1,3-Dipolar Character of Six-membered Aromatic Rings. Part 33.[1] Transformations of Cycloadducts derived from 3-Oxido-1-triazinylpyridiniums

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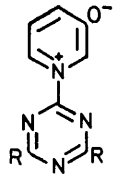
1-(4,6-Diphenyl- and 4,6-dimethoxy-*s*-triazin-2-yl)-3-oxidopyridinium betaines were prepared as dimers which dissociate to yield adducts with a variety of 2 and 4 π-electron dipolarophiles. Transformations of the adducts are described, including examples of the hydrolytic removal of the triazinyl group.

THE betaines 1-methyl-, 1-phenyl-, 1-(2,4-dinitrophenyl)-, and 1-(5-nitro-2-pyridyl)-3-oxidopyridinium form a series which displays increasing reactivity in pericyclic reactions. We have previously shown that aza-substitution in the 2- and 6-positions of the phenyl ring of 3-oxido-1-phenylpyridinium will lower the betaine LUMO and increase the reactivity of the betaine in pericyclic reactions. Thus the *s*-triazinylpyridinium betaines (1) and (2), in which the 2-, 4-, and 6-carbon atoms of the phenyl ring have been replaced by nitrogen, should be of particular interest. Furthermore, the *s*-triazine ring is readily ruptured by nucleophiles; this indicated that it might be possible to remove the substituent *after* cycloaddition had occurred.

3-Hydroxypyridine was readily quaternised by 2-chloro-4,6-diphenyl-*s*-triazine [2] and 2-chloro-4,6-dimethoxy-*s*-triazine [3] to yield the quaternary salts (3), m.p. 179—180 °C, and (4), m.p. 167—168 °C, respectively. The i.r. spectra of both salts show characteristic O–H stretching frequencies and triazine skeletal bands.[4] The ^{1}H n.m.r. spectrum of the salt (4) in D_2O showed the



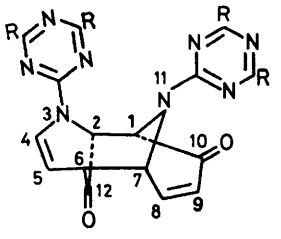
(1) R = Ph
(2) R = OMe
(3) R = Ph,HCl
(4) R = OMe,HCl

characteristic pattern of an ABCD system. That of the salt (3) could not be obtained owing to rapid formation of the dimer in D_2O. In the mass spectrometer, both

[1] Part 32, N. Dennis, A. R. Katritzky, H. Wilde, E. Gavuzzo, and A. Vaciago, *J.C.S. Perkin II*, 1977, 1304.
[2] R. Hirt, N. Nidecker, and R. Berchtold, *Helv. Chim. Acta*, 1950, **33**, 1365.
[3] Ciba, Swiss Pat. 106,407/1924 (cited in ref. 15, pp. 72—73).
[4] H. K. Reimschuessel and N. T. McDevitt, *J. Amer. Chem. Soc.*, 1960, **82**, 3756.

salts (3) and (4) lose HCl to yield prominent peaks at *m/e* 326 (100%) and 234 (60%) corresponding to the betaines (1) and (2); for neither is the molecular ion peak observed.

A solution of the salt (4) in D_2O became turbid within 1 h and precipitated the dimer (6). The salt (3) reacted



(5) R = Ph
(6) R = OMe

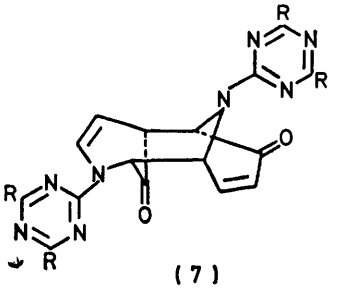
in D_2O to yield the dimer (5) immediately. Both salts were readily converted into the corresponding dimers using triethylamine. Although the dimer (6) was readily soluble in $CDCl_3$, the dimer (5) was insoluble in most solvents except deuteriated trifluoroacetic acid.

The i.r. spectra of the dimers (5) and (6) 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 1 650 cm^{-1}. The structure and stereochemistry of the dimer (6) [and by analogy the dimer (5)] were elucidated from spectral evidence; the n.m.r. spectrum (Figure 1) * was especially significant and assignments were confirmed by double irradiation experiments (Figure 2).* The spectrum shows three singlets at δ 3.60 (3 H), 3.95 (6 H), and 4.10 (3 H) assignable to the methoxy-protons of two triazine groups in different environments. That *three* OMe peaks are seen indicates lack of fast rotation about only one triazine–N bond. In the olefinic region, the downfield double doublet at δ 7.30 was assigned to H-8 and irradiation at this frequency simplified the patterns of H-7 (δ 6.50, quintet collapsed to a triplet) and of H-9 (doublet to singlet). Irradiation at the H-7 frequency confirmed the coupling of H-7 to H-6 by 2.0 Hz since the sextet at δ 3.03 collapsed to a double doublet. Irradiation at the frequency of H-6 confirmed the coupling of H-6 to H-5 by 6.0 Hz, and as H-5 is in turn coupled to H-4 by 8.2 Hz, the positional sequence H-4 to H-9 was thus unambiguously established.

The signal of the bridgehead proton, H-6, not located α to a nitrogen atom, occurs at higher field than those of the other three bridgehead protons, further supporting the *syn*-structure (6) as against the *anti*-form (7). The *exo*-configuration of the dimer is supported by the H-2,-H-6 coupling of 2.0 Hz. Molecular models demonstrate that only in the *exo*-structure does the four-bond system connecting H-2 and H-6 assume a planar configuration necessary for W-type coupling; the system deviates sharply from coplanarity in the *endo*-form.

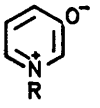
The mass spectrum of the dimer (6) exhibited a molecular ion at *m/e* 468 (60%) and an intense peak at *m/e* 234 (100%) corresponding to the betaine (2), the product of dimer dissociation by retrocycloaddition.[5] The molecular ion of the dimer (5) was not detected at *m/e* 652, while the betaine (1) peak appeared at *m/e* 326 (49%). The marked variation in relative ion abundances of the two betaines (1) and (2) at identical ionisation potentials further supports the higher reactivity of the betaine (1) relative to (2) and consequently the higher stability of the dimer (5) than of (6).

Dimerisation.—The ease of thermal dimerisation of an *N*-substituted 3-oxidopyridinium is a function of the nature of the *N*-substituent.[6] In terms of PMO–FMO theory, the activation of a betaine by the *N*-substituent is the result of a lowering of the LUMO energy while the HOMO energy level is maintained. The more electron-withdrawing the *N*-substituent, the smaller is the energy



(7)

difference between the frontier orbitals of the two reacting betaine molecules and the more favoured is dimerisation. The *N*-(dimethoxy-*s*-triazinyl)- (2) and *N*-(diphenyl-*s*-triazinyl)-betaine (1) possess more strongly electron-withdrawing *N*-substituents and thus more readily dimerise than previously described *N*-pyridyl-[7] (8) and *N*-pyrimidinyl-[7] (9) betaines. The observed (see later) difference between the rates of dimerisation of the triazinyl betaines [(1) > (2)] is the result of the 4,6-diphenyl-*s*-triazinyl nucleus being even more electron-withdrawing than the 4,6-dimethoxy-*s*-triazinyl nucleus.



(8) R = 5-nitro-2-pyridyl
(9) R = 4,6-dimethylpyrimidin-2-yl
(10) R = 2,4-dinitrophenyl

The dimerisations can be considered as concerted suprafacial [$_\pi2 + _\pi4$] or [$_\pi4 + _\pi6$] additions between two

* These Figures are available as Supplementary Publication No. SUP 22074 (4 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1976, Index issue.

[5] Y. Nomura, F. Furusaki, and Y. Takeuchi, *J. Org. Chem.*, 1972, **37**, 502.

[6] N. Dennis, B. Ibrahim, and A. R. Katritzky, *J.C.S. Chem. Comm.*, 1975, 425.

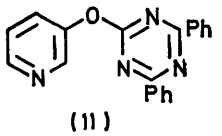
[7] N. Dennis, B. Ibrahim, and A. R. Katritzky, *J.C.S. Perkin I*, 1976, 2296.

molecules of betaine (1) or (2). As previously described for dimerisation of betaines of this type, the initially formed adduct is the *syn*-dimer [(5)/(6)] rather than the *anti*-dimer (7) since bonding at the sites of largest coefficients will give rise to a larger stabilisation energy for the *syn*-transition state than the *anti*-transition state (*cf.* 1-methyl-3-oxidopyridinium [7]).

$[{}_{\pi}4_s + {}_{\pi}6_s]$ Pericyclic reactions are predicted to yield *exo*-adducts [8] (*cf.* dimerisation of 1*H*-azepines [9]) and this is observed in the present dimerisations. The transition state needed for the formation of the *endo*-adduct is highly crowded and destabilised as compared with that needed for the formation of the *exo*-adduct, which is thus more stable.

