DISIC ACIDS

A STUDY OF A NEW SERIES OF STRONG ORGANIC ACIDS AND THEIR CONDENSATION PRODUCTS WITH ALDEHYDES

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(Received in UK 4 December 1974; Accepted for publication 4 March 1975)

Abstract—4-(p-Nitrophenyl)-3,5-dihydroxyisoxazole is a remarkably strong acid which possesses unique chemical reactivity towards carbonyl compounds. It has been shown that these properties are encountered in a series of related 3,5-dihydroxyisoxazole derivatives. It appears that this isoxazole system is very electron deficient, a fact that together with a neighboring group effect is responsible for the exceptional acidity and reactivity. The electron deficiency is also reflected in the deshielding of the aromatic protons. Comparison of the NMR spectra served as a criterion for the electron deficiency of the isoxazole moiety. This new class of acids yield a variety of novel systems. The influence of substitution on the visible spectrum of the aldimonium system obtained with derivatives of benzaldehyde is discussed.

A. Acidity and UV absorptions. The first member of this series i.e. 4-phenyl-3,5-dihydroxyisoxazole (1, R=C₆H₅) was reported' in 1971. For convenience the shorter name phenyldisic acid has been adopted. The pK_a of this compound is 1.86 and it has some very unusual physical' and chemical² properties. We have now prepared several derivatives of disic acid, which have different aryl groups at the 4 position (1). p-Nitrophenyldisic acid (1, R = p-NO₂-C₆H₄) has a remarkable acidity and is probably one of the strongest organic acids. It has a pK_a of -0.1 which is lower than that of picric acid ($pK_a = 0.3$) or trifluoroacetic acid ($pK_a =$ 0.23).

The dianion of p-nitrophenyldisic acid has a deep red color ($\lambda_{max} = 438$, $\epsilon = 16600$). The first ionization could be followed by a change in the UV absorption ($\lambda_{max} = 388$, $\epsilon = 12800$ for the monoanion and $\lambda_{max} = 349$, $\epsilon = 11400$ for the undissociated acid). This enabled the determination of the first ionization constant unlike phenyldisic acid' where the absorption does not change considerably on the first ionization. In other derivatives slight changes in UV absorptions could be observed (Table 1). In the case of p-nitrophenyldisic acid (1, R = p-NO₂-C₆H₄) the protonation pK_a could also be determined. This fact excludes the possibility of confusion between this pK_a and the acidic dissociation.



The acidity which is shown here is explained by the various canonical formulations of the anion (Scheme 1). Out of the four tautomeric species shown in the scheme the saturated one is the most unfavorable. The numerous resonative formulae could be summarized in the resonance hybrids 2-4. Resonance formulations which involve the benzene ring like 5 will have only a minor contribution but for p-nitrophenyldisic acid the canonical 6 should be considered. The contribution of this kind of delocalization is demonstrated by the increase in acidity and by the great bathochromic shift in the light absorption. In all other derivatives a significant shift is observed only on the second ionization. The strong acidity, comparable to inorganic acids, is manifested in p-nitrophenylidisic acid by the orange color that its crystals acquire in saline solutions down to a concentration of 0.3 M NaCl.

The dianion of disic acid can be represented by several resonance hybrids (Scheme 2). The deep red color of the dianion of p-nitriophenyldisic acid is probably due to the quinonoid hybrids as 10 (Scheme 2).

