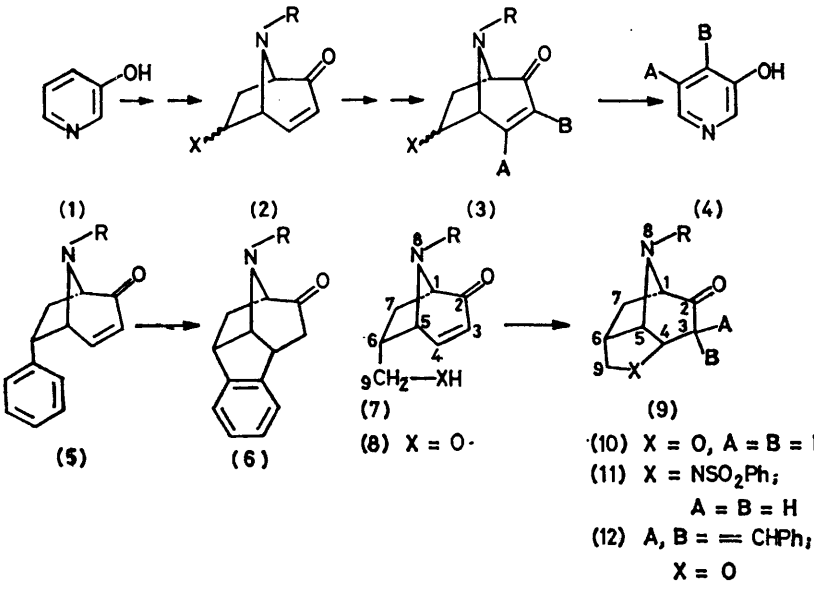
1,3-Dipolar Character of Six-membered Aromatic Rings. Part 43.[1] Cycloadditions leading to Tricyclic Adducts

By **Alan R. Katritzky,* Nicholas Dennis, Gebran J. Sabongi,‡ and Lemi Turker,** School of Chemical Sciences, University of East Anglia, Norwich NR4 4TJ

Allyl alcohol reacts with 1-heteroaryl-3-oxidopyridiniums to give a tricyclic product (10) in which the OH group has added to the αβ-unsaturated ketone. Analogous products are obtained from *N*-allylbenzenesulphonamide, acrylic acid, and 2-vinylpyridine. Further transformations of the primary adducts are described.

A MAJOR aim of our cycloaddition work is the development of new synthetic methods in pyridine chemistry. Thus, the reversibility of cycloadditions suggests the conversion of cycloadducts (2) into derivatives (3) which should allow the substitution of 3-hydroxypyridine in the 4- and/or 5-positions [(1)→(4)]. We have described the preparation of 4-bromo-3-hydroxypyridine by this method.[2] However, attempts to change the OH function of 3-hydroxypyridine by an analogous route are hindered by the preferential reaction [2] of nucleophiles with the C=C bond in (2). We therefore examined methods of protecting this double bond. The facile conversion [3] of styrene adducts (5) into the tetracyclic derivatives (6) suggested that suitable *endo*-adducts of type (7) should undergo spontaneous cyclisation to the tetracycles (9). The present paper describes these and related systems.

The betaines used in this study (13a—d) were generated *in situ* either from their salts (14a—d) or from their dimers. Each betaine formed initially the *syn*-dimer (15a—d), but in the pyrimidinyl case, (15b) equilibrated to give mainly (16b).



RESULTS AND DISCUSSION

Allyl Alcohol.—Whereas the pyridyl betaine (13a) reacted with allyl acetate to give the normal cycloadduct (17a), shown to have the *endo* structure by its n.m.r.

‡ Previously transliterated as G. J. Sabounji.

spectrum (Table 1), the reactions of betaines (13a), (13b), and (13c) with allyl alcohol each gave a product [(10a), (10b), and (10c) in 48%, 85%, and 10% yield, respectively] in which cyclisation of the intermediates (8a—c) had taken place. Structures (10) were proved by the n.m.r. spectra (see below) (Table 2), together with the i.r. spectra [saturated ν(C=O) at 1 720—1 730 cm^{-1}] and elemental analysis. The reaction with the pyrimidinyl dimer (16b) also yielded 14% of the *exo*-adduct (22b), in which cyclisation of the type (7)→(9) cannot occur. The poor yield obtained of (10c) is due to the addition of allyl alcohol to the triazinyl dimer (15c) to give (24c). Similar products have been obtained previously from the pyridyl dimer (15a).[4] Structure (24c) was proved by the n.m.r. and i.r. spectrum: the αβ-unsaturated carbonyl band of the dimer (16c) was lost, the new saturated ν(C=O) evidently overlapping with the other saturated ν(C=O). The ^1H n.m.r. spectrum showed the disappearance of the αβ-olefinic protons.

Further Transformations of Allyl Alcohol Tricycles.—The pyrimidinyl derivative (10b) reacted with phenylhydrazine to give the corresponding phenylhydrazone

TABLE 1

^1H N.m.r. data (100 MHz) for adducts by addition at the 2,6-positions of the pyridine ring [a]

