 ml) was set aside for 20 min and the precipitated $NN'$-dicyclohexylurea (1.77 g, 79%) was filtered off. The filtrate was evaporated and the residue recrystallised from aqueous ethanol to yield the ester (3.1 g, 80%), identified by m.p., mixed m.p., and its i.r. spectrum.

*Deprotonation of Diphenylmethylenesuccinisoimidium Salts* (4).—A stirred suspension of the appropriate isoimidium perchlorate (0.01M) in acetonitrile (freshly distilled from $P_2O_5$) (15 ml) was treated with triethylamine (1.01 g, 1 mol. equiv.), whereupon the orange conjugate base crystallised. The products decomposed on keeping and on attempted recrystallisation. The following 2,3-*dihydro*-3-*diphenyl-methylenefuran*-2-*ones* were obtained: 5-*morpholino*- (5a) (2.9 g, 85%), m.p. 157° (decomp.), $\nu_{max.}$ 1 780, 1 642, 1 580, and 1 110 cm$^{-1}$, $\delta(CDCl_3)$ 7.3 (s, 2Ph), 5.03 (s, CH), and 3.8—3.14 (8 H, m, morpholino), $m/e$ 333 ($M^+$) and 305 ($M^+$ − CO) (Found: C, 75.2; H, 5.8; N, 4.25. $C_{21}H_{19}NO_3$ requires C, 75.65; H, 5.75; N, 4.2%); 5-*piperidino*- (5b) (3.1 g, 94%), hygroscopic, m.p. 142° (decomp.), $\nu_{max.}$ 1 772 and 1 632 cm$^{-1}$, $\delta(CDCl_3)$ 7.27 (s, 2Ph), 5.00 (s, CH), and 3.2br (4 H, s) and 1.58br (6 H, s) (piperidino), $m/e$ 331 ($M^+$), 303 ($M^+$ − CO), and 247 ($M^+$ − piperidino) (Found: C, 78.0; H, 6.45; N, 3.9. $C_{22}H_{21}NO_2,0.5H_2O$ requires C, 77.9; H, 6.4; N, 4.05%), and 5-*diethylamino*- (5c) (2.8 g, 88%), decomposes within 24 h, m.p. 133° (decomp.), $\nu_{max.}$ 1 774 and 1 629 cm$^{-1}$, $\delta(CDCl_3)$ 7.26 (s, 2Ph), 4.92 (s, CH), and 3.21 (4 H, q) and 1.12 (6 H, t) (2Et) (Found: C, 76.0; H, 6.65; N, 4.4. $C_{21}H_{21}NO_2,0.5H_2O$ requires C, 76.05; H, 6.85; N, 4.25%).

*Reaction of the Butenolide* (5a) *with Perchloric Acid.*—A solution of compound (5a) (0.2 g) in acetonitrile (5 ml) was treated with perchloric acid until the orange colour was discharged; addition of ether precipitated the perchlorate (4a) (0.22 g, 85%), identified by its i.r. spectrum.

N-(3-*Morpholinocarbonyl*-4,4-*diphenylbut*-3-*enoyl)morpholine* (7).—(a) A solution of the butenolide (5a) (0.66 g) in benzene (10 ml) was refluxed for 10 h and then cooled, whereupon the dimorpholide (0.38 g, 90%) crystallised; it was identified (m.p., i.r., and t.l.c.) with the sample described

under (b). The filtrate was evaporated; t.l.c. and i.r. of the residue showed that it was essentially diphenyl-methylenesuccinic anhydride. Similar results were obtained when the thermolysis was carried out in boiling toluene or acetonitrile.

(b) Addition of the perchlorate (4a) (4.33 g, 0.01M) to a solution of morpholine (1.04 g, 1.2 mol. equiv.) and tri-ethylamine (1.01 g, 1 mol. equiv.) in acetonitrile (15 ml) gave a precipitate of the *dimorpholide* (7) (3.35 g, 79%), m.p. 229.5—231.5° (from benzene), $\nu_{max.}$ 1 635, 1 610, and 1 113 cm$^{-1}$, $\delta(CDCl_3)$ 7.75—6.9 (m, 2Ph), 3.87 (s, CH$_2$), and 3.69—2.6 (16 H, m, 2 × morpholino), $m/e$ 420 ($M^+$), 333 ($M^+$ − morpholino), and 308 ($M^+$ − morpholino − carbonyl) (Found: C, 71.4; H, 6.8; N, 6.8. $C_{25}H_{28}N_2O_4$ requires C, 71.4; H, 6.7; N, 6.65%).