R	pK _{a1}	p <i>K</i> _{a2}	Dianion	Monoanion	Neutral	Cation	
p-NO ₂ -C ₄ H ₄ ^a		9.05	438(16.6)	388(12.8)	349(11.4)	277(14.0)	
,,		-	232(12.7)	236(15-1)	235(14.5)		
p-Cl-C+H+	1.3	9.60	283(11.7)	260(15.3)	256(14-5)	_	
p-CHO-CH	2.0	10.36	269(12.8)	256(20.8)	250(14-5)	_	
I-C10H7	0.9	9-55	322(7.5)	292(11.9)	282(7.0)	270(30-0)	
				280(11.9)	222(60.0)	222(62.0)	
$2 - C_{10}H_7$	1.0	9.90	347(2.6)	302(9.7)	280sh	256(24-6)	
			310(13-2)	291(10.6)	252(19.6)	223(53-0)	
			267(21-2)	259(34-0)	223(44.0)		
			. ,	216(44-0)			
p-CH ₃ CONH-C ₆ H ₄		-	292(17.0)	271(19.3)	259(21.6)	239(13-6)	
C ₆ H,	1.86	9.98	277(12-5)		254(21-0)		

Table 1. Dissociation constants and UV spectra of disic acids (1). $\lambda_{max}(\epsilon \times 10^3)$

" pKa of protonation = -4.6.







B. IR and NMR properties. The OH absorption of disic acids in the IR region is diffuse and is shifted to higher wavelengths as observed in phenyldisic acid.' The CO absorption in the solid state is also weak and in the case of *p*-nitrophenyldisic acid (1, $R = p - NO_2 - C_6H_4$) it has almost disappeared. There is a slight shoulder at 1670 cm⁻¹ in the solid state (nujol) but on dissolving in DMSO a strong CO absorption is observed at 1750 cm⁻¹. All derivatives have a weak absorption in the solid state (1680-1690 cm⁻¹) and a strong one when dissolved in DMSO (1730-1740 cm⁻¹). The spectral properties of disic acids indicate a dimeric structure in the solid state and probably also in solution.¹ p-Chlorophenyldisic acid (1, $R = p - Cl - C_6 H_4$ and 2-naphthalenedisic acid (1, R = $2-C_{10}H_{7}$) remain as semihydrates.

The two acidic protons of disic acids give a single peak in the NMR spectra at a very low field; about δ 12.0 in DMSO-d₆. On increasing the content of water this peak moves upfield and at the same time its integration increases as a result of exchange processes. The semihydrates absorb at about δ 9.5 (a shift of 2.5 ppm) and the "dihydrates" at about δ 6.6.

The remarkable electron withdrawing effect of the dihydroxyisoxazole moiety is also illustrated in its deshielding of the phenyl protons in phenyldisic acid¹ which is associated with splitting of the aromatic protons' bands. In the para substituted phenyldisic acids we were able to observe a non-first-order AB quartet in which the two inner bands increase as the deshielding caused by the substituent approaches that of the dihydroxyisoxazole group (Table 2). With the nitro group the two outermost bands dwindle to zero and a singlet is observed. Thus we may conclude that the deshielding effect of the heterocyclic ring in disic acids is comparable to that of a nitro group. In diethyl α -(p-nitrophenyl)malonate (Table 3) the protons ortho to the nitro group (H_A) absorb at δ 7.95 $(\Delta_{AB} = 32 \text{ c/s}, J = 9 \text{ c/s})$. While on ring closure to p-nitrophenyldisic acid the two bands coincide at δ 7.95.

Assuming that the heterocyclic moiety in disic acids has the same deshielding effect as a nitro group we may

Table 2. NMR absorptions of the phenyl protons in para substituted phenyldisic acids. δ in DMSO-d₆

x	H	Нав	H₽	Δ_{AB}	JAB			
CH ₃ O	6·75 d		7.60 d	51 c/s	9 c/s			
CI	7∙10 d		7•70 d	35 c/s	9 c/s			
CH ₃ CONH	7•40 d		7∙60 d	12 c/s	8 c/s			
O₂N	-	7∙95 s	—	0	0			

Table 3. NMR absorptions of the phenyl protons in para substituted diethyl phenylmalonates, δ , in CCl₄

$X - CH COOC_2H_3$									
х	H	Нав	Нв	Δ_{AB}	J _{ab}				
CH₃O Cl CH₃CONH° O₂N	6·60 d 7·40 d 7·95 d	7∙10 s	7·10 d 7·28 d 7·40 d	30 c/s 0 12 c/s 32 c/s	8 c/s 0 8 c/s 9 c/s				