(*a*) Chemical shifts

Proton	(17a) [b]	(18a) [c]	(19d) [b]	(20b) [b]	(21b) [b]	(22b) [b]	(23d) [b]	(37) [b]	(38) [c]	(40) [b]	(41) [b]	(42) [b]	(43) [b]
1	4.82 [g]	5.01 [g]	4.32 [h]	5.12 [g]	5.12 [g]	4.96 [g]	4.41 [h]	5.20 [h]	5.00 [g]	5.48 [g]	5.17 [g]	5.09 [g]	5.04 [h]
3	6.11 [h]	5.86 [h]	5.98 [h]	5.94 [h]	5.80 [g]	5.78 [h]	5.98 [h]	5.92 [h]	6.06 [h]	5.88 [h]	5.89 [h]	6.09 [h]	5.92 [h]
4	7.28 [h]	7.40 [j]	7.18 [h]	6.76 [h]	6.96 [h]	7.25 [h]	7.24 [h]	7.06 [h]	6.94 [h]	7.27 [h]	7.20 [h]	7.32 [h]	7.20 [h]
5	5.35 [k]	5.16 [k]	4.66 [k]	5.50 [k]	5.70 [k]	5.16 [g]	4.75 [g]	5.31 [g]	5.63 [k]	5.12 [g]	5.53 [g]	5.52 [k]	5.50 [k]
6	3.10 [l]	2.80 [j]	3.50 [m]	3.92 [l]	4.13 [l]	3.98 [n]	2.98 [j]	3.61 [h]	*o*	3.02 [h]	3.06 [h]	3.36 [m]	3.54 [j]
7-*exo*	2.78 [n]	2.56 [j]	2.70 [n]	2.92 [n]	2.86 [l]	2.20 [j]	2.84 [j]	2.76 [l]	*o*	2.74 [n]	2.79 [n]	2.90 [n]	2.70 [l]
7-*endo*	1.56 [h]	1.60 [h]	2.13 [h]	2.02 [h]	2.86 [l]	1.89 [h]	2.06 [h]	2.30 [j]	*o*	2.00 [h]	2.25 [j]	2.01 [h]	2.12 [h]
Aromatic		6.7—	7.5—	6.3—	6.3—	6.27 [i]	7.4—	6.3—	6.6—	6.27 [i]	6.38 [i]	6.38 [i]	6.38 [i]
		8.9 [l]	7.7 [l]	8.5 [l]	8.5 [l]		7.5 [j]	8.5 [l]	9.1 [l]				
CMe			1.45 [i]	2.25 [i]	2.25 [i]	2.20 [i]	1.45 [i]	2.22 [i]	2.25 [i]	2.25 [i]	2.25 [i]	2.25 [i]	2.27 [i]
CH_2	4.30 [h]	2.56 [j]				3.60 [h]							
	3.88 [h]	2.80 [j]				3.40 [h]							
OMe	2.15 [i]												3.68 [i]
$\overset{+}{N}$–Me									4.49 [i]				

Proton	(44) [b]	(45) [b]	(46) [b]	(47) [b]	(48) [b]	(49) [b]	(50) [d]	(51) [b]	(52) [b]	(53) [b]	(54) [b,e]	(55) [b,f]	
1	5.14 [h]	4.92 [g]	4.96 [g]	5.00 [g]	5.12 [h]	5.06 [h]	4.80 [h]	5.26 [i]	5.58 [g]	5.10 [j]	5.62 [i]	5.62 [i]	
3	5.89 [h]	6.05 [h]	6.07 [h]	5.98 [g]	6.08 [h]	5.99 [h]	5.83 [h]	5.88 [h]	5.90 [h]	5.89 [h]	5.50 [j]	5.66 [j]	
4	7.34 [h]	7.18 [h]	7.14 [h]	7.19 [h]	7.16 [h]	7.08 [h]	7.02 [h]	7.18 [h]	7.39 [h]	7.26 [h]	7.55 [j]	7.20—7.60 [j]	
5	5.55 [g]	5.41 [k]	5.57 [k]	5.60 [k]	5.76 [g]	5.42 [g]	5.35 [g]	5.58 [k]	5.45 [g]	5.22 [j]	5.71 [g]	5.83 [g]	
6	2.96 [j]	4.49 [n]	5.43 [n]	4.84 [j]				3.32 [g]	4.00 [i]	2.60 [l]			
7-*exo*	2.96 [j]	2.84 [m]	2.98 [m]	2.70 [l]	3.49 [h]	3.10 [h]	2.56 [h]		3.49 [g]	2.50 [l]			
7-*endo*	2.02 [h]	1.65 [h]	1.67 [h]	1.85 [j]	2.38 [g]	1.76 [g]	2.02 [j]	4.00 [i]					
Aromatic	6.38 [i]	6.36 [i]	6.39 [i]	6.32 [i]	6.40 [i]	6.38 [i]	6.29 [i]	6.38 [i]	6.36 [i]	6.32 [i]			
CMe	2.27 [i]	1.20 [p]	2.25 [i]	2.25 [i]	2.25 [i]	2.25 [i]	1.74 [i]	1.22 [k]	1.22 [k]	2.24 [i]	1.26 [k]	1.32 [k]	
		2.25 [i]				1.50 [i]	2.25 [i]	2.22 [i]	2.22 [i]				
CH_2		3.56 [k]						4.10 [p]	4.10 [p]	1.20—	4.24 [p]	4.29 [p]	
										2.00 [j]			
OMe	3.68 [i]		2.04 [i]				1.94 [i]						

(*b*) Coupling constants (Hz)

	(17a)	(18a)	(19d)	(20b)	(21b)	(22b)	(23d)	(37)	(38)	(40)	(41)	(42)	(43)
J(1,3)	1	1	2	1	0.5	2	2	1		1	1	1	2
J(1,7-*exo*)	8	7	7	8	8	10	8	8	8	5	8	8	8
J(3,4)	10	12	10	9	10	11	10	10	10	10	10	10	10
J(4,5)	5	5	5	6	6	5	5	5	5	8	5	6	5
J(5,6)	5	5	5	6	6				5			6	5
J(6,7-*exo*)	8	*o*	5	9	10	*o*	4	4	*o*	9	3	8	9
J(6,7-*endo*)	6	5	6	7	8	5	10	9	*o*	4	8	6	6
J(6,9A)	5	*o*				11							
J(6,9B)	10	*o*				8							
J(7-*exo*,7-*endo*)	14	13	14	14	16	10	14	14	*o*	15	14	14	14
J(9A,9B)	11	*o*				12							

	(44)	(45)	(46)	(47)	(48)	(49)	(51)	(51)	(52)	(53)	(54)	(55)
J(1,3)	2	2	1		1	1	2	1	1	1	1	1
J(1,7-*exo*)	8	8	9	7	8	8	9		5	6		
J(3,4)	10	10	10	10	10	10	10	10	10	10	10	10
J(4,5)	5	5	5	5	6	5	5	6	8	5	5	5
J(5,6)	5	5	5	5				6	0.5	5		
J(6,7-*exo*)	*o*	10	9	9						*o*		
J(6,7-*endo*)	9	5	4	6						*o*		
J(7-*exo*,7-*endo*)	14	14	14	14	14	14	14					
J(9A,9B)										*o*		

[a] In p.p.m. relative to $SiMe_4$ as internal standard. [b] In $CDCl_3$. [c] In $(CD_3)_2SO$. [d] In CCl_4. [e] Isomer, m.p. 155 °C. [f] Isomer m.p. 162 °C. [g] Doublet. [h] Double doublet. [i] Singlet. [j] Overlap with other signals. [k] Triplet. [l] Multiplet. [m] Double triplet. [n] Quartet of doublets. [o] Not measurable due to signal overlap. [p] Quartet.