*Reactions of the Morpholinobutenolide* (5a) *with Aldehydes.* —(a) A solution of the butenolide (0.666 g, 0.002M) and benzaldehyde (0.212 g, 1 mol. equiv.) in acetonitrile (10 ml) was refluxed for 2 h. The solvent was removed *in vacuo*. The n.m.r. spectrum of the residual cis- and trans-*tetrahydro*-4-*morpholinocarbonyl*-5-*phenyl*-3-*diphenylmethylenefuran*-2-*one* (8a) (0.85 g, 97%) showed $\delta(CDCl_3)$ 7.5—7.0 (m, 3Ph), 5.78 (d) and 4.39 (d) ($J_{AB}$ 6.5 Hz), 5.43 (d) and 4.39 (d) ($J_{AB}$ 6.0 Hz), 5.68 (d) and 3.8 (d) ($J_{AB}$ 2.4 Hz), and 3.8—3.0 (8 H, m, morpholino), cis : trans 3 : 1. Recrystallisation from ethanol gave the cis-*isomer*, m.p. 209—211° (softens at 202°), $\nu_{max.}$ 1 760, 1 630, 1 620, and 1 110 cm$^{-1}$, $\delta(CDCl_3)$ 7.4—7.2 (m, 3Ph), 5.54 (d) and 4.22 (d) ($J_{AB}$ 6.5 Hz), 5.38 (d) and 4.31 (d) ($J_{AB}$ 6.0 Hz), and 3.6—2.5 (8 H, m, morpholino) (the n.m.r. spectrum did not change over the temperature range 35—100°) (Found: C, 76.2; H, 5.7; N, 3.05. $C_{28}H_{25}NO_4$ requires C, 76.5; H, 5.75; N, 3.2%).

(b) A similar reaction of the butenolide with *p*-nitro-benzaldehyde on a 0.001M scale gave a 7 : 1 mixture of cis- and trans-*tetrahydro*-4-*morpholinocarbonyl*-5-p-*nitrophenyl*-3-*diphenylmethylenefuran*-2-*one* (8b) (0.44 g, 91%), $\delta(CF_3CO_2H)$ 8.5—7.1 (14 H, m, Ar), 6.12 (d) and 4.95 (d) ($J_{AB}$ 7 Hz), 5.87 (d) and 4.86 (d) ($J_{AB}$ 6.3 Hz), 4.36 (d, $J_{AB}$ 1.2 Hz) (the other doublet with $J$ 1.2 Hz appeared to be masked by one of the doublets with 6.3 or 7 Hz), and 4.0—3.1 (8 H, m, morpholino); recrystallisation from ethanol–acetic acid gave the cis-*isomer*, m.p. 249° (softens at 234°), $\nu_{max.}$ 1 762, 1 631, and 1 112 cm$^{-1}$, $\delta(CDCl_3)$ 8.4—7.1 (14 H, m, Ar), 5.68 (d) and 4.39 (d) ($J_{AB}$ 7 Hz), 5.55 (d) and 4.28 (d) ($J_{AB}$ 6.3 Hz) (ratio of 7 Hz: 6.3 Hz doublets 1 : 3), and 3.6—2.5 (8 H, m, morpholino) (Found: C, 69.2; H, 5.05; N, 5.75. $C_{28}H_{24}N_2O_6$ requires C, 69.4; H, 5.0; N, 5.8%); subsequent chromatography on silica gel, using ethyl acetate–light petroleum as eluant, gave a pure cis-isomer, m.p. 250—252°, $\delta(CDCl_3)$ 8.21 (2 H) and 7.45 (2 H) (AB, *p*-NO$_2$·C$_6$H$_4$), 7.45—7.0 (m, 2Ph), 5.65 (d) and 4.35 (d) ($J_{AB}$ 7 Hz), and 3.5—2.6 (8 H, m, morpholino).

