Synthesis and Reactions of 2-Dialkylaminofurans

By **Gerhard V. Boyd** * and **Kenneth Heatherington**, Department of Chemistry, Chelsea College, London SW3 6LX

Treatment of tertiary amides of β-aroylpropionic acids with acetic anhydride and perchloric acid gave 2,3-dihydro-2-furylideneammonium salts (5); intermediate acetoxytetrahydrofurylideneammonium perchlorates (4) were isolated in some instances. In the cases of β-*m*-nitrobenzoylpropionomorpholide and 4-oxovaleromorpholide the reaction stopped at the acetoxytetrahydrofuran stage. The unsaturated iminium salts (5) were deprotonated to yield 2-aryl-5-dialkylaminofurans (6). 2-Morpholino-5-phenylfuran reacted with diazonium fluoroborates to give 3-arylazofurans (9) or their salts; the consitution of the latter is discussed. The hydroperchlorate of 2-morpholino-5-phenylfuran condensed with aromatic aldehydes to form arylidene derivatives (12), which were hydrolysed to the corresponding arylidenebutenolides (13); the condensation product (15) obtained from diphenylcyclopropenone yielded (2-benzoylethyl)diphenylcyclopropenylium perchlorate. Cycloadditions of maleic anhydride and *N*-phenylmaleimide to 2-morpholino-5-phenylfuran resulted in rearranged dihydrohydroxyphthalic acid derivatives. Attempts to prepare primary and secondary aminofurans by the action of acetic anhydride and perchloric acid on the amide and anilide of β-benzoylpropionic acid led, ultimately, to 2-phenyl-Δ^1-pyrrolin-5-one and 1,5-diphenyl-Δ^3-pyrrolin-2-one, respectively.

RELATIVELY few 2-dialkylaminofurans are known; these compounds have usually been obtained by the action of secondary amines on activated 2-halogenofurans, such as 5-chloro-2-furaldehyde,[1] 2-bromo-5-nitrofuran,[2] and 2,3-dibromofuran;[3] but their synthesis from open-chain precursors does not appear in the literature. In the course of our work on the cyclisation of systems of the general formula $-OC{\cdot}X{\cdot}Y{\cdot}CO-$,[4] we have found that tertiary amides of β-aroylpropionic acids are converted into salts of 2-dialkylaminofurans on treatment with acetic anhydride and a strong mineral acid, and we now report on the scope of this reaction and the chemistry of the products.[5]

The required amides (3) (Table 1) were obtained by the action of secondary amines on either 4-arylbut-3-enolides

[1] S. Shimamura, and H. Saikachi, *Yakugaku Zasshi*, 1960, **80**, 41, 429, 1534 (*Chem. Abs.*, 1960, **54**, 13,093c, 19,634e; 1961, **55**, 837g).

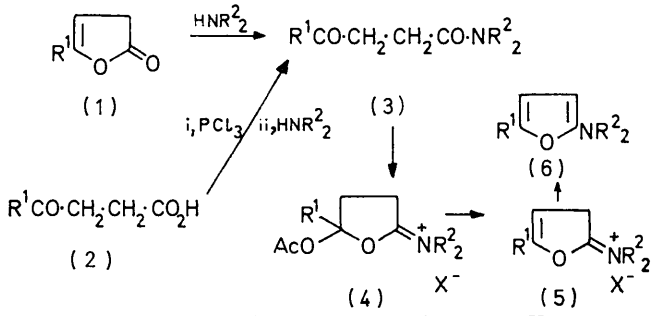
[2] (*a*) Z. N. Nazarova, V. N. Novikov, and V. T. Bukhaeva, *Zhur. obshchei Khim.*, 1964, **34**, 705; (*b*) V. N. Novikov and Z. N. Nazarova, *Zhur. org. Khim.*, 1965, **1**, 2022.

[3] Z. N. Nazarova and G. F. Potemkin, *Zhur. org. Khim.*, 1968, **4**, 722.

[4] G. V. Boyd, *J.C.S. Perkin I*, 1973, 1731, and previous papers.

[5] For a preliminary account, see G. V. Boyd and K. Heatherington, *Chem. Comm.*, 1971, 346.

(1) or, preferably, the chlorides of β-aroylpropionic acids (2). Treatment of β-benzoylpropionomorpholide (3a) with acetic anhydride and perchloric acid below 5° gave a salt whose analytical figures and spectra indicated that it had the cyclic ester structure (4a). The compound absorbed at 1780 (ester carbonyl) and 1715 cm^{-1} ($C=\overset{+}{N}$) in the i.r.; the methylene n.m.r. signals of the tetrahydrofuran ring formed an AA'BB' pattern and those of the morpholinium group appeared as a singlet. The salt was hydrolysed by water or dilute hydrochloric acid to give a mixture of the original morpholide and the butenolide (1a). When the salt was briefly heated in



	R^1	NR^2_2	X
a;	Ph	morpholino	ClO_4
b;	Ph	morpholino	HSO_4
c;	Ph	morpholino	BF_4
d;	Ph	piperidino	ClO_4
e;	Ph	pyrrolidino	ClO_4
f;	*p*-ClC_6H_4	morpholino	ClO_4
g;	*p*-MeC_6H_4	morpholino	ClO_4
h;	*p*-MeO·C_6H_4	morpholino	ClO_4
i;	*m*-O_2N·C_6H_4	morpholino	ClO_4
j;	Me	morpholino	ClO_4

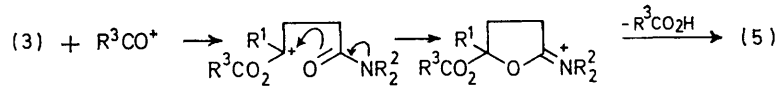
acetic acid on a steam-bath it was converted into the unsaturated iminium perchlorate (5a); the same compound was formed when the morpholide was treated with acetic anhydride–perchloric acid at a higher temperature (20—30°) and by the action of propionic anhydride and perchloric acid at either <5° or 20—30°. The i.r. spectrum of the perchlorate (5a) exhibited the characteristic $C=\overset{+}{N}$ band at 1717 cm^{-1}; its n.m.r. spectrum showed a singlet for the morpholinium protons and the presence of adjacent olefinic and methylene protons. The appearance of these signals and the absence of $\overset{+}{N}H$ stretching vibrations in the i.r. rule out the alternative *N*-protonated structure (7) for the cation. The formation of the iminium salt can be rationalised (see Scheme) by assuming initial attack of an acylium cation on the keto-amide, followed by intramolecular alkylation of the amide group and elimination of acetic or propionic acid. Intermolecular *O*-alkylations of amides are well known [6]

[6] H. Meerwein, P. Borner, O. Fuchs, H. J. Sasse, H. Schrodt, and J. Spille, *Chem. Ber.*, 1956, **89**, 2060.

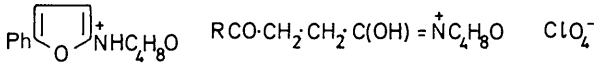
and the proposed mechanism is supported by the isolation of the acetoxyiminium salt (4a). An analogous acetoxy-hydrogen sulphate (4b) was prepared from the morpholide (3a) and acetic anhydride–sulphuric acid and was converted into the unsaturated hydrogen sulphate (5b) on heating. Similarly, in the presence of fluoroboric acid, the fluoroborates (4c) and (5c) were obtained. The action of acetic anhydride and perchloric acid at 20—30° on the piperidide (3d) and the pyrrolidide (3a) resulted in the cyclic perchlorates (5e) and (5d), respectively, and the substituted morpholides (3f—h) similarly yielded the salts (5f—h), respectively. β-*m*-Nitrobenzoylpropionomorpholide (3i), on the other hand, gave the acetoxy-perchlorate (4i) at 20—30°; this salt did not lose acetic acid when heated; instead, it suffered ring-opening to form the hydroperchlorate of the original amide, which probably exists in the *O*-protonated [7] form (8a); the i.r. spectrum (ν_{OH}, 3300—2200, ν_{ArCO} 1680 cm^{-1}) supports this assignment. An analogous hydroperchlorate (8b) was obtained when *p*-chlorobenzoylpropionomorpholide (3f) was treated with acetic anhydride and perchloric acid below 5°. The cyclic salts are listed in Table 2.