TABLE 2

^{1}H N.m.r. data (100 MHz) for tricyclic adducts [a,b]

(*a*) Chemical shifts

Proton	(10a) [c]	(10b) [c]	(10c) [c,d]	(11a) [c]	(11b) [c]	(12b) [c,e]	(25) [f,g]	(26) [c,h]	(27) [c,i]
1	5.38 [l]	5.01 [l]	5.05 [l]	4.68 [l]	4.92 [l]	5.25 [m]	5.70 [l]	4.30 [l]	4.96 [n]
3	2.98 [o]	2.30 [m]	2.43 [p]	2.80 [m]	2.66 [o]		2.00—2.50 [m]	4.05 [l]	2.00 [m]
4	5.32 [m]	4.70 [r]	4.74 [r]	4.27 [q]	4.24 [q]	5.25 [m]	4.50 [s]	4.90 [n]	4.40 [m]
5	5.80 [n]	5.50 [n]	5.54 [n]	5.14 [n]	5.18 [n]	5.58 [n]	5.34 [n]	5.02 [n]	5.28 [n]
6	3.46 [s]	2.94 [s]	3.00 [s]	2.90 [m]	2.84 [m]	3.14 [s]	3.40—3.90 [m]	3.10 [m]	2.40—2.80 [m]
7-*exo*	2.98 [m]	2.50 [m]	2.50 [m]	2.12 [q]		2.60 [s]	2.88 [s]	2.70 [m]	2.40—2.80 [m]
7-*endo*	2.10 [l]	1.62 [q]	1.70 [q]	1.68 [l]	1.50 [l]	1.84 [l]	1.50 [q]	1.58 [m]	1.60 [s]
9-*exo*	4.20 [s]	3.92 [q]	3.70—4.20 [m]	3.40 [q]	3.30 [q]	4.24 [q]	3.40—3.90 [m]	3.50 [q]	3.67 [q]
9-*endo*	4.20 [s]	3.70 [q]	3.70—4.70 [m]	3.16 [q]	3.12 [q]	3.77 [q]	3.40—3.90 [m]	2.70 [m]	3.67 [q]

Proton	(28) [c]	(29) [c]	(30) [q]	(31) [q]	(32) [c,j]	(33) [c,k]	(35a) [c]	(35b) [c]	(36) [c]
1	5.00 [l]	5.65 [l]	5.49 [l]	5.64 [l]	6.00 [l]	5.43 [l]	5.40 [l]	5.08 [l]	5.00 [l]
3	2.20 [m]						3.02 [o]	2.40 [q]	2.75 [l]
4	4.74 [r]	5.04 [l]	4.84 [l]	4.89 [l]	6.53 [l]	6.47 [l]	5.68 [s]	5.22 [r]	6.00 [m]
5	5.50 [n]	5.84 [n]	5.65 [n]	5.84 [n]	5.62 [n]	5.56 [n]	6.10 [n]	5.78 [n]	6.00 [m]
6	2.94 [s]	3.00 [s]	3.00 [m]	2.90 [m]	3.30 [s]	3.12 [s]	3.74 [r]	3.14 [r]	4.50 [s]
7-*exo*	2.20 [m]	2.50 [m]	2.40 [m]	2.40 [m]	2.70 [r]	2.64 [s]	2.95 [m]	2.50 [m]	2.29 [m]
7-*endo*	1.68 [q]	1.66 [q]	1.50 [q]	1.49 [q]	1.95 [l]	1.82 [l]	2.34 [q]	1.98 [q]	1.86 [q]
9-*exo*	3.96 [q]	4.10 [q]	3.90 [q]	3.91 [q]	4.38 [n]	4.24 [n]			
9-*endo*	3.76 [q]	3.69 [q]	3.52 [q]	3.46 [q]	3.50 [q]	3.30 [q]			

(*b*) Coupling constants (Hz)

	(10a)	(10b)	(10c)	(11a)	(11b)	(12b)	(25)	(26)	(27)
J(1,7-*exo*)	9	7	8	8	8	6	8	5	8
J(3-*exo*,4)	*t*	2	*t*	6	5				
J(3-*endo*,4)	*t*	4	*t*	1	1				
J(4,5)	7	7	6	7	6	7	7	8	7
J(5,6)	7	7	6	7	6	7	7	8	7
J(6,7-*exo*)	*t*	6	*t*	6	*t*	*t*	*t*	*t*	*t*
J(6,7-*endo*)	1	2	2		1	1	2	1	2
J(6,9-*exo*)	*t*	5	*t*	4	2	7	4	4	3
J(6,9-*endo*)	*t*	1	*t*	4	5	4	1	*t*	*t*
J(7-*exo*,7-*endo*)	16	13	14	13	14	14	*t*	13	11
J(9-*exo*,9-*endo*)	*t*	10	*t*	10	12	10	12	10	12

	(28)	(29)	(30)	(31)	(32)	(33)	(35a)	(35b)	(36)
J(1,7-*exo*)	6	6	7	7	6	7	8	8	8
J(3-*exo*,4)	5						*t*	7	*t*
J(3-*endo*,4)							*t*	2	*t*
J(4,5)	7	7	8	8	6	6	8	7	*t*
J(5,6)	7	7	8	8	6	6	8	7	*t*
J(6,7-*exo*)	*t*	*t*	*t*	*t*	8	*t*	10	10	*t*
J(6,7-*endo*)	2	3	3	2	1	1	2	2	3
J(6.9-*exo*)	5	6	6	6	9	8			
J(6.9-*endo*)	2	2	3	3	4	4			
J(7-*exo*,7-*endo*)	13	14	14	14	14	14	16	14	14
J(9-*exo*,9-*endo*)	10	10	10	10	9	10			

