X=Y–ZH Systems as Potential 1,3-Dipoles. Part 8.[1] Pyrrolidines and Δ⁵-Pyrrolines (3,7-Diazabicyclo[3.3.0]octenes) from the Reaction of Imines of α-Amino Acids and their Esters with Cyclic Dipolarophiles. Mechanism of Racemisation of α-Amino Acids and their Esters in The Presence of Aldehydes

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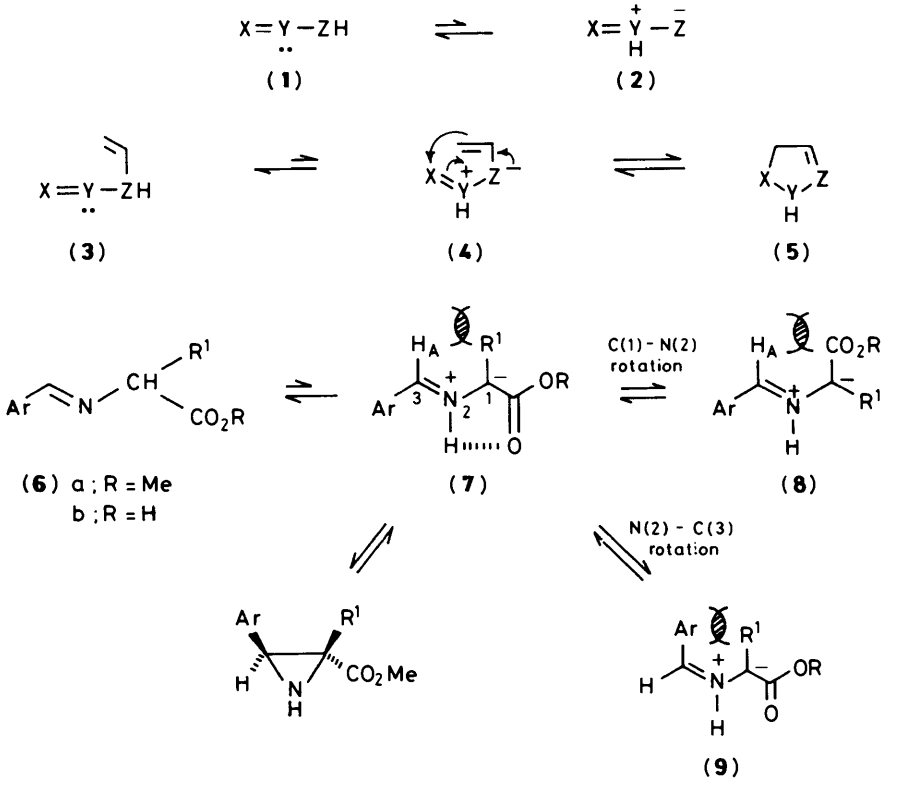
Imines of α-amino acid esters with aromatic, heterocyclic, and aliphatic aldehydes generate azomethine ylides stereospecifically by a prototropic shift on heating in toluene. The azomethine ylides undergo cycloaddition to *N*-phenylmaleimide, maleic anhydride, and *p*-naphthoquinone *via* an *endo*-transition state to give racemic, single diastereoisomeric, cycloadducts. α-Amino acids undergo analogous cycloadditions, without decarboxylation, in hot acetic acid. Mechanisms of racemisation of α-amino acids and their esters in the presence of aldehydes are discussed. The pyrrolidine cycloadducts (**22**) are smoothly oxidised to the corresponding Δ⁵-pyrrolines (**33**) by dichlorodicyano-*p*-benzoquinone.

The concept of a formal 1,2-proton shift in X=Y–ZH systems generating 1,3-dipoles (**1**) ⇌ (**2**)[2] and 1,5-dipoles (**3**) ⇌ (**4**) ⇌ (**5**)[3] has proved mechanistically interesting and synthetically rewarding. It has provided a new perspective on the chemistry of pyridoxal enzymes,[4] and the mechanism of the ninhydrin reaction[5] as well as providing a simple approach to a wide range of heterocyclic systems. The concept originally developed from our new synthesis of dehydroamino acids[6,7] and recently others have reported applications in natural product syntheses.[8]

Imines of amino acid esters when heated in organic solvents generate the 1,3-dipole (**7a**) in a kinetically controlled process (Scheme 1). Stereomutation of (**7**) to (**8**) occurs when the kinetic dipole has two aryl groups at the terminii of the azomethine ylide system (**7a**; R¹ = Ph) and when the dipolarophile is less active than maleimides, *i.e.* maleate and fumarate esters,[1] acrylate esters,[9] acrylontrile[9] *etc.* Thus the occurrence of dipole stereomutation in cycloadditions of (**6a**) is a function of both imine structure and dipolarophile reactivity. The kinetic dipole (**7**) does not stereomutate to (**9**) (Scheme 1) as shown by stereochemical studies of the stereoisomeric pyrrolidines derived from (**6a**) and maleate esters.[1] Thus regiospecific rotation about the C(1)–N(2) bond in (**7a**) occurs and N(2)–C(3) rotation is not observed. In terms of dipole stability (**9**) would be predicted to be the least stable of the three azomethine ylides based on steric considerations. Based on Huisgen's extensive studies[10] of the

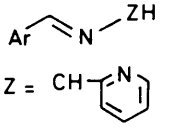


Scheme 1.

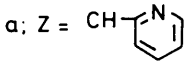
stereomutation of aziridines and the addition of aziridines to dipolarophiles it would be expected that aziridines might feature in the imine-dipole equilibria (Scheme 1). At present we have no evidence for this possibility. The relative order of the steric interactions between H_A and R^1 in (**7**) and H_A and the ester group in (**8**) will depend on the steric bulk of R^1. Studies of intramolecular cycloaddition of (**6a**; R^1 = Ph) to non-activated alkenes suggest (**7a**; R^1 = Ph) and (**8a**; R^1 = Ph) (Scheme 1) have comparable stability, *i.e.* such reactions result in the trapping of (**7a**) and (**8a**) in *ca.* 50:50 ratio.[11] For reactive dipolarophiles such as maleimides the energy barrier to dipole stereomutation is higher than the energy of activation of the cycloaddition, *i.e.* dipole formation (**6a**) ⟶ (**7a**) is the rate determining step.[12] Dipole stereomutation (**7a**) ⇌ (**8a**) involves loss of *ca.* 5—6 kcal of stabilisation due to the intramolecular hydrogen bond in (**7a**). Thus imines lacking a terminal substituent capable of hydrogen bonding might exhibit a lower barrier to stereomutation. We have studied a range of terminal substituents (**10a—e**) together with various lactam and thiolactone substituents.[13] In cases (**10a—c**) where dipole stereomutation might occur, only one dipole, corresponding to (**7a**), is trapped with maleimide dipolarophiles. However, in these cases intramolecular hydrogen bonding, involving the ring imino nitrogen atoms in (**10a**) and (**10b**) and phenolic group in (**10c**), can still occur. In contrast to these observations Tsuge *et al.*,[14] following up earlier French work,[15] using the terminal cyano substituted imines (**11**) have observed dipole stereomutation for (**11a**) and (**11b**) even in cycloadditions with maleimides. Moreover, dipole stereomutation was accelerated in the presence of 0.1—5 mol% of organic acids. In the case of dipoles such as (**12**) and (**13**), derived from (**11**), we would expect lower energy barriers to stereomutation because they lack the 5—6 kcal of stabilisation accruing from intramolecular hydrogen bonding in (**7**). The unexplained affect of weak organic acids lowering the stereoselectivity of the cycloaddition is probably related to the capacity of the acids to further reduce the energy barrier to dipole stereomutation by protonating the nitrile group in the azomethine ylide (**12**) ⟶ (**14**) allowing rotation around the C(1)–N(2) bond. We have earlier reported the rate accelerating effects of Lewis and Bronsted acids on the cycloadditions of (**6a**)[16] but again we only observe the formation of the kinetic dipole (**7a**) in cycloadditions with *N*-phenylmaleimide.

This paper is concerned with the reactions of (**7a**) and (**7b**) with the cyclic dipolarophiles *N*-phenylmaleimide (**15a**), maleic anhydride (**15b**) and *p*-benzoquinone. Heating the imines (**6a**) with these cyclic dipolarophiles in boiling toluene for varying periods of time gave, in general, high yields of substituted pyrrolidines (**16a**, **b**) and (**17**) (Table 1) as single diastereoisomers.

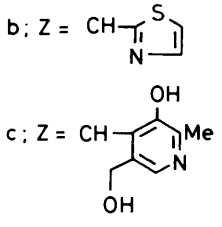
N-Phenylmaleimide (**15a**) proved to be the most convenient dipolarophile for delineating the *scope of* the reaction. Commercial samples of (**15a**) contain small amounts of acidic impurities, presumably the maleamic acid, which accelerate the cycloaddition. A wide variety of both aryl and heterocyclic aldehydes and α-amino acids esters have been successfully employed in these cycloadditions (Table 1). No Diels–Alder adducts were isolated when the imines contained a furan moiety [*i.e.* (**6a**; Ar = 2-furyl)] and optically active α-amino acid esters gave rise, as expected, to racemic products. Imines of aliphatic aldehydes (**18a—f**) also under analogous cycloadditions (Table 1) although the opportunity for imine-enamine equilibration (**19**) ⇌ (**20**) and subsequent reactions of the enamine tautomer frequently makes aliphatic aldehydes less attractive substrates.



(**10**) a; Z =



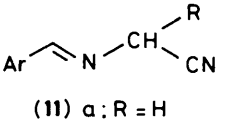
b; Z =



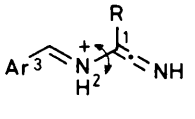
c; Z =

d; Z = fluoren-9-yl

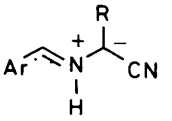
e; Z = dibenzotropan-11-yl



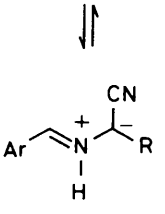
(**11**) a; R = H
b; R = Ph



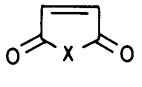
(**14**)



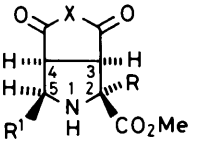
(**12**)



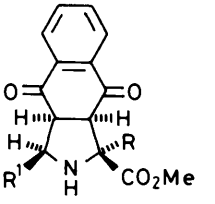
(**13**)



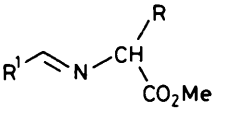
(**15**) a; X = NPh
b; X = O



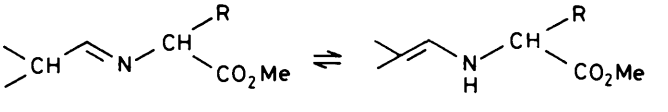
(**16**)* a; X = NPh
b; X = O



(**17**)



(**18**) a; R = Ph, R^1 = Bu^t
b; R = Ph, R^1 = Pr^i
c; R = Ph, R^1 = $CHBu^i$
d; R = Ph, R^1 = $CH(OEt)_2$
e; R = Ph, R^1 = CO_2Et
f; R = Me, R^1 = $CH(OEt)_2$



(**19**) (**20**)

* The numbering employed for n.m.r. purposes differs from that used in the Experimental section for the purposes of systematic nomenclature.

Table 1. The pyrrolidines (**16a, b**) and (**17**) derived from the cycloaddition (toluene, 110 °C) of the imines (**6a**) to cyclic dipolarophiles

Pyrrolidine (16a, b), (17)	R^1	R	Reaction time (h)	Yield (%)[a]	M.p. (°C)
a	*o*-HOC_6H_4	H	48	71	128—130
a[b]	Ph	H	48	62	199—201
a	Ph	Me	48	85	220—222
b	Ph	Me	48	81	207—210
b	2-Furyl	Me	30	72	162—164
a	2-Furyl	Me	48	78	204—206
a	3-Pyridyl	Me	8	75	220—222
b	3-Pyridyl	Me	8	86	164—166
a[c]	Ph	Me	24	54	114—116
a	Ph	CH_2Ph	24	64	232—234
b	Ph	CH_2Ph	24	74	165—168
a	*p*-$MeOC_6H_4$	CH_2Ph	24	83	220—222
a	*p*-$NO_2C_6H_4$	CH_2Ph	24	55	264—266
a	*o*-HOC_6H_4	CH_2Ph	48	56	242—245
a	Ph	CH_2CO_2Me	24	73	180—181
a	Ph	CH_2SCH_2Ph	24	89	151—154
b	Ph	CH_2SCH_2Ph	24	79	106—108
a	Ph	Indol-3-ylmethylene	24	32	282—284
a	*p*-$O_2NC_6H_4$	Indol-3-ylmethylene	48	37	286—288
a	*p*-$MeOC_6H_4$	Et	48	83	154—156
b	Ph	Pr^i	48	76	137—140
a	Ph	Pr^i	48	71	163—164
a	*o*-HOC_6H_4	Pr^i	48	91	173—175
b	Benzothiazol-2-yl	Pr^i	48	23	235—237
a	Ph	Ph	48	86	238—240
b	Ph	Ph	48	61	174—176
a[c]	Ph	Ph	24	75	142—145
a[d]	*p*-$MeOC_6H_4$	Ph	5	84	183—185
b	*p*-$MeOC_6H_4$	Ph	12	73	108—110
a	Me_5C_6	Ph	48	52	216—217
b	*p*-$O_2NC_6H_4$	Ph	48	68	200—202
a[d]	*p*-$O_2NC_6H_4$	Ph	48	54	250—252
b	2-Furyl	Ph	48	85	157—159
a	2-Furyl	Ph	24	77	179—182
a	2-Thienyl	Ph	24	88	253—255
b	2-Thienyl	Ph	48	71	211—213
(**17**)[e]	2-Furyl	Ph	48	48	158—160
(**17**)[e]	Ph	Ph	48	75	186—187
a	3-Pyridyl	Ph	24	87	239—240
a	5-Methylthiazol-2-yl	Ph	48	68	239—240
a	5-Phenylthiazol-2-yl	Ph	24	70	261—263
a	5-Methyl-2-thienyl	Ph	24	52	190—192
a	*N*-Methylpyrrol-2-yl	Ph	12	62	244—246
b	5-Methylthiazol-2-yl	Ph	18	55	194—195
b	5-Phenylthiazol-2-yl	Ph	24	85	211—214
a	5-Methylthiazol-2-yl	Bu^i	48	69	180—182
a	5-Phenylthiazol-2-yl	Bu^i	30	39	215—217
a	5-Methyl-2-thienyl	Bu^i	24	57	190—191
a	*N*-Methylpyrrol-2-yl	Bu^i	24	51	185—187
a	5-Methyl-2-furyl	Bu^i	24	55	188—189
a	Bu^t	Ph	20	95	217—218
b	Bu^t	Ph	19	98	143—145
a	Pr^i	Ph	20	55	183—185
a	$Bu^iCH=$	Ph	19	95	153—155
a	$CH(OEt)_2$	Ph	14	70	181—183
a	CO_2Et	Ph	14	60	135—136
a	$CH(OEt)_2$	Me	17	68	116—118

[a] Isolated yields. [b] Ethyl ester. [c] Allyl ester. [d] Reported previously in ref. 2. [e] Carried out under a nitrogen atmosphere.