^a in CDCl₃.

expect that the influence of a OMe group is in the other direction. In fact the Δ_{AB} in *p*-methoxyphenyldisic acid is of 51 c/s which is 21 c/s larger than in diethyl α -(pmethoxyphenyl)malonate (Table 3). The OMe group has a shielding effect as compared to the malonate residue; the electron deshielding of the latter has a magnitude close to that of a Cl atom as we have observed in diethyl α -(p-chlorophenyl)malonate (δ 7.10, Table 3). By comparing the two Tables (2 and 3) we can see that the minimum of the difference between the electron deshielding effects is in the disic acids at the NO_2 substituent and in the malonates is at the chlorine. In *p*nitrophenylmalonate there is again a large difference but in the opposite direction.

C. Synthesis and chemical properties. The substituted malonates which are the starting materials for disic acids were prepared by methods described earlier.³ Diethyl α -(p-acetamidophenyl)-malonate was prepared by the acetylation of the p-aminophenyl malonate which was obtained from diethyl α -(p-nitrophenyl)malonate by catalytic hydrogenation. The acetylation was carried out either on the isolated diethyl α -(p-aminophenyl)malonate or *in situ* while carrying out the hydrogenation. The cyclization with hydroxylamine was performed by a slight modification of a method described earlier¹ for phenyl-disic acid. The strong p-nitrophenyldisic acid required a large excess of HCl for precipitation.

All the disic acids which are described react spontaneously with aromatic aldehydes to give N-arylmethylidene-4-phenylisoxazo-5-onium enolates (11). For convenience these zwitterionic colored products⁴ are referred below also as aldisates. Unsaturated aldisates like cinnamaldisate and citralaldisate are also quite stable. Some of the new aldisates are reported in the Experimental. A spectral study of the p,p'-disubstituted aldisates (14) is included in section D below. Disic acids yield with acetone a yellow coloration, which then gives a condensation product (12); the same product is obtained from the reaction of disic acids with mesityloxide. Compound 12 yields on gentle heating in alcohols the bicyclic system 13 as was described for the unsubstituted product.² Reaction with acrolein or crotonaldehyde results in a paramagnetic polymer or oligomer.² p-Nitrophenyldisic acid gave an oligomer only with acrolein, whereas with crotonaldehyde an unidentified red product was obtained. Some representative examples are described in the Experimental.

Table 4. The influence of substituents in phenylbenzaldisates on the wavelengths of visible light absorption in dioxane (λ_{max} , nm), (values obtained in TFA are given in brackets)

xY	СН₃О	н	CI	NO₂	λ x- λ _H	λγ-λμ
CH3O	502	466	468	430	-14	+40
Н	520(463)	480(445)	476(453)	440 sh	_	
CI	538(477)	495(458)	490(462)	460	+15	-4
NO ₂	568° (528)	523(498)	522(508)	_	+43	-40

^a In this case the product was insoluble in dioxane and the expected absorption in dioxane is derived by extrapolation from the spectra taken in trifluoroacetic acid(TFA).

bathochromic shift which was earlier observed⁴ in phenylaldisates having a more extended conjugation (e.g. in cinnamaldisate), is caused also by electron withdrawing groups (e.g. NO₂ and Cl) present in the benzylidene group. On the other hand, electron donating groups like a OMe group exert a hypsochromic shift. With substituents on the phenyl disic acid component the reverse phenomenon is observed. The shifts, as compared to hydrogen $(\lambda_x - \lambda_H)$ and $\lambda_y - \lambda_H$), which are caused by the various substituents are shown in Table 4.