Attempts to prepare an alkyl-substituted unsaturated iminium salt failed. 4-Oxovaleromorpholide (3j) [8] reacted with acetic anhydride and perchloric acid below 5° or at elevated temperatures to form the acetoxy-compound (4j); with propionic anhydride the corresponding propionate was obtained. Neither salt could be converted into the iminium perchlorate (5j) under any conditions tried. Prolonged heating of the acetate in acetic acid gave the protonated amide (8c).

The aryliminium salts (5a—h) were readily deprotonated by the action of triethylamine to give the corresponding 2-dialkylaminofurans (6) (Table 3); treatment of the furans with the appropriate acid regenerated the salts. 2-Morpholino-5-phenylfuran (6a), together with the amide (3a), was also formed from the acetoxy-salt (4a) and triethylamine; but the esters (4i) and (4j) yielded solely the corresponding amides on similar treatment.



SCHEME



(7) (8)

a; R = *m*-O_2N·C_6H_4
b; R = *p*-ClC_6H_4
c; R = Me

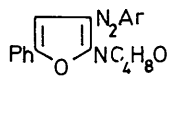
Table 4 summarises the spectroscopic properties of the dialkylaminofurans. They absorb maximally at 310—340 nm and their n.m.r. spectra exhibit doublets due to

[7] G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, 1970, **70**, 561.

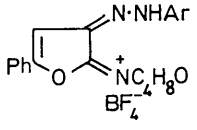
[8] R. Chiron and Y. Graff, *Bull. Soc. chim. France*, 1970, 575.

the furan protons at τ *ca.* 3·5 and 4·9. Since, in the morpholinofurans, variation of the aryl substituent affects the chemical shifts of the signals at low field but leaves those at higher field unchanged, the former are assigned to the protons at C-4. Furthermore, the signals of H-3 at τ *ca.* 4·9 in the spectra of compounds (6a, d, and e) are more sensitive to the nature of the dialkylamino-group than are those at τ 3·5, in agreement with the assignment.

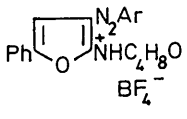
The dialkylaminofurans are stable; they resist the action of water or aqueous alkali but are hydrolysed by dilute hydrochloric acid to the corresponding butenolides. This behaviour, like the formation of iminium salts by *C*-protonation, is characteristic of enamines.[9] Another typical enamine reaction of 2-morpholino-5-phenylfuran is its ability to couple [10] with diazonium salts: treatment with arenediazonium fluoroborates in the presence of triethylamine gave highly coloured 3-arylazofurans (9a—g); in the absence of triethylamine, the corresponding hydrotetrafluoroborates were formed. The azofurans and their salts were interconvertible. These compounds are listed in Table 5. Two structures for the salts have to be considered: the bases can be protonated on the azo-group to yield arylhydrazono-compounds (10) or on the morpholine nitrogen atom giving the azofurylmorpholinium salts (11). We believe that the solid salts all exist in the arylhydrazono-form because the i.r. spectrum of each compound displays a single sharp band at 3260—3270 cm^{-1} and there is no sign of multiple $\overset{+}{N}H$ stretching vibrations [11] at 2330—2700 cm^{-1} as required by structure (11). In dichloromethane solution, the salts of the furans (9a—d) likewise appear to exist in the form (10) since a bathochromic shift in the longest-wave



(9)



(10)



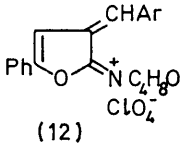
(11)

a; Ar = Ph
b; Ar = *p*-MeC_6H_4
c; Ar = *p*-$MeO{\cdot}C_6H_4$
d; Ar = *p*-ClC_6H_4
e; Ar = *p*-$EtO_2C{\cdot}C_6H_4$
f; Ar = *p*-AcC_6H_4
g; Ar = *p*-$O_2N{\cdot}C_6H_4$

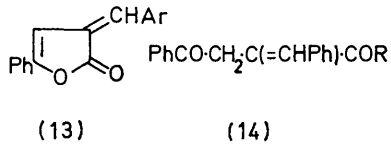
absorption band is observed when comparing the visible spectrum of an azofuran with that of its fluoroborate; the opposite effect would be expected if the cations had the less conjugated structure (11). The visible spectra of the salts of compounds (9e—g), however, do not conform to this pattern. They display shoulders at a longer wavelength than that of the parent bases and, in addition, strong bands at shorter wavelengths. The appearance of the latter bands may indicate admixture with the other protonated species.

[9] G. H. Alt, in ' Enamines: Synthesis, Structure and Reactions,' ed. A. G. Cook, Marcel Dekker, New York, 1969, p. 117.

Attempts to bring about other electrophilic substitution reactions of 2-morpholino-5-phenylfuran failed: no products could be isolated when the base was treated with acetyl chloride, benzoyl chloride, copper(II) nitrate–acetic anhydride, bromine, or *N*-bromosuccinimide under various conditions, although reactions were evidently taking place. Its hydroperchlorate (5a), however, readily condensed with benzaldehyde in hot acetic acid to yield the red benzylideneiminium salt (12a). We suggest that the reaction occurs by preliminary proton exchange between the salt and the aldehyde, followed by electrophilic attack of the resulting cation, $Ph\overset{+}{C}HOH$, on the free base, and subsequent dehydration. The same condensation product was obtained from the acetoxy-salt (4a) and benzaldehyde and by cyclisation of β-benzoyl-α-benzylidenepropionomorpholide (14a) with acetic anhydride and perchloric acid. The iminium salt (5a) was treated with a number of other aromatic aldehydes to



(12)



(13) (14)

a; Ar = Ph
b; Ar = *p*-ClC_6H_4
c; Ar = *p*-MeC_6H_4
d; Ar = *p*-$MeO{\cdot}C_6H_4$
e; Ar = 3,4-$CH_2O_2{\cdot}C_6H_3$
f; Ar = *p*-$HO{\cdot}C_6H_4$
g; Ar = *p*-$Me_2N{\cdot}C_6H_4$
h; Ar = *p*-$O_2N{\cdot}C_6H_4$

a; R = morpholino
b; R = OH

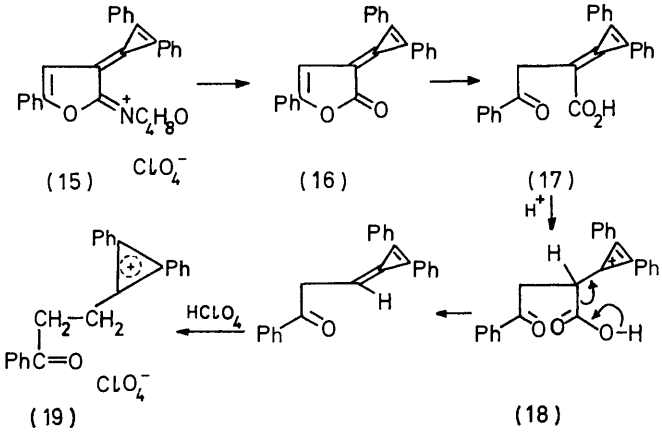
give analogous highly coloured arylmethylene derivatives (12b—g) (Table 6); with diphenylcyclopropenone, the orange cyclopropenylidene salt (15) was obtained. In contrast, the reaction with *p*-nitrobenzaldehyde was accompanied by hydrolysis to form *p*-nitrobenzylidenephenylbutenolide (13h); it remains to be seen if the use of other aromatic aldehydes containing electron-withdrawing groups gives analogous results.