Stereochemistry and ^{1}H *N.m.r. Spectra of the Pyrrolidines* (**16a, b**) *and* (**17**).—A single-crystal *X*-ray structure[7] on the cycloadduct (**16a**; R^1 = 2-furyl, R = Ph) provided definitive proof of stereochemistry and co-incidentally characterised the configuration of the kinetic dipole as (**7a**). A comparison of the ^{1}H n.m.r. coupling constants (Table 2) of the pyrrolidines (**16a**) and (**16b**) with those of (**16a**; Ar = 2-furyl, R = Ph) suggests that all the adducts have the same relative stereochemistry. The range of coupling constants observed ($J_{4,5}$ 7.3—9.5 Hz, and $J_{3,4}$ 7.0—8.3 Hz, Table 2) accords well with the typical values of J_{cis} 9 Hz and J_{trans} 0.5 Hz found for pyrrolidines derived by 1,3-dipolar cycloaddition of azomethine ylides, derived from aziridines, to (**15a**) and (**15b**).[10]

The coupling constant data in Table 2 accords with the proposed stereochemistry of the pyrrolidines but the magnitude of the coupling constants is, unfortunately, not always a reliable

Table 2. ^{1}H N.m.r. data ($CDCl_3$ + 1 drop D_2O) for pyrrolidines (**16a**), (**16b**), and (**17**)

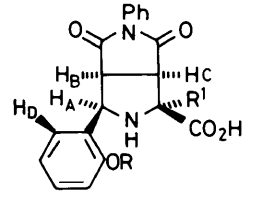
Pyrrolidine (**16a, b**), (**17**)	R^1	R	δ(3-H)	δ(4-H)	δ(5-H)	$J_{3,4}$/Hz	$J_{4,5}$/Hz
a[a]	Ph	H	3.7[b]	3.7[b]	4.7	*b*	8.0
a	Ph	Me	3.45	3.65	4.9	7.6	8.8
b	Ph	Me	3.57	3.7	4.85	8.1	8.5
b	2-Furyl	Me	3.65	3.75	4.9	8.0	9.0
a	2-Furyl	Me	3.5	3.7	4.9	7.9	8.5
a	3-Pyridyl	Me	3.46	3.72	4.88	7.7	8.8
b	3-Pyridyl	Me	3.58	3.68	4.87	8.3	8.3
a[c]	Ph	Me	3.5	3.7	4.8	7.5	7.5
a	Ph	CH_2Ph	3.6	3.7	4.95	6.6	8.6
a	*p*-$O_2NH_6H_4$	CH_2Ph	3.63	3.75	5.0	7.5	9.0
a	Ph	CH_2CO_2Me	3.4	3.6	4.8	7.7	8.8
a	Ph	CH_2SCH_2Ph	3.4	3.4	4.35		8.4
a	Ph	Pr^i	3.63	3.75	4.93	7.5	9.0
a	Ph	Ph	4.15	3.4	4.45	7.5	9.5
b	Ph	Ph	4.35	3.55	4.35	7.7	9.3
a[c]	Ph	Ph	4.2	3.47	4.4	7.5	9.1
a	2-Furyl	Ph	4.3	3.45	4.5	7.6	9.0
a	2-Thienyl	Ph	4.3	3.5	4.7	7.6	8.5
(**17**)	2-Furyl	Ph	4.25	3.55	4.8	7.5	9.5
(**17**)	Ph	Ph	4.2	3.65	4.8		
a	5-Methylthiazol-2-yl	Ph	4.23	3.49	4.56	7.3	9
a	5-Phenylthiazol-2-yl	Ph	4.39	3.83	4.77	7.3	9
a	5-Methyl-2-thienyl	Ph	4.19	3.41	4.53	7.3	9.2
a	*N*-Methylpyrrol-2-yl	Ph	4.21	3.42	4.5	7	9
b	5-Methylthiazol-2-yl	Ph	4.36	3.60	4.56	7.8	9
b	5-Phenylthiazol-2-yl	Ph	4.33	3.62	4.63	7.8	9
a	5-Methylthiazol-2-yl	Bu^i	3.37	3.62	4.91	7.8	8.7
a	5-Phenylthiazol-2-yl	Bu^i	3.39	3.65	4.97	7.8	8.7
a	5-Methyl-2-furyl	Bu^i	3.39	3.53	4.66	7.5	8.4
a	5-Methyl-2-thienyl	Bu^i	3.35	3.58	4.89	7.5	8.7
a	*N*-Methylpyrrol-2-yl	Bu^i	3.37	3.62	4.77	7.5	8.7
a	Bu^t	Ph	4.2	3.31	2.93	7.6	8.3
b	Bu^t	Ph	4.32	3.33	2.94	7.8	8.8
a	Pr^i	Ph	4.10	3.40	2.81	7.6	7.6
a	Bu^iCH=	Ph	4.16	3.33	2.95	7.6	8.2
a	$CH(OEt)_2$	Ph	4.13	3.55	3.55	7.4	
a	CO_2Et	Ph	4.22	3.58	3.94	7.6	8.7
a	$CH(OEt)_2$	Me	3.32	3.5	3.38	8.1	7.3

[a] Ethyl ester. [b] Overlapping triplets. [c] Allyl ester.

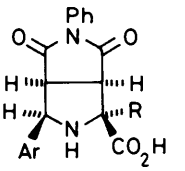
guide to stereochemistry in pyrrolidines.[10] However, the early work on pyrrolidines derived from aziridines showed that chemical-shift data gave useful stereochemical information[10] and related trends can be discerned from our data in Table 2. Thus the chemical shift of 3-H is markedly dependent on the *cis*-2-substituent. The presence of a *cis*-phenyl group at C-2 (Table 2; R = Ph) causes deshielding of 3-H with respect to the same proton in pyrrolidines (**16a**, **b**; R = alkyl) (Table 2). The chemical shift of 4-H is little affected by change of substitution on the pyrrolidine, suggesting a constant stereochemical *trans*-relationship between 4-H and the 5-aryl group. Proton assignments 3-H to 5-H were confirmed by exchange of the NH proton (D_2O) and decoupling. The deshielding of 3-H and the shielding of 5-H by *cis*-vicinal phenyl substituents observed for (**16a**, **b**) is the reverse of the trend reported for similar *N*-alkyl or -aryl mono 2-substituted pyrrolidines.[10]

Cycloadditions of Imines of α-Amino Acids.—We have briefly reported the catalytic effect of Lewis and Bronsted acids on the formation of 1,3-dipoles from imines of α-amino acid esters[16] and this allows many cycloadditions to be carried out at room temperature, *e.g.* the reaction of (**6a**; Ar = *o*-$MeOC_6H_4$, R = Me, R^1 = Ph) with (**15b**) in acetic anhydride containing 6% acetic acid is complete in 30 min at ambient temperature giving (**16b**; R^1 = *o*-$MeOC_6H_4$, R = Ph) in 85% yield. Heating (L)-amino acids with salicylaldehyde, *o*-methoxybenzaldehyde, benzaldehyde, or pyridine-2-carbaldehyde and (**15a**) in acetic protons of the benzyl group (R^1) (8%). The product, (**21a—e**) and (**22a—c**) in >65% yield.[17]

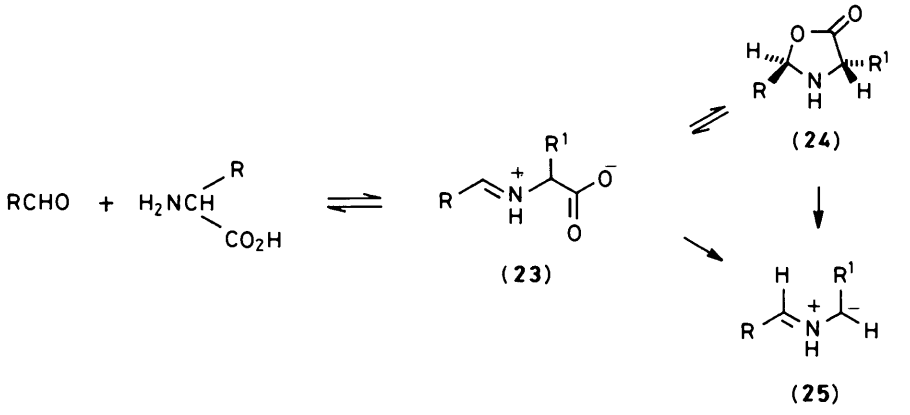
The stereochemistry of the cycloadducts (**21a—e**) and (**22a—c**) were established using n.O.e. difference spectroscopy. This technique was not available to us when the earlier work with imines (**6a**) was carried out. Thus (**21b**) in deuteriopyridine solution gave the following n.O.e. enhancements when H_A was irradiated: H_B (16.6%), H_D (19%) and one of the diastereotopic protons of the benzyl group (R^1) (8%). The product, (**21a—e**) and (**22a—c**), stereochemistry indicates stereospecific trapping of the 1,3-dipole (**7b**) *via* an *endo*-transition state and thus exactly parallels the situation observed for imines of α-amino acid esters. We have not, as yet, carried out any studies of the stability of (**7b**) to stereomuation when treated with less active dipolarophiles.[1] However, we have carried out extensive studies[18–20] of the reactions of α-amino acids with aldehydes and dipolarophiles in a range of solvents such as methanol, acetonitrile, dimethylformamide, methylene dichloride and water–organic solvent mixtures which result in generation and trapping of azomethine ylides *via* a decarboxylative route (Scheme 2). Originally[18] we proposed that the zwitterion (**23**) lost carbon dioxide directly to give (**25**) but recent stereochemical studies[19] suggest an oxazolidin-5-one (**24**)



(21) a; R = H, R^1 = CH_2Ph
b; R = Me, R^1 = CH_2Ph
c; R = H, R^1 = $(CH_2)_2SMe$
d; R = H, R^1 = CH_2CHMe_2
e; R = H, R^1 = CH_2OH

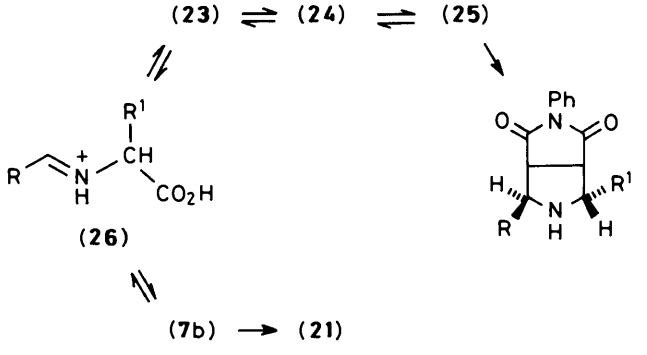


(22) a; Ar = 2-pyridyl, R = CH_2Ph
b; Ar = Ph, R = CH_2Ph
c; Ar = Ph, R = Me



Scheme 2.

(Scheme 2) is the species that loses carbon dioxide *via* a stereospecific 1,3-cyclo-reversion.[20] The oxazolidin-5-ones are usually formed stereospecifically or with a high degree of stereoselectivity with *trans*-stereochemistry favoured. The cycloreversion of the *trans*-oxazolidinone then generates the *anti*-dipole (**25**) (Scheme 2).[19,20] The formation of (**21a**—**e**) and (**22a**—**c**) in acetic acid thus involves suppression of decarboxylation and since the 1,3-cycloreversion is expected to be essentially insensitive to solvent the acetic acid must inhibit the cyclisation (**23**) ⇌ (**24**). The initial protonated imine (**26**) will progress to either (**7b**) or (**25**) (Scheme 3) depending on the



Scheme 3.

relative rates of the various processes. Progression to (**25**) will be retarded in acetic acid due to the formation of hydrogen bonded dimers/oligomers involving the imine carboxy group and the acetic acid solvent. This will reduce the nucleophilicity of the carboxy group by suppressing ionisation of the carboxy group and impede cyclisation to (**24**). Cyclisation (**26**) ⟶ (**24**) can also be slowed relative to dipole (**7b**) formation by ring-strain effects. Thus Seebach[21] reports stereospecific oxazolidinone (**27a**) formation from (L)-proline and pivalaldehyde without racemisation in pentane, whilst (L)-azetidine-2-carboxylic acid under the same conditions gives a racemic (**27b**). The formation of racmic (**27b**) implicates a dipole analogous to (**7b**).