A simple rule of additivity is observed in the 15 combinations which were studied here. The shift in wavelength which is caused by a certain combination $(\Delta \lambda)$ is the sum of $\Delta \lambda_{XH}$ and $\Delta \lambda_{YH}$ which are $(\lambda_X - \lambda_H)$ and $(\lambda_Y - \lambda_H)$ respectively (Table 4). A comparison between the experimental shifts $(\Delta \lambda)$ and the calculated $\Delta \lambda_{XY} = (\lambda_X - \lambda_H) + (\lambda_Y - \lambda_H)$ is given in Table 5. A very reasonable agreement between the experimental and the calculated values is observed.

Aldisates derived from p-dimethylaminobenzaldehyde (Table 6 and Ref. 4) have intense peaks at 405-415 nm ($\epsilon = 20000-25000$). The wavelength of this band is very



As we have suggested before, the reactivity of the nitrogen towards carbonyl compounds is enhanced by the neighboring acidic OH group. In conclusion, we believe that both the unique acidity and the peculiar reactivity of this heterocyclic system arise from a combination of electron deficiency and group proximity, which are encountered in aryldisic acids.

D. Visible spectra of 4,4'-disubstituted phenylbenzaldisates



The stability of this betaine structure is attributed to electron delocalisation, a spectral study is therefore important for further understanding of the properties and stability of such an unusual structure. The wavelengths of the visible absorptions of some 4,4'-disubstituted phenylbenzaldisates (14) are shown in Table 4. It is evident that a

Table 5. Experimental shifts in wavelengths $(\Delta \lambda)$ compared to the calculated $(\Delta \lambda_{XY} = \Delta \lambda_{XH} + \Delta \lambda_{YH})$, nm

Combination		Δλ°					
X	Y	Found	Calcd.				
CH,0	CI	-12	-18				
CH3O	NO2	-50	-54				
Cl	CH3O	+58	+55				
Cl	CI	+10	+11				
NO ₂	Cl	+39	+42				
CL	NO ₂	-20	-25				
CH3O	CH ₁ O	+22	+36				
NO ₂	CH ₃ O	+88	+83				

^a It expresses the difference between the substituted phenylbenzaldisates and the unsubstituted product where X = Y = H.

little dependent on the substituent in the phenyldisic acid component. The small effect which is observed is rather in the opposite direction. p-Dimethylaminobenzaldisates are very stable, their stability permits preparation even in IN HCl. None of the other aldisates is preparable in water. The delocalization in phenylbenzaldisate and its derivatives may be expressed by several dipolar structures. Besides of the permanent charges of the betaine moiety there may be hybrids of a quinonoid structure with charges at the *para* and *ortho* positions in both phenyl groups. Representative of the hybrids for the parent unsubstituted phenylbenzaldisate are structures 15 and 16.



The coplanar conjugated system with the numerous ionic forms as shown in Structure 15 and 16 bring about stabilization and an over all decrease in the differences between the energies of the ground and excited states. This explains why these aldisates are formed and the long wavelengths of its absorptions, e.g. 480 nm for the parent unsubstituted phenylbenzaldisate.

When substituents are present in the *para* positions of both phenyl groups they may stabilize the quinonoid structure by the extension of conjugation. They may either share a pair of electrons or accept an electron, as in the case of a nitro group, yielding hybrids with charges on one or on both substituents as shown in Structures 17 and 18. benzylidene group) should decrease stability. In general, destabilization by substituents is followed by a hypsochromic effect. (b) An electron withdrawing substituent on the phenyldisic acid component and an electron releasing substituent on the benzylidene group should stabilize the products because of the extension of conjugation in the favored direction. In this case a bathochromic shift is predicted.

In fact, these speculations are verified only in regards to stabilization of phenylbenzaldisates. Introducing the appropriate substituents or combination of substituents results in products which differ considerably in their stability towards hydrolysis and readiness of formation. This phenomenon is very much pronounced in the case of the aldehydic component. The extreme examples are the derivatives of p-dimethylaminobenzaldehyde which are remarkably stable.

