1,3-Dipolar Character of Six-membered Aromatic Rings. Part 49.[1] 3-Oxido-1-(4-pyridyl)pyridinium, 3-Oxido-1-(2-pyridyl)pyridinium, 3-Oxido-1-(quinoxolin-2-yl)pyridinium, 3-Oxido-1-(5,6-diphenyl-1,2,4-triazin-3-yl)pyridinium, and 3-Oxido-1-(5-phenyl-1,2,4-triazin-3-yl)pyridinium

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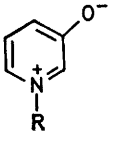
The title betaines are prepared: the two triazinyl betaines undergo spontaneous thermal dimerisation, and all add a variety of 2π, 4π, and/or 6π dipolarophiles. The regio- and stereo-chemistry of the addition are elucidated and rationalised. The pyridyl adducts undergo quaternisation and ring opening to tropolones.

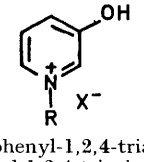
1-METHYL-3-OXIDOPYRIDINIUM (1) has been shown [2] to react with activated addends to give 8-azabicyclo[3.2.1]-oct-3-en-2-ones which are readily converted into tropones and tropolones.[3] Cycloadducts are obtained more easily from 3-oxido-1-phenylpyridinium [4] (2) but these are *N*-alkylated [5] only with difficulty, by use of methyl fluorosulphonate [6] and methyl trifluoromethanesulphonate.[7] *N*-(Pyridyl) substituents should activate the betaine towards cycloaddition and it was expected that they could be cleaved readily from the cycloadducts: Schmid and Wolkoff [8] made alkenes by facile thermal eliminations of 4-alkoxy-*N*-methylpyridinium iodides. We therefore undertook the preparation of the *N*-2-pyridyl (6) and *N*-4-pyridyl (3) betaines and analogues with other heterocyclic substituents.



(1) R = Me
(2) R = Ph
(3) R = 4-Pyridyl
(4) R = 2,4-Dinitrophenyl
(5) R = 5-Nitro-2-pyridyl
(6) R = 2-Pyridyl
(7) R = Quinoxolin-2-yl
(8) R = 5-Phenyl-1,2,4-triazin-3-yl
(9) R = 5,6-Diphenyl-1,2,4-triazin-3-yl

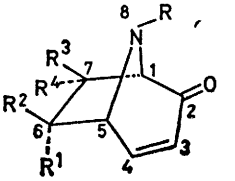
RESULTS AND DISCUSSION

3-Oxido-1-(4-pyridyl)pyridinium (3) *and 3-Oxido-1-(2-pyridyl)pyridinium* (6).—3-Hydroxy-1-(4-pyridyl)-pyridinium chloride (14) (prepared from 3-hydroxypyridine and 4-chloropyridine), when treated with IRA-401 (OH) [9] resin, gives the hydrated betaine (3), m.p. 105—106 °C (*m/e* 172). The analogous 3-hydroxy-1-(2-pyridyl)pyridinium chloride (12), characterised as



(10) R = 5,6-Diphenyl-1,2,4-triazin-3-yl; X = Cl
(11) R = 5-Phenyl-1,2,4-triazin-3-yl; X = Cl
(12) R = 2-Pyridyl; X = Cl
(13) R = 2-Pyridyl; X = ClO_4
(14) R = 4-Pyridyl; X = Cl
(15) R = Quinoxolin-2-yl; X = Cl
(16) R = Quinoxolin-2-yl; X = ClO_4

the perchlorate (13), when treated with triethylamine yielded the 2-pyridyl betaine (6). Like 3-oxido-1-



(17) R = 4-Pyridyl; R^1 = CN; R^2 = R^3 = R^4 = H
(18) R = 4-Pyridyl; R^1 = CO_2Me; R^2 = R^3 = R^4 = H
(19) R = 4-Pyridyl; R^1 = Ph; R^2 = R^3 = R^4 = H
(20) R = 4-Pyridyl; R^1 = OEt; R^2 = R^3 = R^4 = H
(21) R = Quinoxolin-2-yl; R^1 = CN; R^2 = R^3 = R^4 = H
(22) R = Quinoxolin-2-yl; R^1 = R^3 = R^4 = H; R^2 = CN
(23) R = Quinoxolin-2-yl; R^1,R^2 = Cl,CN; R^3 = R^4 = H
(24) R = Quinoxolin-2-yl; R^1 = CO_2Me; R^2 = R^3 = R^4 = H
(25) R = Quinoxolin-2-yl; R^1 = R^3 = R^4 = H; R^2 = CO_2Me
(26) R = Quinoxolin-2-yl; R^1 = Ph; R^2 = R^3 = R^4 = H
(27) R = 2-Pyridyl; R^1 = Ph; R^2 = R^3 = R^4 = H
(28) R = 2-Pyridyl; R^2 = R^3 = R^4 = H; R^1 = CO_2Me
(29) R = 2-Pyridyl; R^1 = R^3 = R^4 = H; R^2 = CO_2Me
(30) R = 2-Pyridyl; R^2 = R^3 = R^4 = H; R^1 = OEt
(31) R = 2-Pyridyl; R^1 = 3-ClC_6H_4; R^2 = R^3 = R^4 = H
(32) R = 2-Pyridyl; R^1,R^2 = Cl,CN; R^3 = R^4 = H
(33) R = 2-Pyridyl; R^1 = R^3 = CO_2Et; R^2 = R^4 = H
(34) R = 2-Pyridyl; R^1 = R^3 = R^4 = H; R^2 = CN
(35) R = 2-Pyridyl; R^1 = CN; R^2 = R^3 = R^4 = H
(36) R = 2-Pyridyl; R^1 = R^2 = R^3 = H; R^4 = CN
(37) R = 5,6-Diphenyl-1,2,4-triazin-3-yl; R^1,R^2 = Cl,CN; R^3 = R^4 = H
(38) R = 5,6-Diphenyl-1,2,4-triazin-3-yl; R^1 = CO_2Me; R^2 = R^3 = R^4 = H
(39) R = 5,6-Diphenyl-1,2,4-triazin-3-yl; R^1 = R^3 = H; R^2 = R^4 = CO_2Et
(40) R = 5-Phenyl-1,2,4-triazin-3-yl; R^1 = Ph; R^2 = R^3 = R^4 = H
(41) R = 5-Phenyl-1,2,4-triazin-3-yl; R^1 = CN; R^2 = R^3 = R^4 = H
(42) R = 5-Phenyl-1,2,4-triazin-3-yl; R^1 = CO_2Me; R^2 = R^3 = R^4 = H
(43) R = 5,6-Diphenyl-1,2,4-triazin-3-yl; R^1 = CN; R^2 = R^3 = R^4 = H
(44) R = 5,6-Diphenyl-1,2,4-triazin-3-yl; R^1 = R^3 = R^4 = H; R^2 = CN
(45) R = 5,6-Diphenyl-1,2,4-triazin-3-yl; R^1 = Ph; R^2 = R^3 = R^4 = H
(46) R = 5-Phenyl-1,2,4-triazin-3-yl; R^1 = R^3 = R^4 = H; R^2 = CN
(47) R = 5-Phenyl-1,2,4-triazin-3-yl; R^1 = R^2 = R^3 = H; R^4 = CN
(48) R = 5-Phenyl-1,2,4-triazin-3-yl; R^1 = R^3 = R^4 = H; R^2 = CO_2Me
(49) R = 4-Pyridyl; R^2 = R^3 = H; R^1,R^4 = CON(Ph)CO
(50) R = 2-Pyridyl; R^2 = R^3 = H; R^1,R^4 = CON(Ph)CO
(51) R = 5,6-Diphenyl-1,2,4-triazin-3-yl; R^2 = R^3 = H; R^1,R^4 = CON(Ph)CO
(52) R = 5,6-Diphenyl-1,2,4-triazin-3-yl; R^1 = R^2 = H; R^2,R^3 = CON(Ph)CO

phenylpyridinium [4] (2), and unlike the 5-nitro-2-pyridyl analogue (5),[10] these 2- (6) and 4-pyridyl (3) betaines do not undergo thermal dimerisation.

Betaines (3) and (6) react with monosubstituted olefins to give good yields of the expected [4] cycloadducts: thus acrylonitrile yields the 6-*endo*- [(17) and (35)], 6-*exo*- (34), and 7-*endo*-derivatives (36); methyl acrylate yields the 6-*endo*- [(18) and (28)] and 6-*exo*-derivatives (29); styrene yields exclusively the 6-*endo*-adducts [(19) and (27)]; ethyl vinyl ether also yields exclusively the 6-*endo*-adducts [(20) and (30)]. 3-Chlorostyrene reacts with betaine (6) to yield the 6-*endo*-aryl adduct (31) (*cf.* reactions of 3-oxido-1-phenylpyridinium and substituted styrenes).[5] The structures were confirmed by i.r. and n.m.r. spectroscopy. The splitting patterns of the two bridgehead protons, 1-H and 5-H, characterise [4] the 6-*endo*-stereochemistry of the cycloadducts, since $J_{5,6\text{-}endo}$ is negligibily small whereas $J_{5,6\text{-}exo}$ is relatively large (5 Hz).* 2-Chloroacrylonitrile cycloadds with the 2-pyridyl betaine (6) to produce a single cycloadduct (32) of unknown stereochemistry at C-6. Dimethyl fumarate reacts with betaine (6) to yield the single *trans*-isomer (33).

Acenaphthylene, a strained olefin, readily reacted with betaine (3) to produce exclusively the *exo*-adduct (53), m.p. 264—266 °C. However, the addition to the betaine (6) produced both the *exo*- (54) and the *endo*-adducts (56). The n.m.r. spectra (Table 1, and Table 2 of SUP 22631) confirm the *exo*-stereochemistry of compounds (53) and (54) since 6-H and 7-H form an AB quartet and the bridgehead protons, 1-H and 5-H, exhibit a singlet and a doublet, respectively (*endo*-stereochemistry would cause the bridgehead protons, 1-H and 5-H, to exhibit a doublet or double doublet, and a triplet respectively).

Unlike 3-oxido-1-phenylpyridinium,[4] both the pyridyl betaines (3) and (6) with *N*-phenylmaleimide yield single *endo*-adducts, (49) and (50) respectively. The *endo*-stereochemistry was demonstrated for (49) and (50) by the n.m.r. spectra (Table 1 and Table 2 of SUP 22631), as 1-H and 5-H exhibit a doublet and a triplet respectively.