The benzylidene derivative (12a) was hydrolysed by water or dilute hydrochloric acid to the butenolide (13a); when aqueous sodium carbonate was used the butenolide was accompanied by a small amount of the corresponding acid (14b). The butenolides (13b—g) were obtained by acidic hydrolysis of the corresponding iminium salts; the cyclopropenylidene salt (15), however, resisted prolonged heating with water, concentrated hydrochloric acid, or 2N-sodium hydroxide. Boiling with a mixture of acetic and concentrated hydrochloric acid gave a colourless perchlorate, to which we assign the cyclopropenylium structure (19) on the basis of its analytical figures and i.r. (ν_{CO} 1674 cm^{-1}) and n.m.r. spectra (four methylene protons with accidentally identical chemical shifts). The salt is presumably formed by successive hydrolysis of the original perchlorate to the lactone (16) and the acid (17). Protonation of the latter, followed by decarboxylation

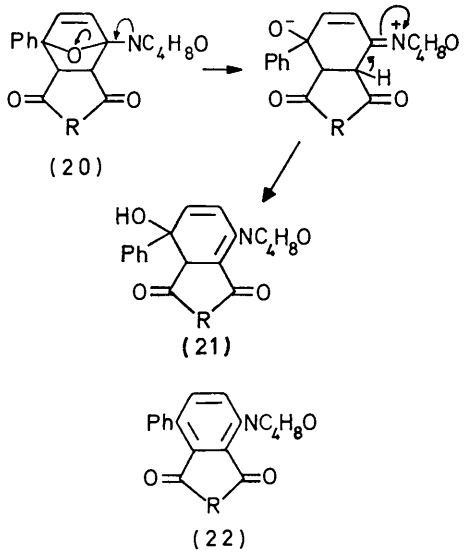
[10] Ref. 9, p. 158.
[11] N. B. Colthup, L. H. Daly, and F. E. Wiberley, ' Introduction to Infrared and Raman Spectroscopy,' Academic Press, London, 1964, p. 282.

[*cf.* (18)] and renewed protonation yields the aromatic product.*

The chemical properties of 2-morpholino-5-phenylfuran described so far are typical of those of enamines; however, unlike simple enamines [12] it did not function as a

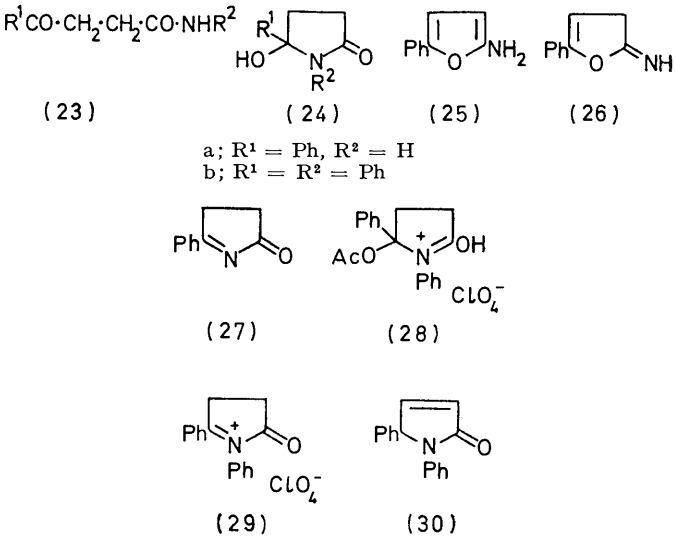


dipolarophile towards diphenylnitrilimine or *p*-nitrophenyl azide, being recovered after treatment with these reagents. Its furanoid character was shown in Diels–Alder reactions with maleic anhydride and *N*-phenylmaleimide. The isolated products (21a and b) are



formed by rearrangement of the initial adducts (20a and b); the ring opening may be assisted by the presence of the dialkylamino-group (see arrows). The phthalic acid derivatives (22a and b) were obtained by dehydration with acetic anhydride.

We attempted to prepare furans containing a primary or secondary amino-substituent by the cyclisation of appropriate γ-oxoamides. There is extensive literature [13] on the chain–ring tautomerism [(23 ⇌ (24)] of these amides; i.r., u.v., and n.m.r. spectroscopy indicate that the equilibrium depends on the nature both of the amide and of the solvent. It appears to be established [13] that the two amides were used, β-benzoylpropionamide (23a) and the corresponding anilide (23b) both exist in the open-chain form in the solid state and in various solvents. Reaction of the amide (23a) with acetic anhydride and perchloric acid gave an oily perchlorate which, on treatment with triethylamine, yielded a base which was evidently neither the expected aminofuran (25) nor its imino-tautomer (26) since its i.r. spectrum lacked NH vibrations but exhibited carbonyl absorption at 1690 cm^{-1} and its n.m.r. spectrum showed the presence of two adjacent methylene groups. We consider that these characteristics are consistent only with the 2-phenyl-Δ^1-pyrrolin-5-one formula (27), a rare structural type.[14] We



attribute the formation of this lactam to the presence of the cyclic tautomer (24a) in the reaction mixture. A similar result was obtained when the anilide (23b) was submitted to the usual treatment. The product, a cyclic acetoxy-perchlorate containing two adjacent methylene groups, lost the elements of acetic acid on heating briefly in acetic acid to give the lactam salt (29); the presence of two methylene n.m.r. triplets and the high carbonyl i.r. absorption at 1840 cm^{-1} in the spectra of this salt rule out any structures containing a dihydrofuran ring. The precursor is consequently formulated as the *O*-protonated [7] salt (28).† Deprotonation of the oxo-

* An alternative mechanism, suggested by a referee, involves direct decarboxylation of compound (17) *via* a four-membered cyclic transition state, followed by protonation.

† We now prefer this structure to the *N*-protonated form given in our original communication.[5]

[12] (*a*) R. Fusco, G. Bianchetti, and D. Pocar, *Gazzetta*, 1961, **91**, 849, 933; (*b*) M. E. Kuehne, S. J. Weaver, and P. Franz, *J. Org. Chem.*, 1964, **29**, 1582.

[13] (*a*) Ref. 8; (*b*) R. Chiron and Y. Graff, *Bull. Soc. chim. France*, 1967, 3715; 1971, 2145; (*c*) W. Flitsch, *Chem. Ber.*, 1970, **103**, 3205; (*d*) M. Sekiya and Y. Terao, *Chem. and Pharm. Bull. (Japan)*, 1970, **18**, 947; 1971, **19**, 391; (*e*) O. Keller and V. Prelog, *Helv. Chim. Acta*, 1971, **54**, 2572.

[14] For a review on pyrrolin-2-ones, see G. Rio and D. Masure, *Bull. Soc. chim. France*, 1972, 4598.

pyrrolinium perchlorate (29) with triethylamine yielded the Δ^3-pyrrolin-2-one (30), whose n.m.r. spectrum did not exhibit a methylene resonance, thus excluding the tautomeric Δ^4-form.[15]

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus and microanalyses with a Perkin-Elmer 240 instrument. I.r. spectra were recorded for Nujol mulls, unless otherwise stated, with a Perkin-Elmer 521 spectrometer and u.v. spectra were determined for solutions in 95% ethanol, unless otherwise stated, with a Unicam SP 700C instrument. ^{1}H N.m.r. spectra were recorded at 100 MHz with a Varian HA 100 spectrometer and refer to deuteriochloroform solutions, unless stated otherwise. Perchloric acid was of 70% strength.

Preparation of Tertiary Amides (3) *of β-Aroylpropionic Acids* (*Table* 1).—The aroylpropionic acid (10·0 g) was suspended in anhydrous diethyl ether (200 ml) and phosphorus trichloride (3·0 g) was added drop by drop with stirring. Stirring was continued for 1 h; the solution was then decanted from a gummy residue and stirred, and a solution of the appropriate secondary amine (12·5 g) in ether (50 ml) was added. The mixture was stirred for 1 h and the precipitate was filtered off and washed with ether (2 × 50 ml). The combined filtrate and washings were evaporated, leaving the product.