[a] In p.p.m. relative to $SiMe_4$ as internal standard. [b] Numbering is non-systematic, for comparison only. [c] In $CDCl_3$. [d] OMe, 4.00 (footnote *p*). [e] C–C*H*$_3$, 2.27 (footnote *p*). [f] N*H*, 9.11 (footnote *p*). [g] In $(CD_3)_2SO$. [h] 2″-H,6″-H, 2.70 (footnote *m*); 3″-H,-5″-H, 3.10 (footnote *m*); CMe, 2.22 (footnote *p*). [i] 2-H, 4.40 (footnote *m*). [j] CMe, 2.20 (footnote *p*). [k] CMe, 2.15 (footnote *p*). [l] Doublet. [m] Overlapped with other signals. [n] Triplet. [o] Pseudo-singlet. [p] Singlet. [q] Double doublet. [r] Quartet of doublets. [s] Multiplet. [t] Not measurable owing to signal overlap.

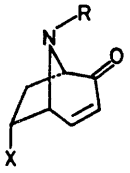
(25), but several attempts to achieve a Fischer indole synthesis [5] failed. Similarly, attempts at the Pfitzinger [6] and Friedlaender quinoline [7] synthesis failed. Cycloadduct (10b) condensed with benzaldehyde to the styryl derivative (12b) and with morpholine to form the enamine (26), which did not condense smoothly with methyl vinyl ketone. Borohydride reduction of (10b) gave the corresponding alcohol (27).

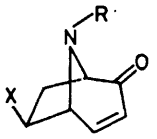
Under acidic conditions, bromination of (10b) occurred exclusively in the pyrimidine ring to give the *N*-(5-bromo-4,6-dimethylpyrimidin-2-yl) derivative (28). In pyridine solution, (10b) yielded the tribrominated compound (29) whereas the 2-pyridyl tricyclic adduct (10a) gave a mixture of the dibromo- (30) and tribromo- (31) compounds. The value of ν(C=O) in (29)—(31) was raised by the α-halogenation to 1 750—1 740 cm^{-1}.

Benzofuroxan reacted with (10b) to form the quinoxaline 1,4-dioxide (32) in an example of the ' Bierut reaction '.[8] The dioxide (32) was stereospecifically reduced by KBH_4 to the monoxide (33). Structures (32) and (33) were established by spectroscopic evidence: in the i.r. spectrum no ν(C=O) or ν(OH/NH) was present; the aromatic ring-stretch showed at 1 580 cm^{-1} and the *N*-oxide ν(N–O) at 1 360—1 370 cm^{-1} (*cf.* ref. 9). This last band was considerably weaker in (33) than in (32).

Allylamine and Derivatives.—Allylamine itself, under

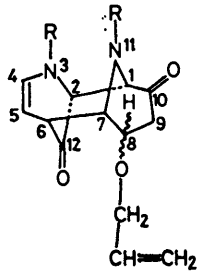
various conditions did not react with betaine (13b) but only with the dimer (16b) to give the dimer addition product (34), whereas with (13a) no homogeneous product





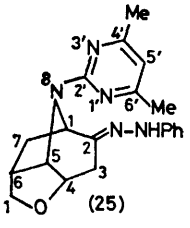
(17) X = CH_2OCOMe
(18) X = CH_2NHSO_2Ph
(19) X = CO_2Bu^t
(20) X = 4-Pyridyl
(21) X = 2-Pyridyl

(22) X = CH_2OH
(23) X = CO_2Bu^t



(24) a; R = 5-Nitro-2-pyridyl
b; R = 4,6-Dimethylpyrimidin-2-yl
c; R = 4,6-Dimethoxy-1,3,5-triazin-2-yl
d; R = 3-*p*-Bromophenyl-3-oxopropen-1-yl

could be isolated. However, the cyclised products (11a and b) were obtained in 22 and 68% yield by the reaction of *N*-allylbenzenesulphonamide with the betaines (13a and b), respectively: again structures are supported by



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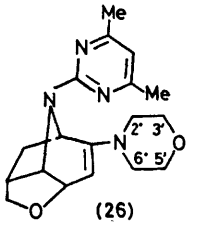

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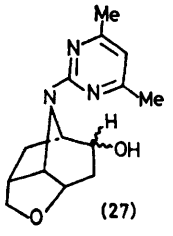

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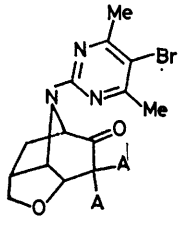
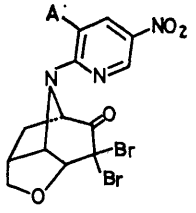


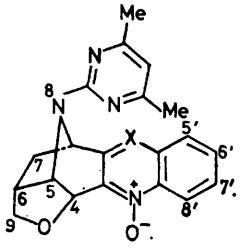
(28) A = H
(29) A = Br



(30) A = H
(31) A = Br

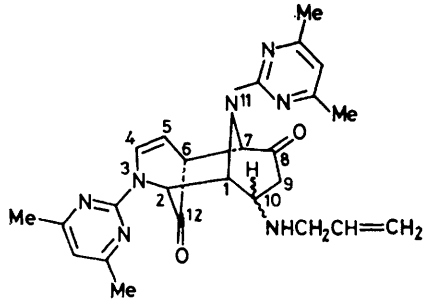
n.m.r. spectra (see below) and i.r. spectra [ν(C=O) in Nujol at 1 730 and 1 720 cm^{-1}]. The former reaction also afforded 20% of the uncyclised 6-*endo*-cycloadduct (18a). Surprisingly no cycloadducts were obtained from attempted reaction of *N*-alkylbenzenesulphonamide with (16c and d), nor from *N*-allylacetamide with (16a and b).