As regards to the influence on the wavelengths, in all cases the reverse of the predicted changes are observed. These are explained as follows:

(i) When there is an electron donating group on the phenyldisic acid component as well as when there is an electron withdrawing substituent on the benzylidene group, delocalization is enhanced and extended, as shown in structures 19–22 respectively. There is no way where one of these substituents may compensate one of the charges on the isoxazole moiety, thus the conjugation has to stretch along the whole molecule. The shift here is therefore larger, (Table 4 and 5). When there is a combination like $X = NO_2$, $Y = CH_3O$, a very large bathochromic shift is observed (88 nm, Table 5). In such a case both substituents promote delocalization to the same direction resulting in structure 17 where it is extended to both substituents.

(ii) Where there is an electron donating group on the benzylidene group and an electron withdrawing group on



It was shown above that disic acids are electron deficient compounds so that the favored electron donor should always be the aldehydic component. The electron transfer from one component to the other is, in fact, responsible for the stability of aldisates. On this basis the effect of *para* substituents on the stability and spectra should be as follows: (a) An electron donating group on the phenyldisic acid component as well as an electron withdrawing group in the aldehydic component (on the the disic acid component, there is in both cases a certain decrease in conjugation by partial counterbalancing the charges of the betaine moiety as shown in structures 23 and 24 respectively.

In structure 23 an uncharged trivalent nitrogen is formed instead of the evidently less stable imonium cation. This should, of course, explain the enhanced stabilization that comes together with a hypsochromic shift. A combination where $Y = NO_2$, $X = OCH_3$ yields a



product that absorbs at 138 nm shorter wavelength than its isomer $(X = NO_2, Y = OCH_3)$. The band at about 410 nm which is observed in all derivatives of *p*dimethylaminobenzaldehyde is derived from the

chromophore \longrightarrow N Me₂ with very little conjuga-

tion across the phenyldisic acid component.* The higher extinction coefficient in these derivatives which is about 5-10 times greater than in the other derivatives, is probably a result of the marked change in the dipole moment in passing from the ground state to the excited state. It may also involve a transition between two ground states in one of which the dimethylamino nitrogen is cationized. The second part of the molecule generally absorbs in the UV region. In the case where $X = N(CH_3)_2$, $Y = NO_2$, the phenyldisic acid moiety probably absorbs in the visible light. This is expressed by an inflection at about 440 nm. This absorption probably comes from structure 25 where the enolate charge is on the nitro group yielding two separate chromophores. In fact, the dianion of p-nitrophenyldisic acid (10) which has a structure similar to a part of 25, absorbs at 438 nm (Table 1).



EXPERIMENTAL

The NMR spectra were determined with a Varian T-60 spectrometer with internal TMS as reference. Electronic spectra were taken with a Varian Techtron model 635 and IR spectra with Perkin Elmer model 237 spectrophotometer. IR in DMSO was taken by placing a thin layer of a concentrated soln between NaCl windows.

p-Nitrophenyldisic acid (1, $R = p - NO_2 - C_6H_3$). Hydroxylamine hydrochloride (7.0 g) was dissolved in boiling MeOH (80 ml) and cooled to 40°. KOH (11.2 g) was dissolved with heating in 50 ml MeOH and cooled at 20°. The two methanolic solns were combined by the addition of the KOH soln to the hydroxylamine soln with shaking and cooling on ice. After cooling for additional 5 min the precipitated KCl was filtered off and a soln of diethyl α -(p-nitrophenyl)malonate (9.0 g) in MeOH (40 ml) was added. The red soln was kept 48 hr at room temp. and evaporated in vacuo to a volume of 20 ml. p-Nitrophenyldisic acid was precipitated by the addition of 35% HCl (50 ml) with cooling in ice bath. The yellow ppt was collected and dried in the air. It was recrystallized by dissolving in THF and adding light petroleum (40-60). The yield was 6.4 g (90%), m.p. 232°. A sample was dried in vacuo on P2O5 at 100°. (Found: C, 48.64; H, 2.81; N, 12.62. Calcd. for C₉H₆N₂O₅: C, 48.66; H, 2.72; N, 12.61%).