6-(*p*-Methoxyphenyl)fulvene with the betaine (3)

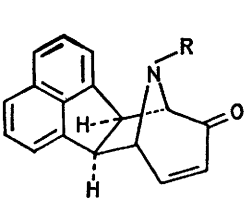
TABLE 1

^{1}H N.m.r. spectra of 4-pyridyl cycloadducts [a],*

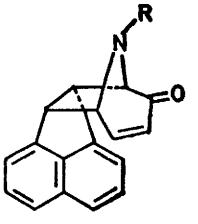
Chemical shifts (δ)	(18) [b]	(19) [b]	(20) [b]	(49) [c]	(53) [b]	(59) [c]	(78) [c]	(79) [c]	(80) [c]	(81) [c]	(82) [c]	(83) [c]
1	4.30 [d]	4.42 [d]	4.40 [e]	5.20 [e]	4.62 [f]	5.20 [f]	5.29 [e]	5.22 [e]	5.14 [e]	5.22 [e]	5.02 [e]	5.24 [e]
3	5.77 [d]	5.82 [d]	6.06 [e]	6.13 [d]	6.05 [d]	5.48 [d]	6.15 [d]	6.28 [e]	6.05 [d]	6.04 [d]	6.12 [e]	6.26 [e]
4	6.94 [d]	6.55 [d]	7.05 [g]	7.26 [g]	7.48 [g]	6.06 [d]	7.62 [g]	7.66 [g]	7.47 [g]	7.10 [d]	7.48 [g]	7.66 [g]
5	4.77	4.73 [h]	4.86 [h]	5.47 [h]	4.87 [e]	5.30 [e]	5.58 [e]	5.71 [h]	5.58 [h]	5.76 [h]	5.60 [h]	5.71 [h]
6-*endo*					4.36 [e]	3.80 [i]	4.54 [e]					
6-*exo*	3.53 [j]	3.86 [j]	4.46 [j]	4.30 [d]				3.98 [j]	3.80 [j]	4.00 [j]	4.56 [j]	4.00 [j]
7-*endo*	2.02 [d]	2.12 [d]	1.72 [d]		4.20		4.40 [e]	2.13 [d]	2.00 [d]	2.12 [d]	1.55 [d]	2.14 [d]
7-*exo*	2.60 [j]	2.80 [j]	2.91 [j]	3.32 [d]				3.30 [j]	2.92 [j]	3.15 [j]	3.04 [j]	3.24 [j]
2′,6′	8.08 [e]	8.08 [e]	8.26 [i]	4.08 [e]	8.10 [e]		8.13 [e]	8.42 [e]	8.36 [e]	8.32 [e]	8.36 [e]	8.40 [e]
3′,5′	6.38 [e]	6.42 [e]	6.54 [e]	6.86 [e]	6.40 [e]		7.16 [e]	7.31 [e]	7.34 [e]	7.26 [i]	7.31 [e]	7.26 [e]
CO_2Me	3.53 [f]								3.67 [f]			
Ph		7.12 [i]		7.26 [i]	7.48 [i]	6.80 [i]	7.62 [i]			7.26 [i]		
CH_2CH_3			3.56 [g]								3.58 [g]	
CH_2CH_3			1.24 [h]								1.16 [h]	
NMe						3.80 [f]	3.80 [f]	3.98 [f]		3.93 [f]	3.94 [f]	4.00
OMe						3.80 [f]						
Coupling constants (Hz)												
1,3	1.0	1.0	2.0	1.0	1.5	1.0	1.0	1.5	1.0	1.0	2.0	1.5
1,7-*exo*	8.0	8.0	8.0	8.0				7.0	8.0	8.0	8.0	7.0
1,7-*endo*	1.0	1.0			1.0		1.0	1.0	1.0	1.0		1.0
3,4	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
4,5	5.0	4.0	5.0	6.0	5.0	5.0	5.0	5.0	5.0	4.0	5.0	5.0
5,6-*exo*	6.0	6.0	5.0	6.0				5.0	5.0	6.0	5.0	5.0
6-*endo*, 7-*endo*					7.0		7.0					
6-*exo*, 7-*endo*	7.0	6.0	6.0					6.0	6.0	8.0	6.0	6.0
6-*exo*, 7-*exo*	10.0	10.0	9.0	10.0				8.0	10.0	10.0	9.0	8.0
7-*endo*, 7-*exo*	14.0	16.0	14.0					14.0	14.0	14.0	14.0	14.0
2′,3′	5.0	6.0	6.0	6.0	6.0		6.0	7.0	7.0	8.0	6.0	7.0
5′,6′	5.0	6.0	6.0	6.0	6.0		6.0	7.0	7.0	8.0	6.0	7.0
CH_2CH_3			8.0								8.0	

* See formulae for numbering which is non-systematic.

[a] Internal standard $SiMe_4$. [b] In $CDCl_3$. [c] In $(CD_3)_2SO$. [d] Double doublet. [e] Doublet. [f] Singlet. [g] Quartet. [h] Triplet. [i] Complex. [j] Quartet of doublets.



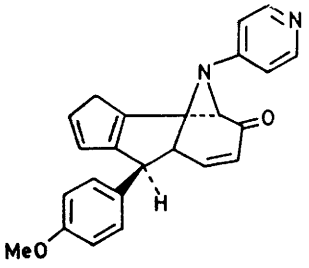
(53) R = 4-Pyridyl
(54) R = 2-Pyridyl
(55) R = 5,6-Diphenyl-1,2,4-triazin-3-yl



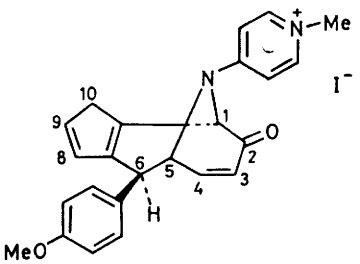
(56) R = 2-Pyridyl
(57) R = 5,6-Diphenyl-1,2,4-triazin-3-yl

* See Table 2 of SUP 22631 (8 pp.); for details of the Supplementary Publications scheme see Notice to Authors No. 7, *J.C.S. Perkin I*, 1979, Index issue.

produced the adduct (58) which on treatment with methyl iodide yielded a single quaternary salt (59), m.p. 220 °C, in 20% yield. We have previously reported [11]



(58)



(59)

the addition of 1-(5-nitro-2-pyridyl)- and 1-(4,6-dimethylpyrimidin-2-yl)-3-oxidopyridinium with 6π-electron addends.

3-Oxido-1-(5,6-diphenyl-1,2,4-triazin-3-yl)pyridinium (9) *and 3-Oxido-1-(5-phenyl-1,2,4-triazin-3-yl)pyridinium* (8).—3-Hydroxypyridine was readily quaternised by 3-chloro-5,6-diphenyl-1,2,4-triazine * and 3-chloro-5-phenyl-1,2,4-triazine [12] to yield the quaternary salts (10), m.p. 215—218 °C, and (11), m.p. 234—236 °C, respectively. The ^{1}H n.m.r. spectra of these salts in $(CD_3)_2SO$ show the characteristic pattern of an ABCD system (Table 3 of SUP 22631).

Treatment of the salts (11) and (10) with aqueous $NaHCO_3$ yielded, in place of the expected betaines (8) and (9), the corresponding dimers (61) and (60), respectively. The i.r. spectra of the dimers (61) and (60) both show two carbonyl stretching frequencies at 1 740 (saturated) and 1 680 cm^{-1} (conjugated αβ-unsaturated), and an enamine C=C frequency at 1 640 cm^{-1}. The structure and stereochemistry of the dimers (61) and (60) were elucidated from spectral evidence; the n.m.r.

TABLE 2

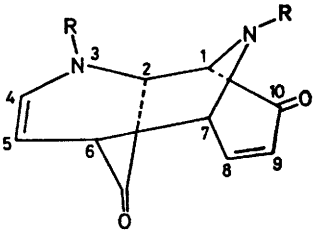
^{1}H N.m.r. spectra of dimers [a,b,*]

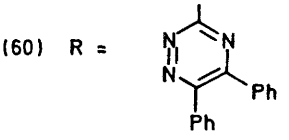
Chemical shifts (δ)	(60) [c]	(61) [d]	(71) [e]
1	6.26 [f]	6.54 [g]	5.22 [g]
2	5.48 [f]	5.38 [f]	5.22 [g]
4	7.20 [h]	7.12 [i]	7.30 [g]
5	5.18 [j]	5.17 [k]	5.22 [j]
6	3.45 [i]	3.44 [l]	3.36 [g]
7	5.48 [f]	5.38 [f]	6.04 [g]
8	7.20 [h]	7.38 [g]	2.89 [g]
9	6.32 [i]	6.36 [i]	2.89 [g]
Ph	7.20 [h]	7.38 [g]	7.30 [g]

* See formulae for numbering which is non-systematic.

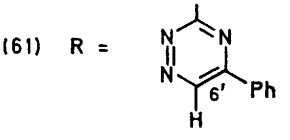
[a] Internal standard $SiMe_4$. [b] In $CDCl_3$. [c] $J_{1,2} = J_{2,6} = J_{1,7} = J_{6,7} = 2.0$ Hz; $J_{4,5}$ 8.0 Hz; $J_{8,9}$ 10 Hz; $J_{5,6}$ 7.0 Hz. [d] 6′-H = 8.86,[f] 8.98;[f] $J_{2,6} = J_{6,7} = 2.5$ Hz; $J_{4,5}$ 7.5 Hz; $J_{5,6}$ 7.0 Hz; $J_{8,9}$ 10.0 Hz. [e] 10-H = 3.36;[g] 11-H = 12-H = 6.04;[g] 13-H = 2.89;[g] 14-*endo*-H = 14-*exo*-H = 1.50;[g] $J_{4,5}$ 8.0 Hz; $J_{5,6}$ 7.0 Hz; $J_{1,2} = J_{6,7} = 2.0$ Hz; $J_{1,7} = J_{2,6} = 1.5$ Hz. [f] Singlet. [g] Multiplet. [h] Complex. [i] Doublet. [j] Triplet. [k] Double doublet. [l] Triplet of doublets.

spectra (Table 2) were especially significant and assignments were made by analogy with the corresponding *N*-(diphenyl-1,3,5-triazinyl)- (62) and *N*-(dimethoxy-1,3,5-triazinyl)-dimers (63) previously reported.[13] Assignments were confirmed by double-irradiation experiments. The signal of the bridgehead proton not located α to a nitrogen atom, absorbs at higher field than those of the *syn*-structure [(61) or (60)] as against the *anti*-form (64). The *exo*-configuration of both dimers was supported by the 2-H–6-H coupling, 2.0—2.5 Hz. Molecular models show that only in the *exo*-structure does the four-bond system connecting 2-H and 6-H assume a planar configuration required for W-type coupling.