Cyclisation of Tertiary γ-Oxoamides to yield Compounds (4) *or* (5) (*Table* 2).—A stirred suspension of the amide (2·0 g) in acetic or propionic anhydride (25 ml) was slowly treated with perchloric acid (1 ml) or 40% tetrafluoroboric acid (2 ml) or concentrated sulphuric acid (1 ml) with cooling such that the temperature was kept either at 20—30° or below 5°. When the addition was complete the resulting solution was stirred for a further 30 min and then slowly treated with ether (200 ml). The salt usually separated as a crystalline solid, which was collected and washed thoroughly with ether. If an oil was obtained it was induced to solidify by trituration with acetonitrile.

Reactions of N-(5-*Acetoxytetrahydro-5-phenyl-2-furylidene*)-*morpholinium Perchlorate* (4a).—(*a*) A solution of the salt (1·0 g) in acetic acid (5 ml) was heated on the steam-bath for 15 min; *N*-(2,3-dihydro-5-phenyl-2-furylidene)morpholinium perchlorate (5a) (0·75 g, 89%) was deposited on cooling.

(*b*) Treatment of the salt (0·5 g) with water (25 ml) gave 5-phenylfuran-2(3*H*)-one (1a) (0·077 g, 37%), m.p. 88—89° (lit.,[16] 91—92°), $\nu_{max.}$ 1800, 1780infl, 1123, and 1015 cm^{-1}

TABLE 1

Tertiary amides (3) of β-aroylpropionic acids

Compound	Yield (%)	M.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N	$\nu_{max.}$/cm^{-1}
(3a)	88	86—87 [a]								1683, 1638, 1110 [b]
(3d)	62	51—52 [c]								1680, 1625
(3e)	59	88 [d]	72·6	7·6	5 9	$C_{14}H_{17}NO_2$	72·7	7·4	6·1	1678, 1630
(3f)	88	97 [d]	59·8	5·9	5·1	$C_{14}H_{16}ClNO_3$	59·7	5·7	5·0	1680, 1640, 1110
(3g)	46	85 [d]	68·8	7·5	5·4	$C_{15}H_{19}NO_3$	68·9	7·3	5·4	1683, 1635, 1110
(3h)	76	86—87 [d]	65·4	6·9	4·9	$C_{15}H_{19}NO_4$	65·0	6·9	5·0	1683, 1640, 1240, 1164, 1114
(3i)	70	93 [d]	57·3	5·6	9·6	$C_{14}H_{16}N_2O_5$	57·5	5·5	9·6	1683, 1638, 1530, 1350, 1105

[a] N. H. Cromwell, P. L. Creger, and K. E. Cork (*J. Amer. Chem. Soc.*, 1956, **78**, 4412) give m.p. 85—87°. [b] Morpholine ether. [c] H. Moehrle (*Arch. Pharm.*, 1965, **298**, 612) gives m.p. 51·5—52·5°. [d] Obtained analytically pure without recrystallisation.

TABLE 2

Di- and tetra-hydro-2-furylideneammonium salts (4) and (5) from γ-oxoamides

Compound	Yield (%)	M.p. (°C) [a] (decomp.)	Found (%) C	H	N	Formula	Required (%) C	H	N	$\nu_{max.}$/cm^{-1}
(4a)	92 [b]	153—155	49·4	5·1	3·6	$C_{16}H_{20}ClNO_8$	49·3	5·2	3·6	1780, 1715, 1100 [c]
(4b)	28 [d]	150—153	50·1	5·2	3·8	$C_{16}H_{21}NO_8S$	49·6	5·5	3·6	2600—2000, 1780, 1715, 1165, 1110
(4c)	87 [d]	114—115	50·7	5·4	3·7	$C_{16}H_{20}BF_4NO_4$	50·9	5·4	3·7	1780, 1715, 1110
(4i)	87 [d]	120—121	44·3	4·6	6·5	$C_{16}H_{19}ClN_2O_{10}$	44·2	4·4	6·4	1768, 1712, 1530, 1100
(4j)	88 [b], 90 [d]	105—106	40·3	5·4	4·3	$C_{11}H_{18}ClNO_8$	40·3	5·5	4·3	1755, 1690, 1100 [e]
(4j) [f]	90 [b], 95 [d]	93—94	42·1	5·9	4·4	$C_{12}H_{20}ClNO_8$	42·2	5·9	4·1	1750, 1695, 1100
(5a)	83 [d], 97 [g]	173—174	51·0	5·0	4·3	$C_{14}H_{16}ClNO_6$	51·0	4·9	4·2	1717, 1658, 1100 [h]
(5b)	29 [i]	147—148	51·0	5·3	4·3	$C_{14}H_{17}NO_6S$	51·4	5·2	4·3	2800—2000, 1715, 1654, 1170, 1107
(5c)	75 [i]	138—140	52·7	5·1	4·3	$C_{14}H_{16}BF_4NO_2$	53·0	5·1	4·4	1722, 1654, 1115
(5d)	81 [b], 92 [d]	153	54·9	5·5	4·4	$C_{15}H_{18}ClNO_5$	55·0	5·5	4·3	1720, 1660, 1100
(5e)	85 [b], 92 [d]	144—145	53·6	5·2	4·5	$C_{14}H_{16}ClNO_5$	53·6	5·1	4·5	1738, 1652, 1100
(5f)	77 [d]	159—161	46·1	4·1	3·6	$C_{14}H_{15}Cl_2NO_6$	46·2	4·1	3·8	1715, 1655, 1100
(5g)	88 [d]	192—193	52·4	5·3	3·9	$C_{15}H_{18}ClNO_6$	52·4	5·3	4·1	1718, 1658, 1100
(5h)	77 [b], 88 [d]	165	50·5	5·1	4·0	$C_{15}H_{18}ClNO_7$	50·1	5·0	3·9	1715, 1650, 1260, 1100

[a] From acetonitrile. [b] Prepared in the presence of acetic anhydride below 5°. [c] τ (CF_3·CO_2H) 1·8—2·6 (m, Ph), 5·86 (8H, s, morpholine), 6·2 (2H, m) and 6·6 (2H, m) (AA′BB′, CH_2·CH_2), and 7·75 (s, Me). [d] Prepared in the presence of acetic anhydride at 20—30°. [e] τ (CF_3·CO_2H) 5·9 (8H, m, morpholine), 6·4 (2H, m), and 7·1 (2H, m) (AA′BB′, CH_2·CH_2), 7·75 (s, MeCO), and 7·99 (s, Me). [f] $EtCO_2$ in place of AcO. [g] Prepared by using propionic anhydride–perchloric acid below 5°. [h] τ (CF_3·CO_2H) 2·5 (m, Ph), 3·84 (t, *J* 2·6 Hz, =CH), 5·84 (d, *J* 2·6 Hz, CH_2), and 5·7 (8H, s, morpholine). [i] Prepared by heating the corresponding acetoxy-salt with acetic acid at 100° for 2 h.

[15] For a discussion of the tautomerism of pyrrolin-2-ones, see A. R. Katritzky and J. M. Lagowski, *Adv. Heterocyclic Chem.*, 1963, **2**, 1; and ref. 14.

[16] R. Fittig and M. Ginsberg, *Annalen*, 1897, **299**, 1.

(Found: C, 75·2; H, 5·2. Calc. for $C_{10}H_8O_2$: C, 75·0; H, 5·0%). The filtrate was extracted with ether and the extract was evaporated. The i.r. spectrum (1683, 1638, and 1110 cm^{-1}) of the oily residue (0·033 g) suggested that it was mainly *N*-(β-benzoylpropionyl)morpholine (3a), contaminated with a small amount of the butenolide (1a).