The racemisation of α-amino acids and their derivatives has been the subject of numerous studies.[22–25] Racemisation of α-imino acids in the presence of aldehydes[23–25] (stoicheiometric or catalytic amounts) could involve one of three species, the dipole (**7b**), the metallo-1,3-dipole (**28**),[26,27] or the aza-allyl anion (**29**)[28–31] depending on the solvent and the presence of acids, bases or metal ions.

The ability of organic acids to racemise imines has been used in an elegant kinetic resolution of esters of DL-phenylglycine to the pure D- or L-phenylglycine esters by use of (+)-tartaric acid in the presence of aldehydes.[24] Thus weak acids favour imine racemisation *via* the dipole (**7b**) whilst bases effect racemisation *via* (**29**).

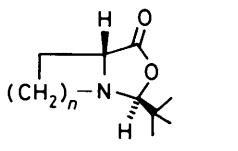
The cycloaddition of the imine of serine (**6b**; Ar = *o*-HOC_6H_4, R^1 = CH_2OH) to (**15a**) in acetic acid (100 °C, 15 min) gives an 8:3 mixture of (**21e**) and (**30**). The ratio of (**21e**) to (**30**) remains unchanged after a further 1 h at 100 °C in acetic acid showing that (**21e**) is not a direct precursor of (**30**) *via* fragmentation (**31**; arrows) and enamine ⇌ imine tautomerism. A possible mechanism for the formation (**30**) involves condensation of (**21e**) with benzaldehyde to give (**32**) followed by fragmentation (**32**; arrows) and subsequent tautomerism of the enamine.

Oxidation of Pyrrolidines to Δ^5*-Pyrrolines.*—The pyrrolidines (**16a**) and (**16b**) are dehydrogenated to the corresponding Δ^5-pyrrolines (**33**) by dichlorodicyano-*p*-benzoquinone (DDQ) in benzene at room temperature (Table 3). Under similar conditions *o*-chloranil was ineffective, reflecting the higher

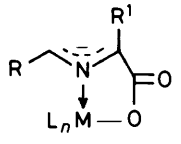
Table 3. ^{1}H N.m.r. data ($CDCl_3$) for Δ^5-pyrrolines (**33a, b**)

Pyrroline	Ar	R	Reaction temp. (°C)	Reaction time (h)	Yield (%)[a]	δ(3-H)	δ(4-H)	$J_{3,4}$/Hz
a	Ph	Me	25	24	96	3.55	4.85	9
a	Ph	CH_2SCH_2Ph	25 80	12 4	93	3.75	4.9	9
a	Ph	CH_2CO_2Me	25	48	83	4.15	5.0	9
a	Ph	CH_2Ph	25	80	87	3.85	3.85	
b	Ph	CH_2Ph	25 80	12 4	80	3.9	3.9	
a	Ph	Pr^i	25	48	91	3.7	4.8	9
b	Ph	Pr^i	25 80	12 4	79	3.8	4.9	
b	Me_5C_6	Ph	25	48	64	4.15	4.5	9
b	2-Thienyl	Ph	25 80	12 4	74	4.15	4.9	10
a	2-Thienyl	Ph	25	72	70	4.0	4.65	10
a[b]	Ph	H	25 80	24 1	99	4.1	4.88	9

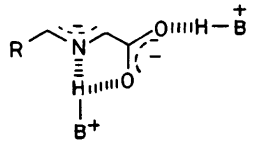
[a] Isolated yield. [b] Ethyl ester.



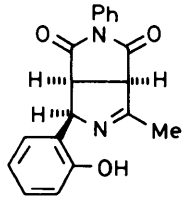
(**27**) a ; n = 2
b ; n = 1



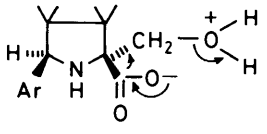
(**28**)



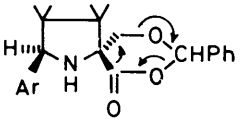
(**29**)



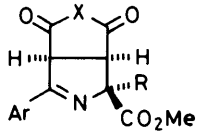
(**30**)



(**31**)



(**32**)



(**33**) a ; X = NPh
b ; X = O

oxidation potential of DDQ (DDQ 1.0 V, *o*-chloranil 0.83 V).[3,2] Attempts to further oxidise (**33**) to the corresponding pyrroles under more forcing conditions (boiling xylene, DDQ) were unsuccessful.

The ^{1}H n.m.r. spectra of (**33a, b**) indicate that the C(3)–C(4) pyrrolidine stereochemistry is retained upon oxidation (Table 3). As expected 4-H is deshielded in (**33a, b**) (Table 3) with respect to the analogous proton in (**16a, b**) (Table 2) due to its azallylic environment. The 3-H, 4-H coupling constants in (**33a, b**) are 9—10 Hz in accord with a *cis*-ring junction. Deshielding of 3-H is again observed when a *cis*-2-Me group is replaced by a *cis*-2-phenyl group. Interestingly, the presence of a *cis*-2-benzyl group causes a marked shielding of 4-H.

Experimental

General spectroscopic details were as previously noted.[2] Most imines were prepared by methods A and B as described previously.[2] A third general method, method C was also employed and is described below. Light petroleum refers to the fraction b.p. 40—60 °C.

Preparation of Imines (**6a**).—*Methyl N-o-hydroxybenzylideneglycinate* (**6a**; Ar = *o*-HOC_6H_4, R^1 = H). Prepared (21%) by method B, the imine crystallised from dichloromethane–hexane as pale yellow needles, m.p. 182—183 °C (Found: C, 61.95; H, 5.5; N, 7.05. $C_{10}H_{11}NO_3$ requires C, 62.15; H, 5.75; N, 7.25%); $\nu_{max.}$ 1 720 and 1 630 cm^{-1}; δ 8.3 (s, 1 H, CH=N), 7.0 (m, 4 H, ArH), 4.3 (s, 2 H, CH_2), and 3.7 (s, 3 H, OMe).

Methyl N-(*3-pyridylmethylene*)*alaninate* (**6a**; Ar = 3-pyridyl, R^1 = Me). Prepared (60%) by method B, the imine distilled as a colourless oil, b.p. 98—100 °C/0.1 mmHg (Found: C, 62.6; H, 6.35; N, 14.4. $C_{10}H_{12}N_2O_2$ requires C, 62.5; H, 6.3; N, 14.6%); *m*/*z*(%) 192 (M^+, 1) and 133 (M − CO_2Me, 100); $\nu_{max.}$(film) 1 745 and 1 645 cm^{-1}; δ 8.9, 8.6, and 8.5 (3 × 1 H, pyridyl H), 8.4 (s, 1 H, CH=N), 7.3 (dd, 1 H, pyridyl H), 4.2 (q, 1 H, C*H*Me), 7.3 (s, 3 H, CO_2Me), and 1.45 (d, 3 H, CH*Me*).

Allyl N-*benzylidenealaninate* (**6a**; Ar = Ph, R^1 = Me, allyl ester). Prepared (94%) by method C (below) as a colourless oil, the material was used without further purification; δ 8.3 (s, 1 H, CH=N), 7.9—7.3 (m, 5 H, ArH), 6.0 (m, 1 H, C*H*=CH_2), 5.3 (m, 2 H, CH=CH_2), 4.6 (d, 2 H, CH_2), 4.2 (q, 1 H, C*H*Me), and 8.5 (d, 3 H, Me).

Methyl N-p-*methoxybenzylidene*(*phenyl*)*alaninate* (**6a**; Ar = *p*-$MeOC_6H_4$, R^1 = CH_2Ph). Prepared (81%) by method A modified by the subsitution of sodium hydroxide for sodium carbonate, the *product* crystallised from ether–light petroleum as colourless prisms, m.p. 54—57 °C (Found: C, 72.65; H, 6.65; N, 4.7. $C_{18}H_{19}NO_3$ requires C, 72.7; H, 6.45; N, 4.7%); *m*/*z*(%) 297 (M^+, 2), 238 (M − CO_2Me, 17), and 206 (M − CH_2Ph, 100); $\nu_{max.}$ 1 730 and 1 635 cm^{-1}; δ 7.8 (s, 1 H, CH=N), 7.65 (d, 2 H, ArH), 7.2 (s, 5 H, ArH), 6.85 (d, 2 H, ArH), 4.15 (dd, 1 H,

$CHCH_2$), 3.8 and 3.7 (2 × s, 2 × 3 H, OMe), and 3.22 (m, 2 H, $CHCH_2$).

Methyl N-p-*nitrobenzylidene(phenyl)alaninate* (**6a**; Ar = *p*-$O_2NC_6H_4$, R^1 = CH_2Ph). Prepared (62%) by method A, the imine crystallised as colourless prisms from carbon tetrachloride, m.p. 65—67 °C (Found: C, 64.95; H, 4.85; N, 9.05. $C_{17}H_{16}N_2O_4$ requires C, 65.4; H, 5.15; N, 8.95%); $\nu_{max.}$ 1 740, 1 645, 1 530, and 1 350 cm^{-1}; δ 8.2 and 7.8 (2 × d, 2 × 2 H, ArH), 7.85 (s, 1 H, CH=N), 4.2 (q, 1 H, $CHCH_2$), 3.75 (s, 3 H, OMe), and 3.25 (dd, 2 H, $CHCH_2$).

Methyl N-o-*hydroxybenzylidene(phenyl)alaninate* (**6a**; Ar = *o*-HOC_6H_4, R^1 = CH_2Ph). Prepared (89%) by method A, the imine crystallised from dichloromethane–light petroleum as yellow needles, m.p. 49—50 °C (Found: C, 72.35; H, 6.2; N, 5.00. $C_{17}H_{17}NO_3$ requires C, 72.05; H, 6.05; N, 4.95%); *m/z*(%) 283 (M^+, 20), 282 (100), 224 ($M - CO_2Me$, 20) and 192 ($M - CH_2Ph$, 70); $\nu_{max.}$ 1 760 and 1 640 cm^{-1}; δ 8.0 (s, 1 H, CH=N), 7.2 (s, 5 H, ArH), 7.0 (m, 4 H, ArH), 4.1 (dd, 1 H, $CHCH_2$), 3.7 (s, 3 H, OMe), and 3.2 (dd, 2 H, $CHCH_2$).

Dimethyl N-*benzylideneaspartate* (**6a**; Ar = Ph, R^1 = CH_2CO_2Me). Prepared (15%) by method A, the imine crystallised from ether–hexane as colourless prisms, m.p. 37—39 °C (Found: C, 62.60; H, 5.95; N, 5.75. $C_{13}H_{15}NO_4$ requires C, 62.65; H, 6.05; N, 5.6%); *m/z*(%) 249 (M^+, 8) and 190 ($M - CO_2Me$, 100); δ 8.5 (s, 1 H, CH=N), 7.8 (m, 2 H, ArH), 7.5 (m, 3 H, ArH), 4.55 (dd, 1 H, $CHCH_2$), 3.8 and 3.7 (2 × s, 2 × 3 H, OMe), and 7.0 (t, 2 H, $CHCH_2$).

Methyl N-*benzylidene*-S-*benzylcysteinate* (**6a**; Ar = Ph, R^1 = CH_2SCH_2Ph). The imine, prepared (55%) by method A, crystallised from ether–light petroleum as colourless prisms, m.p. 87—88 °C (Found: C, 68.75; H, 5.85; N, 4.2. $C_{18}H_{19}NO_2S$ requires C, 69.00; H, 6.1; N, 4.45%); δ 8.15 (s, 1 H, CH=N), 7.7 (m, 2 H, ArH), 7.3 (m, 3 H, ArH), 7.2 (s, 5 H, ArH), 4.0 (dd, 1 H, $CHCH_2$), 3.7 (s, 5 H, OMe + SCH_2), and 3.0 (dd, 2 H, $CHCH_2S$).

Methyl N-p-*nitrobenzylidenetryptophanate* (**6a**; Ar = *p*-$O_2NC_6H_4$, R^1 = indoly-3-ylmethylene). Prepared (60%) by method B, the imine crystallised from dichloromethane–hexane as pale yellow prisms, m.p. 82—85 °C (Found: C, 64.45; H, 4.85; N, 11.65. $C_{19}H_{17}N_3O_4$ requires C, 64.95; H, 4.99; N, 11.95%); *m/z*(%) 351 (M^+, 5), 292 ($M - CO_2Me$, 1) and 130 (100); $\nu_{max.}$ 3 400, 1 750, and 1 635 cm^{-1}; δ 8.1 (d, 2 H, ArH), 7.9 (s, 1 H, CH=N), 7.7 (m, 3 H, ArH), 4.4 (dd, 1 H, $CHCH_2$), 3.8 (s, 3 H, OMe), and 3.5 (dd, 2 H, $CHCH_2$).