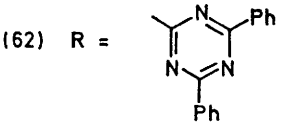




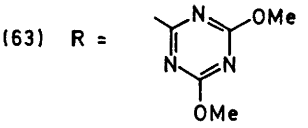
(60) R =



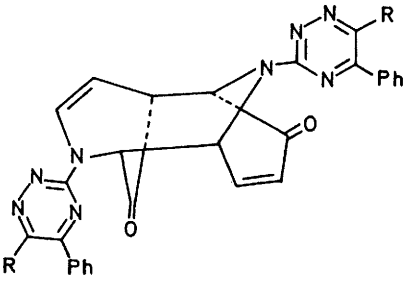
(61) R =



(62) R =



(63) R =



(64) R = H or Ph

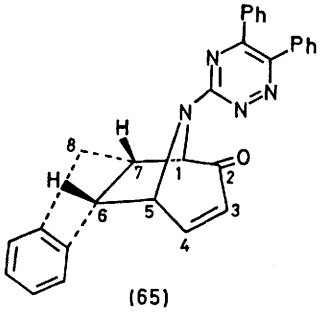
The triazinyl betaine dimers (60) and (61) evidently undergo reversible de-dimerisation readily, for they form cycloadducts derived from the monomeric betaines (8) and (9) readily with a variety of 2π and 4π dipolarophiles. Thus acrylonitrile yields the expected [4] 6-*endo*-[(41) and (43)] and 6-*exo*-derivatives [(46) and (44)];

* Kindly supplied by Dr. E. Lunt, May and Baker, Dagenham, Essex.

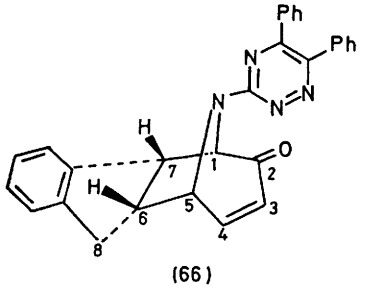
methyl acrylate yields the 6-*endo*- [(42) and (38)] and the 6-*exo*-derivatives (48); styrene yields exclusively the 6-*endo*-adducts [(40) and (45)]. In the reaction of the monophenyltriazinyl betaine (8), the 7-*endo*-carbonitrile (47) was produced in 15% yield along with the expected 6-carbonitriles [(41) 38% and (46) 24%]. The diphenyl betaine (9) combines with 2-chloroacrylonitrile to produce a single 6-substituted isomer (37). The spectral data for all these ethylenic adducts are consistent with the structures proposed (see Table 5 of SUP 22631 for n.m.r. data and Experimental section for i.r. data).

Diethyl fumarate with the diphenyltriazinyl betaine (9) produced a single *trans*-cycloadduct (39). The n.m.r. spectrum of (39) (Table 5 of SUP 22631) exhibits a double doublet ($J_{1,7\text{-}exo}$ 8.0; $J_{1,3}$ 1.5 Hz) for 1-H and a doublet ($J_{4,5}$ 6.0 Hz) for 5-H.

Indene readily reacted as a 2π addend with the diphenyltriazinyl betaine (9) to yield two *endo*-adducts (65) and (66) in low yields. The n.m.r. spectra (Table 5 of SUP 22631) of these indene adducts (65) and (66) exhibit double doublets for 1-H confirming the *endo*-stereochemistry of the cycloadducts. Further structural features were elucidated by exhaustive spin–spin decoupling techniques. The strained 2π addend, acenaphthylene, cycloadded to the diphenyltriazinyl betaine (9) to produce both the *endo*- (57) and the *exo*-adducts (55): the n.m.r. spectrum (Table 5 of SUP 22631) confirms the stereochemistry in each case. The diphenyltriazinyl betaine (9) with *N*-phenylmaleimide



(65)

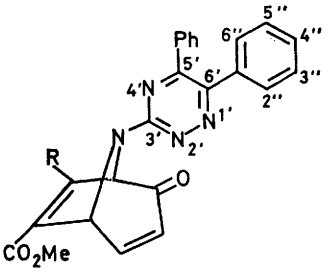


(66)

yields both *endo*- (51) and *exo*-adducts (52). The *endo*-stereochemistry of (51) was demonstrated by the n.m.r. spectrum (Table 5 of SUP 22631) since 1-H and 5-H exhibit a doublet and a triplet respectively. The *exo*-stereochemistry of (52) was demonstrated by the n.m.r. spectrum (Table 5 of SUP 22631) since 1-H and 5-H show a singlet and a doublet respectively.

Cycloadditions were also achieved readily with acetylenic dipolarophiles: dimethyl but-2-ynedioate and methyl prop-2-ynoate reacted with the betaine (9) to yield the 2,6-adducts (68) and (67) respectively. The n.m.r. spectra (Table 5 of SUP 22631) for both adducts exhibit a doublet (J 5 Hz) for 5-H confirming the presence of a methoxycarbonyl group at C-6.

1,3-Dienes can react as either 2π- or 4π-electron



(67) R = H
(68) R = CO_2Me

components. Heating the diphenyltriazinyl dimer (60) with cyclopentadiene gives a mixture of the products [(69)—(71)] which were separated by chromatography. The dimer (60) itself undergoes, without de-dimerisation, a Diels–Alder cycloaddition with cyclopentadiene acting as a diene to yield the compound (71). The dimer (60) also acts as a source of the triazinyl betaine (9) which reacts with cyclopentadiene, at elevated temperature, to yield the 2,6-adduct (69). Adduct (69), in part, undergoes a Diels–Alder reaction with more cyclopentadiene giving the adduct (70). We have previously reported [14] the comparable double addition of cyclopentadiene to 1-(5-nitro-2-pyridyl)-3-oxidopyridinium (5). The evidence for the structures of (70) and (71) includes the absence of the αβ-unsaturated carbonyl stretching frequency initially present in the 2,6-adduct (69) and the dimer (64; R = Ph), respectively. No simple 2,4-adducts were detected in the reaction of dimer (60) and cyclopentadiene, in contrast to the reaction [14] of pyrimidinyl betaine dimer with cyclopentadiene. We believe that the absence of 2,4-adducts is a result of the 2,6-adduct being thermodynamically more stable. However, 2,3-dimethylbuta-1,3-diene reacts with the betaine (9) to yield the 2,4-adduct (73), and buta-1,3-diene (prepared *in situ* from 2,5-dihydrothiophen sulphone) also combines as a diene with both betaines (9) and (8) to afford the 2,4-adducts (74) and (72) respectively. The i.r. spectra of the 2,4-adducts exhibit saturated carbonyl-stretching frequencies for the bridgehead carbonyl groups at 1 720—1 725 cm^{-1}; their structures and the *exo*-stereochemistry were confirmed by the n.m.r. spectra (Table 5 of SUP 22631).

3-*Oxido*-1-(*quinoxolin*-2-*yl*)*pyridinium* (7).—2-Chloroquinoxoline and 3-hydroxypyridine readily afforded the corresponding quaternary salt (15) which was characterised as the crystalline perchlorate, m.p. 195—197 °C. From this salt, the quinoxolinyl betaine (7) was readily prepared *in situ* by the addition of triethylamine. The 2π addends acrylonitrile, 2-chloroacrylonitrile, methyl

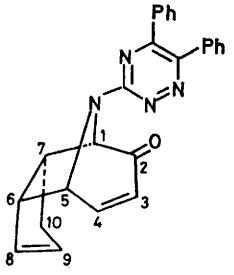
TABLE 3

Yields (%) of *endo*- and *exo*-cycloadducts from $[4n + 2]\pi$ addition of electron-deficient addends with betaines

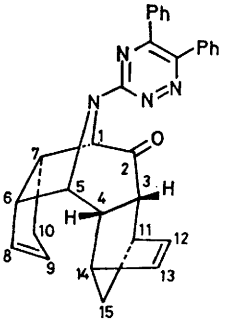
	Betaine (3)		Betaine (6)		Betaine (7)		Betaine (8)		Betaine (9)	
	endo	*exo*	*endo*	*exo*	*endo*	*exo*	*endo*	*exo*	*endo*	*exo*
CH_2=CH–CO_2Me	100 *	0	54	46	56	44	30	70	100 *	0
CH_2=CH–CN	100	0	59	41	57	43	69	31	52	48
N-Phenylmaleimide	100	0	100	0					21	79
Styrene	100	0	100	0	100	0	100	0	100	0
CH_2=CH–OEt	100	0	100	0						
Acenaphthylene	0	100	43	57					31	69

* Only one adduct isolated from mixture.

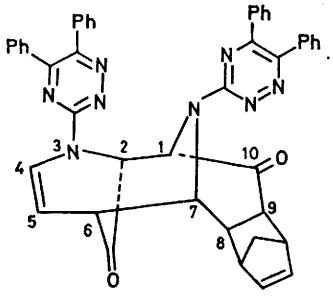
acrylate, and styrene reacted with the quinoxolinyl betaine (7) to produce the expected [4] cycloadducts (21)—(26) in moderate yields. The n.m.r. spectra (Table 6 of SUP 22631) of these cycloadducts are in agreement with the structures proposed.



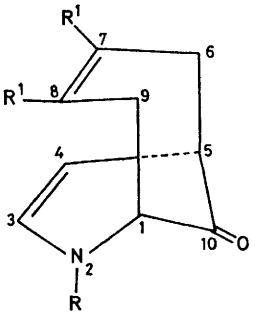
(69)



(70)



(71)



(72) R = 5-Phenyl-1,2,4-triazin-3-yl; R^1 = H
(73) R = 5,6-Diphenyl-1,2,4-triazin-3-yl; R^1 = Me
(74) R = 5,6-Diphenyl-1,2,4-triazin-3-yl; R^1 = H

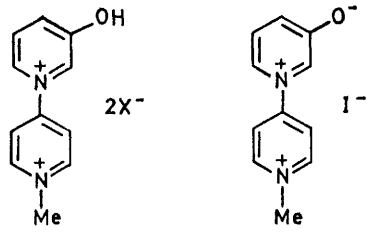
Stereoselectivity and Regioselectivity.—*endo*-Addition of conjugated olefins is favoured by secondary orbital overlap [15] but disfavoured by steric factors and dipole–dipole interactions.[16] The exclusive formation of the *endo*-adduct from the reaction of *N*-phenylmaleimide and the betaines (3) and (6) is the result of strong interaction between the lowest-unoccupied molecular orbital (LUMO) of the betaine and the highest-occupied molecular orbital (HOMO) of *N*-phenylmaleimide, *cf.* the dinitrophenyl [17] (4) and nitropyridyl [14] (5) betaines which also give exclusively the *endo*-adducts. The formation of the thermodynamically more stable *exo*-product (52) in the reaction of *N*-phenylmaleimide and betaine (9) is probably the result of thermal isomerism of the initially formed kinetic product, the *endo*-isomer (51) [*cf.* the *N*-(diphenyl-1,3,5-triazinyl)-dimer (62)].[13]

Generally, stereoselectivity is lost in the addition of *N*-aryl betaines to acrylonitrile, methyl acrylate, and methyl vinyl ketone: here the secondary overlap is weaker and the steric and dipole–dipole interactions are stronger, which leads to considerable formation of the *exo*-adduct (see Table 3), with the exception of betaine (3) with which acrylonitrile and methyl acrylate yield exclusively the *endo*-adducts. The conjugated dipolarophile, styrene, yields exclusively the *endo*-adduct since the secondary overlap predominates over the weak dipole–dipole interaction. However, with acenaphthylene steric factors lead to the formation of the *exo*-isomer as the predominant isomer. Reversal of polarity of ethyl vinyl ether leads to a favourable dipole–dipole interaction which is responsible for the sole formation of the *endo*-adduct.