*Tetrahydro*-3-*diphenylmethylene*-2-*oxothiophen*-5-*thiones* (9).—(a) A mixture of the morpholinobutenolide (5a) (3.33 g, 0.01M), carbon disulphide (7.6 g, 10 mol. equiv.), and acetonitrile (20 ml) was stirred for one week, during which time the orange 4-*morpholinocarbonyl derivative* (9a) (4.07 g, 99.6%) separated; it had m.p. 227—229° (decomp.) (from ethanol), $\nu_{max.}$ 1 695, 1 617, and 1 118 cm$^{-1}$, $\delta(CDCl_3)$ 7.5—7.0 (m, 2Ph), 3.9—2.8 (8 H, m, morpholino), and 2.0br (s, CH), $m/e$ 409 ($M^+$), 333 ($M^+$ − CS$_2$), and 3.23 ($M^+$ − morpholino) (Found: C, 64.2; H, 4.55; N, 3.05; S, 15.5. $C_{22}H_{19}NO_3S_2$ requires C, 64.5; H, 4.7; N, 3.4; S, 15.65%).

(b) A similar reaction of the piperidinobutenolide (5b) (0.331 g, 0.001M) gave the 4-*piperidinocarbonyl derivative*

(9b) (0.39 g, 93%), orange needles (from ethanol), m.p. 218—220°, $\nu_{max.}$ 1 698 and 1 612 cm⁻¹, δ(CDCl₃) 7.5—7.1 (2Ph, m), 3.6—2.5 (4 H, m), and 1.7—1.0 (6 H, m) (piperidino), and 2.05br (s, CH), m/e 407 (M⁺) and 323 (M⁺ − piperidino) (Found: C, 67.8; H, 5.0; N, 3.45; S, 16.1. C₂₃H₂₁NO₂S₂ requires C, 67.75; H, 5.2; N, 3.45; S, 15.7%).

*Reaction of the Butenolides (5) with Arenediazonium Salts.*—Triethylamine (0.101 g, 1 mol. equiv.) was slowly added to a stirred mixture of a butenolide (5) (0.001M), the appropriate arenediazonium fluoroborate (0.001M), and acetonitrile (20 ml); the resulting solution was stirred for 30 min, acetonitrile was removed, and the residue was washed with water. The following red 4-*diphenylmethylene-2-pyrazolin-5-ones* were obtained: 3-*morpholinocarbonyl-1-phenyl-* (11a) (0.404 g, 92%), m.p. 224—226.5° (from aqueous ethanol), $\nu_{max.}$ 1 690, 1 648, 1 585, and 1 112 cm⁻¹, δ(CDCl₃) 8.05—7.05 (m, 3Ph) and 3.8—3.1 (8 H, m, morpholino) (Found: C, 73.8; H, 5.3; N, 9.4. C₂₇H₂₃N₃O₃ requires C, 74.1; H, 5.3; N, 9.6%); 1-p-*chlorophenyl-3-morpholinocarbonyl-* (11b) (0.39 g, 83%), m.p. 225.5—227° (from acetone), $\nu_{max.}$ 1 710, 1 688, 1 650, 1 580, and 1 110 cm⁻¹, δ(CDCl₃) 7.86 (2 H) and 7.29 (2 H) (AB, p-ClC₆H₄), 7.43 (m, 2Ph), and 3.7—3.1 (8 H, m, morpholino) (Found: C, 68.6; H, 4.7; N, 8.8. C₂₇H₂₂ClN₃O₃ requires C, 68.7; H, 4.7; N, 8.9%); 3-*morpholinocarbonyl-1-p-nitrophenyl-* (11c) (0.404 g, 84%), m.p. 152—154° (from benzene), $\nu_{max.}$ 1 695, 1 642, 1 630, 1 590, and 1 110 cm⁻¹, δ(CDCl₃) 8.18 (2 H) and 7.2 (2 H) (AB, p-NO₂·C₆H₄), 7.46 (m, 2Ph), and 3.8—3.1 (8 H, m, morpholino) (Found: C, 66.9; H, 4.7; N, 11.5. C₂₇H₂₂N₄O₅ requires C, 67.2; H, 4.6; N, 11.6%); 3-*morpholinocarbonyl-1-m-nitrophenyl-* (11d) (0.419 g, 87%), m.p. 217—219° (from ethanol), $\nu_{max.}$ 1 698, 1 652, 1 584, and 1 112 cm⁻¹, δ(CDCl₃) 8.77—7.14 (14 H, m, Ar and 2Ph) and 3.8—3.1 (8 H, m, morpholino) (Found: C, 66.9; H, 4.65; N, 11.5%); 1-p-*methoxyphenyl-3-morpholinocarbonyl-* (11e) (0.42 g, 90%), m.p. 207.5—209° (from ethanol), $\nu_{max.}$ 1 688, 1 642, 1 630, 1 580, and 1 115 cm⁻¹, δ(CDCl₃) 7.74 (2 H) and 6.86 (2 H) (AB, p-MeOC₆H₄), 7.42—7.1 (m, 2Ph), 3.78 (s, Me), and 3.78—3.12 (8 H, m, morpholino) (Found: C, 71.5; H, 5.35; N, 8.8. C₂₈H₂₅N₃O₄ requires C, 71.9; H, 5.4; N, 8.9%); 1-*phenyl-3-piperidinocarbonyl-* (11f) (0.392 g, 90%), m.p. 192—194° (from ethanol), $\nu_{max.}$ 1 695, 1 640, and 1 584 cm⁻¹, δ(CDCl₃) 7.9—7.1 (m, 3Ph) and 3.5—2.9 (4 H, m), and 1.7—1.2 (6 H, m) (piperidino) (Found: C, 77.1; H, 5.7; N, 9.6. C₂₈H₂₅N₃O₂ requires C, 77.2; H, 5.8; N, 9.65%); 1-p-*chlorophenyl-3-piperidinocarbonyl-* (11g) (0.39 g, 83%), m.p. 194—195° (from ethanol), $\nu_{max.}$ 1 697, 1 640, and 1 587 cm⁻¹, δ(CDCl₃) 7.91 (2 H) and 7.31 (2 H) (AB, p-ClC₆H₄), 7.45br (s, 2Ph), and 3.6—3.0 (4 H, m), and 1.5—1.3 (6 H, m) (piperidino) (Found: C, 71.2; H, 5.1; Cl, 7.6; N, 8.7. C₂₈H₂₄ClN₃O₂ requires C, 71.55; H, 5.15; Cl, 7.55; N, 8.95%); and 1-p-*chlorophenyl-3-diethylcarbamoyl-* (11h) (0.404 g, 88%), m.p. 165.5—167° (from acetone), $\nu_{max.}$ 1 695, 1 644, and 1 585 cm⁻¹, δ(CDCl₃) 7.88 (2 H) and 7.3 (2 H) (AB, p-ClC₆H₄), 7.4br (s, 2Ph), 3.45 (2 H, q) and 1.28 (3 H, t) (Et), and 3.05 (2 H, q) and 0.78 (3 H, t) (Et) (Found: C, 70.3; H, 5.25; Cl, 7.8; N, 9.1. C₂₇H₂₄ClN₃O₂ requires C, 70.8; H, 5.3; Cl, 7.75; N, 9.2%).