Methyl N-o-*hydroxybenzylidenevalinate* (**6a**; Ar = *o*-HOC_6H_4, R^1 = Pr^i). The imine was prepared by method A but with sodium hydroxide replacing sodium carbonate. The *product* (91%) crystallised as yellow needles from dichloromethane–light petroleum, m.p. 74—75 °C (Found: C, 66.55; H, 7.5; N, 5.65. $C_{13}H_{17}NO_3$ requires C, 66.35; H, 7.3; N, 5.95%); $\nu_{max.}$ 3 430, 1 740, and 1 635 cm^{-1}; δ 10.3 (br, s, 1 H, OH), 8.1 (s, 1 H, CH=N), 7.2—6.8 (m, 4 H, ArH), 3.8 (s, 3 H, OMe), 3.75 (d, 1 H, CH), 3.6 (m, 1 H, $CHMe_2$), and 1.9 (2 × d, 2 × 3 H, Me).

Methyl N-*benzothiazol*-2-*ylmethylenevalinate* (**6a**; Ar = thiazol-2-yl, R^1 = Pr^i). An excess of sodium carbonate was added to a solution of methyl L-valinate hydrochloride (1.67 g, 0.01 mol) in water (25 ml), and the solution extracted with ether (4 × 25 ml). The ether extract was dried ($MgSO_4$) and benzothiazole-2-carbaldehyde (1.63 g, 0.01 mol) added together with molecular sieves (type 3A). The solution was kept at ambient temperature for 2 h, filtered, and the filtrate evaporated to leave a pale yellow oil, from which the *product* (2.35 g, 8.5%) was obtained as colourless needles, m.p. 79—80 °C, by crystallisation from ether–light petroleum at −20 °C (Found: C, 61.05; H, 6.00; N, 9.95; S, 11.65. $C_{14}H_{16}N_2O_2S$ requires C, 60.85; H, 5.85; N, 10.15; S, 11.6%); *m/z*(%) 276 (M^+, 0.5) and 91 (100); $\nu_{max.}$ 1 750 and 1 640 cm^{-1}; δ 8.6 (s, 1 H, CH=N), 7.8 (m, 4 H, ArH), 3.9 (d, 1 H, CH), 3.8 (s, 3 H, OMe), 2.5 (m, 1 H, $CHMe_2$), and 1.0 (d, 6 H, $CHMe_2$).

Methyl N-*pentamethylbenzylidene(phenyl)glycinate* (**6a**; Ar = Me_5C_6, R^1 = Ph). The imine, prepared (86%) by method A, crystallised from ether–light petroleum as fine needles, m.p. 90—91 °C (Found: C, 77.95; H, 7.8; N, 4.2. $C_{21}H_{25}NO_2$ requires C, 78.00; H, 7.8; N, 4.35%); $\nu_{max.}$(Nujol) 1 740 and 1 640 cm^{-1}; δ 8.8 (s, 1 H, CH=N), 7.5 (m, 5 H, ArH), 5.3 (s, 1 H, CH), 3.8 (s, 3 H, OMe), and 7.3—8.2 (overlapping s, 15 H, ArMe).

Methyl N-2-*thienylmethylene(phenyl)glycinate* (**6a**; Ar = 2-thienyl, R^1 = Ph). The imine, prepared (72%) by method A, crystallised from dichloromethane–light petroleum as colourless prisms, m.p. 60—61 °C (Found: C, 65.1; H, 5.15; N, 5.55. $C_{14}H_{13}NO_2S$ requires C, 64.85; N, 5.05; N, 5.4%); *m/z*(%) 259 (M^+, 1) and 200 ($M - CO_2Me$, 100); $\nu_{max.}$ 1 735 and 1 640 cm^{-1}; δ 7.7—7.3 (m, 6 H, ArH and thienyl 5-H), 7.1 (m, 2 H, thienyl H), 5.25 (s, 1 H, CH), and 3.75 (s, 3 H, OMe).

Methyl N-3-*pyridylmethylene(phenyl)glycinate* (**6a**; Ar = 3-pyridyl, R^1 = Ph). The imine, prepared (58%) by method A, crystallised from dichloromethane–light petroleum as pale yellow prisms, m.p. 67—68 °C (Found: C, 70.4; H, 5.5; N, 10.8. $C_{15}H_{14}N_2O_2$ requires C, 70.85; H, 5.55; N, 11.0%); *m/z*(%) 254 (M^+, 0.5) and 195 ($M - CO_2Me$, 100); $\nu_{max.}$ 1 750 and 1 645 cm^{-1}; δ 9 (m, 1 H, pyridyl H), 8.75 (q, 1 H, pyridyl H), 8.45 (s, 1 H, CH=N), 8.3 (m, 2 H, pyridyl H), 7.5 (m, 5 H, ArH), 5.3 (s, 1 H, CH), and 3.75 (s, 3 H, OMe).

Allyl N-*benzylidene(phenyl)glycinate* (**6a**; Ar = R^1 = Ph, allyl ester). This imine was prepared by method C. Triethylamine (60.6 g, 6 × 10^{-1} mol) was added dropwise to a stirred mixture of benzaldehyde (10.6 g, 1 × 10^{-1} mol) and allyl phenylglycinate toluene-*p*-sulphonic acid salt (36.3 g, 1 × 10^{-2} mol) in dichloromethane (200 ml) containing anhydrous magnesium sulphate (50 g). The mixture was stirred at room temperature for 24 h, filtered, and the filtrate washed with water (2 × 50 ml), dried ($MgSO_4$), and evaporated under reduced pressure to afford the *product* (26.5 g, 95%) as a colourless oil which was used without further purification; δ 8.35 (s, 1 H, CH=N), 7.9—7.2 (m, 10 H, ArH), 5.9 (m, 1 H, $CH{=}CH_2$), 5.2 (m, 5 H, CH_2, $CH{=}CH_2$, and CH), and 4.65 (m, 2 H, OCH_2).

Methyl N-(2-*methylthiazol*-5-*ylmethylene(phenyl)glycinate* (**6a**; Ar = 2-methylthiazol-5-yl, R^1 = Ph). Prepared (92%) by method A, the imine crystallised as colourless plates from ether–light petroleum, m.p. 113—114 °C (Found: C, 61.2; H, 5.2; N, 10.00. $C_{14}H_{14}N_2O_2S$ requires C, 61.3; H, 5.1; N, 10.2%); *m/z*(%) 274 (M^+, 2) and 215 (100); $\nu_{max.}$ 1 745 and 1 630 cm^{-1}; δ 8.36 (s, 1 H, CH=N), 7.81 (s, 1 H), 7.42—7.28 (m, 5 H, ArH), 5.2 (s, 1 H, CHPh), 3.72 (s, 3 H, OMe), and 2.7 (s, 3 H, Me).

Methyl N-(2-*phenylthiazol*-5-*ylmethylene(phenyl)glycinate* (**6a**; Ar = 2-phenylthiazol-5-yl, R^1 = Ph). Prepared (70%) by method B, the imine crystallised from ether–light petroleum as colourless plates, m.p. 114—115 °C (Found: C, 67.9; H, 4.9; N, 8.4. $C_{19}H_{16}N_2O_2S$ requires C, 67.85; H, 4.75; N, 8.35%); *m/z*(%) 336 (M^+, 8) and 227 (100); $\nu_{max.}$ 1 745 and 1 630 cm^{-1}; δ 8.5 (s, 1 H, CH=N), 8.1 (s, 1 H), 8.2—7.8 and 7.7—7.35 (2 × m, 10 H, ArH), 5.3 (s, 1 H, CHPh), and 3.8 (s, 3 H, OMe).

Methyl N-(5-*methyl*-2-*thienylmethylene(phenyl)glycinate* (**6a**; Ar = 5-methyl-2-thienyl, R^1 = Ph). Prepared (66%) by method B, the imine crystallised from ethanol as colourless rods, m.p. 65—67 °C (Found: C, 65.75; H, 5.55; N, 5.00. $C_{15}H_{15}NO_2S$ requires C, 65.95; H, 5.5; N, 5.15%); *m/z*(%) 373 (M^+, 4) and 214 (100); $\nu_{max.}$ 1 735 and 1 630 cm^{-1}; δ 8.3 (s, 1 H, CH=N), 7.6—7.28 (m, 6 H, ArH + thienyl H), 7.17 (d, 1 H), 6.74 (m, 1 H), 5.2 (s, 1 H, CHPh), 3.76 (s, 3 H, OMe), and 2.52 (s, 3 H, Me).

Methyl N-(N-*methylpyrrol*-2-*ylmethylene(phenyl)glycinate* (**6a**; Ar = *N*-methylpyrrol-2-yl, R^1 = Ph). Prepared (36%) by method B, the imine crystallised as colourless rods from ether–light petroleum, m.p. 45—47 °C (Found: C, 70.45; H, 6.25; N, 10.9. $C_{15}H_{16}N_2O_2$ requires C, 70.3; H, 6.25; N, 10.95%); *m/z*(%)

256 (M^+, 18) and 197 (M − CO_2Me, 100); $\nu_{max.}$ 1 745 and 1 460 cm^{-1}; δ 8.1 (s, 1 H, CH=N), 7.68—7.15 (m, 5 H, ArH), 6.67, 6.47, and 6.1 (3 × m, 3 × 1 H, pyrrolyl H), 4.95 (s, 1 H, CHPh), 4.0 (s, 3 H, OMe), and 3.7 (s, 3 H, NMe).

Methyl N-(2-*methylthiazol*-5-*yl*)*leucinate* (**6a**; Ar = 2-methylthiazol-2-yl, $R^1 = CH_2Pr^i$). Prepared (40%) by method A, the imine distilled as a colourless oil, b.p. 107—108 °C/0.05 mmHg (Found: C, 56.45; H, 7.25; N, 11.05. $C_{12}H_{18}N_2O_2S$ requires C, 56.7; H, 7.1; N, 11.00%); m/z(%) 254 (M^+, 4) and 195 (M − CO_2Me, 100); $\nu_{max.}$(film) 1 730 and 1 630 cm^{-1}; δ 8.59 (s, 1 H, CH=N), 7.83 (s, 1 H), 4.1 (t, 1 H, CH), 3.72 (s, 3 H, OMe), 2.71 (s, 3 H, Me), 1.7 (m, 3 H, CH_2CHMe_2), and 0.95 (2 × d, 2 × 3 H, Me).

Methyl N-(2-*phenylthiazol*-5-*ylmethylene*)*leucinate* (**6a**; Ar = 2-phenylthiazol-5-yl, $R^1 = CH_2Pr^i$). Prepared (71%) by method B, the imine precipitated as an amorphous colourless solid from methanol, m.p. 65—66 °C (Found: C, 64.75; H, 6.5; N, 8.9. $C_{17}H_{20}N_2O_2S$ requires C, 64.55; H, 6.35; N, 8.85%); m/z(%) 316 (M^+, 30) and 257 (M − CO_2Me, 100); $\nu_{max.}$ 1 725 and 1 625 cm^{-1}; δ 8.4 (s, 1 H), 8.0 (s, 1 H), 8.13—7.8 and 7.56—7.3 (2 × m, 5 H, ArH), 4.1 (t, 1 H, $CHCO_2Me$), 3.73 (s, 3 H, OMe), 1.66 (m, 3 H, CH_2CHMe_2), and 0.96 (2 × d, 2 × 3 H, Me).

Methyl N-(N-*methylpyrrol*-2-*ylmethylene*)*leucinate* (**6a**; Ar = N-methylpyrrol-2-yl, $R^1 = CH_2Pr^i$). Prepared (48%) by method B, the imine distilled as a colourless oil, b.p. 92—93 °C/0.01 mmHg (Found: C, 66.1; H, 8.65; N, 11.95. $C_{13}H_{20}N_2O_2$ requires C, 66.1; H, 8.45; N, 11.86%); m/z(%) 236 (M^+, 43) and 177 (M − CO_2Me, 100); $\nu_{max.}$(film) 1 740 and 1 640 cm^{-1}; δ 8.1 (s, 1 H, CH=N), 6.67, 6.47 and 6.08 (3 × m, 3 × 1 H, pyrrolyl H), 4.18 (t, 1 H, $CHCO_2Me$), 3.9 (s, 3 H, OMe), 3.77 (s, 3 H, NMe), 1.68 (m, CH_2CHMe_2), and 0.91 (2 × d, 2 × 3 H, Me).

Methyl N-(2,2-*dimethylpropylidene*)*phenylglycine* (**18a**). Prepared (80%) by method B, the imine was a colourless oil, b.p. 90—92 °C/0.3 mmHg; m/z 233.141 64 (M^+, requires 233.141 57); $\nu_{max.}$(film) 1 750 and 1 670 cm^{-1}; δ 7.33 (m, 5 H, ArH), 7.62 (d, 1 H, CH=N, J 0.7 Hz), 4.95 (br s, 1 H, CH), 3.69 (s, 3 H, OMe), and 1.11 (s, 9 H, Bu^t)

Methyl N-*isopropylidene*(*phenyl*)*glycinate* (**18b**). Prepared (85%) by method B, the imine was a colourless oil, b.p. 90—92 °C/0.1 mmHg m/z 219.125 99 (M^+ requires 219.125 92); $\nu_{max.}$(film) 1 750 and 1 670 cm^{-1}; δ 7.33 (m, 5 H, ArH), 7.57 (d, 1 H, CH=N, J 6 Hz), 4.9 (s, 1 H, CH), 3.63 (s, 3 H, OMe), 2.53 (m, 1 H, $CHMe_2$), and 1.07 and 1.03 (2 × d, 2 × 3 H, Me).