p-Methoxyphenyldisic acid (1, R=CH₃O-C₆H₃). Free hydroxylamine was prepared as above in MeOH (220 ml) from hydroxylamine hydrochloride (24 g) and KOH (36.8 g). A soln of diethyl α -(p-methoxyphenyl)malonate (24 g) in MeOH (80 ml) was added and the yellow soln was kept 24 hr at room temp and then concentrated *in vacuo* to about 40 ml. The product was



precipitated by the addition of 17.5% HCl (160 ml) and cooling overnight. The ppt was dried in the air and recrystallized from EtOAc-light petroleum (40-60), 11.6 g (62%) m.p. 175°. A sample was dried in vacuo on P_2O_3 at 100°. (Found: C, 57.76; H, 4.56; N, 6.87. Calcd. for $C_{10}H_9NO_4$: C, 57.97; H, 4.38; N, 6.76%).

p-Chlorophenyldisic acid (1, R=Cl-C₆H₄). Diethyl α -(p-chlorophenyl)-malonate (19·3 g) in MeOH (80 ml) was added to a soln of free hydroxylamine prepared from hydroxylamine hydrochloride (17·5 g) in MeOH (120 ml) and KOH (28·0 g) in MeOH (80 ml) as above. After keeping for 48 hr at room temp. the MeOH was concentrated *in vacuo* to 40 ml and the product precipitated by the addition of water (80 ml) followed by 35% HCl (80 ml); p-chlorophenyldisic acid was recrystallized from EtOAc-light petroleum (40-60), 7·1 g (55%), m.p. 169°. After drying *in vacuo* at 80° the product still held a half a molecule of water. (Found: C, 48·88; H, 3·19; N, 6·22. Calcd. for C₉H₆NO₃Cl.1/2H₂O: C, 49·04; H, 3·01; N, 6·02%).

Upon drying on P_2O_5 at 110° the anhydrous acid was obtained. (Found: C, 50.92; H, 3.16; N, 6.55. Calcd. for $C_9H_6NO_3Cl$: C, 51.06; H, 2.89; N, 6.65%).

1-Naphthalenedisic acid (1, $R=C_{10}H_7$). This product was prepared by a procedure close to those described above. The quantities were 14g of hydroxylamine hydrochloride in 80 ml MeOH, 23g KOH in 60 ml MeOH and 18g diethyl α -(1naphthyl)malonate in 150 ml of MeOH. The mixture had to be kept at room temp. for 5 days, concentrated *in vacuo* to 50 ml and the product was precipitated by the addition of 17.5% HCl (100 ml) with cooling. It was recrystallized from EtOAc-light petroleum (40-60), 5·2g (37%), m.p. 165°. 1-Naphthyldisic acid is the only derivative which did not crystallize as a semihydrate. (Found: C, 68-60; H, 4·01; N, 6·12. Calcd. for C₁₃H₉NO₃: C, 68·72; H, 3·99; N, 6·16%).

2-Naphthalenedisic acid (1, $R=C_{10}H_7$). The same procedure was used as above with the same quantities as for 1-naphthalenedisic acid, starting from 18 g diethyl α -(2-naphthyl)malonate. The yield was 5-1 g (35%). The product was recrystallized by dissolving in EtOAc and precipitating with chloroform, m.p. 148°. The product turns brown on heating. 2-Naphthalenedisic acid was obtained as a semihydrate. (Found: C, 65-95; H, 4-11; N, 5-75. Calcd. for C₁₃H₉NO₃.1/2H₂O: C, 66-10; H, 4·26, N, 5·93%).