Acrylic Acid Derivatives.—Triethylammonium acrylate reacted with the pyridyl (13a) and pyrimidinyl (13b) betaines [but not with (16c or d)] forming the tricyclic



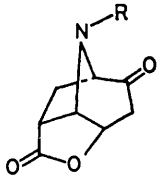
(32) X = $\overset{+}{N}\text{-}\bar{O}$
(33) X = N

products (35a and b) in 44 and 52% yield, respectively. The i.r. spectra of both products showed the lactone ν(C=O) at 1 770—1 780 and the ketone ν(C=O) at 1 720



(34)

cm^{-1}. The n.m.r. spectra are discussed below. Betaines (13c and d) failed to react with acrylic acid.

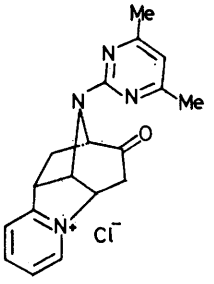


(35) a; R = 5-Nitro-2-pyridyl
b; R = 4,6-Dimethylpyrimidin-2-yl

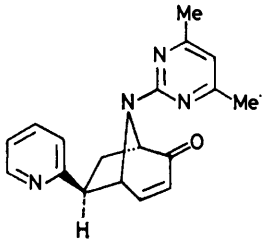
t-Butyl acrylate reacted with betaine (13d) to give a mixture of *endo*- (19d) and *exo*- (23d) adducts. It is interesting that the acrylate esters gave both stereoisomers, whereas from acrylic acid only products of the *endo*-addition were isolated.

Vinylpyridines.—Betaine (13b) reacted normally with 4-vinylpyridine to give the *endo*-adduct (20b); the corresponding adduct (21b) from 2-vinylpyridine formed a cation which cyclised spontaneously to give (36). A low yield of the 6-*exo*-adduct (37) was also isolated. Reaction of (36) with aqueous base regenerated (21b). Quaternisation of adduct (21b) with methyl iodide gave a quaternary salt (38) ($\overset{+}{N}$-*Me* at δ 4.49).

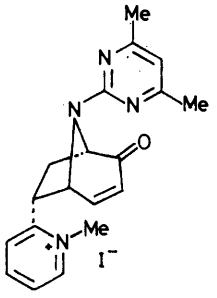
Hydrogen-1 *N.M.R. Spectra of Tricyclic Adducts* (*Table* 2).—The usual olefinic protons 3-H and 4-H were absent from the ^1H n.m.r. spectra of these compounds.



(36)

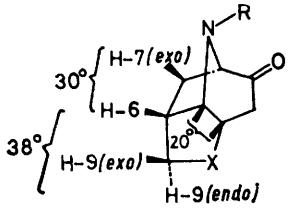


(37)



(38)

The ^1H n.m.r. spectra and decoupling experiments of the tricyclic compound (10b) are representative of this new class. Double irradiation at 5-H collapsed the 4-H multiplet at δ 4.70 into a broad singlet, and simplified the 6-H multiplet at δ 2.94. Protons 6-H, 9-*exo*-H, and 9-*endo*-H constitute an ABX spin system in which the coupling of 5.0 Hz between 6-H and 9-*exo*-H correlates with a dihedral angle (φ) of 38° between 6-*exo*-H and 7-H. The coupling of 7.0 Hz between 4-H and 5-H corresponds to a dihedral angle [10] of 20° [see (39)].



(39)

Other Cycloadditions at the 2,6-*Positions of the Pyrimidinyl Betaine* (13b).—Considerable further positive work is summarised in Table 3,[9] whereas attempted cycloadditions failed with the following dipolarophiles: phenyl isocyanate, phenyl isothiocyanate, benzalaniline, dicyclohexylcarbodi-imide, dihydropyran, allyl disulphide, and acrylamide.

The electron-rich dipolarophiles, ethyl vinyl ether, vinyl acetate, and *N*-vinylpyrrolidin-2-one yielded exclusively the 6-*endo*-isomers (45), (46), and (47), respectively. In the case of isopropenyl acetate, it was not possible to determine the stereochemistry of the acetate group of the single isomer (50). As expected, the electron-deficient dipolarophiles acrylonitrile and methyl acrylate produced the 6-*endo*–6-*exo*-mixtures of isomers (42–41) and (43–44) respectively. Both α-

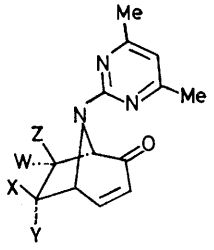
TABLE 3

Preparation of cycloadducts

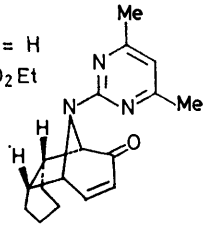
Cyclo-adduct	Dipolarophile	Solvent	Vol (ml)	Reaction time/d	Yield (%)	M.p. (°C)	Crystallisation solvent [a]	Analysis: Found C	H	N	Formula	Required C	H	N
(40)	Methyl vinyl ketone	MeCN	20	3	17	130—131	Et_2O–EtOH	66.3	6.4	15.4	$C_{15}H_{17}N_3O_2$	66.4	6.3	15.5
(41)	Acrylonitrile	MeCN	15	4	44	206—207	EtOH	66.1	5.8	22.2	$C_{14}H_{14}N_4O$	66.1	5.5	22.0
(42)	Acrylonitrile	MeCN	15	4	8	216—217	EtOH	66.1	5.7	22.3	$C_{14}H_{14}N_4O$	66.1	5.5	22.0
(43)	Methyl acrylate	MeCN	10	2	40	110—111	Et_2O–C_6H_{12}	63.0	6.2	14.4	$C_{15}H_{17}N_3O_3$	62.7	5.9	14.6
(44)	Methyl acrylate	MeCN	10	2	29	87—88	Et_2O–C_6H_{12}	62.9	6.3	14.5	$C_{15}H_{17}N_3O_3$	62.7	5.9	14.6
(45)	Ethyl vinyl ether [b]	1,2-dichloroethane	20	4	41	126—127	EtOH	65.9	7.0	15.5	$C_{15}H_{19}N_3O_2$	66.0	7.0	15.4
(46)	Vinyl acetate	EtOH	50	1	60	150—151	EtOH	62.8	6.1	14.5	$C_{15}H_{17}N_3O_3$	62.7	5.9	14.6
(47)	*N*-Vinylpyrrolidin-2-one			3	4	180—181	C_6H_{12}	65.2	6.6	17.7	$C_{17}H_{20}N_4O_2$	65.4	6.4	17.9
(48)	α-Chloroacrylonitrile	MeCN	15	5	41	151—152	EtOH	58.0	4.2	19.7	$C_{14}H_{13}ClN_4O$	58.2	4.5	19.4
(49)	α-Methylacrylonitrile	MeCN	15	2	34	186—187	EtOH	67.5	6.1	20.6	$C_{15}H_{16}N_4O$	67.2	6.0	20.9
(50)	Isopropenyl acetate [b]	EtOH	15	2	6	92—93	Et_2O–EtOH	63.4	6.4	13.6	$C_{16}H_{19}N_3O_3$	63.8	6.3	14.0
(51)	Diethyl maleate	MeCN	15	2	40	100—101	EtOH	61.3	6.2	11.0	$C_{19}H_{23}N_3O_5$	61.1	6.1	11.3
(52)	Diethyl maleate	MeCN	15	2	45	90—91	EtOH	61.0	6.2	11.1	$C_{19}H_{23}N_3O_5$	61.1	6.1	11.3
(53)	Cyclohexene [b]	EtOH	15	1	8	162—163	EtOH–Et_2O (1 : 10)	71.8	7.5	14.4	$C_{17}H_{21}N_3O$	72.1	7.4	14.8
(54)	Ethyl phenylpropiolate	Chlorobenzene	20	7	15	155—156	EtOH [c]	64.6	4.7	10.5	$C_{21}H_{17}N_3O_5$	64.5	4.3	10.7
(55)	Ethyl phenylpropiolate	Chlorobenzene	20	7	6	162—163	EtOH [c]	64.4	4.5	10.5	$C_{21}H_{17}N_3O_5$	64.5	4.3	10.7