Methyl N-(5-*methylhex*-2-*enylidene*) *phenylglycinate* (**18c**). Prepared (80%) by method B, the imine was a colourless oil, b.p. 106—107 °C/0.1 mmHg (Found: C, 74.15; H, 8.3; N, 5.55. $C_{16}H_{21}NO_2$ requires C, 74.1; H, 8.15; N, 5.4%); m/z(%) 259 (M^+, 56) and 200 (M − CO_2Me, 100); $\nu_{max.}$(film) 1 745 and 1 660 cm^{-1}; δ 7.32 (m, 5 H, ArH), 7.55 (s, 1 H, CH=N), 6.68 (m, 1 H, CH=CH_2), 5.0 (m, 2 H, CH=CH_2), 4.92 (s, $CHCO_2Me$), 3.65 (s, 3 H, OMe), 2.18 (d, 2 H, CH_2), and 1.05 (s, 6 H, Me).

Methyl N-(2,2-*diethoxyethylidene*)*phenylglycinate* (**18d**). Prepared (85%) by method B, the imine was a thick oil and was used without further purification.

Methyl N-*ethoxycarbonylmethylene*(*phenyl*)*glycinate* (**18e**). Prepared (85%) by method C as a thick oil, the imine was used directly for cycloadditon.

Methyl N-2,2-*diethoxyethylidenealaninate* (**18f**). Prepared (46%) by method B, the imine distilled as a colourless oil, b.p. 101—102 °C/0.05 mmHg (Found: C, 55.7; H, 9.1; N, 6.25. $C_{10}H_{19}NO_4$ requires C, 55.3; H, 8.8; N, 6.45%); m/z(%) 217 (M^+, 0.5) and 103 (100); δ 7.54 (d, 1 H, CH=N), 4.83 [d, 1 H, $CH(OR)_2$], 4.02 (q, 1 H, $CHCO_2Me$), 3.74 (s, 3 H, OMe), 3.67 (m, 4 H, 2 × CH_2Me), 1.46 (d, 1 H, $CHMe$), and 1.24 (t, 6 H, 2 × CH_2Me).

Cycloaddition of Imines and Cyclic Dipolarophiles.—Except where otherwise stated, all reactions employed equimolar (10 mmol) amounts of imines and dipolarophiles in toluene (50 ml). Reaction conditions are summarised in Table 1 and important n.m.r. data for many of the adducts are summarised in Table 2. The method described below is typical for the whole series.

Methyl 4-o-*hydroxyphenyl*-7-*phenyl*-6,8-*dioxo*-3,7-*diazabicyclo*[3.3.0]*octane*-2-*carboxylate* (**16a**; R^1 = *o*-HOC_6H_4, R = H). A solution of methyl *N*-*o*-hydroxybenzylideneglycinate (1.93 g, 10 mmol) and *N*-phenylmaleimide (**15a**) (1.73 g, 10 mmol) in toluene was boiled under reflux for 48 h during which time the initially yellow solution became almost colourless. Removal of the solvent under reduced pressure gave a white paste which was triturated with ether, filtered, and the solid crystallised from dichloromethane–light petroleum to give the *product* (2.6 g, 71%) as colourless prisms, m.p. 128—130 °C (Found: C, 65.7; H, 4.95; N, 7.4. $C_{20}H_{18}N_2O_5$ requires C, 65.55; H, 4.95; N, 7.65%); m/z(%) 336 (M^+, 18), 307 (M − CO_2Me, 10), and 193 (M − phenylmaleimide, 100); $\nu_{max.}$(Nujol) 3 820, 1 750, and 1 705 cm^{-1}.

Ethyl 6,8-*dioxo*-4,7-*diphenyl*-3,7-*diazabicyclo*[3.3.0]*octane*-2-*carboxylate* (**16a**; R^1 = Ph, R = H, ethyl ester). Obtained as colourless prisms (62%) from dichloromethane–light petroleum (Found: C, 69.6; H, 5.45; N, 7.65. $C_{21}H_{20}N_2O_4$ requires C, 69.2; H, 5.55; N, 7.7%); m/z(%) 364 (M^+, 12), 291 (M − CO_2Et, 86) and 191 (M − phenylmaleimide, 100); $\nu_{max.}$ 3 480, 3 320, and 1 750 cm^{-1}.

Methyl 2-*methyl*-6,8-*dioxo*-4,7-*diphenyl*-3,7-*diazabicyclo*-[3.3.0]*octane*-2-*carboxylate* (**16a**; R^1 = Ph, R = Me). Obtained as a coloulress fluffy solid (85%) from dichloromethane–ether (Found: C, 69.3; H, 5.4; N, 7.3. $C_{21}H_{20}N_2O_4$ requires C, 69.2; H, 5.55; N, 7.7%); m/z(%) 264 (M^+, 3), 305 (M − CO_2Me, 56), and 191 (M − phenylmaleimide, 100); $\nu_{max.}$ 3 250 and 1 710 cm^{-1}.

Methyl 2-*methyl*-6,8-*dioxo*-4-*phenyl*-7-*oxa*-3-*azabicyclo*-[3.3.0]*octane*-2-*carboxylate* (**16b**; R^1 = Ph, R = Me). Obtained as colourless plates from dichloromethane–light petroleum (Found: C, 62.0; H, 5.25; N, 4.95. $C_{15}H_{15}NO_5$ requires C, 62.3; H, 5.25; N, 4.85%); m/z(%) 289 (M^+, 1) and 230 (M − CO_2Me, 100); $\nu_{max.}$ 3 325, 1 860sh, 1 775, and 1 735 cm^{-1}.

Methyl 4-(2-*furyl*)-2-*methyl*-6,8-*dioxo*-7-*oxa*-3-*azabicyclo*-[3.3.0]*octane*-2-*carboxylate* (**16b**; R^1 = 2-furyl, R = Me). Obtained as colourless prisms (72%) from dichloromethane–light petroleum (Found: C, 55.95; H, 4.75; N, 4.8. $C_{13}H_{13}NO_6$ requires C, 55.9; H, 4.7; N, 5.00%); m/z(%) 279 (M^+, 0.1), 220 (M − CO_2Me, 78) and 181 (M − maleic anhydride, 91); $\nu_{max.}$(Nujol) 3 300, 1 840sh, 1 765, and 1 725 cm^{-1}.

Methyl 4-(2-*furyl*)-2-*methyl*-6,8-*dioxo*-7-*phenyl*-3,7-*diazabicyclo*[3.3.0]*octane*-2-*carboxylate* (**16a**; R^1 = 2-furyl, R = Me). Obtained as colourless plates (78%) from dichloromethane–light petroleum (Found C, 64.55; H, 5.15; N, 7.75; $C_{19}H_{18}N_2O_5$ requires C, 64.4; H, 5.1; N, 7.9%); m/z(%) 354 (M^+, 5), 295 (M − CO_2Me, 40), 181 (M − phenylmaleimide, 100); $\nu_{max.}$(Nujol) 3 315, 1 775sh, 1 740, and 1 710 cm^{-1}.

Methyl 2-*methyl*-6,8-*dioxo*-7-*phenyl*-4-(3-*pyridyl*)-3,7-*diazabicyclo*[3.3.0]*octane*-2-*carboxylate* (**16a**; R^1 = 3-pyridyl, R = Me). Obtained as colourless needles from methanol (Found: C, 65.9; H, 5.00; N, 11.6. $C_{20}H_{19}N_3O_4$ requires C, 65.75; H, 5.25; N, 11.5%; m/z(%) 365 (M^+, **1**), and 306 (M − CO_2Me, 100).

Methyl 2-*methyl*-6,8-*dioxo*-4-(3-*pyridyl*)-7-*oxa*-3-*azabicyclo*-[3.3.0]*octane*-2-*carboxylate* (**16b**; R^1 = 3-pyridyl, R = Me). The *product* crystallised from benzene as colourless plates (Found: C, 58.15; H, 4.8; N, 9.55. $C_{14}H_{14}N_2O_5$ requires C, 57.95; H, 4.85; N, 9.65%); m/z(%) 291 (M + 1, 1) and 231 (M − CO_2Me, 100); $\nu_{max.}$ 2 900, 1 780, and 1 730 cm^{-1}.

Allyl 2-*methyl*-6,8-*dioxo*-4,7-*diphenyl*-3,7-*diazabicyclo*[3.3.0]-*octane*-2-*carboxylate* (**16a**; R^1 = Ph, R = Me, allyl ester). Obtained as colourless prisms from dichloromethane–hexane (Found: C, 70.8; H, 5.75; N, 7.3. $C_{23}H_{22}N_2O_4$ requires C, 70.75;

H, 5.7; N, 7.2%); *m/z*(%) 390 (M^+, 0.3) and 305 ($M - CO_2C_3H_5$, 100); $\nu_{max.}$(Nujol) 3 350, 1 780sh, 1 740, and 1 705 cm^{-1}

Methyl 2-benzyl-6,8-dioxo-4,7-diphenyl-3,7-diazocyclo[3.0.0]*octane-2-carboxylate* (**16a**; R^1 = Ph, R = CH_2Ph). Obtained as colourless prisms from dichloromethane–light petroleum (Found: C, 73.8; H, 5.4; N, 6.2. $C_{27}H_{24}N_2O_4$ requires C, 73.6; H, 5.5; N, 6.35%); *m/z*(%) 440 (M^+, 0.2), 381 ($M - CO_2Me$, 5) and 349 ($M - CH_2Ph$, 100); $\nu_{max.}$ 3 340, 1 750, and 1 715 cm^{-1}.

Methyl 2-benzyl-6,8-dioxo-4-phenyl-7-oxa-3-azabicyclo[3.3.0]*octane-2-carboxylate* (**16b**; R^1 = Ph, R = CH_2Ph). Obtained as colourless plates from dichloromethane–hexane (Found: C, 68.9; H, 5.3; N, 3.9. $C_{21}H_{19}NO_5$ requires C, 69.05; H, 5.25; N, 3.85%); *m/z*(%) 365 (M^+, 0.4), 306 ($M - CO_2Me$, 4), and 274 ($M - CH_2Ph$, 100); $\nu_{max.}$ 3 420, 1 860sh, 1 780, and 1 740 cm^{-1}.

Methyl 2-benzyl-4-p-methoxyphenyl-6,8-dioxo-7-phenyl-3,7-diazabicyclo[3.3.0]*octane-2-carboxylate* (**16a**; R^1 = *p*-$MeOC_6H_4$, R = CH_2Ph). Obtained as colourless prisms from dichloromethane–hexane (Found: C, 70.9; H, 5.7; N, 5.9. $C_{28}H_{26}N_2O_5$ requires C, 70.5; H, 5.95; N, 5.6%); *m/z*(%) 470 (M^+, 0.5), 411 ($M - CO_2Me$, 21), and 379 ($M - CH_2Ph$, 100); $\nu_{max.}$ 3 330, 1780sh, 1 730, and 1 710 cm^{-1}.

Methyl 2-benzyl-4-p-nitrophenyl-6,8-dioxo-7-phenyl-3,7-diazabicyclo[3.3.0]*octane-2-carboxylate* (**16a**; R^1 = *p*-$O_2NC_6H_4$, R = CH_2Ph). Obtained as colourless prisms from dichloromethane–ether (Found: C, 66.85; H, 4.8; N, 8.6. $C_{27}H_{23}N_3O_6$ requires C, 66.8; H, 4.8; N, 8.65%); *m/z*(%) 485 (M^+, 0.1) and 394 ($M - CH_2Ph$, 100); $\nu_{max.}$ 3 350, 1 785sh, 1 755, and 1 710 cm^{-1}.

Methyl 2-benzyl-4-o-hydroxyphenyl-6,8-dioxo-7-phenyl-3,7-diazabicyclo[3.3.0]*octane-2-carboxylate* (**16a**; R^1 = *o*-HOC_6H_4, R = CH_2Ph). Obtained as a white powder from dichloromethane–light petroleum (Found: C, 70.3; H, 5.4; N, 6.15. $C_{27}H_{24}N_2O_5$ requires C, 71.00; H, 5.3; N, 6.1%); *m/z*(%) 456 (M^+, 4) and 365 ($M - CH_2Ph$, 100).

Methyl 2-methoxycarbonylmethyl-6,8-dioxo-4,7-diphenyl-3,7-diazabicyclo[3.3.0]*octane-2-carboxylate* (**16a**; R^1 = Ph, R = CH_2CO_2Me). Obtained as colourless needles from ether–hexane (Found: C, 65.35; H, 5.3; N, 6.45. $C_{23}H_{22}N_2O_6$ requires C, 65.4; H, 5.25; N, 6.35%); *m/z*(%) 422 (M^+, 14), 363 ($M - CO_2Me$, 40) and 331 (100); $\nu_{max.}$ 3 350, 3 290, and 1 710 cm^{-1}.

Methyl 2-benzylthiomethyl-6,8-dioxo-4,7-diphenyl-3,7-diazabicyclo[3.3.1]*octane-2-carboxylate* (**16a**; R^1 = Ph, R = CH_2SCH_2Ph). Obtained as colourless plates from dichloromethane–hexane (Found: C, 69.35; H, 5.5; N, 5.7. $C_{28}H_{26}N_2O_4$ requires C, 69.1; H, 5.4; N, 5.75%); *m/z*(%) 486 (M^+, 1), 427 ($M - CO_2Me$, 2), 395 ($M - CH_2Ph$, 2), and 363 ($M - SCH_2Ph$, 4); $\nu_{max.}$ 3 340, 1 735, and 1 705 cm^{-1}.

Methyl 2-benzylthiomethyl-6,8-dioxo-7-oxa-3-azabicyclo[3.3.0]*octane-2-carboxylate* (**16b**; R^1 = Ph, R = CH_2SCH_2Ph). Obtained as a colourless powder from dichloromethane–hexane (Found: C, 64.2; H, 5.25; N, 3.3. $C_{22}H_{21}NO_5S$ requires C, 64.2; H, 5.15; N, 3.4%); *m/z*(%) 411 (M^+, 3), 352 ($M - CO_2Me$, 6), and 274 ($M - CH_2SCH_2Ph$, 100); $\nu_{max.}$ 3 320, 1 860sh, 1 780, and 1 740 cm^{-1}.