3-*Morpholinocarbonyl-4,4-diphenylbut-3-enoic Acid* (3a).— A mixture of the dimorpholide (7) (4.20 g), potassium hydroxide (4.5 g), ethanol (60 ml), and water (5 ml) was heated under reflux for one week. The resulting solution was acidified with hydrochloric acid to give the *amic acid*

(3.6 g, 90%), m.p. 189—190° (from benzene), $\nu_{max.}$ 1 730, 1 580, and 1 110 cm⁻¹, δ(CDCl₃) 8.32br (s, disappears on adding D₂O, CO₂H), 7.5—7.0 (m, 2Ph), 3.38 (s, CH₂), and 3.6—2.8 (8 H, m, morpholino), m/e 351 (M⁺), 334 (M⁺ − OH), and 306 (M⁺ − CO₂H) (Found: C, 71.6; H, 5.85; N, 3.95. C₂₁H₂₁NO₄ requires C, 71.8; H, 6.0; N, 4.0%).

*Tetrahydro-5-morpholino-4-diphenylmethylenefuran-2-one Perchlorate* (12).—Perchloric acid (1.5 ml) was cautiously added to a suspension of the amic acid (3a) (3.51 g, 0.01M) in acetic anhydride (12 ml); the resulting solution was treated with ether to incipient turbidity whereupon the pale yellow *salt* (4.1 g, 94%) crystallised. It had m.p. 154—156°, $\nu_{max.}$ 1 870, 1 662, and 1 100br cm⁻¹, δ(CD₃CN) 7.65—7.05 (m, 2Ph), 3.97 (s, CH₂), and 3.8—3.2 (8 H, m, morpholino) (Found: C, 56.7; H, 4.75; N, 3.35. C₂₁H₂₀ClNO₇,0.5H₂O requires C, 57.0; H, 4.75; N, 3.15%). Addition of the salt (0.433 g) to a solution of morpholine (0.096 g, 1.1 mol. equiv.) in acetonitrile (6 ml) gave the dimorpholide (7) (0.39 g, 92%), identified by its i.r. spectrum.