(*c*) The salt (0·5 g) was added to 2N-hydrochloric acid (25 ml) and the mixture was worked up as in (*b*), yielding the butenolide (0·089 g, 43%) and the morpholide (0·018 g, 6%).

(*d*) The salt (0·5 g) was dissolved in 2N-sodium hydroxide (25 ml). The pale-yellow solution was extracted with ether and the dried ($MgSO_4$) extract was evaporated. The residual oil deposited the morpholide (3a) (0·102 g, 33%). The i.r. spectrum of the oily filtrate (1618, 1598, 1560, and 1118 cm^{-1}) indicated the presence of 2-morpholino-5-phenylfuran (6a) contaminated with a little of the morpholide (3a).

(2H, d) (*J* 8·5 Hz, Ar), 5·9br (8H, s, morpholine), and 6·3 (m) and 6·7 (m) (CH_2·CH_2) (Found: C, 43·9; H, 4·5; N, 3·7. $C_{14}H_{17}Cl_2NO_7$ requires C, 44·0; H, 4·5; N, 3·7%). The compound gave an almost quantitative yield of the morpholide (3f) on treatment with water or ethereal triethylamine.

(*c*) Heating *N*-(5-acetoxytetrahydro-5-methyl-2-furylidene)morpholinium perchlorate (4j) (1·0 g) in acetic acid (20 ml) at 100° for 24 h gave N-(*1-hydroxy-4-oxopentylidene*)-*morpholinium perchlorate* (8c) (0·61 g, 70%), m.p. 160—162° (decomp.), $\nu_{max.}$ 3500—2300, 1718, 1660, and 1080 cm^{-1}, τ (CF_3·CO_2H) 5·7 (8H, m, morpholine), 6·8 (m, 2 × CH_2), and 7·28 (s, Me) (Found: C, 37·4; H, 5·6; N, 4·8. $C_9H_{16}ClNO_7$ requires C, 37·8; H, 5·6; N, 4·9%).

Preparation of 5-Aryl-2-dialkylaminofurans (6) (*Table* 3). —A 2,3-dihydro-2-furylideneammonium salt (5) (1·0 g) was suspended in ether and triethylamine (0·5 ml) was added dropwise with stirring. After 30 min the solution was

TABLE 3

2-Dialkylamino-5-arylfurans (6)

Compound	Yield (%)	M.p. (°C) [a]	Found (%) C	H	N	Formula	Required (%) C	H	N
(6a)	96	72—73	72·9	6·7	6·0	$C_{14}H_{15}NO_2$	73·3	6·6	6·1
(6d)	100	<20	79·0	7·7	6·0	$C_{15}H_{17}NO$	79·3	7·5	6·2
(6e)	87	<20	78·7	7·1	6·6	$C_{14}H_{15}NO$	78·8	7·1	6·6
(6f)	92	106—107	63·9	5·4	5·2	$C_{14}H_{14}ClNO_2$	63·8	5 4	5 3
(6g)	87	109	74·0	7·2	6·0	$C_{15}H_{17}NO_2$	74·0	7·0	5·8
(6h)	97	102	69·5	6·6	5·4	$C_{15}H_{17}NO_3$	69·5	6·6	5·4

[a] From diethyl ether.

TABLE 4

Spectroscopic properties of the 2-dialkylamino-5- arylfurans (6)

Compound	τ Values (*J*/Hz) Ar	4-H	3-H	NR^2_2	Me	$\nu_{max.}$/cm^{-1}	$\lambda_{max.}$/nm (ε)
(6a)	2·45—2·95m	3·53d(3·5)	4·82d(3·5)	6·23, 6·88(A_2B_2)		1618, 1598, 1584, 1560, 1120	217 (9200), 230infl (7000), 318 (17,200)
(6d)	2·4—2·9m	3·52d(3·5)	4·88d(3·5)	6·8—7·0m, 8·2—8·5m		1610, 1590, 1575, 1552	219 (10,700) 325 (18,800)
(6e)	2·4—2·9m	3·48d(3·5)	5·07d(3·5)	6·4—6·8m, 7·9—8·2m		1615, 1590, 1577, 1555	222 (10,100), 340 (19,500)
(6f)	2·63d(8·0), 2·79d(8·0)	3·55d(3·5)	4·82d(3·5)	6·20, 6·87(A_2B_2)		1617, 1592, 1577, 1552, 1118	224 (11,000), 330 (21,800)
(6g)	2·62d(8·0), 2·92d(8·0)	3·59d(3·5)	4·82d(3·5)	6·23, 6·90(A_2B_2)	7·72s	1617, 1598, 1576, 1500, 1120	221 (10,700), 316 (21,000)
(6h)	2·58d(8·0), 3·18d(8·0)	3·67d(3·5)	4·82d(3·5)	6·20, 6·88(A_2B_2)	6·23s	1620, 1605, 1584, 1566, 1247, 1118	224 (10,000), 310 (21,800)

A similar result was obtained when the salt was treated with ethereal triethylamine.

Hydroperchlorates of γ-Oxoamides.—(*a*) *N*-(5-Acetoxytetrahydro-5-*m*-nitrophenyl-2-furylidene)morpholinium perchlorate (4i) (1·0 g) and acetic acid (15 ml) were heated together at 100° for 30 min. N-(*1-Hydroxy*-3-m-*nitrobenzoylpropylidene*)*morpholinium perchlorate* (8a) (0·27 g, 30%) crystallised on cooling; it had m.p. 176—178° (decomp.), $\nu_{max.}$ 3300—2200, 1680, 1650infl, 1525, and 1110 cm^{-1} (Found: C, 43·4; H, 4·3; N, 7·1. $C_{14}H_{17}ClN_2O_9$ requires C, 42·8; H, 4·4; N, 7·1%).

(*b*) Treatment of *N*-(β-*p*-chlorobenzoylpropionyl)morpholine (3f) (2·0 g) with acetic anhydride and perchloric acid in the usual way, below 5°, gave N-(3-p-*chlorobenzoyl*-1-*hydroxypropylidene*)*morpholinium perchlorate* (8b) (1·40 g, 52%), m.p. 190° (decomp.) (from acetonitrile), $\nu_{max.}$ 3000—2100, 1680, and 1080 cm^{-1}, τ (CF_3·CO_2H) 1·97 (2H, d) and 2·47 decanted from the oily triethylammonium perchlorate and the residue was washed with ether (2 × 10 ml). The combined ethereal solutions were evaporated, leaving an oil which usually crystallised on trituration with ether.

Reprotonation.—A solution of a dialkylaminofuran (0·05 g) in ether (20 ml) and acetic anhydride (1 ml) was treated with the appropriate acid (0·3 ml) whereupon the iminium salt separated in 73—99% yield.

Hydrolysis of 2-Morpholino-5-phenylfuran (6a) *and Its Hydroperchlorate* (5a).—(*a*) The furan was recovered after being heated under reflux with water or 2N-sodium hydroxide for 30 min.

(*b*) Addition of the furan (1·0 g) to 2N-hydrochloric acid (20 ml) caused the immediate precipitation of 5-phenylfuran-2(3*H*)-one (1a) (0·65 g, 92%).

(*c*) The same compound (0·17 g, 70%) was deposited when the iminium perchlorate (0·5 g) was briefly heated with water

(25 ml) or treated with 2N-hydrochloric acid (25 ml) at room temperature.

(*d*) The salt (5a) (0·5 g) was briefly heated with 2N-sodium hydroxide (25 ml); the precipitated butenolide (1a) (0·1 g, 41%) was collected and the filtrate was acidified and extracted with ether. Evaporation of the extract left β-benzoylpropionic acid (0·038 g, 14%).

ally pure; if necessary, it was recrystallised from acetonitrile. More of the product could be obtained by concentrating the dichloromethane mother liquors.

(*b*) The same procedure, applied to a mixture of 2-morpholino-5-phenylfuran and triethylamine (2 mol. equiv.), gave 3-arylazofurans (9).