A thermal intramolecular N ⟶ O migration reaction of the 4,6-diphenyl-*s*-triazinyl betaine (1) led to the isomeric ether (11) [*cf.* 1-(2,4-dinitrophenyl)-3-oxidopyridinium [10]]. The i.r. spectrum displayed characteristic bands at 1 570 and 1 540 cm^{-1} for the triazine ring [4] and a strong band at 1 100 cm^{-1} for the ether C–O.[11]

Cycloadditions to 2 π-Electron Addends.—(i) *Olefin dipolarophiles.* The dimers (5) and (6) are stable crystalline compounds which are convenient sources of the corresponding nascent betaines (1) and (2) by thermal retrocycloaddition. In the presence of various dipolarophiles, the betaines are trapped by cycloaddition reactions. Yields of cycloadducts from the dimer (5) are



(11)

lower than from (6): although the betaine (1) is more reactive than (2) the dimer (5) is more stable than (6) to thermal retrocycloaddition.

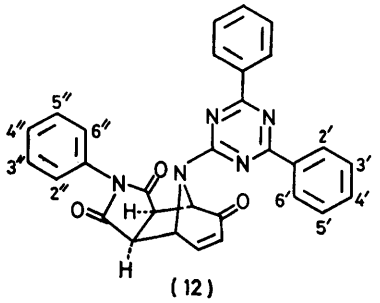
The triazinyl betaines (1) and (2) gave good yields of mixed *exo*- and *endo*-adducts with electron-deficient

TABLE 1

Percentage yields of *endo*- and *exo*-cycloadducts from $[4n + 2]\pi$ addition of electron-deficient addends with the triazinyl betaines (1) and (2)

	Betaine (1)		Betaine (2)	
	endo (%)	*exo* (%)	*endo* (%)	*exo* (%)
CH_2:CH·CO_2Me	50	50	40	60
CH_2:CH·CN	80	20	50	50
N-Phenylmaleimide	0	100	0	100
Styrene	80	20	100	0

acrylic addends (Table 1). With styrene the *endo*-isomeric adduct predominated (Table 1), and with *N*-phenylmaleimide only the *exo*-adducts (12) and (13) were obtained. The ^1H n.m.r. spectra (Table 2) of both adducts (12) and (13) show the H-1 signal as a broadened singlet ($J_{1,3}$ 2.0 Hz) and the H-5 signal as a doublet ($J_{4,5}$ 6.0, $J_{5,6\text{-}endo}$ 0 Hz); both H-6 and H-7 gave doublets



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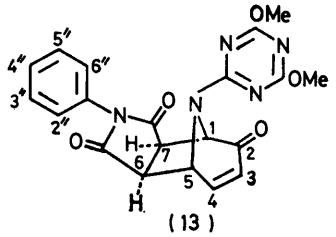


(13)

($J_{6,7}$ 9.0 Hz), conclusively proving the *exo*-configuration for the cycloadduct.

In the ^1H n.m.r. spectra of the acrylonitrile, methyl acrylate, and styrene adducts (14)—(24), the H-1 signal appears as a doublet ($J_{1,7\text{-}exo}$ 8.0—10.0 Hz), and that of H-5 as a double doublet ($J_{4,5}$ 6.0 Hz) for the *exo*-isomers and a triplet ($J_{4,5}$ 6.0, $J_{5,6\text{-}exo}$ 6.0 Hz) for the *endo*-isomers. In the *exo*-isomers (17), (18), and (22)—(24), H-6-*endo* gives a double doublet ($J_{6\text{-}endo,7\text{-}exo}$ 8, $J_{6\text{-}endo,7\text{-}endo}$ 10 Hz); for the *endo*-isomers (14)—(16) and (19)—(21) H-6-*exo* gives a quartet of doublets because of significant additional coupling ($J_{5,6\text{-}exo}$ 6 Hz). In the spectra of all eleven compounds, H-7-*exo* gives either a quartet of doublets or a doublet of triplets and H-7-*endo* a double doublet. All the above assignments were confirmed by exhaustive double resonance experiments involving all ring protons: *e.g.* irradiation at the frequency of H-5 caused the H-4 double doublet to collapse to a doublet in every case.

The cycloadducts (14)—(18) showed the expected singlet at δ 3.82—3.90 characteristic of the methoxy-protons of the 4,6-dimethoxy-*s*-triazine group; the adducts (19)—(24) exhibited a multiplet at *ca.* δ 8.50 for the *ortho*-protons of the phenyl rings of the 4,6-diphenyl-*s*-triazine group.

The u.v. spectra of all the cycloadducts (14)—(24) exhibit maxima in the region 200—275 nm for the $n \longrightarrow \pi^*$ transitions of the aryl–nitrogen substituents. The mass spectra of the cycloadducts (14)—(24) show a peak corresponding to the respective betaine together with the associated molecular ion peak indicating the expected retrocycloaddition.

[8] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 1965, **87**, 4388.

[9] L. A. Paquette, J. H. Barrett, and D. E. Kuhla, *J. Amer. Chem. Soc.*, 1969, **91**, 3616; I. C. Paul, S. M. Johnson, J. H. Barrett, and L. A. Paquette, *Chem. Comm.*, 1969, 6.

[10] N. Dennis, B. Ibrahim, A. R. Katritzky, I. G. Taulov, and Y. Takeuchi, *J.C.S. Perkin I*, 1974, 1883.

[11] A. D. Cross and R. A. Jones, 'An Introduction to Practical Infra-Red Spectroscopy,' Butterworths, London, 1969, p. 83.

(a) *Stereoselectivity*. *N*-Phenylmaleimide reacted with the triazinyl betaines (1) and (2) to yield exclusively the *exo*-adducts (12) and (13) (Table 1), respectively. This is contrary to PMO–FMO theory for $[2_s + 4_s]$ processes which should proceed preferentially *via* the *endo*-transition state [*cf.* dinitrophenyl [10] and nitropyridyl [12] betaines (10) and (8) which yield exclusively the *endo*-adducts]. In view of the long reaction time (4—5 days) under reflux, it is suspected that initially formed *endo*-adducts (25) are isomerised to the more thermodynamically stable *exo*-adducts (13) and (12) (*cf.* addition of furan to maleic anhydride [13]).

In the reaction of styrene with the dimethoxybetaine (2), the expected *endo*-adduct was the sole product (Table 1), whereas with the diphenyl betaine (1) both *endo*- and *exo*-products were isolated. Steric crowding caused by non-bonded interactions between the 2,6-diphenyl-*s*-triazinyl group and the phenyl group of the addend disfavour *exo*-approach; the 20% of *exo*-product is attributed to the high reactivity of the betaine (1) and fast non-stereospecific addition.

Stereoselectivity is however lost in the addition of the triazinyl betaines to acrylonitrile and methyl acrylate (Table 1), as has previously been shown to be the case with other aryl betaines.[14] The observed secondary orbital overlap leading to the *endo*-product is weak in these cases while steric and dipolar factors are considerably stronger and lead to the formation of *exo*-product in larger amounts.

TABLE 2

Proton n.m.r. spectra of ene cycloadducts [a,b]

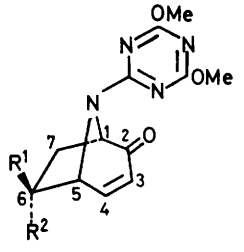
Chemical shifts (δ)

	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(21)	(22)	(23)	(24)	(26)
1	5.45 [c]	5.15 [c]	5.00 [d]	5.10 [d]	5.20 [d]	5.10 [d]	5.20 [d]	5.35 [d]	5.40 [d]	5.45 [d]	5.50 [d]	5.50 [d]	5.55 [d]	5.90 [c]
3	6.10 [d]	6.10 [d]	5.90 [d]	6.20 [d]	6.05 [d]	5.85 [d]	5.95 [d]	6.05 [d]	6.20 [d]	6.10 [d]	6.00 [d]	6.05 [d]	6.00 [d]	5.55 [d]
4	7.80 [d]	7.80 [d]	7.20 [d]	7.40 [d]	6.90 [d]	7.30 [d]	7.25 [d]			6.90 [d]				7.50 [d]
5	5.90 [e]	5.50 [e]	5.00 [f]	5.50 [f]	5.50 [f]	5.50 [e]	5.50 [e]	5.80 [f]	5.80 [f]	5.70 [f]	5.85 [e]	5.85 [e]	5.70 [e]	5.90 [e]
6-*endo*	3.85 [e]					*g*	3.10 [d]				3.70 [d]	3.70 [d]	4.20 [d]	
6-*exo*			3.50 [h]	3.40 [h]	3.90 [h]			3.70 [h]	3.50 [h]	4.00 [h]				
7-*endo*	3.70 [e]		2.10 [d]	2.05 [d]	2.10 [d]	2.05 [d]	2.25 [d]	2.20 [d]	2.15 [d]	2.15 [d]	2.15 [d]	2.30 [d]	2.30 [d]	
7-*exo*			2.70 [h]	2.90 [h]	2.90 [i]	2.80 [h]	2.75 [i]	2.80 [h]	3.00 [h]	3.00 [i]	3.10 [i]	3.00 [i]	2.90 [i]	
CO_2Me			3.60 [e]			3.60 [e]		3.70 [e]			3.70 [e]			3.85 [e]
2′,6′	8.55 [j]							8.60 [j]	8.50 [j]	8.60 [j]	8.55 [j]	8.50 [j]	8.60 [j]	8.55 [j]
3′,4′,5′	7.55 [j]							7.50 [j]	7.50 [j]	7.40 [j]	7.50 [j]	7.50 [j]	7.50 [j]	7.50 [j]
OMe		3.80 [e]	3.82 [e]	3.90 [e]	3.90 [e]	3.82 [e]	3.90 [e]							
Ph					7.20 [j]					7.20 [j]			7.20 [j]	
2″,6″	7.05 [j]	7.10 [j]												8.55 [j]
3″,4″,5″	7.30 [j]	7.45 [j]												7.50 [j]