Methyl 2-indol-3-ylmethyl-6,8-dioxo-4,7-diphenyl-3,7-diazabicyclo[3.3.0]*octane-2-carboxylate* (**16a**; R^1 = Ph, R = indol-3-ylmethyl). Obtained as colourless prisms from dichloromethane–light petroleum (Found: C, 72.35; H, 5.25; N, 8.75. $C_{29}H_{25}N_3O_4$ requires C, 72.1; H, 5.45; N, 8.75%); *m/z*(%) 479 (M^+, 1) and 349 (M – indolylmethyl, 100); $\nu_{max.}$ 3 360, 1 740, and 1 705 cm^{-1}.

Methyl 2-indol-3-ylmethyl-4-p-nitrophenyl-6,8-dioxo-7-phenyl-3,7-diazabicyclo[3.3.0]*octane-2-carboxylate* (**16a**; R^1 = *p*-$O_2NC_6H_4$, R = indol-3-ylmethyl). Obtained as pale yellow prisms from dichloromethane–ether (Found: C, 66.65; H, 4.6; N, 10.6. $C_{29}H_{24}N_4O_6$ requires C, 66.4; H, 4.6; N, 10.7%); $\nu_{max.}$(Nujol) 3 410, 1 745, and 1 705 cm^{-1}.

Methyl 2-ethyl-4-p-methoxyphenyl-6,8-dioxo-7-phenyl-3,7-diazabicyclo[3.3.0]*octane-2-carboxylate* (**16a**; R^1 = *p*-$MeOC_6H_4$, R = Et). Obtained as colourless prisms from dichloromethane–hexane (Found; C, 67.9; H, 6.1; N, 7.1. $C_{23}H_{24}N_2O_5$ requires C, 67.65; H, 5.9; N, 6.85%); *m/z*(%) 408 (M^+, 3) and 349 ($M - CO_2Me$, 21); $\nu_{max.}$(Nujol) 3 350, 1 780sh, 1 740, and 1 720 cm^{-1}.

Methyl 2-isopropyl-6,8-dioxo-4-phenyl-7-oxa-3-azabicyclo[3.3.0]*octane-2-carboxylate* (**16b**; R^1 = Ph, R = Pr^i). Obtained as colourless plates from dichloromethane–light petroleum (Found: C, 64.3; H, 6.2; N, 4.25. $C_{17}H_{19}NO_5$ requires C, 64.35; H, 6.05; N, 4.4%); *m/z*(%) 317 (M^+, 2) and 274 ($M - Pr^i$, 100); $\nu_{max.}$ 3 340, 1 865sh, 1 790, and 1 730 cm^{-1}.

Methyl 2-isopropyl-6,8-dioxo-4,7-diphenyl-3,7-diazabicyclo[3.3.0]*octane-2-carboxylate* (**16a**; R^1 = Ph, R = Pr^i). Obtained as colourless plates from dichloromethane–ether (Found: C, 70.35; H, 6.2; N, 7.25. $C_{23}H_{24}N_2O_4$ requires C, 70.4; H, 6.15; N, 7.15%); *m/z*(%) 392 (M^+, 0.5) and 349 ($M - Pr^i$, 100); $\nu_{max.}$(Nujol) 3 370, 1 775sh, and 1 720 cm^{-1}.

Methyl 4-o-hydroxyphenyl-2-isopropyl-6,8-dioxo-7-phenyl-3,7-diazabicyclo[3.3.0]*octane-2-carboxylate* (**16a**; R^1 = *o*-HOC_6H_4, R = Pr^i). Obtained as a colourless solid from dichloromethane–light petroleum (Found: C, 67.5; H, 5.85; N, 6.55. $C_{23}H_{24}N_2O_5$ requires C, 67.65; H, 5.9; N, 6.85%); *m/z*(%) 408 (M^+, 1) 349 ($M - CO_2Me$; 4), and 235 (M – phenylmaleimide, 40); $\nu_{max.}$(Nujol) 1 780sh and 1 700 cm^{-1}.

Methyl 4-benzothiazol-2-yl-2-isopropyl-6,8-dioxo-7-oxa-3-azabicyclo[3.3.0]*octane-2-carboxylate* (**16b**; R^1 = benzothiazol-2-yl, R = Pr^i). Obtained as colourless plates from dichloromethane–hexane (Found: C, 57.5; H, 4.9; N, 7.35. $C_{18}H_{18}N_2O_5S$ requires C, 57.75; H, 4.85; N, 7.5%); *m/z*(%) 374 (M^+, 24) and 315 ($M - CO_2Me$, 100); $\nu_{max.}$ 3 320 (NH), 1 860sh, 1 780, and 1 720 cm^{-1}.

Methyl 6,8-dioxo-2,c-4,7-triphenyl-3,7-diazabicyclo[3.3.0]*octane-r-2-carboxylate* (**16a**; R^1 = R = Ph). Obtained as colourless prisms (Found: C, 72.95; H, 5.25; N, 6.3. $C_{26}H_{22}N_2O_4$ reqires C, 73.2; H, 5.2; N, 6.55%); *m/z*(%) 426 (M^+, 0.5) and 367 ($M - CO_2Me$, 100); $\nu_{max.}$ 3 340, 1 785sh, 1 750, and 1 730 cm^{-1}.

Methyl 6,8-dioxo-2,c-4-diphenyl-7-oxa-3-azabicyclo[3.3.0]*octane-r-2-carboxylate* (**16a**; R^1 = R = Ph). Obtained as colourless prisms from dichloromethane–light petroleum (Found: C, 68.9; H, 4.9; N, 3.75. $C_{20}H_{17}NO_5$ requires C, 68.55; H, 4.9; N, 4.00%), *m/z*(%) 351 (M^+, 0.3) and 292 ($M - CO_2Me$, 100); $\nu_{max.}$ 3 335, 1 860, 1 780, and 1 745 cm^{-1}.

Allyl 6,8-dioxo-2,4,7-triphenyl-3,7-diazabicyclo[3.3.0]*octane-2-carboxylate* (**16a**; R^1 = R = Ph, allyl ester). Obtained as colourless prisms from dichloromethane–hexane (Found: C, 74.0; H, 5.3; N, 6.0. $C_{28}H_{24}N_2O_4$ requires C, 74.3; H, 5.35; N, 6.2%); *m/z*(%) 452 (M^+, 0.2) and 367 ($M - CO_2Me$, 100); $\nu_{max.}$(Nujol), 3 340, 1 780sh, 1 720, and 1 705 cm^{-1}.

Methyl c-4-p-methoxyphenyl-6,8-dioxo-2-phenyl-7-oxa-3-azabicyclo[3.3.0]*octane-2-carboxylate* (**16b**; R^1 = *p*-$MeOC_6H_4$, R = Ph). Obtained as colourless prisms from dichloromethane–light petroleum (Found: C, 70.7; H, 5.15; N, 5.8. $C_{27}H_{24}N_2O_5$ requires C, 71.05; H, 5.3; N, 6.15%); $\nu_{max.}$ 3 420, 1 855sh, 1 780, and 1 720 cm^{-1}.

Methyl 6,8-dioxo-4-pentamethylphenyl-2,7-diphenyl-3,7-diazabicyclo[3.3.0]*octane-2-carboxylate* (**16a**; R^1 = Me_5C_6, R = Ph). Obtained as colourless prisms from dichloromethane–ether. (Found: C, 74.8; H, 6.3; N, 5.5. $C_{31}H_{32}N_2O_4$ requires C, 74.95; H, 6.50; N, 5.65%); $\nu_{max.}$(Nujol) 3 330, 1 775sh, 1 735, and 1 705 cm^{-1}

Methyl c-4-(4-nitrophenyl)-6,8-dioxo-2-phenyl-7-oxa-3-azabicyclo[3.3.0]*octane-2-carboxylate* (**16b**; R^1 = *p*-$O_2NC_6H_4$, R = Ph). Obtained as pale yellow needles from dichloromethane–light petroleum (Found: C, 59.8; H, 4.2; N, 6.3. $C_{20}H_{16}N_2O_7$ requires C, 60.6; H, 4.05; N, 7.05%); *m/z*(%), 396 (M^+, 0.3) and 337 ($M - CO_2Me$, 100); $\nu_{max.}$ 3 370, 1 865sh, 1 785, and 1 730 cm^{-1}.

Methyl c-4-(2-*furyl*)-6,8-*dioxo*-2,7-*diphenyl*-7-*oxa*-3-*azabicyclo*[3.3.0]*octane*-r-2-*carboxylate* (**16b**; R^1 = 2-furyl, R = Ph). Obtained as colourless flakes from dichloromethane–light petroleum (Found: C, 63.15; H, 3.95; N, 4.35. $C_{18}H_{15}NO_6$ requires C, 63.35; H, 4.45; N, 4.1%); *m*/*z*(%) 341 (M^+, 0.7) and 282 ($M - CO_2Me$, 100); $\nu_{max.}$ 3 340, 1 860sh, 1 780, an 1 740 cm^{-1}.

Methyl c-4-(2-*furyl*)-6,8-*dioxo*-2,7-*diphenyl*-3,7-*diazabicyclo*[3.3.0]*octane*-r-2-*carboxylate* (**16a**; R^1 = 2-furyl, R = Ph). Obtained as colourless prisms from dichloromethane–ether (Found: C, 69.25; H, 4.9; N, 6.5. $C_{24}H_{20}N_2O_5$ requires C, 69.2; H, 4.9; N, 6.75%); *m*/*z*(%) 416 (M^+, 1) and 357 ($M - CO_2Me$, 100); $\nu_{max.}$ 3 320, 1 780sh, 1 740, and 1 710 cm^{-1}. The *X*-ray crystal structure of this compound was determined.[7]

Methyl 2,7-*diphenyl*-6,8-*dioxo*-c-4-(2-*thienyl*)-3,7-*diazabicyclo*[3.3.0]*octane*-r-2-*carboxylate* (**16a**; R^1 = 2-thienyl, R = Ph). Obtained as colourless prisms from dichloromethane–light petroleum (Found: C, 66.9; H, 4.65; N, 6.35. $C_{24}H_{20}N_2O_4S$ requires C, 66.65; H, 4.65; N, 6.5%); *m*/*z*(%) 432 (M^+, 1.5) and 373 ($M - CO_2Me$, 100); $\nu_{max.}$ 3 320, 1 740, and 1 710 cm^{-1}.

Methyl 6,8-*dioxo*-2,7-*diphenyl*-c-4-(2-*thienyl*)-7-*oxa*-3-*azabicyclo*[3.3.0]*octane*-r-2-*carboxylate* (**16b**; R^1 = 2-thienyl, R = Ph). Obtained as colourless plates from dichloromethane–light petroleum (Found: C, 60.35; H, 4.3; N, 3.8. $C_{18}H_{15}NO_5S$ requires C, 60.5; H, 4.25; N, 3.92%); *m*/*z*(%) 357 (M^+, 1) and 298 ($M - CO_2Me$, 100); $\nu_{max.}$ 3 340, 1 865sh, 1 790, and 1 735 cm^{-1}.

Methyl c-3-(2-*furyl*)-4,9-*dioxo*-1-*phenyl*-2,3,3a,9a-*tetrahydrobenz*[f]*isoindole*-r-2-*carboxylate* (**17**; R^1 = 2-furyl, R = Ph). Obtained as pale pink needles from dichloromethane–light petroleum (Found: C, 71.9; H, 4.8; N, 3.35. $C_{24}H_{19}NO_5$ requires C, 71.8; H, 4.75; N, 3.5%); *m*/*z*(%) 401 (M^+, 3), 342 ($M - CO_2Me$, 52), and 184 (100); $\nu_{max.}$ 3 360, 1 725, 1 700, and 1 685 cm^{-1}.

Methyl 4,9-*dioxo*-1,c-3-*diphenyl*-2,3,3a,9a-*tetrahydrobenz*[f]-*isoindole*-r-2-*carboxylate* (**17**; R^1 = R = Ph). Obtained as off-white prisms from dichloromethane-hexane; $\nu_{max.}$ 3 390, 1 730, 1 680, and 1595 cm^{-1}.

Methyl 6,8-*dioxo*-2,7-*diphenyl*-c-4-(3-*pyridyl*)-3,7-*diazabicyclo*[3.3.0]*octane*-r-2-*carboxylate* (**16a**; R^1 = 2-pyridyl, R = Ph). Obtained as colourless prisms from dichloromethane–light petroleum (Found: C, 68.75; H, 4.95; N, 9.4. $C_{25}H_{21}N_3O_4$ requires C, 68.75; H, 4.95; N, 9.4. $C_{25}H_{21}N_3O_4$ requires C, 70.25; H, 4.95; N, 9.85%); *m*/*z*(%) 427 (M^+, 5) and 368 ($M - CO_2Me$, 100); $\nu_{max.}$ 3 460, 3 320, 1 735, and 1 710 cm^{-1}.

Methyl 6,8-*dioxo*-c-4-(5-*methylthiazol*-2-*yl*)-2,7-*diphenyl*-3,7-*diazabicyclo*[3.3.0]*octane*-r-2-*carboxylate* (**16a**; R^1 = 5-methylthiazol-2-yl, R = Ph). Obtained as colourless rods from methanol (Found: C, 64.9; H, 4.75; N, 9.45. $C_{24}H_{21}N_3O_4S$ requires C, 64.4; H, 4.7; N, 9.4%); *m*/*z*(%) 447 (M^+, 1) and 388 ($M - CO_2Me$, 100); $\nu_{max.}$ 3 100, 1 790, 1745, and 1 725 cm^{-1}.