We have previously [14] shown that frontier molecular orbital [11] theory correctly predicts that electron-donating, electron-accepting, and conjugated monosubstituted olefins all add to give exclusively the 6-regioisomers; this holds also in the present case.

Our present studies have shown that the 3-oxido-1-heteroarylpyridinium betaines form a series which displays increasing reactivity in pericyclic reactions with olefinic dipolarophiles *viz.* (8) ≈ (9) > (7) > (6) > (3) > (2) > (1). The ease of thermal dimerisation of an *N*-substituted 3-oxidopyridinium is a function of the *N*-substituent. In general, the more electron-withdrawing the *N*-substituent, the smaller is the energy difference between the frontier orbitals of the two reacting betaine molecules and the more favoured is dimerisation. The *N*-(5,6-diphenyl-1,2,4-triazin-3-yl) (9) and *N*-(5-phenyl-1,2,4-triazin-3-yl) betaine (8) possess strong electron-withdrawing *N*-substituents and readily dimerise, although not as readily as the analogous symmetrical triazinyl betaine (62).[13]

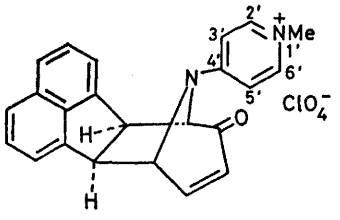
The 4′-aza-substituent in 3-oxido-1-phenylpyridinium should exert [11] a considerable lowering effect on the LUMO resulting in a smaller frontier-orbitals energy separation. The present study has shown that this activation is not sufficient for dimerisation. To further increase this reactivity, the pyridyl betaine (3) was methylated with MeI to yield the bis-salt (75), characterised as the perchlorate (76). However, attempts to prepare the corresponding betaine (77) by base treatment proved unsuccessful; presumably the betaine (77) is unstable.



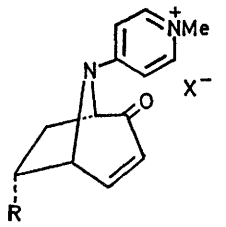
(75) X = I
(76) X = ClO_4

(77)

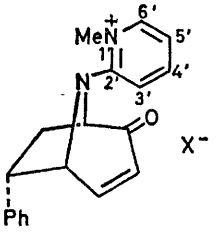
Tropone Formation.—The cycloadducts (17)—(20), (53), (27), (26), and (24) were readily quaternised by methyl iodide, methyl perchlorate, or methyl toluene-*p*-sulphonate on the ring nitrogen, as expected, to give the salts (78)—(83), (85), (84), (86), and (87). Hofmann degradation [3] of the methiodide (81) with Ag_2O produced



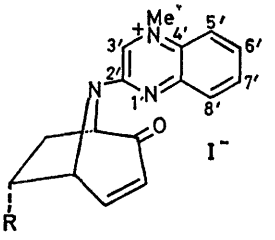
(78)



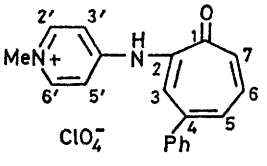
(79) R = CN, X = I
(80) R = CO_2Me, X = I
(81) R = Ph, X = I
(82) R = OEt, X = I
(83) R = CN, X = ClO_4



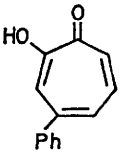
(84) X = I
(85) X = OTs



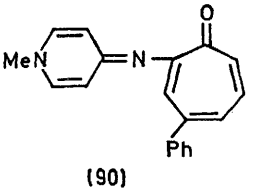
(86) R = Ph
(87) R = CO_2Me



(88)



(89)



(90)

the corresponding tropone perchlorate (88), m.p. 250 °C. Further hydrolysis [18] of this perchlorate to the corresponding tropolone (89) proved unsuccessful, presumably owing to the intervention of the tautomer (90) under basic conditions. Pietra *et al.*[19] have described the facile nucleophilic displacement of chlorine and the tosyloxy-group from 2-chloro- and 3-tosyloxy-tropones by alkoxide. Attempted acid-catalysed hydrolysis of the diphenyltriazinyl adduct (45) yielded only benzil, derived from the hydrolysis [20] of the triazinyl ring.

EXPERIMENTAL

M.p.s were determined with a Reichert apparatus. The spectra were recorded with a Perkin-Elmer 257 grating i.r. spectrophotometer, a Hitachi-Perkin-Elmer RMU-6E mass spectrometer, and a Varian HA-100 n.m.r. spectrometer. Compounds were purified until they were observed as single spots on t.l.c. using Kieselgel GF 254 (Type 60).

3-Hydroxy-1-(4-pyridyl)pyridinium Chloride (14).—4-Chloropyridine (2.0 g, 1.8 × 10^{-2} mol) and 3-hydroxypyridine (1.0 g, 0.01 mol) in tetrahydrofuran (15 ml) were heated under reflux for 60 h. A pale yellow precipitate (1.9 g, 86.6%) was recrystallised to yield (14) as colourless *needles*, m.p. 226—227 °C (MeOH–EtOAc) (Found: C, 57.7; H, 4.6; N, 13.2; Cl, 16.7. $C_{10}H_9ClN_2O$ requires C, 57.6; H, 4.3; N, 13.4; Cl, 17.0%); $\nu_{max.}$ (Nujol) 2 800—2 500 (phenolic OH), 1 630 (C=C–N), and 1 590 cm^{-1} (C=C).

3-Oxido-1-(4-pyridyl)pyridinium (3).—An aqueous solution of salt (14) (1.0 g, 4.8 × 10^{-3} mol) was filtered through a column of Amberlite IRA-401 (OH). The eluant was evaporated *in vacuo* to give the *title compound* (3) (0.7 g, 77%) as a brown amorphous solid, m.p. 105—106 °C (MeCN–Et_2O) (Found: C, 62.8; H, 5.0; N, 14.5. $C_{10}H_8N_2O{\cdot}H_2O$ requires C, 63.2; H, 5.3; N, 14.7%); $\nu_{max.}$ (Nujol) 3 500 (OH) and 1 650 cm^{-1} (C=C–N).

3-Hydroxy-1-(2-pyridyl)pyridinium Chloride (12) *and Perchlorate* (13).—3-Hydroxypyridine (8 g, 8.6 × 10^{-2} mol) and 2-chloropyridine (10 g, 8.8 × 10^{-2} mol) were heated at 130 °C for 9 h to yield the *chloride* (12) (11 g, 62%) as microcrystals, m.p. 180—181 °C (EtOH–EtOAc) (Found: C, 57.2; H, 4.2; N, 13.3. $C_{10}H_9ClN_2O$ requires C, 57.6; H, 4.4; N, 13.4%); $\nu_{max.}$ (Nujol) 1 630 (enamine, C=C–N) and 1 595 cm^{-1} (C=C). Treatment of the chloride (12) (1.0 g, 0.005 mol) in MeOH (10 ml) with $HClO_4$ (0.7 g, 0.007 mol) followed by treatment with Et_2O yielded the *perchlorate* (13) as colourless needles (1.2 g, 92%), m.p. 155—157 °C (EtOH–Et_2O) (Found: C, 43.8; H, 3.6; N, 10.1. $C_{10}H_9ClN_2O_5$ requires C, 44.1; H, 3.3; N, 10.2%); $\nu_{max.}$ (Nujol) 1 630 (enamine, C=C–N), 1 600 (C=C), and 1 100 cm^{-1} (ClO_4^-).

Similarly prepared were: *1-(5,6-diphenyl-1,2,4-triazin-3-yl)-3-hydroxypyridinium chloride* (10) (64.2%), m.p. 215—218 °C as off-white needles (MeOH–EtOAc) (Found: C, 66.2; H, 4.3; N, 15.2. $C_{20}H_{15}ClN_4O$ requires C, 66.2; H, 4.2; N, 15.4%); $\nu_{max.}$ (Nujol) 2 480 (OH) and 1 590 cm^{-1} (C=C); *3-hydroxy-1-(5-phenyl-1,2,4-triazin-3-yl)pyridinium chloride* (11) (83%), m.p. 234—236 °C, as white needles (MeOH) (Found: C, 58.6; H, 4.0; N, 19.3. $C_{14}H_{11}ClN_4O$ requires C, 58.7; H, 3.9; N, 19.5%); $\nu_{max.}$ (Nujol) 2 500 (OH) and 1 600 cm^{-1} (C=C).

3-Hydroxy-1-(quinoxolin-2-yl)pyridinium Perchlorate (16).—3-Hydroxypyridine (0.7 g, 7.4 mmol) and 2-chloro-

quinoxoline (1.2 g, 7.3 mmol) in $[CH_2]_4O$ (10 ml) were heated under reflux (b.p. 66 °C) for 84 h to give the chloride (15) (0.8 g, 42.5%) which was characterised as the *perchlorate* (16) (0.7 g, 71%) as light brown needles, m.p. 195—197 °C (from MeOH–EtOAc) (Found: C, 48.5; H, 3.4; N, 12.6. $C_{13}H_{10}ClN_3O_5$ requires C, 48.2; H, 3.1; N, 12.9%); $\nu_{max.}$ (Nujol) 1 630, 1 590, and 1 100 cm^{-1}.

2-*Oxo*-8-(4-*pyridyl*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo-*carbonitrile* (17).—A well-stirred suspension of (14) (5 g, 2.4×10^{-2} mol), acrylonitrile (15 g, 2.9×10^{-1} mol), and quinol (20 mg) in MeCN (25 ml) was heated to reflux, and NEt_3 (5 g, 4.9×10^{-2}) was added dropwise. The reaction mixture was heated under reflux for a further 24 h, and then solvent was removed *in vacuo* to yield the endo-*adduct* (17) which was treated with MeI to produce the *methiodide* (79) (8 g, 81.7%) as a yellow amorphous solid, m.p. 253—255 °C (EtOH) (Found: C, 44.9; H, 4.2; N, 11.4. $C_{14}H_{14}IN_3O \cdot 0.5H_2O$ requires C, 44.7; H, 4.0; N, 11.2%); $\nu_{max.}$ (Nujol) 3 500 (OH), 2 220 (C≡N), 1 700 (αβ-unsaturated C=O), and 1 650 cm^{-1} (C=C–N): the *perchlorate* (83) (7.4 g, 100%) was isolated as pale brown needles, m.p. 238—240 °C (EtOH) (Found: C, 48.7; H, 4.3; N, 11.9. $C_{14}H_{14}ClN_3O_5 \cdot 0.5H_2O$ requires C, 48.2; H, 4.3; N, 12.0%); $\nu_{max.}$ (Nujol) 3 500 (O–H), 2 220 (C≡N), 1 690 (αβ-unsaturated C=O), 1 650 (C=C–N), and 1 100 cm^{-1} (ClO_4^-).