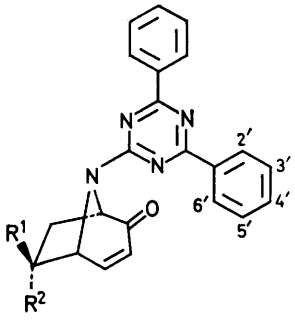
Coupling constants (Hz)

	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(21)	(22)	(23)	(24)	(26)
1,3	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
1,7-*exo*			8.0	8.0	10.0	8.0	8.0	8.0	8.0	10.0	8.0	8.0	8.0	
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	10.0	10.0
4,5	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
5,6-*exo*			6.0	6.0	6.0			6.0	6.0	6.0				
6,7-*exo*			10.0	10.0	10.0	*g*	8.0	10.0	10.0	10.0	8.0	8.0	8.0	
6,7-*endo*	9.0	*g*	8.0	6.0	8.0	10.0	10.0	8.0	8.0	8.0	10.0	10.0	10.0	
7-*exo*,7-*endo*			14.0	12.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	

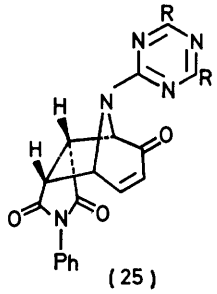
[a] Me_4Si as internal standard. [b] In $CDCl_3$. [c] Singlet. [d] Double doublet. [e] Doublet. [f] Triplet. [g] Overlap. [h] Quartet of doublets. [i] Double triplet [j] Multiplet.



(14) $R^1 = H, R^2 = CO_2Me$
(15) $R^1 = H, R^2 = CN$
(16) $R^1 = H, R^2 = Ph$
(17) $R^1 = CO_2Me, R^2 = H$
(18) $R^1 = CN, R^2 = H$



(19) $R^1 = H, R^2 = CO_2Me$
(20) $R^1 = H, R^2 = CN$
(21) $R^1 = H, R^2 = Ph$
(22) $R^1 = CO_2Me, R^2 = H$
(23) $R^1 = CN, R^2 = H$
(24) $R^1 = Ph, R^2 = H$



(25)

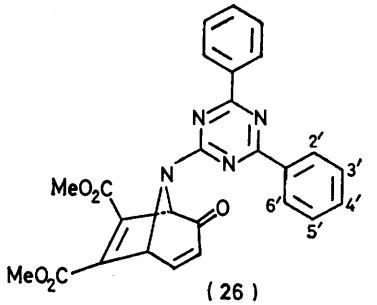
[12] N. Dennis, B. Ibrahim, and A. R. Katritzky, *J.C.S. Perkin I*, 1976, 2307.

[13] N. Entwistle, 'Orbital Symmetry Correlations in Organic Chemistry. A Guide to the Woodward-Hoffmann Rules,' Van Nostrand Reinhold Co., London, 1972, p. 33.

[14] B. Ibrahim, Ph.D. Thesis, University of East Anglia, 1975, p. 157.

(b) *Regioselectivity.* The addition of monosubstituted dipolarophiles (acrylonitrile and methyl acrylate) to triazinyl-3-oxidopyridinium betaines (1) and (2) is highly regioselective in favour of the 6-isomer, as previously found for 3-oxidopyridiniums.[12]

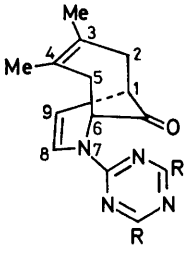
(ii) *Acetylenic dipolarophiles.* Dimethyl but-2-ynedioate readily reacted with the betaine (1) to yield the single 2,6-adduct (26) (53%). The i.r. spectrum exhibits a broad carbonyl band at 1 740 cm^{-1} (αβ-unsaturated ketone and αβ-unsaturated ester) and characteristic[4] triazine bands at 1 530 and 1 570 cm^{-1}. The mass spectrum shows a molecular ion at *m/e* 470 together with a peak (*m/e* 326) corresponding to the betaine (1) derived from the parent ion by retrocycloaddition. Betaines (1) and (2) were both unreactive towards diphenylacetylene.



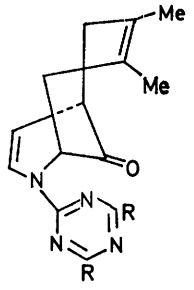
(26)

Cycloadditions to 4π-Electron Addends.—2,3-Dimethylbuta-1,3-diene with the betaines (1) and (2) yields 2,4-adducts (27) and (28), respectively. The i.r. spectra exhibit strong ν(C=O) bands at 1 730 cm^{-1} for the saturated cyclic ketone and a medium ν(C=C) band at 1 640—1 650 cm^{-1} for the enamine double bond together with triazine ring bands at 1 530 and 1 570 cm^{-1}. The ^1H n.m.r. spectra of (27) and (28) (Table 3) are consistent only with 2,4-adducts and are characterised by a low-field doublet for H-8 at δ 7.55—8.50, a double doublet for H-9 at δ 4.90, and a doublet for H-6 at δ 5.00—5.15. Other assignments were obtained by double resonance techniques. Irradiation at the frequencies of H-6 and H-9 affected the broad double doublet (2 H) at δ *ca.* 3.0 which was assigned to overlapping H-5-*endo* and H-1 signals. Further, irradiation at the frequency of the double doublet at *ca.* δ 3.0 affected the broad three-proton doublet at *ca.* δ 2.40 assignable to H-5-*exo*, H-2-*exo*, and H-2-*endo*. The vinyl methyl groups absorb at δ 1.45, 1.60, and 1.65.

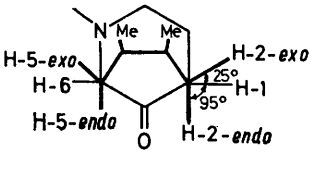
The dihedral angles (θ) between H-1 and H-2, and H-5 and H-6, are sensitive to the stereochemistry of the adduct. In the *endo*-conformation [(27) and (28)], θ(H-1,H-2-*exo*) = θ(H-6,H-5-*exo*) ≃ 25° is consistent with the large observed coupling constant (*ca.* 8.0 Hz), while θ(H-1,H-2-*endo*) = θ(H-6,H-5-*endo*) ≃ 95° [*i.e.* (31)] is consistent with the absence of coupling between H-1 and H-2-*endo*. However, in the *exo*-conformation [(29) and (30)] the corresponding angles are 25 and 145° [*i.e.* (32)], respectively, resulting in large coupling constants for both *exo*- and *endo*-protons.



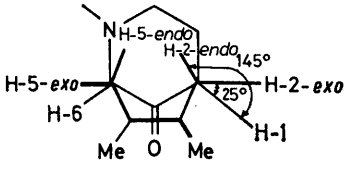
(27) R = Ph
(28) R = OMe



(29) R = Ph
(30) R = OMe



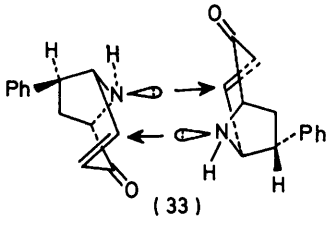
(31)



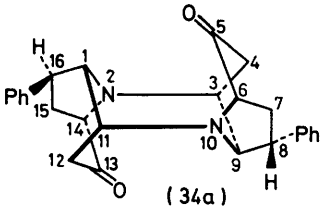
(32)

C=C bonds omitted for clarity

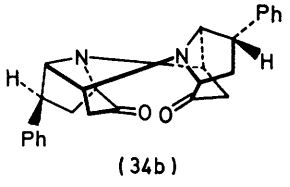
Both 2,4-adducts (27) and (28) undergo ready electron-impact-induced retrocycloaddition in the mass spectrometer to give the molecular ions of the respective betaines (1) and (2) as base peaks.