[a] Prisms unless otherwise stated. [b] Under sealed tube conditions at 80 °C. [c] Plates.

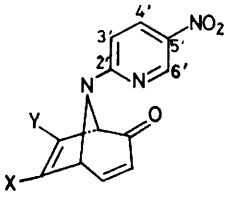
chloroacrylonitrile and α-methylacrylonitrile formed the single 6-C isomers (48) and (49) respectively of unknown stereochemistry. Methyl vinyl ketone yielded the single 6-*exo*-isomer (40). The reaction of diethyl maleate with



(40) X = COMe; W = Z = Y = H
(41) X = CN; W = Z = Y = H
(42) X = H; Y = CN; W = Z = H
(43) X = H; Y = CO_2Me; W = Z = H
(44) X = CO_2Me; W = Z = Y = H
(45) X = H; W = Z = H; Y = OEt
(46) X = H; W = Z = H; Y = OCOMe
(47) X = H; Y =  ; W = Z = H
(48) X, Y = Cl, CN; W = Z = H
(49) X, Y = Me, CN; W = Z = H
(50) X, Y = Me, OCOMe; W = Z = H
(51) X = H; Y = CO_2Et; Z = CO_2Et; W = H
(52) X = CO_2Et; Z = H; Y = H; W = CO_2Et



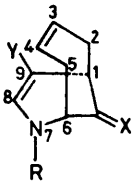
(53)



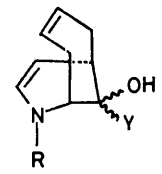
(54) and (55) X,Y = Ph, CO_2Et

the pyrimidinyl betaine, generated *in situ* with triethylamine, yielded the two *trans*-isomers (51) and (52). FMO calculations [9] predict the formation of the 6-*endo*,7-*endo*-bis(ethoxycarbonyl) adduct. Presumably base-catalysed isomerism [11] of the initially formed kinetically controlled *cis*-product produced the less strained *trans*-isomers. Cyclohexene yielded a single 6,7-*endo*-adduct (53), the formation of which attests to the high reactivity of the pyrimidinyl betaine. The acetylenic dipolarophile, ethyl phenyl propiolate readily produced the adducts (54) and (55), whose structures could not be differentiated by spectral means.

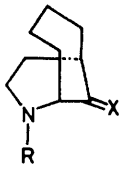
Adducts with Dienes.—Butadiene reacted across the 2,4-positions of betaines (13a and b) to give the expected adducts (56a and b); we have previously reported [12] the analogous reaction with (13c). Bromination of (56a and b) occurred exclusively at the enamine group to yield (57a and b) as shown by the n.m.r. spectra (see below) (Table 4). The pyrimidinyl adduct (56b) formed the oxime (58b), while the pyridyl adduct (56a) yielded the phenylhydrazone (59a). Reduction of (56b) with sodium borohydride gave the alcohol (60b) and with PhMgBr the alcohol (61b). Catalytic reduction of the adduct (56b) gave the saturated ketone (62b) which formed an oxime (63b) and was reduced to the alcohol (64b).



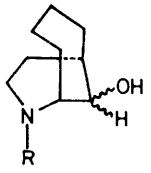
(56) X = O, Y = H
(57) X = O, Y = Br
(58) X = NOH, Y = H
(59) X = NNHPh, Y = H



(60) Y = H
(61) Y = Ph



(62) X = O
(63) X = NOH



(64)

a; R = 5-Nitro-2-pyridyl
b; R = 4,6-Dimethylpyrimidin-2-yl

EXPERIMENTAL

The melting points were determined on a Reichert apparatus. Spectra were recorded with a Perkin-Elmer 257 grating infrared spectrophotometer, a Unicam ultraviolet 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 a single spot on t.l.c. (Kieselgel GF 254, type 60), and Kieselgel PF 254 was used for the preparative t.l.c. operations.