6-endo-*Ethoxy*-8-(4-*pyridyl*)-8-*azabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (20).—3-Oxido-1-(4-pyridyl)pyridinium (3) (0.5 g, 2.9×10^{-3} mol) and ethyl vinyl ether (10 g, 1.4×10^{-1} mol) in EtOH (25 ml) were heated under reflux (65—70 °C) for 7 d. The reaction mixture was evaporated off *in vacuo* to give a black solid which crystallised to yield the *adduct* (20) (0.120 g, 17%) as yellow needles, m.p. 164—165 °C (EtOH–Et_2O) (Found: C, 68.9; H, 6.5; N, 11.5. $C_{14}H_{16}N_2O_2$ requires C, 68.8; H, 6.6; N, 11.5%); $\nu_{max.}$ (Nujol) 1 680 cm^{-1} (αβ-unsaturated C=O). Treatment with MeI yielded the *methiodide* (82) (0.16 g, 84%), as yellow needles, m.p. 233—235 °C (EtOH) (Found: C, 46.5; H, 5.3; N, 7.2. $C_{15}H_{19}IN_2O_2$ requires C, 46.6; H, 5.0; N, 7.3%); $\nu_{max.}$ (Nujol) 1 680 cm^{-1} (αβ-unsaturated C=O). Similarly prepared was 6-endo-*ethoxy*-8-(2-*pyridyl*)-8-*azabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (30) (36.7%), m.p. 51—53 °C, as yellow needles (EtOH) (Found: C, 68.6; H, 6.6; N, 11.3. $C_{14}H_{16}N_2O_2$ requires C, 68.8; H, 6.6; N, 11.5%); $\nu_{max.}$ (Nujol) 1 680 (αβ-unsaturated C=O), 1 590 (C=C), and 1 100 cm^{-1} (C–O–C).

6-endo-*Phenyl*-8-(4-*pyridyl*)-8-*azabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (19).—A well stirred suspension of (14) (1.0 g. 4.7×10^{-3} mol), quinol (20 mg), and an excess of styrene (3 ml) in MeCN (200 ml) was treated with NEt_3 (3 ml) as described above to give the endo-*cycloadduct* (19) (270 mg, 20.4%) as yellow needles, m.p. 195—197 °C (EtOH–Et_2O) (Found: C, 77.9; H, 5.8; N, 9.9. $C_{18}H_{16}N_2O$ requires C, 78.2; H, 5.8; N, 10.1%); $\nu_{max.}$ (Nujol) 1 680 (αβ-unsaturated C=O) and 1 600 cm^{-1} (benzene, C=C). The *methiodide* (81) was a white amorphous solid (1.3 g, 63%), m.p. 295—297 °C (EtOH–H_2O) (Found: C, 54.3; H, 4.7; N, 6.6. $C_{19}H_{19}IN_2O$ requires C, 54.5; H, 4.6; N, 6.7%); $\nu_{max.}$ (Nujol) 1 680 (αβ-unsaturated C=O) and 1 650 cm^{-1} (C=C–N).

Similarly prepared were: 6-endo-*phenyl*-8-(2-*pyridyl*)-8-*azabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (27) (46%), m.p. 125—126 °C, as yellow needles (EtOH) (Found: C, 78.1; H, 5.6; N. 10.1. $C_{18}H_{16}N_2O$ requires C, 78.2; H, 5.8; N, 10.1%); $\nu_{max.}$ (Nujol) 1 675 (αβ-unsaturated C=O) and 1 600 cm^{-1} (C=C); 6-endo-(3-*chlorophenyl*)-8-(2-*pyridyl*)-8-*azabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (31) (39%), m.p. 84—86 °C, as yellow needles (EtOH) (Found: C, 69.3; H, 4.9; N, 9.0. $C_{18}H_{15}ClN_2O$ requires C, 69.6; H, 4.9; N, 9.0%); $\nu_{max.}$ (Nujol) 1,690 (αβ-unsaturated C=O) and 1 600 cm^{-1} (C=C); 8-(5,6-*diphenyl*-1,2,4-*triazin*-3-*yl*)-2-*oxo*-6-endo-*phenyl*-8-*azabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (45) (16.1%), m.p. 203—205 °C, as yellow needles (EtOH) (Found: C, 77.5; H, 5.4; N, 12.9. $C_{28}H_{22}N_4O$ requires C, 77.4; H, 5.4; N, 12.7%); $\nu_{max.}$ (Nujol) 1 680 cm^{-1} (αβ-unsaturated C=O); 6-endo-*phenyl*-8-(5-*phenyl*-1,2,4-*triazin*-3-*yl*)-8-*azabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (40) (38%), m.p. 160—162 °C, as yellow needles (EtOH) (Found: C, 74.4; H, 5.3; N, 15.5. $C_{22}H_{18}N_4O$ requires C, 74.6; H, 5.1; N, 15.8%); $\nu_{max.}$ (Nujol) 1 685 (αβ-unsaturated C=O) and 1 600 cm^{-1} (C=C); *m/e* 354 ($M^{+\cdot}$) 40%; 6-endo-*phenyl*-8-(*quinoxolin*-2-*yl*)-8-*azabicyclo*-[3.2.1]*oct*-3-*en*-2-*one* (26) (11.8%), m.p. 191—192 °C, as yellow needles (EtOH) (Found: C, 77.0; H, 5.5; N, 12.6. $C_{21}H_{17}N_3O$ requires C, 77.0; H, 5.2; N, 12.8%); $\nu_{max.}$ (Nujol) 1 690 (αβ-unsaturated C=O) and 1 590 cm^{-1} (C=C).

Methyl 2-*Oxo*-8-(4-*pyridyl*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo-*carboxylate* (18).—A well stirred suspension of the 3-hydroxy-1-(4-pyridyl)pyridinium chloride (14) (1.0 g, 4.7×10^{-3} mol), quinol (20 mg), and an excess of methyl acrylate (10 g, 1.2×10^{-1} mol) in MeCN (15 ml) was treated with NEt_3 (3 ml) as described above for (17) to yield a yellow oil. The endo-*cycloadduct* (18) (120 mg, 9.7%) crystallised as yellow needles, m.p. 143—145 °C (EtOH–Et_2O) (Found: C, 65.2; H, 5.2; N, 10.6. $C_{14}H_{14}N_2O_3$ requires C, 65.1; H, 5.4; N, 10.8%); $\nu_{max.}$ (Nujol) 1 730 (ester carbonyl C=O) and 1 680 cm^{-1} (αβ-unsaturated C=O).

Treatment with MeI yielded the *methiodide* (80) (0.7 g, 34%) as colourless needles, m.p. 179—181 °C (EtOH) (Found: C, 44.3; H, 4.3; N, 6.7. $C_{15}H_{17}IN_2O_3 \cdot 0.5H_2O$ requires C, 44.0; H, 4.4; N, 6.8%); $\nu_{max.}$ (Nujol) 3 500 (OH), 1 730 (ester C=O), 1 690 (αβ-unsaturated C=O), and 1 640 cm^{-1} (C=C–N).

Similarly prepared were *methyl* 2-*oxo*-8-(2-*pyridyl*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo- *and* -6-exo-*carboxylates* (28) and (29); 6-endo-*isomer* (28) (18.5%), m.p. 96—97 °C, as yellow needles (EtOH) (Found: C, 65.0; H, 5.3; N, 10.5. $C_{14}H_{14}N_2O_3$ requires C, 65.1; H, 5.5; N, 10.9%); $\nu_{max.}$ (Nujol) 1 725 (ester C=O), 1 690 (αβ-unsaturated C=O), and 1 600 cm^{-1} (C=C); 6-exo-*isomer* (29) (16%), m.p. 68—70 °C, as yellow needles [Et_2O–light petroleum (60—80 °C)] (Found: C, 64.9; H, 5.4; N, 11.1. $C_{14}H_{14}N_2O_3$ requires C, 65.1; H, 5.5; N, 10.9%); $\nu_{max.}$ (Nujol) 1 730 (ester C=O), 1 690 (αβ-unsaturated C=O), and 1 600 cm^{-1} (C=C); *methyl* 8-(5,6-*diphenyl*-1,2,4-*triazin*-3-*yl*)-2-*oxo*-8-*azabicyclo*[3.2.1]-*oct*-3-*ene*-6-endo-*carboxylate* (38) (21.8%), m.p. 184—185 °C, as yellow needles (EtOH) (Found: C, 70.0; H, 5.0; N, 13.2. $C_{24}H_{20}N_4O_3$ requires C, 70.0; H, 5.0; N, 13.6%); $\nu_{max.}$ (Nujol) 1 730 (saturated C=O) and 1 690 cm^{-1} (αβ-unsaturated C=O); *methyl* 2-*oxo*-8-(5-*phenyl*-1,2,4-*triazin*-3-*yl*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo- and -6-exo-*carboxylates*, (42) and (48); 6-endo-*isomer* (42) (21.4%), m.p. 129—130 °C, as yellow needles (EtOH) (Found: C, 64.2; H, 4.9; N, 16.4. $C_{18}H_{16}N_4O_3$ requires C, 64.3; H, 4.8; N, 16.7%); $\nu_{max.}$ (Nujol) 1 735 (ester C=O), 1 690 (αβ-unsaturated C=O), and 1 600 cm^{-1} (C=C); 6-exo-*isomer* (48) (49.2%), m.p. 50—52 °C, as yellow needles [EtOAc–light petroleum (b.p. 60—80 °C) (1 : 2)] (Found: C, 64.0; H, 5.1; N, 16.2. $C_{18}H_{16}N_4O_3$ requires C, 64.4; H, 4.8; N, 16.7%); $\nu_{max.}$ (Nujol) 1 735 (ester C=O), 1 690 (αβ-unsaturated C=O), and 1 600 cm^{-1} (C=C); *methyl* 2-*oxo*-8-(*quinoxolin*-2-*yl*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo- and -6-exo-*carboxylates*,

(24) and (25); 6-endo-*adduct* (24) (10%), m.p. 169—170 °C, as yellow needles (EtOH) (Found: C, 65.8; H, 5.0; N, 13.5. $C_{17}H_{15}N_3O_3$ requires C, 66.0; H, 4.9; N, 13.6%); $\nu_{max.}$ (Nujol) 1 735 (ester C=O), 1 680 (αβ-unsaturated C=O), and 1 580 cm^{-1} (C=C); 6-exo-*adduct* (25) (8.2%), m.p. 135—137 °C, as yellow needles (Et_2O) (Found: C, 64.8; H, 5.0; N, 12.8%. $C_{17}H_{15}N_3O_3 \cdot 0.33H_2O$ requires C, 64.7; H, 4.9; N, 13.3%); $\nu_{max.}$ (Nujol) 3 400 (H_2O), 1 730 (αβ-unsaturated C=O), and 1 580 cm^{-1} (C=C).