(33)



(34a)



(34b)

SCHEME 1

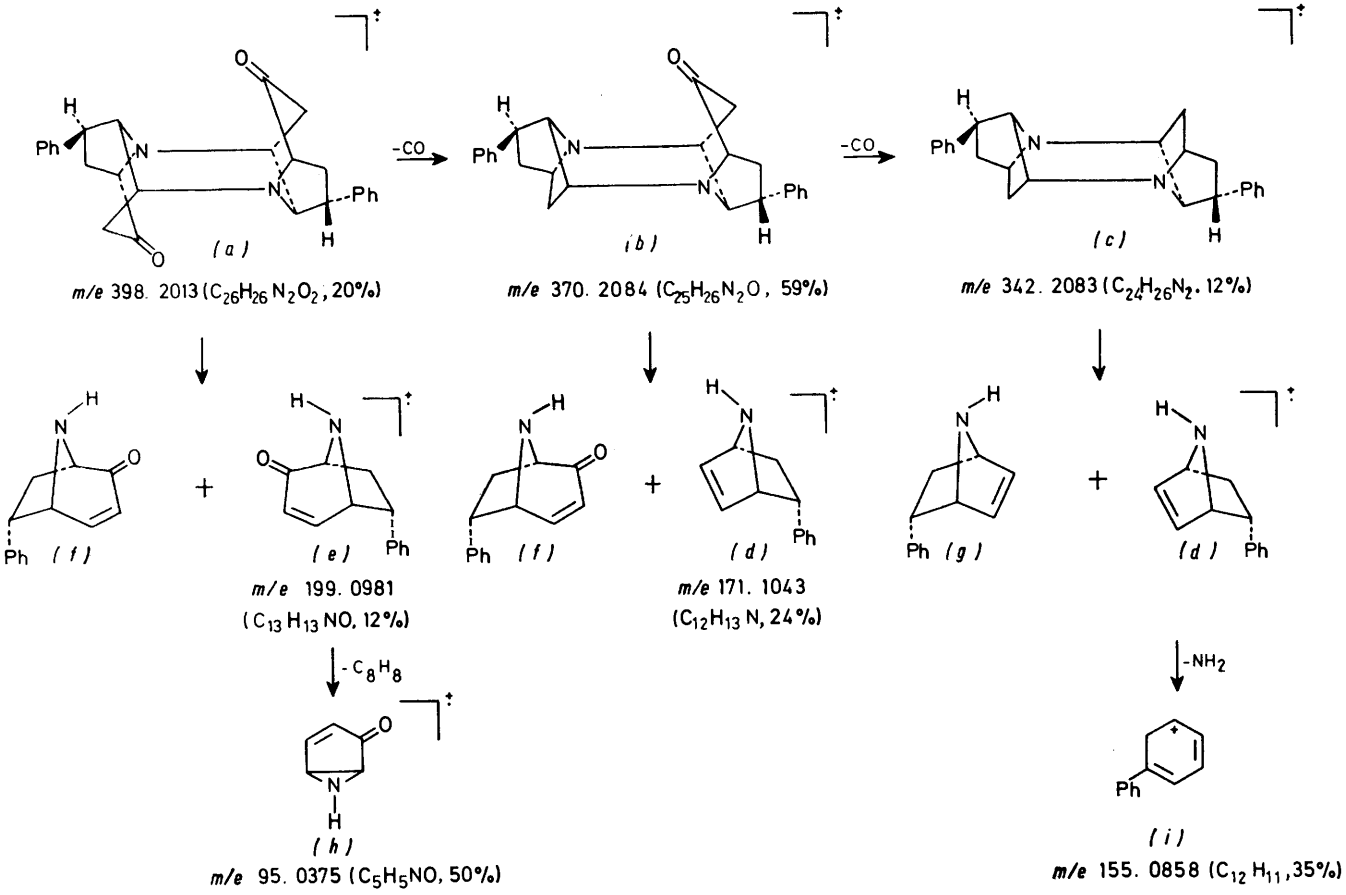
Cycloadduct Transformations.—*2π-Electron addends.* Alkoxy-*s*-triazines are hydrolysed by acid [15] to cyanuric acid (*cf.* 1,3,5-trimethoxy-*s*-triazine). The styrene adduct (16) with refluxing concentrated HCl–H_2O (1 : 1) gave cyanuric acid and a crystalline product, m.p. >280 °C. Elemental analysis ($C_{26}H_{26}N_2O_2$) and the molecular ion peak at *m/e* 398 indicate the dimeric nature of the product. The i.r. band at 1 710 cm^{-1} is typical of a saturated carbonyl group. The ^1H n.m.r. spectrum

[15] E. M. Smolin and L. Rapoport, '*s*-Triazines and their Derivatives,' in the series 'The Chemistry of Heterocyclic Compounds,' ed. A. Weissberger, Interscience, New York and London, 1959, p. 67.

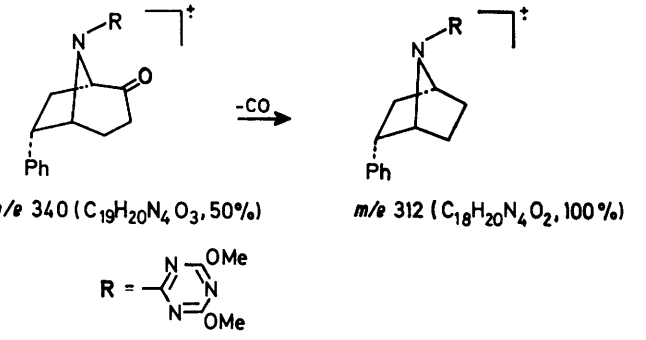
showed only saturated and aromatic protons; peaks for the vinylic protons H-3 and H-4 usually associated with the bicyclo[3.2.1] system [16] were absent.

The physical data of the product of m.p. >280 °C are consistent with the dimeric structure (34a), which is the result of Michael-type addition between an enantiomeric pair of molecules of the initially formed monomer (33) (Scheme 1); *i.e.* the bridge nitrogen (N-8) of one cycloadduct adds to C-4 of a second molecule whose bridge nitrogen adds to C-4 of the first-mentioned cycloadduct. The *trans*-structure (34a) in which the central piperazine ring assumes a non-strained chair conformation is preferred by us to the *cis*-structure (34b) with the central piperazine in the boat conformation.

High-resolution mass spectrometry confirms the assigned structure (Scheme 2). The molecular ion peak [*m/e* 398, (*a*), $C_{26}H_{26}N_2O_2$] fragments by two principal pathways. In the first, initial symmetrical dedimerisation to the cycloadduct ion (*e*) (*m/e* 199, $C_{13}H_{13}NO$) is followed by retrocycloaddition (loss of styrene) to give the betaine ion (*h*) (*m/e* 95). A second fragmentation route involves two successive losses of CO accompanied by ring contraction to the ion (*c*) (*m/e* 342, $C_{24}H_{26}N_2$) *via* the ion (*b*) (*m/e* 370, $C_{25}H_{26}N_2O$). *N*-Aryl-6-*endo*-phenyl-8-azabicyclo[3.2.1]-octan-2-ones (Scheme 3) undergo similar ready loss of CO, since the electron-impact-induced retrocycloaddition [5,17] observed with *N*-aryl-6-*endo*-phenyl-8-azabicyclo[3.2.1]oct-3-en-2-ones is impossible. The ion (*b*) (Scheme 2) can dedimerise to give the fragments (*f*) and (*d*); the ion (*c*) dedimerises to give the fragments (*d*) and (*g*). The fragment (*d*) loses NH_2 to yield the phenylcyclohexadiene ion (*i*), *m/e* 155.



SCHEME 2

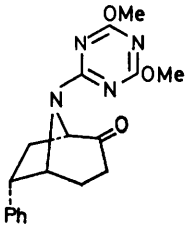


SCHEME 3

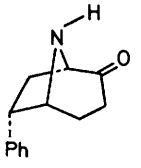
[16] N. Dennis, A. R. Katritzky, T. Matsuo, S. K. Parton, and Y. Takeuchi, *J.C.S. Perkin I*, 1974, 746.

[17] G. J. Sabounji, Ph.D. Thesis, University of East Anglia, 1976, p. 186.

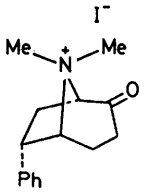
Catalytic hydrogenation (Pd–C) of the triazine (16) yielded the dihydro-ketone (35), m.p. 124—125 °C, whose i.r. spectrum showed a saturated ketone band at 1 720 cm^{-1}. Acid-catalysed hydrolysis ($HCl–H_2O$) yielded cyanuric acid and 6-*endo*-phenyl-8-azabicyclo[3.2.1]-octan-2-one (36), $\nu_{max.}$ 1 720 (saturated ketone) and 3 400 cm^{-1} (N–H). The saturated adduct (36) is readily quaternised with methyl iodide to yield the methiodide



(35)



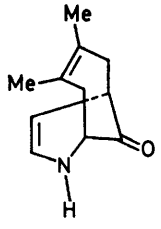
(36)



(37)

(37), m.p. 115—117 °C, whose i.r. spectrum shows a saturated ketone band at 1 730 cm^{-1}. The ^1H n.m.r. spectrum (Experimental section) exhibits two methyl signals at δ 3.50. In the mass spectrum of the salt (37), the molecular ion ($C_{15}H_{20}INO$) is absent, since MeI is lost on pyrolysis to yield the fragment *m/e* 215 (2%).

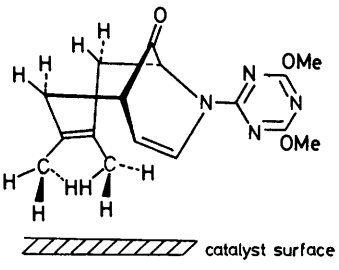
4π-Electron addends. Acid-catalysed hydrolysis of the triazinyl group from the adduct (28) gave cyanuric acid. However, the expected bicyclic fragment (38) was not isolated presumably because of side-reactions involving the enamine double bond.



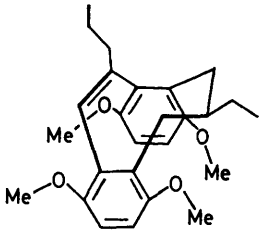
(38)

Attempts to reduce the enamine double bond with hydrogen over palladium–charcoal in ethanol, ethyl acetate, or acetic acid failed. Molecular models of (28) reveal that the bulky 3- and 4-methyl groups and the triazinyl group on the ball-like molecule will prevent both the 3,4- and the 8,9-double bonds from approaching the catalyst surface [*cf.* structure (39)]. Stork *et al.*[18] have reported similar behaviour for the intermediate (40) in the synthesis of (±)-byssochlamic acid. Sodium borohydride in methanol also failed to reduce the enamine double bond, since steric crowding prevents approach of the borohydride ion. However, in the presence of sodium borohydride, the alcohol (41), m.p. 157—158 °C, was isolated in 92% yield. The i.r. spectrum exhibited ν(O–H) at 3 400 cm^{-1} and enamine ν(C=C) at 1 650 cm^{-1}.