(*c*) Triethylamine (0·5 ml) was added to a suspension of

TABLE 5

3-Arylazo-2-morpholino-5-phenylfurans (9) and their hydrofluoroborates

Compound	Yield (%)	M.p. (°C)	Colour	Found (%) C	H	N	Formula	Required (%) C	H	N	$\nu_{max.}$/cm^{-1}	$\lambda_{max.}$[a]/nm (ε)
(9a)	78	146—147 [b,c]	Orange	71·4	5·3	12·6	$C_{20}H_{19}N_3O_2$	72·0	5·7	12·6	1600, 1580, 1355, 1247, 1110	247 (22,200), 333 (17,800), 463 (34,100) [d]
(9a), HBF_4	81	274—275 [b,e]	Red	57·0	4·7	10·0	$C_{20}H_{20}BF_4N_3O_2$	57·0	4·8	10·0	3270, 1660, 1545, 1275, 1115, 1070	263 (16,700), 270 (16,700), 294 (18 300), 480 (32,800), 500infl (28,600)
(9b)	93	157 [c]	Orange	73·0	6·1	12·1	$C_{21}H_{21}N_3O_2$	72·6	6 1	12·1	1605, 1580, 1353, 1250, 1114	246 (18,300), 333 (14,500), 461 (27,800)
(9b), HBF_4	90	253 [b,g]	Red	58·1	5·1	9·6	$C_{21}H_{22}BF_4N_3O_2$	58·0	5·1	9·7	3260, 1660, 1545, 1280, 1118, 1080	267 (16,200), 276(16,600), 294 (17,500), 488 (36,500)
(9c)	89	168 [c]	Orange	69·2	5·9	11·5	$C_{21}H_{21}N_3O_3$	69·4	5·8	11·6	1605, 1570, 1360, 1240, 1113	241 (21,600), 333 (16,400), 463 (30,500)
(9c), HBF_4	87	244—246 [b,e]	Red	55·9	5·0	9·5	$C_{21}H_{22}BF_4N_3O_3$	55·9	4·9	9·3	3260, 1660, 1550, 1285, 1253, 1113, 1080	242 (14,700), 258 (14,700), 295 (17,600), 507 (33,900)
(9d)	95	175 [g]	Orange	65·5	5·0	11·4	$C_{20}H_{18}ClN_3O_2$	65·3	4·9	11·4	1600, 1578, 1344, 1235, 1108	254 (18,200), 331 (14,600), 470 (31,100)
(9d), HBF_4	89	253—254 [b,g]	Red	52·8	4·3	9·2	$C_{20}H_{19}BClF_4N_3O_2$	52·7	4·2	9·2	3260, 1665, 1543, 1280, 1115, 1090	267 (18,700), 276 (18,300), 294 (17,900), 483 (39,100)
(9e)	80	177 [c]	Red	68·3	5·8	10·5	$C_{23}H_{23}N_3O_4$	68·1	5·7	10·4	1698, 1608, 1580, 1320, 1275, 1248, 1113	268 (21,200), 332 (15,900), 490 (37,700)
(9e), HBF_4	81	250 [b,g]	Orange-red	56·0	5·0	8·5	$C_{23}H_{24}BF_4N_3O_4$	56·0	4·9	8·5	3260, 1710, 1662, 1538, 1270, 1100	274 (24,500), 296infl (16,800), 478 (41,300), 500infl (36,500)
(9f)	79	211 [c]	Red	70·7	5·7	11·3	$C_{22}H_{21}N_3O_3$	70·4	5·6	11·2	1670, 1604, 1575, 1325, 1248, 1109	275 (19,300), 321 (16,100), 495 (37,700)
(9f), HBF_4	78	260—262 [b,e]	Orange	56·8	4·9	9·3	$C_{22}H_{22}BF_4N_3O_3$	57·0	4·8	9·1	3260, 1675, 1660infl, 1538, 1270, 1245, 1110, 1080	282 (23,000), 483 (40,000), 505infl (36,500)
(9g)	87	230—231 [b,c]	Green	63·3	4·8	14·7	$C_{20}H_{18}N_4O_4$	63·5	4·8	14·8	1600, 1576, 1300, 1248, 1100	284 (14,600), 328 (16,300), 526 (34,100)
(9g), HBF_4	73	261—262 [b,e]	Orange	51·5	4·1	11·9	$C_{20}H_{19}BF_4N_4O_4$	51·5	4·1	12·0	3260, 1675, 1530, 1270, 1110, 1060	286 (18,400), 478 (37,300), 502 (38,000), 570infl (6300)

[a] In dichloromethane. [b] Decomp. [c] From ethyl acetate. [d] τ 2·3—2·8 (m, 2 × Ph), 2·85 (s, 4-H), and 5·9—6·1 (8H, m, morpholine). [e] From acetonitrile. [f] τ [$(CD_3)_2SO$] 2·2—2·9 (m, 2 × Ph and 4-H), 5·65br (s, NH), and 6·05br (8H, s, morpholine). [g] Pure without recrystallisation.

Azo-coupling (*Table* 5).—(*a*) A solution of 2-morpholino-5-phenylfuran (1·15 g) in dichloromethane (25 ml) was stirred at 0—10° during the addition in portions of an arenediazonium tetrafluoroborate (1 mol. equiv.). A strongly coloured solution formed which deposited the crystalline hydrofluoroborate (10) of the corresponding arylazofuran (9) within a few minutes. The product was usually analytic-

N-(2,3-dihydro-5-phenyl-3-phenylhydrazono-2-furylidene)-morpholinium tetrafluoroborate (10a) (0·1 g) in ether (25 ml); a yellow solution formed, which, after a few minutes, deposited 2-morpholino-5-phenyl-3-phenylazofuran (9a) (0·057 g, 72%).

(*d*) A solution of the azofuran (9a) (0·05 g) in ether (30 ml), containing a few drops of acetic anhydride, when treated

with a little 40% tetrafluoroboric acid, deposited the fluoroborate (10a) (0·053 g, 84%).

N-(3-*Arylmethylene*-2,3-*dihydro*-5-*phenyl*-2-*furylidene*)*morpholinium Perchlorates* (12) *and* (15) (*Table* 6).—(*a*) The iminium perchlorate (5a) (1·65 g) was dissolved in acetic acid (50 ml) by heating on a steam-bath and an aromatic aldehyde or diphenylcyclopropenone (2—3 mol. equiv.) was gradually added to the hot solution. Heating was continued for 30 min and the strongly coloured solution was then allowed to cool; the product usually crystallised. If it did not, it was precipitated by the dropwise addition of ether. Gummy products were induced to crystallise by trituration with acetonitrile.

(*b*) A suspension of 3-benzylidene-5-phenylfuran-2(3*H*)-one [17] (13a) (3·1 g) in benzene (20 ml) was slowly treated with morpholine (1·2 g) and the resulting solution was heated under reflux for 1 h and then concentrated to 5 ml. A paste separated overnight; gentle warming with ethanol (5 ml) gave N-(β-*benzoyl*-α-*benzylidenepropionyl*)*morpholine* (14a) [18] (3·1 g, 75%), needles, m.p. 114—115°, $\nu_{max.}$ 1680, 1610, and 1105 cm^{-1}, τ 2·0—2·1 (m) and 2·4—2·8 (m) (2 × Ph), 3·43 (s, =CH), 5·81 (s, CH_2), and 6·5 (8H, m, morpholine) (Found: C, 75·3; H, 6·5; N, 4·3. $C_{21}H_{21}NO_3$ requires C, 75·2; H, 6·3; N, 4·2%). This morpholide (2·0 g) was treated with acetic anhydride and perchloric acid at 20—30° in the usual way, giving *N*-(3-benzylidene-2,3-dihydro-5-phenyl-2-furylidene)morpholinium perchlorate (12a) (1·9 g, 77%).