2-*Oxo*-8-(2-*pyridyl*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo- *and* -6-exo-*carbonitrile* [(35) *and* (34)] *and* -7-endo-*carbonitrile* (36).—A well-stirred suspension of the 1-(2-pyridyl)-3-hydroxypyridinium chloride (12) (1.0 g, 4.8×10^{-3} mol), quinol (20 mg), and an excess of acrylonitrile (10 g, 1.9×10^{-1} mol) in MeCN was treated with NEt_3 (3 ml) as described above for (17) to yield a yellow oil (three-compound mixture by t.l.c.). The mixture was purified by preparative t.l.c. [light petroleum (b.p. 60—80 °C)–EtOAc (2 : 1)]. The 6-endo-*isomer* (35) (0.175 g, 16%) was obtained as yellow needles, m.p. 119—120 °C (EtOH) (Found: C, 69.0; H, 4.9; N, 18.6. $C_{13}H_{11}N_3O$ requires C, 69.3; H, 4.9; N, 18.7%); $\nu_{max.}$ (Nujol) 2 215 (C≡N), 1 700 (αβ-unsaturated C=O), and 1 600 cm^{-1} (C=C). The 6-exo-*isomer* (34) (0.140 g, 13%) was isolated as yellow needles, m.p. 136—137 °C (EtOH) (Found: C, 69.2; H, 4.8; N, 18.4. $C_{13}H_{11}N_3O$ requires C, 69.3; H, 4.9; N, 18.7%); $\nu_{max.}$ (Nujol) 2 215 (C≡N), 1 690 (αβ-unsaturated C=O), and 1 600 cm^{-1} (C=C); the 7-endo-*isomer* (36) (0.035 g, 3%) was separated as yellow needles, m.p. 139—140 °C (EtOH) (Found: C, 69.1; H, 5.2; N, 18.5. $C_{13}H_{11}N_3O$ requires C, 69.3; H, 4.9; N, 18.7%); $\nu_{max.}$ (Nujol) 2 215 (C≡N), 1 690 (αβ-unsaturated C=O), and 1 600 cm^{-1} (C=C).

Similarly prepared were: 8-(5,6-*diphenyl*-1,2,4-*triazin*-3-*yl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo- and -6-exo-*carbonitriles* (43) and (44); 6-endo-*isomer* (43) (28%), m.p. 225—226 °C, as yellow needles (EtOH) (Found: C, 72.6; H, 4.6; N, 18.1. $C_{23}H_{17}N_5O$ requires C, 72.8; H, 4.5; N, 18.5%); $\nu_{max.}$ (Nujol) 1 690 cm^{-1} (αβ-unsaturated C=O); 6-exo-*isomer* (44) (25.8%), m.p. 175—177 °C, as yellow needles (EtOH) (Found: C, 72.7; H, 4.8; N, 18.1. $C_{23}H_{17}N_5O$ requires C, 72.8; H, 4.5; N, 18.5%); $\nu_{max.}$ (Nujol) 1 700 cm^{-1} (αβ-unsaturated C=O); 2-*oxo*-8-(5-*phenyl*-1,2,4-*triazin*-3-*yl*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo-, -6-exo-, *and* -7-endo-*carbonitriles* (41), (46), and (47); 6-endo-*adduct* (41) (38.0%), m.p. 209—210 °C, as yellow needles (EtOH) (Found: C, 66.9; H, 4.6; N, 22.8. $C_{17}H_{13}N_5O$ requires C, 67.3; H, 4.3; N, 23.1%); $\nu_{max.}$ (Nujol) 2 220 (C≡N), 1 695 (αβ-unsaturated C=O), and 1 600 cm^{-1} (C=C); 6-exo-*adduct* (46) (24%), m.p. 181—183 °C, as yellow needles (EtOH) (Found: C, 67.7; H, 4.4; N, 23.1. $C_{17}H_{13}N_5O$ requires C, 67.3; H, 4.3; N, 23.1%); $\nu_{max.}$ (Nujol) 2 220 (C≡N), 1 705 (α,β-unsaturated C=O), and 1 600 cm^{-1} (C=C); *m/e* 302 ($M^{+\cdot}$); 7-endo-*adduct* (47) (15.2%), m.p. 198—200 °C, as yellow needles (EtOH) (Found: C, 66.2; H, 4.6; N, 22.7. $C_{17}H_{13}N_5O \cdot 0.25H_2O$ requires C, 66.3; H, 4.4; N, 22.8%); $\nu_{max.}$ (Nujol) 2 220 (C≡N), 1 700 (α,β-unsaturated C=O), and 1 600 cm^{-1} (C=C); 2-*oxo*-8-(*quinoxolin*-2-*yl*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo- and -6-exo-*carbonitriles* (21) and (22); 6-endo-*adduct* (21) (19.5%), m.p. 178—179 °C, as yellow needles (EtOH) (Found: C, 69.7; H, 4.5; N, 20.0. $C_{16}H_{12}N_4O_2$ requires C, 69.6; H, 4.4; N, 20.3%); $\nu_{max.}$ (Nujol) 2 220 (C≡N), 1 690 (αβ-unsaturated C=O), and 1 590 cm^{-1} (C=C); 6-exo-*adduct* (22) (15%), m.p. 218—220 °C, as yellow needles (EtOH) (Found: C, 69.4; H, 4.3; N, 20.0. $C_{16}H_{12}N_4O_2$ requires C, 69.6; H, 4.4; N, 20.3%); $\nu_{max.}$ (Nujol) 2 220 (C≡N), 1 690 (αβ-unsaturated C=O), and 1 590 cm^{-1} (C=C).

6-*Chloro*-8-(5,6-*diphenyl*-1,2,4-*triazin*-3-*yl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-*carbonitrile* (37).—The dimer (60) (0.5 g, 0.000 8 mol) and 2-chloroacrylonitrile (5 ml) in MeCN (25 ml) were heated under reflux for 8 h. The reaction mixture was evaporated to dryness *in vacuo* to yield a brown solid which was purified by preparative t.l.c. [light petroleum (b.p. 60—80 °C)–EtOAc (2 : 1)] to give the *cycloadduct* (37) (0.21 g, 33%) as yellow needles, m.p. 169—170 °C (EtOH) (Found: C, 66.4; H, 4.1; N, 16.6; Cl, 8.5. $C_{23}H_{16}ClN_5O$ requires C, 66.8; H, 3.9; N, 16.9; Cl, 8.6%); $\nu_{max.}$ (Nujol) 1 700 cm^{-1} (αβ-unsaturated C=O).

Similarly prepared were: 6-*chloro*-2-*oxo*-8-(2-*pyridyl*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-*carbonitrile* (32) (44%), m.p. 98—99 °C, as yellow needles (EtOH) (Found: C, 60.1; H, 3.9; N, 16.2; Cl, 13.7. $C_{13}H_{10}ClN_3O$ requires C, 60.4; H, 4.0; N, 15.9; Cl, 13.6%); $\nu_{max.}$ (Nujol) 2 220 (C≡N), 1 705 (αβ-unsaturated C=O), and 1 590 cm^{-1} (C=C); 6-*chloro*-2-*oxo*-8-(*quinoxolin*-2-*yl*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-*carbonitrile* (23) (6%), m.p. 170—172 °C, as yellow needles (EtOH) (Found: C, 61.7; H, 3.7; N, 17.7. $C_{16}H_{11}ClN_4O$ requires C, 61.8; H, 3.9; N, 18.0%); $\nu_{max.}$ (Nujol) 1 705 (αβ-unsaturated C=O) and 1 575 cm^{-1} (C=C).

Diethyl 8-(5,6-*Diphenyl*-1,2,4-*triazin*-3-*yl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-exo,7-endo-*dicarboxylate* (39).—The dimer (60) (0.3 g, 0.003 5 mol), dimethyl fumarate (0.51 g, 0.003 5 mol), and MeCN (20 ml) were heated under reflux for 24 h. The solvent was evaporated off (30 °C at 10 mmHg), and the residual oil chromatographed on silica gel (B.D.H.). Elution with light petroleum (60—80 °C)–EtOAc (1 : 7) gave the *cycloadduct* (39) (0.07 g, 37.1%) as yellow needles, m.p. 129—131 °C (EtOH) (Found: C, 67.3; H, 5.4; N, 11.0. $C_{28}H_{26}N_4O_5$ requires C, 67.5; H, 5.3; N, 11.2%); $\nu_{max.}$ (Nujol) 1 735 (ester C=O) and 1 690 cm^{-1} (αβ-unsaturated C=O).

Similarly prepared was *diethyl* 2-*oxo*-8-(2-*pyridyl*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo,7-exo-*dicarboxylate* (33) (30%), m.p. 95—96 °C as yellow needles (EtOH) (Found: C, 62.9; H, 5.8; N, 8.1. $C_{18}H_{20}N_2O_5$ requires C, 62.8; H, 5.9; N, 8.1%); $\nu_{max.}$ (Nujol) 1 730 (ester C=O), 1 690 (αβ-unsaturated C=O), and 1 590 cm^{-1} (C=C).

6b(SR),7(RS),11(RS),11a(RS)-*Tetrahydro*-12-(4-*pyridyl*)-7,11-*iminocyclohept*[a]*acenaphthylen*-8-*one* (53).—A well stirred suspension of (14) (1.0 g, 4.8×10^{-3} mol), acenaphthylene (0.75 g, 4.8×10^{-3} mol), and quinol (0.1 g) in MeCN (30 ml) was treated with NEt_3 (2 g, 1.9×10^{-2} mol) as described above to produce the exo-*adduct* (53) (0.025 g, 1.6%) as yellow needles, m.p. 264—266 °C (EtOH) (Found: C, 81.3; H, 4.9; N, 8.4. $C_{22}H_{16}N_2O$ requires C, 81.5; H, 4.9; N, 8.6%); $\nu_{max.}$ (Nujol) 1 675 (αβ-unsaturated C=O) and 1 590 cm^{-1} (aromatic C=C). Treatment of the crude adduct from above with MeI followed by $NaClO_4$ (aqueous) yielded the *perchlorate* (78) (2.5 g, 39%) as a pale brown amorphous solid, m.p. 275—278 °C (EtOH–Me_2CO) (Found: C, 61.4; H, 4.4; N, 6.4. $C_{23}H_{19}ClN_2O_5 \cdot 0.5H_2O$ requires C, 61.6; H, 4.5; N, 6.3%); $\nu_{max.}$ (Nujol) 3 500 (OH), 1 680 (αβ-unsaturated C=O), 1 650 (C=C–N), 1 600 (aromatic C=C), and 1 110 cm^{-1} (ClO_4^-).