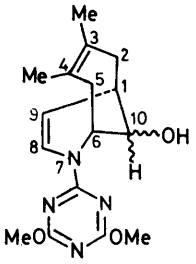
The ^1H n.m.r. spectrum (Table 3) confirmed the structure (41) for the alcohol, although it is not possible to assign the stereochemistry of the OH group. The assignments were confirmed by extensive spin–spin decoupling



(39)



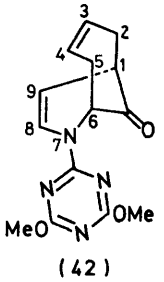
(40)



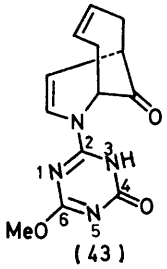
(41)

experiments, *e.g.* irradiation at the frequency of the H-9 double doublet at δ 5.80 caused the H-8 doublet at δ 7.40 and the H-1 broad quartet at δ 2.35 to collapse to a singlet and a sharp double doublet, respectively.

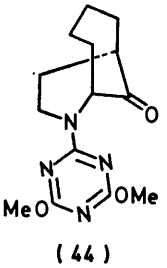
The mass spectrum of alcohol (41) showed the molecular ion [M^+ 318 (45%)] which lost 2,3-dimethylbuta-1,3-diene and a hydroxy-radical to yield the base peak, *m/e* 219 (100%).



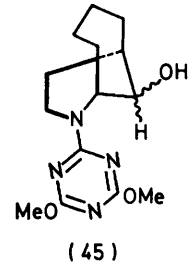
(42)



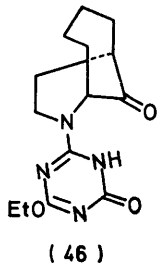
(43)



(44)



(45)



(46)

7-(4,6-Dimethoxy-*s*-triazin-2-yl)-7-azabicyclo[4.3.1]-deca-3,8-dien-10-one (42) was readily prepared from butadiene and the triazinyl dimer (6). Base-catalysed hydro-

[18] G. Stork, J. M. Tabak, and J. F. Blount, *J. Amer. Chem. Soc.*, 1972, **94**, 4735.

TABLE 3

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

Chemical shifts (δ)

	(27)	(28)	(41)	(42)	(43)	(44) [c]	(45)	(46)
1	3.40 [d]	3.10 [d]	2.35 [e]	3.12 [f]	3.19 [f]	2.92 [f]	3.22 [f]	
2	2.30 [d]	2.50 [d]	1.70 [e]	1.90—2.40 [d]	1.90—2.70 [d]	1.20—2.00 [d]	1.40—2.10 [d]	1.40—2.30 [d]
			2.95 [g]					
3				5.66 [h]	5.73 [h]	1.20—2.00 [d]	1.40—2.10 [d]	1.40—2.30 [d]
4				5.66 [h]	5.73 [h]	1.20—2.00 [d]	1.40—2.10 [d]	1.40—2.30 [d]
5	2.30 [d]	2.50 [d]	2.35 [e]	1.90—2.40 [d]	1.90—2.70 [d]	1.20—2.00 [d]	1.40—2.10 [d]	1.40—2.30 [d]
	3.40 [d]	3.10 [g]						
6	5.15 [g]	5.00 [g]	4.55 [h]	5.00 [h]	5.09 [f]	5.19 [h]	4.45 [d]	4.90—5.30 [d]
8	8.50 [g]	7.55 [g]	7.40 [g]	7.50 [g]	7.53 [g]	3.94 [f]	4.52 [j]	3.74 [f]
						4.40 [i]	3.22 [j]	
9	4.90 [e]	4.90 [e]	5.80 [e]	4.72 [e]	4.86 [e]	1.20—2.00 [f]	1.40—2.50 [d]	2.90 [f]
10			4.10 [h]				3.94 [f]	
OMe		3.95 [k]		3.85 [k]	3.88 [k]	3.94 [k]	3.94 [k]	
NH					7.60 [k]			3.31 [k]
					7.69 [k]			3.96 [k]
CMe	1.45 [k]	1.65 [k]	1.35 [k]					
	1.60 [k]		1.45 [k]					

Coupling constants (Hz)

	(27)	(28)	(41)	(42)	(43)	(44) [c]	(45)	(46)
1,6						1.0		
1,9				5.0	5.0			
1,10			6.0					
3,4				5.0	5.0			
5,6	8.0	8.0	8.0			5.0	3.0	
6,10							5.0	
8-*endo*,8-*exo*						14.0	14.0	14.0
8,9	8.0	8.0	8.0	9.0	9.0			
8-*exo*,9						5.0	5.0	5.0
8-*endo*,9							5.0	

[a] Me_4Si as internal standard. [b] In $CDCl_3$. [c] OCH_2CH_3 δ 4.44 (q), OCH_2CH_3 δ 1.38 (t) (*J* 8.0 Hz). [d] Overlap [e] Double doublet. Multiplet. [g] Doublet. [h] Triplet. [i] Doublet of triplets. [j] Quartet of doublets. [k] Singlet.

lysis of (42) failed to remove the triazinyl moiety but succeeded only in the demethylation of one of the 4,6-dimethoxy-substituents to yield the adduct (43), whose structure was confirmed by n.m.r. (Table 3).

Unlike the 2,3-dimethylbutadiene adduct (28), the butadiene adduct (42) suffered catalytic reduction to the tetrahydro-derivative (44) together with the tetrahydro-alcohol (45). As in the case of (42), base-catalysed hydrolysis of (44) in ethanol yielded the mono-demethylated product (46).

EXPERIMENTAL

The m.p.s were determined with a Reichert apparatus. Spectra were recorded with a Perkin-Elmer 257 grating i.r. spectrophotometer, a Perkin-Elmer SP 800 u.v. spectrophotometer, a Hitachi–Perkin-Elmer RMU-6E mass spectrometer, and a Varian HA-100 n.m.r. spectrometer. High resolution mass spectra were recorded on an A.E.I. MS-9 spectrometer coupled to an IBM 1130 computer. Compounds were purified until they were observed as single spots on t.l.c. (Kieselgel PF 254). Isomeric pairs of adducts were separated by preparative thick layer chromatography (prep. t.l.c.) on Kieselgel PF 254.

2-Chloro-4,6-dimethoxy-s-triazine.—Freshly prepared NaOMe (0.2 mol) in dry MeOH (200 ml) was added dropwise during 2 h to cyanuric chloride (18 g, 0.1 mol) in dry benzene (200 ml) at 0 °C. The reaction was monitored by t.l.c. [light petroleum (b.p. 40—60 °C)–EtOAc, 4 : 1]; on completion the NaCl was discarded. The filtrate was evaporated *in vacuo* to yield 2-chloro-4,6-dimethoxy-*s*-triazine (13 g, 72%), m.p. 75—76 °C (lit.,[3] 75—76 °C).

1-(4,6-Diphenyl-s-triazin-2-yl)-3-hydroxypyridinium Chloride (3).—A well stirred solution of 2-chloro-4,6-diphenyl-*s*-triazine (4 g, 0.01 mol) in $[CH_2]_4O$ (10 ml) was treated with 3-hydroxypyridine (2.0 g, 0.01 mol) in $[CH_2]_4O$ (20 ml) at 30 °C as described for (4), to give the *salt* (3) (3.0 g, 80%) as prisms, m.p. 179—180 °C (from MeOH–Et_2O) (Found: C, 65.9; H, 4.1; N, 15.2. $C_{20}H_{15}ClN_4O$ requires C, 66.2; H, 4.1; N, 15.5%); $\nu_{max.}$ (Nujol) 3 080 (Ar–H), 2 500 (O–H), and 1 530 and 1 570 cm^{-1} (C=N); *m/e* 326 (100%).

1-(4,6-Dimethoxy-s-triazin-2-yl)-3-hydroxypyridinium Chloride (4).—3-Hydroxypyridine (2.0 g, 0.01 mol) in $[CH_2]_4O$ (25 ml) was added dropwise with stirring to 2-chloro-4,6-dimethoxy-*s*-triazine (4.0 g, 0.01 mol) in $[CH_2]_4O$ (100 ml) at 0 °C. After stirring for 6 h at 0 °C the precipitate (3.0 g, 50%) was crystallised from EtOH–EtOAc to give the *salt* (4) as needles, m.p. 167—168 °C (Found: C, 43.8; H, 4.1; Cl, 13.4; N, 20.3. $C_{10}H_{11}ClN_4O_3$ requires C, 44.4; H, 4.1; Cl, 13.1; N, 20.3%); $\nu_{max.}$ (Nujol) 3 100 (Ar–H), 2 500 (O–H), 1 570 and 1 530 cm^{-1} (C=N); $\lambda_{max.}$ (EtOH) 217 nm (log ε 5.61); δ (D_2O) 8.60 (1 H, dd, H-6, $J_{5,6}$ 6.0, $J_{2,6}$ 2.2 Hz), 8.55 (1 H, t, H-2, $J_{2,4} \approx J_{2,6}$ = 2.2 Hz), 8.40 (1 H, dd, H-4), 8.15 (1 H, q, H-5, $J_{4,5}$ 8.0 Hz), and 4.22 (6 H, s, OMe); *m/e* 234 (60%).