9-(5-*Nitro*-2-*pyridyl*)-endo-5-*oxa*-9-*azatricyclo*[5.2.1.$0^{4,8}$]-*decan*-2-*one* (10a).—The dimer (15a) (1 g, 0.004 6 mol betaine) in allyl alcohol (20 ml) was heated under reflux for 2 d and the reaction monitored by t.l.c. ($CHCl_3$). Excess of allyl alcohol was removed *in vacuo*. The residue was chromatographed over aluminium oxide (BDH Alumina neutral, 60 g, toluene), followed by preparative t.l.c. ($CHCl_3$). The *decanone* (10a) (0.60 g, 48%), was obtained as yellow prisms, m.p. 217—218 °C (1,2-dichloroethane) (Found: C, 56.6; H, 4.8; N, 15.0. $C_{13}H_{13}N_3O_4$ requires C, 56.7; H, 4.7; N, 15.3%); $\nu_{max.}$ (Nujol) 1 720 cm^{-1} (saturated CO); $\lambda_{max.}$ ($CHCl_3$) 355 nm (log ε 368); *m/e* 275 (58%).

9-(4,6-*Dimethylpyrimidin*-2-*yl*)-endo-5-*oxa*-9-*azatricyclo*-[5.2.1.$0^{4,8}$]*decan*-2-*one* (10b).—A solution of the dimer (16b) (1 g, 0.005 mol betaine) in allyl alcohol (20 ml) was heated under reflux for 2 d. The excess of allyl alcohol was removed *in vacuo*. The residue was washed with light petroleum (b.p. 40—60 °C) (*ca.* 10 ml), and purified by t.l.c. on silica gel ($CHCl_3$) to give the *title compound* (10b) (1.1 g,

TABLE 4

^{1}H N.m.r. data (at 100 MHz) for butadiene adducts [a]

(*a*) Chemical shifts

Proton	(56a) [b]	(56b) [b]	(57a) [b]	(57b) [b]	(58b) [c]	(59a) [c]	(60b) [b]	(61b) [b]	(62b) [b]	(63b) [c]	(64b) [b]
1	3.22 [d]	3.28 [d]	3.46 [e]	3.24 [f]	3.38 [g]	3.40 [g]	3.06 [g]	2.80—3.10 [d]	2.80 [d]	3.30 [d]	3.18 [g]
2-*exo*	2.10 [g]	2.10 [g]	2.12 [g]	1.80—3.00 [d]	2.10—2.80 [d]	2.00—3.00 [d]	2.70 [d]	2.80—3.10 [d]	1.90 [d]	1.50—1.90 [d]	1.40—2.40 [d]
2-*endo*	3.10 [d]	3.28 [d]	3.04 [g]	1.80—3.00 [d]	2.10—2.80 [d]	2.00—3.00 [d]	2.70 [d]	2.80—3.10 [d]	1.90 [d]	1.50—1.90 [d]	1.40—2.40 [d]
3,4	5.72 [e]	5.72 [e]	5.86 [e]	5.68 [e]	5.64 [h]	5.50 [h]	5.48 [d]	5.56 [i]	1.58 [d]	1.50—1.90 [d]	1.40—2.40 [d]
5-*exo*	2.28 [d]	2.40 [d]	2.28 [g]	1.80—3.00 [d]	2.10—2.80 [d]	2.00—3.00 [d]	2.70 [d]	2.80—3.10 [d]	1.90 [d]	1.50—1.90 [d]	1.40—2.40 [d]
5-*endo*	2.40 [g]	2.40 [d]	2.84 [g]	1.80—3.00 [d]	2.10—2.80 [d]	2.00—3.00 [d]	2.70 [d]	2.80—3.10 [d]	1.90 [d]	1.50—1.90 [d]	1.40—2.40 [d]
6	5.05 [j]	5.19 [j]	5.06 [e]	5.06 [f]	5.00 [d]	5.14 [g]	4.80 [g]	5.24 [g]	5.30 [e]	5.05 [g]	5.20 [g]
8	7.16 [i]	7.72 [i]	7.58 [h]	7.98 [h]	6.49 [i] 7.28 [j]	7.10 [d]	7.67 [i]	7.65 [d]	4.42 [f] 3.66 [k]	2.50 [g]	4.50 [k] 3.28 [g]
9	4.87 [j]	4.62 [j]			5.00 [d]	4.86 [j]	4.62 [j]	4.45 [j]	2.80 [d]	1.50—1.90 [d]	1.40—2.40 [d]
10							4.43 [e]				4.06 [e]
3′	6.72 [i]		6.80 [i]			7.34 [i]					
4′	8.29 [j]		8.36 [j]			8.23 [i]					
5′		6.42 [h]		6.36 [h]	6.38 [h]		6.38 [h]	6.38 [h]	6.25 [h]	6.38 [h]	6.20 [h]
6′	9.10 [i]		9.12 [i]			8.96 [i]					
4′,6′ Me		2.28 [h]		2.20 [h]	2.20 [h]		2.29 [h]	2.30 [h]	2.24 [h]	2.20 [h]	2.25 [h]
Ph						7.05 [d]		7.20—7.60 [d]			
N*H*						9.18 [h]					
NO*H*					10.39 10.80 [h]					10.21 [h] 10.46 [h]	

(*b*) Coupling constants (Hz)

	(56a)	(56b)	(57a)	(57b)	(58b)	(59a)	(60b)	(61b)	(62b)	(63b)	(64b)
J(1,2-*exo*)			5	5	*l*	*l*	*l*	*l*	*l*	*l*	*l*
J(1,2-*endo*)	5	5	5	5	*l*	*l*	*l*	*l*	*l*	*l*	*l*
J(1,9)					4	6	6	5	*l*	*l*	*l*
J(1,6)	2	2	2	2				*l*	*l*		
J(1,10)							5	*l*	*l*		6
J(2-*exo*,2-*endo*)	16	16	*l*	*l*	*l*	*l*	*l*	*l*	*l*	*l*	*l*
J(2-*exo*,3)	3	5	5	5	*l*	*l*	*l*	*l*	*l*	*l*	*l*
J(2-*endo*,3)	3	5	5	5	*l*	*l*	*l*	*l*	*l*	*l*	*l*
J(3,4)	*l*	*l*	*l*	*l*	*l*	*l*	7	6	*l*	*l*	*l*
J(4,5-*exo*)	3	5	5	5	*l*	*l*	*l*	*l*	*l*	*l*	*l*
J(4,5-*endo*)	3	5	5	5	*l*	*l*	*l*	*l*	*l*	*l*	*l*
J(5-*exo*,5-*endo*)	14	*l*	*l*	*l*	*l*	*l*	*l*	*l*	*l*		*l*
J(5-*exo*,6)			5	5	*l*	*l*	*l*	*l*	5	*l*	*l*
J(5-*endo*,6)	6	*l*	5	5	*l*	*l*	*l*	*l*	5	*l*	
J(6,10)							5				6
J(8,9)	9	9			8	10	8	9	5, 7	*l*	
J(8A,8B)									14		14
J(3′,4′)	11		*l*	*l*		10					
J(4′,6′)	3		*l*	*l*		3					