Similarly prepared were: 6b(SR),7(RS),11(RS),11a(RS)-*tetrahydro*-12-(2-*pyridyl*)-7,11-*iminocyclohept*[a]*acenaphthylen*-8-*one* (54) *and* 6b(RS),7(RS),11(RS),11a(SR)-*tetrahydro*-12-(2-*pyridyl*)-7,11-*iminocyclohept*[a]*acenaphthylen*-8-*one* (56); endo-*isomer* (56) (3%), m.p. 174—175 °C as yellow needles [Et_2O–light petroleum (60—80 °C)]

(Found: C, 81.2; H, 4.9; N, 8.4. $C_{22}H_{16}N_2O$ requires C, 81.5; H, 5.0; N, 8.6%); $\nu_{max.}$ (Nujol) 1 690 (αβ-unsaturated C=O) and 1 600 cm^{-1} (C=C); exo-*isomer* (54) (4%), m.p. 228—229 °C as yellow needles (EtOH) (Found: C, 81.2 H, 5.0; N, 8.4. $C_{22}H_{16}N_2O$ requires C, 81.5; H, 5.0; N, 8.6%); $\nu_{max.}$ (Nujol) 1 690 (αβ-unsaturated C=O) and 1 590 cm^{-1} (C=C); 12-(5,6-*diphenyl*-1,2,4-*triazin*-3-*yl*)-6b(SR),-7(RS),11(RS),11a(RS)-*tetrahydro*-7,11-*iminocyclohept*[a]*acenaphthylen*-8-*one* (55) *and* 12-(5,6-*diphenyl*-1,2,4-*triazin*-3-*yl*)-6b(RS),7(RS),11(RS),11a(SR)-*tetrahydro*-7,11-*iminocyclohept*[a]*acenaphthylen*-8-*one* (57); endo-*isomer* (57) (9.3%), m.p. 231—233 °C, as yellow needles (EtOH) (Found: C, 80.2; H, 4.8; N, 11.6. $C_{32}H_{22}N_4O$ requires C, 80.3; H, 4.6; N, 11.7%); $\nu_{max.}$ (Nujol) 1 690 cm^{-1} (αβ-unsaturated C=O); exo-*isomer* (55) (21.7%), m.p. 131—132 °C, as yellow needles (EtOH) (Found: C, 80.0; H, 4.9; N, 11.3. $C_{32}H_{22}N_4O$ requires C, 80.3; H, 4.6; N, 11.7%); $\nu_{max.}$ (Nujol) 1 680 cm^{-1} (αβ-unsaturated C=O).

2-*Oxo*-N-*phenyl*-8-(4-*pyridyl*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6,7-endo-*dicarboximide* (49).—A well-stirred suspension of (14) (0.6 g, 2.9×10^{-3} mol), *N*-phenylmaleimide (0.5 g, 0.005 mol), and quinol (12 mg) in MeCN (25 ml) was treated with NEt_3 (3 ml) as described above to yield the endo-*cycloadduct* (49) (80 mg, 4.9%) as yellow needles (EtOH), m.p. 247—249 °C (Found: C, 69.3; H, 4.8; N, 12.4. $C_{20}H_{15}N_3O_3$ requires C, 69.6; H, 4.4; N, 12.2%); $\nu_{max.}$ (Nujol) 1 700 (saturated C=O) and 1 680 cm^{-1} (αβ-unsaturated C=O).

Similarly prepared were 2-*oxo*-N-*phenyl*-8-(2-*pyridyl*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6,7-endo-*dicarboximide* (50) (30%), m.p. 225—227 °C as yellow needles (EtOH) (Found: C, 68.5; H, 4.4; N, 12.0. $C_{20}H_{15}N_3O_3$, $0.25H_2O$ requires C, 68.7; H, 4.5; N, 12.0%); $\nu_{max.}$ (Nujol) 1 710 (imide, C=O), 1 680 (αβ-unsaturated C=O), and 1 590 cm^{-1} (C=C); 8-(5,6-*diphenyl*-1,2,4-*triazin*-3-*yl*)-2-*oxo*-N-*phenyl*-8-*azabicyclo*-[3.2.1]*oct*-3-*ene*-6,7-endo- and -6,7-exo-*dicarboximide* (51) and (52); endo-*isomer* (51) (6.9%), m.p. 253—255 °C, as yellow needles (EtOH) (Found: C, 71.7; H, 4.4; N, 13.8. $C_{30}H_{21}N_5O_3$ requires C, 72.1; H, 4.2; N, 14.0%); $\nu_{max.}$ (Nujol) 1 705 cm^{-1} (αβ-unsaturated C=O); exo-*isomer* (52) (25.7%), m.p. 150—151 °C, as yellow needles (EtOH) (Found: C, 71.9; H, 4.4; N, 13.7. $C_{30}H_{21}N_5O_3$ requires C, 72.1; H, 4.2; N, 14.0%); $\nu_{max.}$ (Nujol) 1 710 cm^{-1} (αβ-unsaturated C=O).

(1RS,7SR,8RS)-7-(4-*Methoxyphenyl*)-12-(4-*pyridyl*)-12-*azatricyclo*[6.3.1.$0^{2,6}$]*dodeca*-2(6),4,9-*trien*-11-*one Methiodide* (59).—A well-stirred suspension of the salt (14) (0.52 g, 2.5×10^{-3} mol), 6-(*p*-methoxyphenyl)fulvene (0.45 g, 2.4×10^{-3} mol), and quinol (10 mg) in MeCN (25 ml) was treated with NEt_3 (1 ml) and then heated under reflux for 12 h. The cooled reaction mixture was washed with light petroleum (50 ml, b.p. 40—60 °C) and extracted with Et_2O (250 ml) to yield a yellow oil (300 mg). Treatment with an excess of MeI in EtOAc for 15 h yielded the *title compound* (59) (250 mg, 19.6%) as a yellow amorphous solid, m.p. 220 °C (decomp.) (EtOAc–Et_2O) (Found: C, 56.9; H, 4.9; N, 5.4. $C_{24}H_{23}IN_2O_2 \cdot 0.5H_2O$ requires C, 56.8; H, 4.8; N, 5.5%); $\nu_{max.}$ (Nujol) 3 500 (OH), 1 680 (αβ-unsaturated C=O), 1 650 (C=C–N), 1 600 (aromatic, C=C), and 1 100 cm^{-1} (C–O–C);

3,12-*Bis*-(5,6-*diphenyl*-1,2,4-*triazin*-3-*yl*)-3,12-*diazatricyclo*[5.3.1.1^{2,6}]*dodeca*-4,8-*diene*-10,11-*dione* (60).—A well stirred suspension of the chloride (10) (1.25 g, 3.4×10^{-3} mol) in water (10 ml) was treated with aqueous $NaHCO_3$ (0.5 g, 0.6×10^{-2} mol) to yield a yellow solid (0.95 g, 84%). The *title dimer* (60) was obtained as yellow needles, m.p. 218—220 °C (EtOH) (Found: C, 73.4; H, 4.4; N, 17.1. $C_{40}H_{28}N_8O_2$ requires C, 73.6; H, 4.3; N, 17.2%); $\nu_{max.}$ (Nujol) 1 740 (saturated C=O), 1 680 (αβ-unsaturated C=O), and 1 640 cm^{-1} (enamine, C=C–N).

Similarly prepared was 3,12-*bis*-(5-*phenyl*-1,2,4-*triazin*-3-*yl*)-3,12-*diazatricyclo*[5.3.1.1^{2,6}]*dodeca*-4,8-*diene*-10,11-*dione* (61) (99%), m.p. 225 °C (decomp.), as yellow needles (EtOH) (Found: C, 66.1; H, 4.3; N, 22.1. $C_{28}H_{20}N_8O_2 \cdot 0.5H_2O$ requires C, 66.0; H, 4.2; N, 22.0%); $\nu_{max.}$ (Nujol) 3 400 (H_2O), 1 740 (saturated C=O), and 1 680 (αβ-unsaturated C=O), and 1 640 cm^{-1} (enamine, C=C–N).

11-(5,6-*Diphenyl*-1,2,4-*triazin*-3-*yl*)-4b(RS),5(RS),-9a(RS),10-*tetrahydro*-5,9(RS)-*iminobenz*[a]*azulen*-6(9H)-*one* (66) *and* 11-(5,6-*Diphenyl*-1,2,4-*triazin*-3-*yl*)-4b(SR),5(RS),-9a(SR),10-*tetrahydro*-5,9(RS)-*iminobenz*[a]*azulen*-6(9H)-*one* (65).—A mixture of the dimer (60) (0.4 g, 6.1×10^{-4} mol) and indene (1 g, 8.6×10^{-3} mol) in MeCN (25 ml) was heated under reflux for 36 h. The solvent was removed *in vacuo* to leave a brown solid (two components by t.l.c.). The solid was purified by preparative t.l.c. [Kieselgel PF 254; light petroleum (b.p. 60—80 °C)–EtOAc (4 : 1)]. The first component, the endo-(6-CH_2) *isomer* (66) (85 mg, 15.7%) was isolated as yellow needles, m.p. 221—223 °C (EtOH) (Found: C, 78.5; H, 5.1; N, 12.4. $C_{29}H_{22}N_4O$ requires C, 78.7; H, 5.0; N, 12.7%); $\nu_{max.}$ (Nujol) 1 680 cm^{-1} (αβ-unsaturated C=O). The second cycloadduct, the endo-(7-CH_2) *isomer* (65) (95 mg, 17.5%) was isolated as yellow needles, m.p. 218—220 °C (EtOH) (Found: C, 78.6; H, 5.1; N, 12.5%); $\nu_{max.}$ (Nujol) 1 685 cm^{-1} (αβ-unsaturated C=O).

Methyl 8-(5,6-*Diphenyl*-1,2,4-*triazin*-3-*yl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*octa*-3,6-*diene*-6-*carboxylate* (67).—The dimer (60) (0.4 g, 1.2 mmol) and methyl prop-2-ynoate (0.5 g, 5 mmol) in MeCN (25 ml) were heated under reflux (75 °C) for 24 h. The mixture was evaporated *in vacuo* to yield a brown residue, which was purified by preparative t.l.c. [light petroleum (b.p. 40—60 °C)–EtOAc (1 : 1)]. The *adduct* (67) (0.05 g, 10%) was isolated as yellow microcrystals, m.p. 160—162 °C [from light petroleum (b.p. 40—60 °C)–Et_2O, 4 : 1] (Found: C, 71.1; H, 4.8. $C_{25}H_{20}N_4O_3$ requires C, 70.8; H, 4.8%); $\nu_{max.}$ (Nujol) 1 740 (ester C=O), 1 695 (αβ-unsaturated C=O), and 1 600 cm^{-1} (C=C).

Dimethyl 8-(5,6-*Diphenyl*-1,2,4-*triazin*-3-*yl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*octa*-3,6-*diene*-6,7-*dicarboxylate* (68).—The dimer (60) (0.5 g, 1.53 mmol) and dimethyl but-2-ynedioate (0.5 g, 3.5 mmol) in MeCN (25 ml) were heated under reflux (80 °C) for 24 h. The mixture was evaporated *in vacuo* to give a brown residue, which was purified by preparative t.l.c. [light petroleum (b.p. 40—60 °C)–EtOAc (1 : 1)]. The *cycloadduct* (68) (0.4 g, 55%) was obtained as yellow microcrystals, m.p. 80—82 °C [from light petroleum (b.p. 40—60 °C)–Et_2O(2 : 1)] (Found: C, 64.7; H, 4.7; N, 11.4. $C_{26}H_{20}N_4O_5 \cdot 0.66H_2O$ requires C, 64.9; H, 4.5; N, 11.7%); $\nu_{max.}$ (Nujol) 1 725 (ester C=O and αβ-unsaturated C=O) and 1 600 cm^{-1} (C=C); *m/e* 468 ($M^{+\bullet}$).