3,11-Bis-(4,6-diphenyl-s-triazin-2-yl)-3,11-diazatricyclo-[5.3.1.1^{2,6}]dodeca-4,8-diene-10,12-dione (5).—The salt (3) (3.6 g, 0.01 mol) in water (10 ml) was stirred for 1 h. The yellow precipitate was crystallised from $[CH_2]_4O$ to give the *dimer* (5) (3.2 g, 98%) as yellow prisms, m.p. >300 °C [Found: C, 73.3; H, 4.4; N, 16.9. $(C_{20}H_{14}N_4O)_2$ requires C, 73.6; H, 4.3; N, 17.2%]; $\nu_{max.}$ ($CHBr_3$) 3 070 (Ar–H), 1 740 (sat. ketone C=O), 1 680 (αβ-unsat. ketone C=O), 1 650 (C=C), 1 530 and 1 570 cm^{-1} (C=N); *m/e* 326 (49%). The dimer (5) could also be obtained in 80% yield by treating the salt (3) with Et_3N at room temperature.

3,11-*Bis*-(4,6-*dimethoxy*-s-*triazin*-2-*yl*)-3,11-*diazatricyclo*-[5.3.1.$1^{2,6}$]*dodeca*-4,8-*diene*-10,12-*dione* (6).—Et_3N (1.0 ml, 0.01 mol) was added to a well stirred suspension of (4) (2.7 g, 0.01 mol) in CH_2Cl_2 (10 ml). When all the salt had dissolved the mixture was evaporated to dryness *in vacuo*. The residue was washed well with water (3 × 5 ml), followed by EtOH (3 × 5 ml) to yield a white solid (1.7 g, 73%). The *dimer* (6) was obtained as needles, m.p. 199—200 °C (from EtOH) [Found: C, 51.3; H, 4.3; N, 23.9. $(C_{10}H_{10}N_4O_3)_2$ requires C, 51.3; H, 4.3; N, 23.9%]; $\nu_{max.}$ ($CHBr_3$ film) 2 950 (C–H), 1 740 (sat. ketone C=O), 1 680 (α,β-unsat. ketone C=O), 1 650 (C=C), and 1 530 and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ (MeCN) 265 (log ε 4.93), 245 (4.96), and 225 nm (4.94); *m/e* 468 (60%) and 234 (100%).

3-(4,6-*Diphenyl*-s-*triazin*-2-*yloxy*)*pyridine* (11).—The dimer (5) (0.2 g, 3.06 × 10^{-4} mol) was heated under reflux with diphenylacetylene (0.1 g) in $[CH_2]_4O$ (20 ml) and chlorobenzene (20 ml) for 48 h. The mixture was evaporated *in vacuo* and the residue purified by prep. t.l.c. [light petroleum (b.p. 40—60 °C)–EtOAc, 9 : 1] to give 3-(4,6-*diphenyl*-s-*triazin*-2-*yloxy*)*pyridine* (11) (90 mg, 45%) as needles, m.p. 102—103 °C (from EtOH) (Found: C, 73.3; H, 4.4; N, 17.2. $C_{20}H_{14}N_3O$ requires C, 73.6; H, 4.3; N, 17.2%); $\nu_{max.}$ ($CHBr_3$ film) 1 570 and 1 540 (C=N) and 1 100 cm^{-1} (Ar–O); $\lambda_{max.}$ ($CHCl_3$) 270 nm (log ε 4.63); *m/e* 326 (100%).

8-(4,6-*Diphenyl*-s-*triazin*-2-*yl*)-2-*oxo*-N-*phenyl*-8-*azabicyclo*-[3.2.1]*oct*-3-*ene*-6,7-exo-*dicarboximide* (12).—The dimer (5) (0.3 g, 4.6 × 10^{-4} mol) was treated with *N*-phenylmaleimide (0.1 g, 0.001 mol) in $[CH_2]_4O$ (20 ml) and chlorobenzene (20 ml) at 130 °C for 72 h as described above. Trituration with EtOH yielded the *cycloadduct* (12) (0.2 g, 58%) as prisms, m.p. 246—265 °C (from MeCN) (Found: C, 72.0; H, 4.1; N, 14.2. $C_{30}H_{21}N_5O_3$ requires C, 72.1; H, 4.2; N, 14.1%); $\nu_{max.}$ ($CHBr_3$ film) 1 710br (C=O), and 1 530 and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ ($CHCl_3$) 268 nm (log ε 4.71); *m/e* 499 (45%).

8-(4,6-*Dimethoxy*-s-*triazin*-2-*yl*)-2-*oxo*-N-*phenyl*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6,7-exo-*dicarboximide* (13).—The dimer (6) (0.2 g, 4.3 × 10^{-4} mol), *N*-phenylmaleimide (0.1 g, 0.001 mol) in $[CH_2]_4O$ (10 ml), and chlorobenzene (10 ml) were heated under reflux (130 °C) for 6 days. The mixture was evaporated *in vacuo* and the residue triturated with Et_2O (5 ml) to yield a precipitate of the *cycloadduct* (13) (0.3 g, 73%) as prisms, m.p. 234—235 °C (from EtOH) (Found: C, 58.5; H, 4.7; N, 16.6. $C_{20}H_{17}N_5O_5$ requires C, 59.0; H, 4.2; N, 17.2%); $\nu_{max.}$ ($CHBr_3$ film) 1 720br (C=O) and 1 530 and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ (MeCN) 227 nm (log ε 4.74) *m/e* 407 (33%).

Methyl 8-(4,6-*Dimethoxy*-s-*triazin*-2-*yl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo- *and* -6-exo-*carboxylate* [(14) *and* (17)].—The dimer (6) (0.4 g, 8.5 × 10^{-4} mol) in chlorobenzene (10 ml) and $[CH_2]_4O$ (10 ml) was refluxed (at 130 °C) with methyl acrylate (10 ml) and hydroquinone (0.2 g) for 4 days. The mixture was evaporated to dryness *in vacuo* to yield a yellow gum (0.50 g, 78%). The mixture of isomers was separated by prep. t.l.c. [light petroleum (b.p. 40—60 °C)–EtOAc, 1 : 1]. The endo-*adduct* (14) (0.20 g, 37%) was isolated as prisms, m.p. 149—150 °C (from EtOH–H_2O) (Found: C, 52.1; H, 4.9; N, 17.0. $C_{14}H_{16}N_4O_5$ requires C, 52.5; H, 5.0; N, 17.5%); $\nu_{max.}$ 1 740 (ester C=O), 1 710 (α,β-unsat. ketone C=O), and 1 530 and 15 70 cm^{-1} (C=N); $\lambda_{max.}$ (MeCN) 218 nm (log ε 4.26); *m/e* 320 (38%). The exo-*adduct* (17) (0.30 g, 56%) was obtained as prisms, m.p. 160—162 °C (from EtOH–H_2O) (Found: C, 52.1; H, 5.3; N, 17.1%); $\nu_{max.}$ ($CHBr_3$ film) 1 740 (ester C=O), 1 700 (αβ-unsat. ketone C=O), and 1 530 and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ (MeCN) 218 nm (log ε 4.81); *m/e* 320 (80%).

8-(4,6-*Dimethoxy*-s-*triazin*-2-*yl*)-2-*oxo*-8-*azabicyclo*[3.2.1]-*oct*-3-*ene*-6-endo- *and* -6-exo-*carbonitrile* [(15) *and* (18)].—A solution of (6) (0.4 g, 8.5 × 10^{-4} mol), acrylonitrile (20 ml), and hydroquinone (0.2 g) in $[CH_2]_4O$ (5 ml) and chlorobenzene (5 ml) was heated under reflux (130 °C) for 4 days. The mixture was evaporated to dryness *in vacuo* to give a gum which was chromatographed [light petroleum (b.p. 40—60 °C)–EtOAc, 1 : 1]. The endo-*adduct* (15) (0.20 g, 40%) was isolated as prisms, m.p. 185—187 °C (from $CHCl_3$–Et_2O) (Found: C, 54.1; H, 4.6; N, 24.0. $C_{13}H_{13}N_5O_3$ requires C, 54.4; H, 4.6; N, 24.4%); $\nu_{max.}$ ($CHBr_3$ film) 2 225 (C≡N), 1 700 (αβ-unsat. ketone C=O), and 1 530 and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ (MeCN) 210 nm (log ε 4.25); *m/e* 287 (70%). The exo-*adduct* (18) (0.24 g, 40%) crystallised from $CHCl_3$–Et_2O as prisms, m.p. 169—170 °C (Found: C, 54.2; H, 4.7; N, 24.4%); $\nu_{max.}$ ($CHBr_3$ film) 2 225 (C≡N), 1 700 (αβ-unsat. ketone C=O), and 1 530 and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ (MeCN) 210 nm (log ε 4.28); *m/e* 287 (100%).