Methyl 6,8-*dioxo*-2,7-*diphenyl*-c-4-(5-*phenylthiazol*-4-*yl*)-3,7-*diazabicyclo*[3.3.0]*octane*-r-2-*carboxylate* (**16a**; R^1 = 5-phenylthiazol-2-yl, R = Ph). Obtained as colourless rods from benzene (Found: C, 68.7; H, 4.55; N, 8.00. $C_{29}H_{23}N_3O_4S$ requires C, 68.35; H, 4.5; N, 8.25%); *m*/*z*(%) 336 (100); $\nu_{max.}$ 3 310, 1 785, 1 740, and 1 715 cm^{-1}.

Methyl 6,8-*dioxo*-2,7-*diphenyl*-c-4-(5-*methyl*-2-*thienyl*)-3,7-*diazabicyclo*[3.3.0]*octane*-r-2-*carboxylate* (**16a**; R^1 = 5-methyl-2-thienyl, R = Ph). Obtained as colourless rods from methanol (Found: C, 67.3; H, 5.05; N, 6.25. $C_{25}H_{22}N_2O_4S$ requires C, 67.25; H, 4.95; N, 6.3%); *m*/*z*(%) 446 (M^+, 1) and 213 (100); $\nu_{max.}$ 3 330, 1 780, and 1 715 cm^{-1}.

Methyl 2,7-*diphenyl*-c-4-N-*methylpyrrol*-2-*yl*)-6,8-*dioxo*-3,7-*diazabicyclo*[3.3.0]*octane*-r-2-*carboxylate* (**16a**; R^1 = *N*-methylpyrrol-2-yl, R = Ph). Obtained as colourless rods from benzene (Found: C, 70.1; H, 5.45; N, 9.7. $C_{25}H_{23}N_3O_4$ requires C, 69.95; H, 5.35; N, 9.8%); *m*/*z*(%) 429 (M^+, 4) and 256 (100); $\nu_{max.}$ 3 325, 1 780, 1 740, and 1 715 cm^{-1}.

Methyl 2-*phenyl*-c-4-(5-*methylthiazol*-2-*yl*)-6,8-*dioxo*-7-*oxa*-3-*azabicyclo*[3.3.0]*octane*-r-2-*carboxylate* (**16b**; R^1 = 5-methylthiazol-2-yl, R = Ph). Obtained as colourless plates from benzene (Found: C, 57.95; H, 4.25; N, 7.7. $C_{18}H_{16}N_2O_5S$ requires C, 58.05; H, 4.3; N, 7.55%); *m*/*z*(%) 372 (M^+, 1) and 313 ($M - CO_2Me$, 100); $\nu_{max.}$ 3 300, 1 870, 1 790, and 1 750 cm^{-1}.

Methyl 6,8-*dioxo*-2-*phenyl*-c-4-(5-*phenylthiazol*-2-*yl*)-7-*oxa*-3-*azabicyclo*[3.3.0]*octane*-2-*carboxylate* (**16b**; R^1 = 5-phenylthiazol-2-yl, R = Ph). Obtained as colourless plates from benzene (Found: C, 63.7; H, 4.2; N, 6.55. $C_{23}H_{18}N_2O_5S$ requires C, 63.6; H, 4.15; N, 6.45%); *m*/*z*(%) 434 (M^+, 3) and 336 (100); $\nu_{max.}$ 3 340, 1 865, 1 790, and 1 750 cm^{-1}.

Methyl c-4-(5-*methylthiazol*-2-*yl*)-6,8-*dioxo*-7-*phenyl*-2-*s*-*butyl*-3,7-*diazabicyclo*[3.3.0]*octane*-r-2-*carboxylate* (**16b**; R^1 = 5-phenylthiazol-2-yl, R = Bu^s). Obtained as colourless rods from benzene (Found: C, 61.65; H, 5.95; N, 9.6. $C_{22}H_{25}N_3O_4S$ requires C, 61.85; H, 5.85; N, 9.85%); *m*/*z*(%) 427 (M^+, 4); $\nu_{max.}$ 3 310, 1 780, 1 740, and 1 710 cm^{-1}.

Methyl 6,8-*dioxo*-c-4-(5-*phenylthiazol*-2-*yl*)-7-*phenyl*-2-*s*-*butyl*-3,7-*diazabicyclo*[3.3.0]*octane*-r-2-*carboxylate* (**16a**; R^1 = 5-phenylthiazol-2-yl, R = Bu^s). Obtained as colourless rods from methanol (Found: C, 66.1; H, 5.45; N, 8.5. $C_{27}H_{27}N_3O_4S$ requires C, 66.25; H, 5.5; N, 8.6%); *m*/*z*(%) 489 (M^+, 7); $\nu_{max.}$ 3 340, 1 775, 1 740, and 1 705 cm^{-1}.

Methyl c-4-(5-*methyl*-2-*thienyl*)-6,8-*dioxo*-7-*phenyl*-2-*s*-*butyl*-3,7-*diazabicyclo*[3.3.0]*octane*-r-2-*carboxylate* (**16a**; R^1 = 5-methyl-2-thienyl, R = Bu^s). Obtained as colourless rods from methanol (Found: C, 64.55; H, 6.05; N, 6.45. $C_{23}H_{26}N_2O_4S$ requires C, 64.8; H, 6.1; N, 6.55%); *m*/*z*(%) 426 (M^+, 4) and 210 (100); $\nu_{max.}$ 3 320, 1785, 1745, and 1 710 cm^{-1}.

Methyl c-4-(N-*methylpyrrol*-2-*yl*)-6,8-*dioxo*-7-*phenyl*-2-*s*-*butyl*-3,7-*diazabicyclo*[3.3.0]*octane*-r-2-*carboxylate* (**16a**; R^1 = N-methylpyrrol-2-yl, R = Bu^s). Obtained as colourless rods from methanol (Found: C, 57.55; H, 6.7; N, 10.25. $C_{23}H_{27}N_3O_4$ requries C, 67.5; H, 6.6; N, 10.25%); *m*/*z*(%) 409 (M^+, 3) and 193 (100); $\nu_{max.}$ 3 300, 1 785, 1 730, and 1 710 cm^{-1}.

Methyl c-4-(5-*methyl*-2-*furyl*)-6,8-*dioxo*-7-*phenyl*-2-*s*-*butyl*-3,7-*diazabicyclo*[3.3.0]*octane*-r-2-*carboxylate* (**16a**; R^1 = 5-methyl-2-furyl, R = Bu^s). Obtained as colourless plates from methanol (Found: C, 67.4; H, 6.4; N, 7.1. $C_{23}H_{26}N_2O_5$ requires C, 67.3; H, 6.35; N, 6.85%); *m*/*z*(%) 410 (M^+, 1) and 194 (100); $\nu_{max.}$ 3 320, 1 780, 1 730, and 1 710 cm^{-1}.

Methyl 6,8-*dioxo*-2,7-*diphenyl*-c-4-*t*-*butyl*-3,7-*diazabicyclo*-[3.3.0]*octane*-r-2-*carboxylate* (**16a**; R^1 = Bu^t, R = Ph). Obtained as colourless needles from methanol (Found: C, 71.15; H, 6.55; N, 6.8. $C_{24}H_{26}N_2O_4$ requires C, 70.9; H, 6.45; N, 6.9%); *m*/*z*(%) 406 (M^+, 0.3) and 349 (100); $\nu_{max.}$ 3 310, 1 780, and 1 720 cm^{-1}.

Methyl 6,8-*dioxo*-2-*phenyl*-c-4-*t*-*butyl*-7-*oxa*-3-*azabicyclo*-[3.3.0]*octane*-r-2-*carboxylate* (**16b**; R^1 = Bu^t, R = Ph). Obtained as colourless needles from ether (Found: C, 65.1; H, 6.35; N, 4.2. $C_{18}H_{21}NO_5$ requires C, 65.25; H, 6.4; N, 4.25%); *m*/*z*(%) 332 (M + 1, 2) and 272 ($M - CO_2Me$, 100); $\nu_{max.}$ 3 370, 1 860, 1 790, and 1 740 cm^{-1}.

Methyl c-4-*isopropyl*-6,8-*dioxo*-2,7-*diphenyl*-3,7-*diazabicyclo*-[3.3.0]*octane*-r-2-*carboxylate* (**16a**; R^1 = Pr^i, R = Ph). Obtained as colourless needles from methanol (Found: C, 70.05; H, 6.15; N, 6.95. $C_{23}H_{24}N_2O_4$ requires C, 70.4; H, 6.15; N, 7.15%); *m*/*z*(%) 392 (M^+, 1) and 333 ($M - CO_2Me$, 100); $\nu_{max.}$ 3 310, 1 780, and 1 720 cm^{-1}.

Methyl c-4-(1,1-*dimethylbut*-3-*enyl*)-6,8-*dioxo*-2,7-*diphenyl*-3,7-*diazabicyclo*[3.3.0]*octane*-r-2-*carboxylate* [**16a**; R^1 = $C(Me)_2CH_2CH{=}CH_2$, R = Ph]. Obtained as colourless needles from methanol (Found: C, 72.15; H, 6.35; N, 6.6. $C_{26}H_{28}N_2O_4$ requires C, 72.2; H, 6.55; N, 6.5%); *m*/*z*(%) 432 (M^+, 2) and 349 (100); $\nu_{max.}$ 3 320, 3 300, 1 770, and 1 710 cm^{-1}.

Methyl c-4-*diethoxymethyl*-6,8-*dioxo*-2,7-*diphenyl*-3,7-*diazabicyclo*[3.3.0]*octane*-r-2-*carboxylate* [**16a**; R^1 = $CH(OEt)_2$, R = Ph]. Obtained as colourless rods from ethanol (Found: C, 66.15; H, 6.3; N, 6.15. $C_{25}H_{28}N_2O_6$ requires C, 66.35; H, 6.25; N, 6.2%); *m/z*(%) 453 (*M* + 1, 1) and 103 (100); $\nu_{max.}$ 3 310, 1 900, and 1 720 cm^{-1}.

Methyl c-4-*ethoxycarbonyl*-6,8-*dioxo*-2,7-*diphenyl*-3,7-*diazabicyclo*[3.3.0]*octane*-r-2-*carboxylate* (**16a**; R^1 = CO_2Et, R = Ph). Obtained as colourless needles from ether–light petroleum (Found: C, 65.35; H, 5.00; N, 6.45. $C_{23}H_{22}N_2O_6$ requires C, 65.4; H, 5.25; N, 6.65%); *m/z*(%) 423 (*M* + 1, 3) and 463 (*M* − CO_2Me, 100); $\nu_{max.}$ 3 300 and 1 705 cm^{-1}.

Methyl c-4-*diethoxymethyl*-2-*methyl*-6,8-*dioxo*-7-*phenyl*-3,7-*diazabicyclo*[3.3.0]*octane*-r-2-*carboxylate* [**16a**; R^1 = $CH(OEt)_2$, R = Me]. Obtained as colourless needles from light petroleum (Found: C, 61.7; H, 6.7; N, 7.15. $C_{20}H_{26}N_2O_6$ requires C, 61.5; H, 6.7; N, 7.2%); *m/z*(%) 390 (M^+, 0.5) and 103 (100); $\nu_{max.}$ 3 300, 2 900, and 1 720 cm^{-1}.

Cycloaddition of Imines of α-Amino Acids: General Procedure.—The arenecarbaldehyde (1.5 mmol), α-amino acid (1.5 mmol), and *N*-phenylmaleimide (1.6 mmol) were suspended in glacial acetic acid and heated at 80—100 °C for 0.25—1.5 h. The solvent was then removed under reduced pressure, and the residue triturated with ether to afford the cycloadduct.

2-*Benzyl*-4-o-*hydroxyphenyl*-6,8-*dioxo*-7-*phenyl*-3,7-*diazabicyclo*[3.3.0]*octane*-2-*carboxylic acid* (**21a**). Obtained (75%) as a colourless solid, m.p. 228—229 °C (Found: C, 70.75; H, 5.05; N, 6.25. $C_{26}H_{23}N_2O_5$ requires C, 70.6; H, 5.00; N, 6.35%); δ([$^2H_5$]pyridine) 7.74—6.88 (m, 14 H, ArH), 5.56 (d, 1 H, H_A, *J* 9.1 Hz), 4.29 (t, 1 H, H_B), 4.05 (d, 1 H, H_C, $J_{B,C}$ 7.8 Hz), 3.95 and 3.5 (2 × d, 2 × 1 H, CH_2Ph, *J* 13.7 Hz).

2-*Benzyl*-4-o-*methoxyphenyl*-6,8-*dioxo*-7-*phenyl*-3,7-*diazabicyclo*[3.3.0]*octane*-2-*carboxylic acid* (**21**). Obtained (77%) as a colourless solid, m.p. 247—250 °C (Found: C, 70.9; H, 5.35; N, 6.15. $C_{27}H_{24}N_2O_5$ requires C, 71.05; H, 5.3; N, 6.15%); *m/z*(%) 456 (M^+, 1) and 91 (100); $\nu_{max.}$ 3 420, 2 920, 1 775, 1 710, and 1 600 cm^{-1}; δ([$^2H_5$]pyridine) 7.78—6.89 (m, 14 H, ArH), 5.51 (d, 1 H, H_A, *J* 8.9 Hz), 4.24 (dd, 1 H, H_B), 3.97 (d, 1 H, H_C, *J* 7.6 Hz), 3.88 and 3.81 (2 × d, 2 × 1 H, CH_2Ph, *J* 13.6 Hz), and 3.81 (s, 3 H, OMe).