Reaction of the Dimer (60) *with Cyclopentadiene*.—The mixture of the dimer (60) (0.5 g, 1.53 mmol) and freshly distilled cyclopentadiene (5 ml) in MeCN (25 ml) were heated under reflux (b.p. 70 °C) for 12 h. The reaction mixture was evaporated to dryness and the residue separated by preparative t.l.c. on Kieselgel PF 254 [light petroleum (b.p. 60—80 °C)–EtOAc (3 : 1)]. 15-(5,6-*Diphenyl*-1,2,4-*triazin*-3-*yl*)-15-*azapentacyclo*[7.5.1.1^{3,6}.$0^{2,7}$.$0^{10,14}$]*hexadeca*-4,12-*dien*-8-*one* (70) (0.075 g, 11%) was isolated as yellow

needles, m.p. 198—200 °C (from EtOH) (Found: C, 79.0; H, 5.7; N, 12.3. $C_{30}H_{26}N_4O$ requires C, 78.6; H, 5.7; N, 12.2%); $\nu_{max.}$ (Nujol) 1 705 (saturated C=O) and 1 600 cm^{-1} (C=C); *m/e* 458 ($M^{+\cdot}$). (1*RS*,2*RS*,6*SR*,7*RS*)-11-(5,6-*Diphenyl*-1,2,4-*triazin*-3-*yl*)-11-*azatricyclo*[5.3.1.$0^{2,6}$]*undeca*-3,9-*dien*-8-*one* (69) (0.1 g, 17%) was isolated as yellow needles, m.p. 150—152 °C (from EtOH) (Found: C, 76.3; H, 5.2; N, 14.4. $C_{25}H_{20}N_4O$ requires C, 76.5; H, 5.1; N, 14.3%); $\nu_{max.}$ (Nujol) 1 680 (αβ-unsaturated C=O) and 1 600 cm^{-1} (C=C); *m/e* 392 ($M^{+\cdot}$). (1RS,9RS,10SR,-14RS)-11,15-*Bis*-(5,6-*diphenyl*-1,2,4-*triazin*-3-*yl*)-11,15-*diazapentacyclo*[7.5.1.$1^{2,7}$.$0^{3,6}$.$0^{10,14}$]*heptadeca*-4,12-*diene*-8,17-*dione* (71) (0.12 g, 10%) crystallised from EtOH as yellow needles, m.p. 227—229 °C (Found: C, 74.5; H, 5.0; N, 15.2. $C_{45}H_{34}N_8O_2 \cdot 0.5H_2O$ requires C, 74.3; H, 4.9; N, 15.4%); $\nu_{max.}$ (Nujol) 3 300 (H_2O), 1 735 (saturated C=O), 1 710 (saturated C=O), and 1 640 cm^{-1} (enamine, C=C–N).

7-endo-(5,6-*Diphenyl*-1,2,4-*triazin*-3-*yl*)-3,4-*dimethyl*-7-*azabicyclo*[4.3.1]*deca*-3,8-*dien*-10-*one* (73).—The dimer (60) (0.4 g, 0.6 mmol) and 2,3-dimethylbuta-1,3-diene (3 g, 37 mmol) in MeCN (20 ml) were heated under reflux (b.p. 81 °C) for 48 h. The reaction mixture was evaporated to dryness to yield a residue which was purified by preparative t.l.c. [light petroleum (b.p. 40—60 °C)–EtOAc (2 : 1)]. The *title compound* (73) (0.06 g, 11.5%) was isolated as yellow microcrystals, m.p. 88—90 °C [from light petroleum (b.p. 40—60 °C)] (Found: C, 73.5; H, 5.9; N, 13.4. $C_{26}H_{24}N_4O \cdot H_2O$ requires C, 73.2; H, 6.1; N, 13.1%); $\nu_{max.}$ (Nujol) 3 400 (H_2O), 1 725 (saturated C=O), and 1 640 cm^{-1} (enamine, C=C–N); *m/e* 426.

7-endo-(5,6-*Diphenyl*-1,2,4-*triazin*-3-*yl*)-7-*azabicyclo*-[4.3.1]*deca*-3,8-*dien*-10-*one* (74).—The dimer (60) (0.5 g, 7.66 × 10^{-6} mol) and thiophen sulphone (2.5 g, 20 mmol) in toluene (20 ml) were heated under reflux (b.p. 120 °C) for 48 h. The reaction mixture was evaporated to dryness *in vacuo* to yield a dark residue which was purified by preparative t.l.c. [light petroleum (b.p. 60—80 °C)–EtOAc (2 : 1)]. The *title compound* (74) (0.078 g, 13%) was isolated as yellow needles, m.p. 178—180 °C (EtOH) (Found: C, 75.7; H, 5.2; N, 14.5. $C_{24}H_{20}N_4O$ requires C, 75.8; H, 5.3; N, 14.7%); $\nu_{max.}$ (Nujol) 1 720 (saturated C=O) and 1 655 (enamine, C=C–N); *m/e* 380 ($M^{+\cdot}$).

Similarly prepared was 7-endo-(5-*phenyl*-1,2,4-*triazin*-3-*yl*)-7-*azabicyclo*[4.3.1]*deca*-3,8-*dien*-10-*one* (72) (22.9%), m.p. 148—150 °C, as yellow needles (EtOH) (Found: C, 70.2; H, 5.3; N, 18.1. $C_{18}H_{16}N_4O \cdot 0.25H_2O$ requires C, 70.0; H, 5.4; N, 18.1%); $\nu_{max.}$ (Nujol) 1 720 (saturated C=O), 1 655 (enamine, C=C–N), and 1 600 cm^{-1} (C=C).

3-*Hydroxy*-1-(1-*methyl*-4-*pyridyl*)*pyridinium Di-iodide* (75).—The pyridinium salt (14) (1.09 g, 5.3 × 10^{-3} mol) and MeI (5 g, 3.5 × 10^{-2} mol) in EtOH (25 ml) were heated under reflux for 10 h. The precipitate (1.7 g, 73%) was crystallised from EtOH–EtOAc to yield the *methiodide* (75) as brown needles, m.p. 162—164 °C (Found: C, 29.5; H, 2.9; N, 6.4. $C_{11}H_{12}I_2N_2O$ requires C, 29.9; H, 2.7; N, 6.3%); $\nu_{max.}$ (Nujol) 1 630 cm^{-1} (C=C–N).

The iodide (75) (1.0 g, 2.3 × 10^{-3} mol) in water (5 ml) was treated with IRA-401 (ClO_4^-) to give the *perchlorate* (76) (0.7 g, 72.2%) as white needles, m.p. 138—140 °C (EtOH) (Found: C, 34.4; H, 3.4; N, 7.5. $C_{11}H_{12}Cl_2N_2O_9$ requires C, 34.1; H, 3.1; N, 7.2%); $\nu_{max.}$ (Nujol) 1 640 (C=C–N) and 1 100 cm^{-1} (ClO_4^-).

Methyl 2-*Oxo*-6-endo-*phenyl*-8-(2-*pyridinium*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene Toluene*-p-*sulphonate* (85).—The cyclo-adduct (27) (4.8 g, 1.7 × 10^{-2} mol) and methyl toluene-*p*-sulphonate (5.0 g, 2.7 × 10^{-2} mol) were heated at 120 °C for 24 h. The black product was washed with EtOAc to yield the required *toluene*-p-*sulphonate* (85) (5.8 g, 76.5%) as colourless needles, m.p. 162—164 °C (EtOH–EtOAc) (Found: C, 67.2; H, 5.6; N, 6.1. $C_{26}H_{26}N_2O_4S$ requires C, 67.5; H, 5.7; N, 6.1%); $\nu_{max.}$ (Nujol) 1 690 (αβ-unsaturated C=O), 1 640 (enamine, C=C–N), and 1 580 cm^{-1} (aromatic C=C).

Methyl 2-*Oxo*-6-endo-*phenyl*-8-(2-*pyridinium*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene Iodide* (84).—The styrene adduct (27) (0.15 g, 0.5 × 10^{-3} mol) and MeI (15 ml) in EtOAc (25 ml) were heated under reflux for 36 h. The white precipitate was collected to yield the *iodide* (84) (70 mg, 30%) as colourless microcrystals, m.p. 185—186 °C (EtOH) (Found: C, 53.3; H, 4.8; N, 6.8. $C_{19}H_{19}IN_2O \cdot 0.5H_2O$ requires C, 53.4; H, 4.7; N, 6.6%); $\nu_{max.}$ (Nujol) 3 400 (H_2O), 1 690 (αβ-unsaturated C=O), 1 640 (enamine, C=C–N), and 1 580 cm^{-1} (aromatic C=C);

Similarly prepared were: *methyl* 2-*oxo*-6-endo-*phenyl*-8-(2-*quinoxolinium*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene iodide* (86) (61%), m.p. 218—220 °C as orange microcrystals (EtOH). Compound (86) was unstable to repeated recrystallisation thus precluding satisfactory elemental analysis; $\nu_{max.}$ (Nujol) 1 690 (αβ-unsaturated C=O) and 1 640 cm^{-1} (enamine, C=C–N); *methyl* 6-endo-*methoxycarbonyl*-2-*oxo*-8-(2-*quinoxolinium*)-8-*azabicyclo*[3.2.1]*oct*-3-*ene iodide* (87) (50%), m.p. 193—195 °C, as yellow microcrystals (EtOH), which was also unstable to repeated recrystallisation thus precluding satisfactory elemental analysis; $\nu_{max.}$ (Nujol) 1 735 (saturated C=O), 1 680 (αβ-unsaturated C=O), and 1 640 cm^{-1} (enamine, C=C–N).

Methyl 4-(1-*Oxo*-4-*phenylcyclohepta*-2,4,6-*trien*-2-*ylamino*)*pyridinium Perchlorate* (88).—The iodide (81) (2.65 g, 6.2 × 10^{-3} mol) and Ag_2O (1.8 g, 7.8 × 10^{-3} mol) were stirred in water (110 ml) at room temperature for 3 h and the solid was then removed by filtration to yield a yellow filtrate. $NaClO_4$ was added dropwise to yield the *perchlorate* (88) (2.09 g, 73.6%) as a yellow amorphous solid, m.p. 250 °C (decomp.) (MeOH) (Found: C, 56.1; H, 4.5; N, 6.6. $C_{19}H_{17}ClN_2O_5 \cdot H_2O$ requires C, 56.1; H, 4.7; N, 6.9%); $\nu_{max.}$ (Nujol) 3 500 (O–H), 1 650 (αβ-unsaturated C=O), and 110 cm^{-1} (ClO_4^-); δ(D_2O) 4.04 (3 H, s, N^+–Me), 7.14 (11 H, br s, 3,5,6,7,3′,5′-H + Ph), and 8.24 (2 H, br s, 2′,6′-H).

We thank Dr. A. D. McNaught (Chemical Society) for help with nomenclature.

[9/131 *Received*, 29*th January*, 1979]

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