(*c*) The same benzylidene compound (0·21 g, 65%) was formed from the acetoxytetrahydrofurylidenemorpholinium perchlorate (4a) (0·3 g) and benzaldehyde in hot acetic acid.

Reaction of the Iminium Perchlorate (5a) *with* p-*Nitrobenzaldehyde*.—The usual procedure yielded 3-*p*-nitrobenzylidene-5-phenylfuran-2(3*H*)-one (13h) (1·02 g, 69%), m.p. 292—294° (lit.,[17] 296°), $\nu_{max.}$ 1760 cm^{-1}. The same compound was formed when the condensation was carried out in acetic anhydride at room temperature.

Hydrolysis of the Arylmethylene Compounds (12).—(*a*) The arylmethylene compound (0·5 g) was heated with 2N-hydrochloric acid (20 ml) at 100° for 30 min; sufficient acetone was then added to the hot mixture to produce a clear solution; the product crystallised on cooling. The following 5-phenylfuran-2(3*H*)-ones (13) were obtained: 3-benzylidene- (13a) (0·23 g, 78%), m.p. 151—152° (lit.,[17] 155°), $\nu_{max.}$ 1760 and 1622 cm^{-1} (Found: C, 82·2; H, 4·8. Calc. for $C_{17}H_{12}O_2$: C, 82·2; H, 4·9%); 3-*p*-chlorobenzylidene- (13b) (0·14 g, 46%), m.p. 228° (lit.,[19] 228—229°), $\nu_{max.}$ 1755 and 1618 cm^{-1} (Found: C, 72·0; H, 3·9. Calc. for $C_{17}H_{11}ClO_2$: C, 72·2; H, 3·9%); 3-*p*-methylbenzylidene- (13c) (0·26 g, 84%), m.p. 160° (lit.,[17] 150°), $\nu_{max.}$ 1760 and 1627 cm^{-1} (Found: C, 82·3; H, 5·3. Calc. for $C_{18}H_{14}O_2$: C, 82·4; H, 5·4%); 3-*p*-methoxybenzylidene- (13d) (0·22 g, 71%), m.p. 171° (lit.,[17] 171°), $\nu_{max.}$ 1762infl, 1750, and 1619 cm^{-1} (Found: C, 77·9; H, 5·2. Calc. for $C_{18}H_{14}O_3$: C, 77·7; H, 5·1%); 3-(3,4-methylenedioxy)benzylidene- (13e) (0·24 g, 76%), m.p. 177° (lit.,[17] 177°), $\nu_{max.}$ 1760infl, 1750, and 1610 cm^{-1} (Found: C, 73·6; H, 4·2. Calc. for $C_{18}H_{12}O_4$: C, 74·0; H, 4·1%); 3-p-*hydroxybenzylidene*- (13f) (0·19 g, 62%), yellow needles, m.p. 179°, $\nu_{max.}$ 3270, 1750, 1738, and 1606 cm^{-1} (Found: C, 77·6; H, 4·9. $C_{17}H_{12}O_3$ requires C, 77·3; H, 4·6%); and 3-*p*-dimethylaminobenzylidene-, isolated as the *hydrochloride* (13g),HCl (0·24 g, 68%), orange prisms, m.p. 180—182°, $\nu_{max.}$ 3600—3200, 2700—2000, 1770, and 1623 cm^{-1} (Found: C, 65·7; H, 5·7; N, 4·0. $C_{19}H_{18}ClNO_2,H_2O$ requires C, 66·0; H, 5·8; N, 4·0%). The free base (13g) (0·061 g, 72%) was obtained by treating a

TABLE 6

N-(3-Arylmethylene-2,3-dihydro-5-phenyl-2-furylidene)morpholinium perchlorates (12) and (15)

Compound	Yield (%)	M.p. (°C) [a]	Colour	Found (%) C	H	N	Formula	Required (%) C	H	N	$\nu_{max.}$/cm^{-1}	$\lambda_{max.}$ [b]/nm (ε)
(12a)	63	235—236 [c]	Red	60·6	4·9	3·4	$C_{21}H_{20}ClNO_6$	60·4	4·8	3·3	1650, 1622, 1580, 1564, 1100	282 (21,100), 336 (10,400), 438 (19,100)
(12b)	65	253 [c]	Red	55·7	4·2	3·2	$C_{21}H_{19}Cl_2NO_6$	55·8	4·2	3·1	1655, 1625, 1574, 1544, 1100	282 (19,000), 348 (9900), 441 (19,700)
(12c)	38	228 [c]	Red	61·3	5·2	3·1	$C_{22}H_{22}ClNO_6$	61·2	5·1	3·2	1648, 1619, 1572, 1550, 1090	284 (21,000), 357 (9100), 450 (24,100)
(12d)	67	233—234 [c]	Red	58·9	5·0	3·3	$C_{22}H_{22}ClNO_7$	59·0	5·0	3·1	1636, 1610, 1560, 1542, 1270, 1166, 1090	284 (18,100), 370 (8000), 481 (28,100)
(12e)	64	235—237 [c]	Red	57·1	4·4	3·0	$C_{22}H_{20}ClNO_8$	57·2	4·4	3·0	1642, 1616, 1560, 1278, 1190	284 (20,400), 339 (5500) 492 (29,000)
(12f)	56	234 [c]	Red	57·9	4·5	3·1	$C_{21}H_{20}ClNO_7$	58·1	4·6	3·2	3600—3000, 1642, 1615, 1550, 1170, 1110	289 (17,600), 366 (8100), 481 (28,700)
(12g)	76	258—259 [d]	Green	60·0	5·5	6·1	$C_{23}H_{25}ClN_2O_6$	59·9	5·5	6·1	1625, 1610, 1530, 1170, 1090	256 (12,800), 302 (18,700), 336infl (6900), 406 (3800) 588 (69,000)
(15)	78	221 [c]	Orange	67·1	4·8	2·8	$C_{29}H_{24}ClNO_6$	67·2	4·7	2·7	1830, 1634, 1607, 1590, 1090	292 (46,000), 410 (22,800) [e]

[a] With decomposition. [b] In dichloromethane. [c] From acetonitrile. [d] From acetic acid. [e] τ [$(CD_3)_2SO$] 1·6—2·6 (m, 3 × Ph), 2·38 (s, 4-H), and 6·15 (m) and 6·25 (m) (8H, morpholine).

[17] F. W. Schueler and C. Hanna, *J. Amer. Chem. Soc.*, 1951, **73**, 3528.

[18] *Cf.* R. Filler and L. M. Hebron, *J. Amer. Chem. Soc.*, 1959, **81**, 391.

[19] R. Filler and H. A. Leipold, *J. Org. Chem.*, 1962, **27**, 4440.

solution of the hydrochloride (0·1 g) in acetonitrile (5 ml) with triethylamine (0·5 ml). It had m.p. 162° (lit.,[17] 175°), $\nu_{max.}$ 1768, 1750, and 1608 cm^{-1} (Found: C, 78·0; H, 6·0; N, 4·9. Calc. for $C_{19}H_{17}NO_2$: C, 78·3; H, 5·9; N, 4·8%).

(*b*) The benzylidene perchlorate (12a) (0·5 g) was heated for 2 h at 100° with 2N-sodium hydrogen carbonate (20 ml); the butenolide (13a) (0·15 g, 51%) separated. It was collected and the filtrate was acidified with concentrated hydrochloric acid. The resulting mixture was extracted with ether and the extract was dried ($MgSO_4$) and evaporated, leaving β-benzoyl-α-benzylidenepropionic acid (14b) (0·042 g, 13%), m.p. 171° (from ether) (lit.,[20] 171°), $\nu_{max.}$ 3200—2200 and 1678 cm^{-1} (Found: C, 76·8; H, 5·4. Calc. for $C_{17}H_{14}O_3$: C, 76·7; H, 5·3%).