*Experiments on* 1-*Acetoxy-3-morpholinocarbonyl-1-phenylnaphthalene* (20a).—(a) *Preparation.* A mixture of the amic acid (3a) (3.51 g) and acetic anhydride (12 ml) was refluxed for 40 h, when t.l.c. indicated that the reaction was complete. The *product* (20a) (3.47 g, 92.5%) crystallised on cooling. It had m.p. 149—150.5° (from ethyl acetate), $\nu_{max.}$ 1 772, 1 640, 1 597, and 1 110 cm⁻¹, δ(CDCl₃) 8.0—7.4 (9 H, m, Ar), 7.26 (s, 2-H), 3.7—2.8 (8 H, m, morpholino), and 2.45 (s, Me), m/e 375 (M⁺) (Found: C, 73.2; H, 5.8; N, 3.55. C₂₃H₂₁NO₄ requires C, 73.55; H, 5.65; N, 3.75%).

(b) *Hydrolysis.* The acetoxynaphthalene (20a) (0.375 g) was refluxed for 2 h with a mixture of aqueous sodium hydrogencarbonate (5%, 10 ml) and acetonitrile (7 ml); the solution deposited 3-*morpholinocarbonyl-4-phenyl-1-naphthol* (20b) (0.27 g, 81%), m.p. 243—245° (from ethyl acetate), $\nu_{max.}$ 1 600 and 1 115 cm⁻¹, δ([²H₆]DMSO) 8.4—7.2 (9 H, m, Ar), 6.98 (s, 2-H), and 3.98—3.05 (9 H, m, morpholino and OH), m/e 333 (M⁺) (Found: C, 75.3; H, 5.8; N, 4.1. C₂₁H₁₉NO₃ requires C, 75.65; H, 5.75; N, 4.2%). The naphthol (0.22 g, 66%) was also produced when the acetate (20a) (0.375 g) was stirred with concentrated hydrochloric acid (5 ml) for 2 h. Treatment of a solution of the naphthol in 2M-sodium hydroxide with p-methoxybenzenediazonium fluoroborate gave a red precipitate. A solution of the naphthol (0.333 g) in acetic acid (6 ml) and acetic anhydride (6 ml) was refluxed for 2.5 h. Addition of water (20 ml) gave the acetoxynaphthalene (20a) (0.29 g, 77%), identified by m.p., mixed m.p., and its i.r. spectrum.

(c) *Alternative synthesis of the acetoxynaphthalene* (20a). A solution of 1-acetoxy-3-carboxy-4-phenylnaphthalene (20e) [9] (1.02 g), morpholine (0.29 g, 1 mol. equiv.), and dicyclohexylcarbodi-imide (0.687 g, 1 mol. equiv.) in dichloromethane (14 ml) was set aside overnight and the precipitated dicyclohexylurea was collected. The filtrate was concentrated to yield the acetoxynaphthalene (20a) (0.6 g, 48%), m.p. 148—150° (from ethyl acetate), identified by its i.r. spectrum.

(d) A mixture of the amic acid (3a) (0.351 g) and acetic anhydride (10 ml) was warmed gently until a clear solution was obtained (ca. 30 s). The acetic anhydride was removed *in vacuo* and the residue (0.112 g) washed with ether. It had m.p. 114—119°, $\nu_{max.}$ 1 820, 1 750, 1 616, and 1 112 cm⁻¹, δ(CDCl₃) 7.4—7.1 (m, 2Ph), 3.42 (s, CH₂), 3.9—3.1 (8 H, m,

morpholino), and 2.18 (s, Me). The analysis was unsatisfactory. Attempted recrystallisation from boiling ethyl acetate gave the naphthalene derivative (20a). The impure solid (0.1 g) was stirred with 2M-sodium hydroxide (20 ml) for three days; acidification of the resulting solution gave the amic acid (3a) (0.03 g). The amic acid was also obtained when the impure solid was warmed with ethanol.