8-(4,6-*Dimethoxy*-s-*triazin*-2-*yl*)-6-endo-*phenyl*-8-*azabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (16).—The dimer (6) (0.4 g, 8.5 × 10^{-4} mol) in $[CH_2]_4O$ (10 ml) and chlorobenzene (10 ml) was heated under reflux (130 °C) with styrene (3 ml) and hydroquinone (0.2 g) for 3 days. The mixture was evaporated *in vacuo* to give a crude solid which was washed with $CHCl_3$. The $CHCl_3$ extracts were collected and evaporated *in vacuo* to give a yellow gum which on trituration with light petroleum (b.p. 40—60 °C) (5 ml) yielded the *cycloadduct* (16) (0.55 g, 75%) as prisms, m.p. 129—130 °C (from EtOH–H_2O) (Found: C, 63.8; H, 5.3; N, 16.3. $C_{18}H_{18}N_4O_3$ requires C, 63.9; H, 5.4; N, 16.6%); $\nu_{max.}$ ($CHBr_3$ film) 1 680 (αβ-unsat. C=O) and 1 530 and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ (EtOH) 210 (log ε 4.15) and 227 nm (4.25); *m/e* 338 (22%).

Methyl 8-(4,6-*Diphenyl*-s-*triazin*-2-*yl*)-2-*oxo*-8-*azabicyclo*-[3.2.1]*oct*-3-*ene*-6-endo- *and* -6-exo-*carboxylate* [(19) *and* (22)].—The dimer (5) (0.4 g, 6.13 × 10^{-4} mol) in $[CH_2]_4O$ (20 ml) and chlorobenzene (20 ml) was treated with methyl acrylate (15 ml), and hydroquinone (0.2 g) at 130 °C for 36 h as described above. Prep. t.l.c. [light petroleum (b.p. 40—60 °C) –EtOAc, 3 : 1] gave the endo-*adduct* (19) (from EtOH) (120 mg, 22%) as prisms, m.p. 209—210 °C (Found: C, 69.7; H, 4.6; N, 13.3. $C_{24}H_{20}N_4O_3$ requires C, 69.9; H, 4.9; N, 13.6%); $\nu_{max.}$ ($CHBr_3$ film) 1 740 (ester C=O), 1 690 (αβ-unsat. C=O), and 1 530 and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ ($CHCl_3$) 270 nm (log ε 4.83); *m/e* 412 (70%). The exo-*adduct* (22) (129 mg, 22%) crystallised from EtOH as prisms, m.p. 195—196 °C (Found: C, 70.1; H, 4.6; N, 13.5%); $\nu_{max.}$ ($CHBr_3$ film) 1 740 (ester C=O), 1 640 (αβ-unsat. ketone C=O), and 1 530 and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ ($CHCl_3$) 270 nm (log ε 4.87); *m/e* 412 (55%).

8-(4,6-*Diphenyl*-s-*triazin*-2-*yl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo- *and* -6-exo-*carbonitrile* [(20) *and* (23)].—The dimer (5) (0.4 g, 6.13 × 10^{-4} mol) in $[CH_2]_4O$ (10 ml) and chlorobenzene (10 ml) was treated with acrylonitrile (15 ml) and hydroquinone (0.2 g) for 36 h as described above. Prep. t.l.c. [light petroleum (b.p. 40—60 °C)–EtOAc, 4 : 1] yielded the endo-*adduct* (20) (120 mg, 24%), as prisms, m.p. 236—237 °C (from EtOH–H_2O) (Found: C, 72.5; H, 4.4; N, 18.2. $C_{23}H_{17}N_5O$ requires C, 72.8; H, 4.5; N, 18.5%); $\nu_{max.}$ 2 240 (C≡N), 1 710 (α,β-unsat. ketone C=O), and 1 530 and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ ($CHCl_3$) 270 nm (log ε 4.49); *m/e* 379 (3.9%). The exo-*adduct* (23) (40 mg, 8%) was isolated

as prisms, m.p. 239—240 °C (EtOH) (Found: C, 72.4; H, 4.3; N, 18.5%); $\nu_{max.}$ 2 240 (C≡N) 1 710 (αβ-unsat. ketone C=O), and 1 530 and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ ($CHCl_3$) 270 nm (log ε 4.62); *m/e* 379 (6%).

8-(4,6-*Diphenyl*-s-*triazin*-2-*yl*)-6-endo- *and* -6-exo-*phenyl*-8-*azabicyclo*[3.2.1]*oct*-3-*en*-2-*one* [(21) *and* (24)].—The dimer (5) (0.4 g, 6.13 × 10^{-4} mol) in $[CH_2]_4O$ (20 ml) and chlorobenzene (20 ml) was treated with styrene (5 ml) and hydroquinone (0.2 g) at 130 °C for 48 h as described above. Prep. t.l.c. [light petroleum (b.p. 40—60 °C)–EtOAc, 9 : 1] yielded the endo-*adduct* (21) (140 mg, 24%) as prisms, m.p. 219—220 °C (from EtOH) (Found: C, 78.2; H, 5.1; N, 13.1. $C_{28}H_{22}N_4O$ requires C, 78.1; H, 5.2; N, 13.0%); $\nu_{max.}$ ($CHBr_3$ film) 1 680 (αβ-unsat. ketone C=O), and 1 530 and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ ($CHCl_3$) 270 nm (log ε 4.57); *m/e* 430 (66%); and the exo-*adduct* (24) (40 mg, 7%) as prisms, m.p. 240—242 °C (from EtOH) (Found: C, 78.1; H, 5.2; N, 13.1%); $\nu_{max.}$ ($CHBr_3$ film) 1 680 (αβ-unsat. ketone C=O), and 1 539 and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ ($CHCl_3$) 270 nm (log ε 4.82); *m/e* 430 (57%).

Dimethyl 8-(4,6-*Diphenyl*-s-*triazin*-2-*yl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*octa*-3,6-*diene*-6,7-*dicarboxylate* (26).—The dimer (5) (0.3 g, 0.001 mol), dimethyl but-2-ynedioate (3 ml) in $[CH_2]_4O$ (20 ml) and chlorobenzene (20 ml) were heated under reflux (130 °C) for 45 min. The mixture was evaporated *in vacuo* to give a yellow residue, which was purified by prep. t.l.c. [light petroleum (b.p. 40—60 °C)–EtOAc, 3 : 1]. The *adduct* (26) (0.25 g, 53%) was isolated as yellow needles, m.p. 207—208 °C (from MeOH–H_2O) (Found: C, 66.5; H, 4.3; N, 11.5. $C_{26}H_{20}N_4O_5$ requires C, 66.7; H, 4.3; N, 12.0%); $\nu_{max.}$ ($CHBr_3$ film) 1 740br (C=O), and 1 530 and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ ($CHCl_3$) 270 (log ε 4.46) and 310 nm (log ε 4.31); *m/e* 470 (32%) and 326 (10%).

7-(4,6-*Diphenyl*-s-*triazin*-2-*yl*)-3,4-*dimethyl*-7-*azabicyclo*[4.3.1]*deca*-3,8-*dien*-10-*one* (27).—The dimer (5) (0.4 g, 6.13 × 10^{-4} mol) was treated with 2,3-dimethylbuta-1,3-diene (5 ml) and hydroquinone (0.1 g) in $[CH_2]_4O$ (10 ml) and chlorobenzene (10 ml) at 130 °C for 36 h, as described above. Preparative thick-layer chromatography [light petroleum–EtOAc, 9 : 1] gave the *cycloadduct* (27) (120 mg, 22%) as yellow prisms, m.p. 165—167 °C (from EtOH) (Found: C, 76.2; H, 5.6; N, 13.5. $C_{26}H_{24}N_4O$ requires C, 76.5; H, 5.9; N, 13.7%); $\nu_{max.}$ ($CHBr_3$ film) 1 730 (sat. ketone C=O), 1 640 (enamine C=C), and 1 530 and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ ($CHCl_3$) 270 nm (log ε 4.66); *m/e* 408 (85%).

7-(4,6-*Dimethoxy*-s-*triazin*-2-*yl*)-3,4-*dimethyl*-7-*azabicyclo*[4.3.1]*deca*-3,8-*dien*-10-*one* (28).—The dimer (6) (0.4 g, 8.5 × 10^{-4} mol), 2,3-dimethylbuta-1,3-diene (5 ml), and hydroquinone (0.1 g) in $[CH_2]_4O$ (10 ml) and chlorobenzene (10 ml) were heated under reflux (130 °C) for 5 days. The mixture was evaporated *in vacuo* and the residue was dissolved in $CHCl_3$. The insoluble hydroquinone was filtered and discarded. The filtrate was evaporated to a yellow residue (0.56 g, 88%) which was purified by prep. t.l.c. [light petroleum–EtOAc, 3 : 1]. The *cycloadduct* (28) was obtained as prisms, m.p. 125—127 °C (EtOH–H_2O) (Found: C, 61.0; H, 6.6. $C_{16}H_{20}N_4O_3$ requires C, 60.8; H, 6.4%); $\nu_{max.}$ ($CHBr_3$ film) 1 730 (sat. ketone C=O), 1 650 (enamine C=C), and 1 530 and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ (MeCN) 270 nm (log ε 4.48); *m/e* 316 (60%).