Hydrolysis of N-(3-*Diphenylcyclopropenylidene*-2,3-*dihydro*-5-*phenyl*-2-*furylidene*)*morpholinium Perchlorate* (15).—The salt was recovered after being boiled with (*a*) water for 8 h, (*b*) 2N-sodium hydroxide for 3 h, (*c*) 2N-hydrochloric acid for 3 h, and (*d*) concentrated hydrochloric acid for 3 h. A mixture of the salt (0·5 g), concentrated hydrochloric acid (15 ml), and acetic acid (15 ml) was heated under reflux. The salt dissolved and a vigorous effervescence occurred. Boiling was continued for 3 h; the solution was then allowed to cool, filtered from a little tar, and poured into water (250 ml), whereupon (2-*benzoylethyl*)*diphenylcyclopropenylium perchlorate* (19) (0·157 g, 40%) separated. It crystallised from acetonitrile as needles, m.p. 194° (decomp.), $\nu_{max.}$ 1674, 1593, 1420, and 1080 cm^{-1}, $\lambda_{max.}$ 225 (ε 23,400), 232 (22,900), 246 (15,100), 292 (20,400), 305 (25,200), and 320 nm (20,200), τ (CD_3·CN) 1·5—2·5 (m, 3 × Ph) and 6·1 (s, 2 × CH_2) (Found: C, 68·4; H, 4·6; Cl, 8·4. $C_{24}H_{19}ClO_5$ requires C, 68·2; H, 4·5; Cl, 8·4%).

Diels–Alder Reactions of 2-*Morpholino*-5-*phenylfuran*.—(*a*) Addition of a solution of the furan (1·15 g) in ether (15 ml) to a solution of maleic anhydride (0·49 g) in ether (10 ml) resulted in an orange solution which, after a few minutes, deposited 2,3-*dihydro*-3-*hydroxy*-6-*morpholino*-3-*phenylphthalic anhydride* (21a) (0·88 g, 54%), yellow needles, m.p. 230—232°, $\nu_{max.}$ 3390, 1800, 1690, 1536, and 1107 cm^{-1} (Found: C, 66·6; H, 5·3; N, 4·3. $C_{18}H_{17}NO_5$ requires C, 66·0; H, 5·2; N, 4·3%). A solution of this adduct (0·5 g) in acetic anhydride (25 ml) was heated under reflux for 2·5 h and then cooled; 6-*morpholino*-2-*phenylphthalic anhydride* (22a) (0·3 g, 64%) separated as amber plates, m.p. 248°, $\nu_{max.}$ 1804, 1760, and 1107 cm^{-1} (Found: C, 69·4; H, 4·9; N, 4·5. $C_{18}H_{15}NO_4$ requires C, 69·9; H, 4·9; N, 4·5%).

(*b*) A solution of the furan (1·15 g) and *N*-phenylmaleimide (0·87 g) in ether (35 ml) deposited 2,3-*dihydro*-3-*hydroxy*-6-*morpholino*-N,3-*diphenylphthalimide* (21b) (1·73 g, 86%) as yellow needles, m.p. 177—179°, $\nu_{max.}$ 3410, 1750, 1665, 1550, and 1116 cm^{-1} (Found: C, 71·3; H, 5·8; N, 6·9. $C_{24}H_{22}N_2O_4$ requires C, 71·6; H, 5·5; N, 7·0%). Dehydration of this compound (0·55 g) as described in (*a*), followed by concentrating the solution, gave 6-*morpholino*-N,3-*diphenylphthalimide* (22b) (0·26 g, 44%), yellow prisms, m.p. 179—180°, $\nu_{max.}$ 1761, 1747, 1705, and 1112 cm^{-1} (Found: C, 75·0; H, 5·3; N, 7·3. $C_{24}H_{20}N_2O_3$ requires C, 75·0; H, 5·3; N, 7·3%).

2-*Phenyl*-Δ^1-*pyrrolin*-5-*one* (27).—Perchloric acid (1·0 ml) was slowly added below 5° to a solution of β-benzoylpropionamide (23a)[8] (1·0 g) in acetic anhydride (50 ml). The resulting solution was stirred for 10 min and then treated with ether (250 ml). The brown oil which separated was thoroughly washed with ether by decantation and then suspended in fresh ether (50 ml), and triethylamine (2 ml) was added. The solution was decanted from a precipitated gum and evaporated, leaving an oil which gradually crystallised. The *pyrrolinone* (0·22 g, 25%) separated from acetone as needles, m.p. 112°, $\nu_{max.}$ 1690, 1600, and 1550 cm^{-1}, τ 2·0—2·8 (m, Ph) and 6·56 (2H, t) and 6·65 (2H, t) (J 4·0 Hz, AA′BB′, CH_2·CH_2), $\lambda_{max.}$ 242 (ε 12,400) and 274infl nm (1200) (Found: C, 75·5; H, 5·7; N, 8·8. $C_{10}H_9NO$ requires C, 75·4; H, 5·7; N, 8·8%).

Cyclisation of β-*Benzoylpropionanilide* (23b).—A suspension of the anilide[8] (2·0 g) in acetic anhydride (40 ml) was treated with perchloric acid (2 ml) below 5°. The resulting solution was stirred for 15 min; addition of ether precipitated 5-*acetoxy*-2-*hydroxy*-1,5-*diphenyl*-Δ^1-*pyrrolinium perchlorate* (28) (2·5 g, 80%), m.p. 88—90° (decomp.) (from acetonitrile), $\nu_{max.}$ 3500—2000, 1770, 1700, and 1100 cm^{-1}, τ (CF_3·CO_2H) 1·8—2·4 (m, CPh), 2·45 (s, NPh), 6·20 (m) and 6·61 (m) (AA′BB′, CH_2·CH_2), and 7·70 (s, Me), $\lambda_{max.}$ (CH_2Cl_2) 247 nm (ε 9500) (Found: C, 54·4; H, 4·7; N, 3·6. $C_{18}H_{18}ClNO_7$ requires C, 54·6; H, 4·6; N, 3·5%). A mixture of this salt (0·5 g) and acetic acid (10 ml) was heated on a steam-bath for 2 min, cooled and treated with ether (50 ml), giving 5-*oxo*-1,2-*diphenyl*-Δ^1-*pyrrolinium perchlorate* (29) (0·2 g, 47%), $\nu_{max.}$ 1840, 1585, 1555, and 1100 cm^{-1}, τ (CF_3·CO_2H) 2·4 (m, 2 × Ph) and 5·73 and 6·59 (AA′BB′, CH_2·CH_2), $\lambda_{max.}$ (CH_2Cl_2) 236 (ε 9400) and 298 nm (2200) (Found: C, 56·9; H, 4·2; N, 4·3. $C_{16}H_{14}ClNO_5$ requires C, 57·2; H, 4·2; N, 4·2%). Triethylamine (2 ml) was added to a suspension of the foregoing salt (0·2 g) in ether (50 ml); after 5 min the mixture was filtered and the filtrate was evaporated. The oily residue solidified in contact with benzene to 1,5-*diphenyl*-Δ^3-*pyrrolin*-2-*one* (30) (0·09 g, 62%), m.p. 167—168° (decomp.) (from benzene), $\nu_{max.}$ 1685 and 1595 cm^{-1}, τ 2·7 (m, CPh), 2·75 (s, NPh), 2·8 (q, 3-H), 3·7 (q, 4-H), and 4·29 (t, 5-H) ($J_{3,4}$ 5·8, $J_{3,5}$ 2·0, $J_{4,5}$ 1·7 Hz), $\lambda_{max.}$ (CH_2Cl_2) 274 nm (ε 4700) (Found: C, 82·0; H, 5·8; N, 6·0. $C_{16}H_{13}NO$ requires C, 81·7; H, 5·6; N, 6·0%).

[3/1125 *Received*, 1*st June*, 1973]

[20] J. Thiele, *Annalen*, 1899, **306**, 145.