4-o-*Hydroxyphenyl*-6,8-*dioxo*-7-*phenyl*-2-(2-*thiomethylethyl*)-3,7-*diazabicyclo*[3.3.0]*octane*-2-*carboxylic acid* (**21c**). Obtained (78%) as a colourless solid, m.p. 205—207 °C (Found: C, 61.7; H, 4.95; N, 6.3. $C_{22}H_{22}N_2O_5S$ requires C, 61.95; H, 5.2; N, 6.55%); δ([$^2H_5$]pyridine) 7.48—6.85 (m, 9 H, ArH), 5.12 (d, 1 H, H_A, *J* 8.8 Hz), 4.07 (t, 1 H, H_B), 3.74 (d, 1 H, H_C, *J* 7.8 Hz), 2.86 (m, 3 H, CH_2S and $CHCH_2S$), 2.37 (m, 1 H, $CHCH_2S$), and 2.12 (s, 3 H, SMe).

4-o-*Hydroxyphenyl*-2-*isobutyl*-6,8-*dioxo*-7-*phenyl*-3,7-*diazabicyclo*[3.3.0]*octane*-2-*carboxylic acid* (**21d**). Obtained (68%) as a colourless solid, m.p. 241—243 °C (Found: C, 67.5; H, 5.8; N, 6.8. $C_{23}H_{24}N_2O_5$ requires C, 67.65; H, 5.9; N, 6.85%); *m/z*(%) 408 (M^+, 0.5) and 190 (100); $\nu_{max.}$ 3 300 and 1 750 cm^{-1}; δ([$^2H_5$]pyridine) 7.51—6.85 (m, 9 H, ArH), 5.1 (d, 1 H, H_A, *J* 8.8 Hz), 4.09 (t, 1 H, H_B), 3.67 (d, 1 H, H_C, *J* 7.75), 2.51 (dd, 1 H), 2.13 (m, 1 H, $CHMe_2$), 1.96 (dd, 1 H), and 1.16 and 1.13 (2 × d, 2 × 3 H, Me).

2-*Hydroxymethyl*-4-o-*hydroxyphenyl*-6,8-*dioxo*-7-*phenyl*-3,7-*diazabicyclo*[3.3.0]*octane*-2-*carboxylic acid* (**21e**). Obtained as an 8:3 mixture with (**29**) as a light brown powder. Attempted separation of the two compounds by acid-base partitioning and by t.l.c. was unsuccessful. The n.m.r. spectrum of the mixture δ([$^2H_5$]pyridine) clearly showed the presence of both compounds as follows: δ (**21e**) 7.64—6.88 (m, 9 H, ArH), 5.43 (d, 1 H, H_A, *J* 8.9 Hz), 4.69 and 4.4 (2 × d, 2 × 1 H, CH_2OH, *J* 10.8 Hz), 4.22 (t, 1 H, H_B), and 4.07 (d, 1 H, H_C, *J* 8 Hz); δ (**29**) 7.64—6.88 (m, 9 H, ArH), 5.35 (d, 1 H, H_A, *J* 8.9 Hz), 4.22 (t, 1 H, H_B), 3.87 (d, 1 H, H_C, *J* 8 Hz), and 1.97 (s, 3 H, Me).

2-*Benzyl*-6,8-*dioxo*-7-*phenyl*-4-(2-*pyridyl*)-3,7-*diazabicyclo*[3.3.0]octane-2-*carboxylic acid* (**22a**). Obtained (65%) as a tan solid, m.p. 210—212 °C (Found: C, 70.1; H, 4.85; N, 10.05. $C_{25}H_{21}N_3O_4$ requires C, 69.7; H, 4.65; N, 10.15%); *m/z*(%) 427 (M^+, 8); δ([$^2H_5$]pyridine) 8.5 (d, 1 H, pyridyl H), 7.76—6.88 (m, 13 H, ArH), 5.24 (d, 1 H, H_A, *J* 8.8 Hz), 4.08 (t, 1 H, H_B), 3.99 (d, 1 H, H_C, *J* 7.7 Hz), and 3.83 and 3.37 (2 × d, 2 × 1 H, CH_2Ph).

2-*Benzyl*-6,8-*dioxo*-4,7-*diphenyl*-3,7-*diazabicyclo*[3.3.0]*octane*-2-*carboxylic acid* (**22b**). Obtained (72%) as colourless prisms from acetone–ether, m.p. 229—231 °C (decomp.) (Found: C, 72.4; H, 5.2; N, 6.8. $C_{26}H_{22}N_2O_4$ requires C, 73.2; H, 5.2; N, 6.55%); *m/z*(%) 427 (*M* + 1, 2); δ([$^2H_5$]pyridine) 7.62—7.16 (m, 15 H, ArH), 5.12 (d, 1 H, H_A, *J* 8.9 Hz), 3.91 (t, 1 H, H_B), 3.82 (d, 1 H, H_C, *J* 7.5 Hz), and 3.76 and 3.3 (2 × d, 2 × 1 H, CH_2Ph).

2-*Methyl*-6,8-*dioxo*-4,7-*diphenyl*-3,7-*diazabicyclo*[3.3.0]*octane*-2-*carboxylic acid* (**22c**). Obtained (67%) as colourless rods from acetone–ether, m.p. 235—238 °C (decomp.) (Found: C, 68.85; H, 5.55; N, 8.4. $C_{20}H_{18}N_2O_4$ requires C, 68.55; H, 5.2; N, 8.0%); δ([$^2H_5$]pyridine) 7.61—7.15 (m, 10 H, ArH), 5.01 (d, 1 H, H_A, *J* 8.7 Hz), 3.94 (t, 1 H, H_B), 3.7 (d, 1 H, H_C, *J* 7.6 Hz) and 1.83 (s, 3 H, Me).

Oxidation of Pyrrolidines to 5-Pyrrolines with DDQ: General Procedure.—A mixture of the pyrrolidine (2 mmol) and DDQ (2 mmol) in benzene (50 ml) was stirred at room temperature for the time indicated in Table 3 and, where appropriate (Table 3), heated at 80 °C for a period of time. Removal of the solvent and trituration of the residue with ether afforded the product which was crystallised from an appropriate solvent. Yields and n.m.r. data are collected in Table 3.

Methyl 2-*methyl*-6,8-*dioxo*-4,7-*diphenyl*-3,7-*diazabicyclo*[3.3.0]*oct*-3-*ene*-2-*carboxylate* (**33a**; Ar = Ph, R = Me). The product crystallised from dichloromethane–light petroleum as colourless needles, m.p. 185—187 °C (Found: C, 69.4; H, 5.1; N, 7.6. $C_{21}H_{18}N_2O_4$ requires C, 69.6; H, 5.00; N, 7.75%); *m/z*(%) 362 (M^+, 6) and 303 (*M* − CO_2Me, 100).

Methyl 6,8-*dioxo*-4,7-*diphenyl*-2-*phenylmethylthiomethyl*-3,7-*diazabicyclo*[3.3.0]*oct*-3-*ene*-2-*carboxylate* (**33a**; Ar = Ph, R = CH_2SCH_2Ph). The *product* crystallised from dichloromethane–light petroleum as colourless plates m.p. 70—72 °C (Found: C, 69.45; H, 5.1; N, 5.5. $C_{28}H_{24}N_2O_4S$ requires C, 69.4; H, 5.00; N, 5.8%); *m/z*(%) 484 (M^+, 14) and 303 (*M* − PhCHS, 100); $\nu_{max.}$ 1 780sh, 1 745, 1 710, and 1 615 cm^{-1}.

Methyl 2-*methoxycarbonylmethyl*-6,8-*dioxo*-4,7-*diphenyl*-3,7-*diazabicyclo*[3.3.0]*oct*-3-*ene*-2-*carboxylate* (**33a**; Ar = Ph, R = CH_2CO_2Me). The *product* crystallised as colourless needles from dichloromethane–light petroleum, m.p. 220—222 °C (Found: C, 65.95; H, 4.9; N, 6.55. $C_{23}H_{20}N_2O_6$ requires C, 65.7; H, 4.8; N, 6.65%); *m/z*(%) 420 (M^+, 17) and 329 (*M* − phenylmaleimide, 100).

Methyl 2-*benzyl*-6,8-*dioxo*-4,7-*diphenyl*-3,7-*diazabicyclo*[3.3.0]*oct*-3-*ene*-2-*carboxylate* (**33a**; Ar = Ph, R = CH_2Ph). The product crystallised as colourless needles from dichloromethane–light petroleum, m.p. 221—222 °C (Found: C, 73.7; H, 5.1; N, 6.25. $C_{27}H_{22}N_2O_4$ requires, C, 73.95; H, 5.05; N, 6.4%); *m/z*(%) 438 (M^+, 48), 379 (*M* − CO_2Me, 30), and 347 (*M* − CH_2Ph, 82).

Methyl 2-*benzyl*-6,8-*dioxo*-4-*phenyl*-7-*oxa*-3-*azabicyclo*[3.3.0]*oct*-3-*ene*-2-*carboxylate* (**33b**; Ar = Ph, R = CH_2Ph). The *product* crystallised as pale pink needles from dichloromethane–light petroleum, m.p. 135—137 °C (Found: C, 69.35; H, 4.8; N, 3.8. $C_{21}H_{17}NO_5$ requires C, 69.4; H, 4.7; N, 3.85%); *m/z*(%) 363 (M^+, 100) and 304 (*M* − CO_2Me, 76); $\nu_{max.}$ 1 865, 1 785, 1 740, and 1 620 cm^{-1}.

Methyl 2-*isopropyl*-6,8-*dioxo*-4,7-*diphenyl*-3,7-*diazabicyclo*-

[3.3.0]*oct*-3-*ene*-2-*carboxylate* (**33a**; Ar = Ph, R = Pr^i). The *product* crystallised from ether at −20 °C as colourless needles, m.p. 185—186 °C (Found: C, 70.55; H, 5.75; N, 7.1. $C_{23}H_{22}N_2O_4$ requires C, 70.75; H, 5.7; N, 7.2%); *m*/*z*(%) 390 (M^+, 2), 347 ($M - C_3H_7$, 10), and 331 ($M - CO_2Me$, 100); $\nu_{max.}$(Nujol) 1 725, 1 705, and 1 610 cm^{-1}.

Methyl 2-*isopropyl*-6,8-*dioxo*-4-*phenyl*-7-*oxa*-3-*azabicyclo*-[3.3.0]*oct*-3-*ene*-2-*carboxylate* (**33b**; Ar = Ph, R = Pr^i). The product crystallised from dichloromethane–light petroleum as colourless plates, m.p. 108—109 °C (Found: C, 64.5; H, 5.5; N, 4.35. $C_{17}H_{17}NO_3$ requires C, 64.74; H, 5.55; N, 4.45%); $\nu_{max.}$(Nujol) 1 860sh, 1 780, and 1 740 cm^{-1}.

Methyl 6,8-*dioxo*-4-*pentamethylphenyl*-2,7-*diphenyl*-3,7-*diazabicyclo*[3.3.0]*oct*-3-*ene*-2-*carboxylate* (**33b**; Ar = Me_5C_6, R = Ph). The *product* was obtained as colourless fine needles from dichloromethane–light petroleum, m.p. 278—279 °C (Found: C, 75.1; H, 6.00; N, 5.45. $C_{31}H_{30}N_2O_4$ requires C, 75.3; H, 6.1; N, 5.65%); $\nu_{max.}$(Nujol) 1 730, 1 695, and 1 640 cm^{-1}.

Methyl 6,8-*dioxo*-2-*phenyl*-4-(2-*thienyl*)-7-*oxa*-3-*azabicyclo*-[3.3.0]*oct*-3-*ene*-2-*carboxylate* (**33b**; Ar = 2-thienyl, R = Ph). The *product* was obtained as pale pink needles from dichloromethane–light petroleum, m.p. 208—210 °C (sublimes at 195 °C) (Found: C, 60.85; H, 3.7; N, 3.85. $C_{18}H_{13}NO_5S$ requires C, 60.85; N, 3.7; N, 3.95%); *m*/*z*(%) 355 (M^+, 3) and 296 ($M - CO_2Me$, 100).

Methyl 6,8-*dioxo*-2,7-*diphenyl*-4-(2-*thienyl*)-3,7-*diazabicyclo*-[3.3.0]*oct*-3-*ene*-2-*carboxylate* (**33a**; Ar = 2-thienyl, R = Ph). The *product* was obtained as pale pink needles from dichloromethane–light petroleum, m.p. 219—221 °C (Found: C, 66.2; H, 4.2; N, 6.35. $C_{24}H_{18}N_2O_4S$ requires C, 66.95; H, 4.2; N, 6.5%); *m*/*z*(%) 430 (M^+, 0.2) and 371 ($M - CO_2Me$, 100); $\nu_{max.}$ 1 785sh, 1 730, 1 710, and 1 605 cm^{-1}.

Ethyl 6,8-*dioxo*-4,7-*diphenyl*-3,7-*diazabicyclo*[3.3.0]*oct*-3-*ene*-2-*carboxylate* (**33a**; Ar = Ph, R = H, ethyl ether). The *product* was obtained as colourless needles from ether–light petroleum, m.p. 128—130 °C (Found: C, 69.4; H, 5.2; N, 7.8. $C_{21}H_{18}N_2O_4$ requires C, 69.6; H, 5.00; N, 7.75%); *m*/*z*(%) 362 (M^+, 22) and 289 ($M - CO_2Et$, 100); $\nu_{max.}$ 1 710 and 1 615 cm^{-1}.

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