Hydrolysis of Compound (16).—A solution of (16) (3.3 g, 0.01 mol) in EtOH (5 ml), conc. HCl (10 ml), and water (10 ml) was refluxed for 2.5 h then cooled; cyanuric acid crystallised out. The filtrate was evaporated *in vacuo* to dryness. The residue was diluted with ice and water, neutralised with $NaHCO_3$, and extracted with hot $CHCl_3$. The extract was dried (Na_2SO_4) and evaporated, and the residue recrystallised from EtOH to give 8,16-*diphenyl*-2,10-*diazapentacyclo*[9.5.0.$0^{2,14}$.$0^{3,9}$.$0^{6,10}$]*hexadecane*-5,13-*dione* (34a) (1 g, 60%) as plates, m.p. >280 °C; $\nu_{max.}$ ($CHBr_3$ film) 1 710 (sat. C=O) and 1 610 cm^{-1} (C=C) [Found: *m/e* 398.2013 (20%). $C_{26}H_{26}N_2O_2$ requires 398.46].

8-(4,6-*Dimethoxy*-s-*triazin*-2-*yl*)-6-endo-*phenyl*-8-*azabicyclo*[3.2.1]*octan*-2-*one* (35).—Compound (16) (3.3 g, 0.01 mol) in EtOH (250 ml) was reduced catalytically over Pd–C (0.3 g at 40 lb in^{-2} at room temp. for 3 h. The catalyst was filtered off and the filtrate evaporated to dryness *in vacuo*. The residue was purified by prep. t.l.c. (EtOAc–light petroleum, 1 : 1) to yield the *cycloadduct* (35) (3 g, 85%) as prisms, m.p. 124—125 °C (from EtOH) (Found: C, 63.2; H, 6.0; N, 16.2. $C_{18}H_{20}N_4O_3$ requires: C, 63.5; H, 5.9; N, 16.5%); $\nu_{max.}$ ($CHBr_3$ film) 1 720 (sat. C=O), and 1 530 and 1 570 cm^{-1} (C=N); *m/e* 340 (20%); δ ($CDCl_3$) 2.20 (6 H, H-3, -4, -7), 3.90 (6 H, CH_3), 3.90 (1 H, H-6), 5.00 (2 H, H-1, -5), and 7.25 (5 H, arom.).

6-endo-*Phenyl*-8-*azabicyclo*[3.2.1]*octan*-2-*one* (36).—A solution of (35) (3.4 g, 0.01 mol) in EtOH (5 ml), conc. HCl (10 ml), and H_2O (10 ml) was heated under reflux for 2.5 h. On cooling, cyanuric acid crystallised out and was filtered off. The filtrate was evaporated to dryness *in vacuo* and the residue in water neutralised ($NaHCO_3$) and extracted with $CHCl_3$. The extract was purified by prep. t.l.c. (EtOAc) to yield the cycloadduct (36) (1.5 g, 68%); $\nu_{max.}$ ($CHBr_3$ film) 1 720 (sat. C=O) and 3 400 cm^{-1} (N–H); compound (36) resisted recrystallisation and was converted into the methiodide salt.

Methiodide salt. A solution of (36) in EtOAc (5 ml) and MeI (20 ml) was left at room temp. overnight. The *methiodide salt* (37) (2.5 g, 100%) crystallised as white needles, m.p. 115—117 °C (from EtOH–Et_2O) (Found: C, 50.2; H, 5.9; N, 3.6. $C_{15}H_{18}INO$ requires C, 50.4; H, 5.6; N, 3.9%); $\nu_{max.}$ ($CHBr_3$ film) 1 730 (sat. C=O) and 3 400 cm^{-1} (N^+–C); δ (D_2O) 2.50 (6 H), 3.50 (2 H), 3.50 (6 H, CH_3), and 7.30 (5 H); *m/e* 215 ($M^{+\cdot}$ − MeI, 2%).

7-(4,6-*Dimethoxy*-s-*triazin*-2-*yl*)-3,4-*dimethyl*-7-*azabicyclo*[4.3.1]*deca*-3,8-*dien*-10-*ol* (41).—$NaBH_4$ (0.35 g) was added slowly to a cooled solution of (28) (2.5 g, 0.006 mol) in MeOH (20 ml). After stirring for 15 min the solution was evaporated *in vacuo* and the residue in water was neutralised (5% HCl) and extracted with $CHCl_3$. The residue obtained was purified by prep. t.l.c. (EtOAc–light petroleum, 1 : 3) to give the *alcohol* (41) (1.71 g, 92%) as needles, m.p. 157—158 °C (from EtOH–H_2O) (Found: C, 60.3; H, 7.0; N, 17.4. $C_{16}H_{22}N_4O_3$ requires C, 60.4; H, 7.0; N, 17.6%); $\nu_{max.}$ ($CHBr_3$) 3 400 (O–H), 1 650 (N–C=C), and 1 550 and 1 570 cm^{-1} (C=N); *m/e* 318 (45%) and 219 (100%).

7-(4,6-*Dimethoxy*-s-*triazin*-2-*yl*)-7-*azabicyclo*[4.3.1]*deca*-3,8-*dien*-10-*one* (42).—The dimer (6) (5 g, 1.07 × 10^{-2} mol), hydroquinone (0.15 g), and liquid butadiene (3 ml) in 1,2-dichloroethane (20 ml) were heated (80—100 °C) in a sealed tube for 3 days. The mixture was filtered and evaporated to dryness. The residue was purified by preparative t.l.c. ($CHCl_3$) to yield the *cycloadduct* (42), m.p. 132 °C, as white prisms (1.85 g, 30%) (from EtOH) (Found: C, 58.8; H, 5.3; N, 19.1. $C_{14}H_{16}N_4O_3$ requires C, 58.3; H, 5.5; N, 19.4%); $\nu_{max.}$ (Nujol) 1 715 (sat. ketone C=O), 1 595, 1 560, and 1 470 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 270 nm (log ε 4.42); *m/e* 288.

7-(3,4-*Dihydro*-6-*methoxy*-4-*oxo*-s-*triazin*-2-*yl*)-7-*azabicyclo*[4.3.1]*deca*-3,8-*dien*-10-*one* (43).—The adduct (42) (0.6 g,

2×10^{-3} mol) in H_2O (15 ml) and Bu^tOH (7.5 ml) containing NaOH (0.2 g) was heated under reflux for 2 h. The product was purified by preparative t.l.c. (MeOH–EtOAc, 2 : 1) to give *compound* (43) (0.23 g, 40%) as white needles, m.p. 205 °C (from EtOH–H_2O) (Found: C, 57.2; H, 5.5; N, 19.6. $C_{13}H_{14}N_4O_3$ requires C, 56.9; H, 5.1; N, 20.4%); $\nu_{max.}$ (Nujol) 1 720 (sat. ketone C=O), 1 660, 1 610, and 1 560 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 278 nm (log ε 4.39); *m/e* 274.

7-(4,6-*Dimethoxy*-s-*triazin*-2-*yl*)-7-*azabicyclo*[4.3.1]*decan*-10-*one* (44).—The cycloadduct (42) (1 g, 3.47×10^{-3} mol) in EtOH (150 ml) and CH_2Cl_2 (10 ml) was hydrogenated over Pd–C (0.2 g) at 30 lb in^{-2} for 4 days. The mixture was filtered and the filtrate evaporated to dryness. The residue (two components by t.l.c.) was separated by preparative t.l.c. ($CHCl_3$). The *cycloadduct* (44) (0.253 g, 25%) was isolated as needles, m.p. 95 °C (from EtOH) (Found: C, 57.4; H, 6.7; N, 19.1. $C_{14}H_{20}N_4O_3$ requires C, 57.5; H, 6.9; N, 19.2%); $\nu_{max.}$ (Nujol) 1 720 cm^{-1} (C=O, sat. ketone); $\lambda_{max.}$ ($CHCl_3$) 248 nm (log ε 3.88); *m/e* 292. The residue was further separated by t.l.c. to yield 7-(4,6-*dimethoxy*-s-*triazin*-2-*yl*)-7-*azabicyclo*[4.3.1]*decan*-10-*ol* (45) (0.31 g, 30%) as white needles, m.p. 153 °C (from EtOH) (Found: C, 56.9; H, 7.3; N, 18.7. $C_{14}H_{22}N_4O_3$ requires C, 57.1; H, 7.5; N, 19.0%); $\nu_{max.}$ (Nujol) 3 320 cm^{-1} (O–H); $\lambda_{max.}$ ($CHCl_3$) 225 (log ε 3.82) and 270 nm (3.51); *m/e* 294.

7-(6-*Ethoxy*-3,4-*dihydro*-4-*oxo*-s-*triazin*-2-*yl*)-7-*azabicyclo*-[4.3.1]*decan*-10-*one* (46).—The saturated adduct (44) (0.25 g, 8.56×10^{-4} mol) in H_2O (15 ml) and EtOH (10 ml) was treated with NaOH (0.2 g). The reaction was monitored by t.l.c. The product was purified by preparative t.l.c. (MeOH–$CHCl_3$, 1 : 15) to give *compound* (46) (0.077 g, 31%) as white needles, m.p. 185 °C (from EtOH) (Found: C, 57.4; H, 6.6; N, 18.8. $C_{14}H_{20}N_4O_3$ requires C, 57.5; H, 6.8; N, 19.2%); $\nu_{max.}$ (Nujol) 1 750, 1 710, 1 660, 1 615, and 1 550 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 250 nm (log ε 4.12); *m/e* 292.

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