p-Acetamidophenyldisic acid (1, R=CH₃CONH-C₈H₄). Diethyl α -(p-acetamido)-malonate (9·7 g) was dissolved in MeOH (60 ml) and added to free hydroxylamine which was prepared as above from hydroxylamine hydrochloride (7 g) in 40 ml MeOH and KOH (11·2 g) in 35 ml MeOH. After keeping for 72 hr at room temp. the solvent was evaporated as above to 20 ml, cooled in ice bath and acidified with 35% HCl (60 ml). The ppt was collected and recrystallized by dissolving in MeOH and reprecipitated by ether and light petroleum, 3·2 g (42%), m.p. 224°. (Found: C, 54·46; H, 4-69; N, 11·38. Calcd. for C₁₁H₁₀N₂O.1/2H₂O: C, 54·32, H, 4·56; N, 11·52.%).

Upon drying on P_2O_5 in vacuo at 110° an anhydrous compound was obtained. (Found: C, 56·16; H, 4·42; N, 11·66. Calcd. for $C_{11}H_{10}N_2O_4$: C, 56·41; H, 4·30; N, 11·96%).

Diethyl α -(p-acetamidophenyl)malonate

Method A. Diethyl α -(p-nitrophenyl)-malonate (5.6 g) was dissolved in AcOH (100 ml). Ac₂O (4 g) and 10% Pd-C (100 mg) were added and the soln was shaken with H₂ (3 atm). The catalyst was then removed by filtration. The soln was concentrated to 50 ml and diethyl α -(p-acetamidophenyl)malonate was precipitated by the addition of water and recrystallized from EtOH, 4.7 g (80%), m, p. 146°. (Found: C, 61·13; H, 6·38; N, 4·96. Calcd. for C₁₅H₁₀NO₅: C, 61·42; H, 6·53; N, 4·78%).

Method B. Diethyl α -(p-nitrophenyl)malonate (3 g) was dissolved in EtOH (40 ml), 10% Pd-C (50 mg) and conc HCl (1 ml) were

^{*}Similar wavelengths are observed in *p*-dimethylaminonitrobenzene and *p*-nitrophenolate.³

R'	R ²	Yield %	Mp ℃	Formula	%C	Calcd. %H	%N	%C	Found %H	%N	Ir (CO) in KBr cm ⁻¹	Vis ^e in dioxane λ _{max} (ε × 10 ³)
p-NO ₂ -C ₆ H ₄	p-Me₂N-C6H4	70	280	C ₁₈ H ₁₅ N ₃ O ₅	61-19	4·28	11.89	61.23	4.30	11.76	1765, 1700	415, 440 in.
$p - NO_2 - C_6H_4$	o,p-diMeO-C ₆ H3	80	262	$C_{12}H_{14}N_{2}O_{7}$	58·38	3.81	7.56	58-43	4.09	7.38	1795, 1740	450 sh
p-NO2-C6H4	p-MeO-C₅H₄	60	250	C17H12N2O6	60.00	3.55	8 ·23	60-30	3.73	8 ∙27	1780, 1710	430(6.4)
p-NO₂-C₅H₄	C&H,CH=CH	85	250	C ₁₈ H ₁₂ N ₂ O ₃	64·29	3.60	8-33	64-35	3.57	7.77	1780, 1720	485
p-NO₂-C6H₄	₽–CI–C₅H₄	40	221	C16H9N2O5Cl	55.75	2.63	8.10	55-47	2.54	7.66	1795, 1740	460(1·0)
p-NO2-C6H4	<i>m</i> - Me O, <i>p</i> -OH-C ₆ H ₃	75°	257	C17H12N2O7	57-31	3.39	7.86	56-00	4.17	7.75	1785, 1730	450 sh
p-NO2-C6H4	С,Н,	70	248	C ₁₆ H ₁₀ N ₂ O ₅	61.94	3.25	9.03	62·15	3.40	9.08	1780, 1740, 1725	440 (1·3)
p-MeO-C ₆ H₄	p-Me₂N-C₅H₄	90	220	$C_{19}H_{18}N_2O_4$	67·95	5.36	8·28	68-45	5.40	8.40	1770, 1685	405(20)
p-MeO-C ₆ H₄	p-MeO-C ₆ H₄	90	205	C18H15NO5	66-46	4-65	4·31	67·61	4.88	4.50	1760, 1700	502(6-1)
p-MeO-C ₆ H₄	o,p-diMeO-C ₆ H3	60	208	C19H17NO6	64·22	4.82	3.94	64-44	4.89	3·91	1785, 1700	505(6-4)
p-MeO-C ₆ H₄	₽-Cŀ-C ₆ H₄	45	215	C ₁₇ H ₁₂ NO ₄ Cl	62.00	3.65	4.25	61.67	3.77	3.97	1820, 1790, 1710	538(1-1)
p-MeO-C ₆ H₄	C&H,CH=CH	85	222	C ₁₉ H ₁₅ NO ₄	71·02	4·71	4.36	70.85	4.78	4.36	1770, 1700	575(8-4)
p-MeO-C ₆ H₄	m-MeO,p-OH-C ₆ H ₃	60	194	C ₁₈ H ₁₅ NO ₆	63-34	4-43	4.10	63·10	4.50	4.00	1790, 1710	501(5-4)
p-MeO-C ₆ H₄	p-OH-C₅H₄	25	198	C17H13NO5	65-59	4·21	4.50	65-40	4.78	4.38	1800, 1730	500(5.0)
pClC₅H₄	p-MeO-C₀H₄	70	242	C ₁₇ H ₁₂ NO ₄ Cl	62.00	3.65	4.25	61.66	3-90	4.04	1760, 1705	468(3-6)
p−Cl−C₅H₄	p-Me₂N-C6H4	90	238	C ₁₈ H ₁₅ N ₂ O ₃ Cl	63·34	4.38	8.18	63·48	4.48	8.03	1765, 1685	410
₽-CI-C₅H₄	°C ₆ H,	65	215	C16H10NO3Cl	64·12	3.34	4.60	63-83	3.42	4.46	1790, 1730, 1710	476(1.2)
pClC₅H₄	С₄Н₃СН=СН	60	221	C ₁₈ H ₁₂ NO ₃ Cl	66-45	3.69	4.30	66·19	3.99	4.14	1790, 1690	525(3.0)
p−Cl−C₅H₄	p-NOz-C6H4	25ª	210	C16H9N2O5Cl	55.75	2.63	8 ·10	55-94	2.88	7.79	1790, 1735	522
1-C10H2	p-McO-C₄H₄	60 ^{*.c}	211	C21H15NO4	73-04	4.38	4.06	72.87	4.15	3.94	1800, 1710	500(2-3)
2C10H7	p-Me₂N-C6H4	80	242	$C_{22}H_{18}N_2O_3$	73.73	5.06	7.82	73·60	5-33	7.33	1755, 1690	413(25.0)
2-C ₁₀ H ₇	p-MeO-C ₆ H₄	85	211	C21H15NO5	73·04	4.38	4.06	73·08	4.49	3.95	1795, 1710	485(5.0)
2C10H7	C.H,	30 ^{*.c}	190	C20H13NO3	76·18	4.16	4.44	76-43	4.25	4.30	1785, 1725	505(1.2)
C6H3	<i>p−</i> CI−C₅H₄	50°	225	C10H10NO3Cl	64·12	3.34	4.60	64 ·17	3.55	4·29	1795, 1720, 1700	495(2-0)

Table 6. N-Arylmethylidene-4-arylisoxazol-5-onium-3-enolates (11).

^a Values of ϵ are approximate because of insolubility and instability in dioxane and sometimes undeterminable. ^b Ether was added to cause precipitation. ^c A few ml of TFA were necessary to start the reaction. ^a The reaction performed in TFA. ^c The product is isolated by evaporation of the solvent and trituration in ether.