[a] In p.p.m. relative to $SiMe_4$ as internal standard. [b] In $CDCl_3$. [c] In $(CD_3)_2SO$. [d] Overlapped with other signals. [e] Triplet. [f] Double triplet. [g] Multiplet. [h] Singlet. [i] Doublet. [j] Double doublet. [k] Quartet of doublets. [l] Not measurable owing to signal overlap.

85%) as prisms, m.p. 120—121 °C (EtOH) (Found: C, 64.4; H, 6.4; N, 15.9. $C_{14}H_{17}N_3O_2$ requires C, 64.9; H, 6.6; N, 16.2%); $\nu_{max.}$ (Nujol) 1 725 cm^{-1} (saturated CO); $\lambda_{max.}$ ($CHCl_3$) 293 (log ε 3.50) and 250 nm (4.10); *m/e* 259 (74%). The reaction also gave 8-(4,6-*dimethylpyrimidin*-2-*yl*)-6-exo-(*hydroxymethyl*)-8-*azabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (22b) (0.2 g, 14%) as a yellow gum which resisted recrystallisation (Found: C, 64.1; H, 7.0; N, 16.4. $C_{14}H_{17}N_3O_2$ requires C, 64.9; H, 6.6; N, 16.2%); $\nu_{max.}$ (Nujol) 1 680 cm^{-1} (αβ-unsaturated ketone CO); $\lambda_{max.}$ ($CHCl_3$) 251 (log ε 6.10) and 295 nm (5.49); *m/e* 259 (65%).

9-(4,6-*Dimethoxy*-s-*triazin*-2-*yl*)-endo-5-*oxa*-9-*azatricyclo*-[5.2.1.$0^{4,8}$]*decan*-2-*one* (10c).—A solution of the dimer (15c) (1 g, 0.004 2 mol betaine) in allyl alcohol (25 ml) was heated under reflux for 2 d and the reaction monitored by t.l.c. ($CHCl_3$). The reaction mixture was then evaporated *in vacuo* and washed with light petroleum (b.p. 40—60 °C) (3 × 5 ml). The residue was purified by preparative t.l.c. ($CHCl_3$) to yield the *title adduct* (10c) (122 mg, 10%) as needles, m.p. 120—121 °C (1,2-dichloroethane) (Found: C, 53.3; H, 5.3; N, 19.0. $C_{13}H_{16}N_4O_4$ requires C, 53.4; H, 5.5; N, 19.2%); $\nu_{max.}$ (Nujol) 1 730 (saturated CO), 1 590, 1 570, and 1 550 cm^{-1} (C–N); $\lambda_{max.}$ ($CHCl_3$) 247 nm (log ε 3.88); *m/e* 292 (43%).

5-*Benzenesulphonyl*-9-(5-*nitro*-2-*pyridyl*)-5,9-*diazatricyclo*-[5.2.1.$0^{4,8}$]*decan*-2-*one* (11a).—A solution of the dimer (15a) (0.5 g, 0.002 3 mol betaine) and allylbenzenesulphonamide (2.8 g, 0.014 2 mol) in toluene (5 ml) was heated under reflux for 2 d and the reaction monitored by t.l.c. ($CHCl_3$). The solvent was evaporated off *in vacuo*, and the brown residue, after treatment with light petroleum (b.p. 40—60 °C) (15 ml), was purified by preparative t.l.c. ($CHCl_3$) to give the pure *compound* (11a) (0.210 g, 22%) as yellow prisms, m.p. 198—199 °C (1,2-dichloroethane) (Found: C, 54.8; H, 4.4; N, 13.4; S, 7.6. $C_{19}H_{18}N_4O_5S$ requires C, 55.1; H, 4.3; N, 13.5; S, 7.7%); $\nu_{max.}$ (Nujol) 1 730 cm^{-1}

(saturated CO); $\lambda_{max.}$ ($CHCl_3$) 245 (log ε 3.74) and 352 nm (4.20); *m/e* 414 (10%). The reaction also gave 6-endo-(*N-benzenesulphonylaminomethyl*)-8-(*5-nitro-2-pyridyl*)-8-*azabicyclo*[3.2.1]*oct-3-en-2-one* (18a) (0.19 g, 20%) as yellow prisms, m.p. 207—208 °C (dichloroethane) (Found: C, 55.3; H, 4.5; N, 13.5; S, 7.7. $C_{19}H_{18}N_4O_5S$ requires C, 55.1; H, 4.3; N, 13.5; S, 7.7%); $\nu_{max.}$ (Nujol) 1 675 cm^{-1} (unsaturated CO); $\lambda_{max.}$ ($CHCl_3$) 245 (log ε 3.65) and 348 nm (4.04); *m/e* 414 (38%).

5-Benzenesulphonyl-9-(4,6-dimethylpyrimidin-2-yl)-5,9-diazatricyclo[5.2.1.$0^{4,8}$]*decan-2-one* (11b).—A solution of the dimer (16b) (0.5 g, 0.002 4 mol betaine) and allylbenzenesulphonamide (3.7 g, 0.018 7 mol) was refluxed in toluene (5 ml) for 2 d with monitoring by t.l.c. ($CHCl_3$). The toluene was removed *in vacuo*, and the semi-solid residue was treated with light petroleum (b.p. 40—60 °C) (20 ml) to remove the excess of dipolarophile. The crude product was purified by preparative t.l.c. ($CHCl_3$) to yield *compound* (11b) (0.65 g, 68%) as prisms, m.p. 212—213 °C (1,2-dichloroethane) (Found: C, 60.0; H, 5.9; N, 14.2; S, 8.2. $C_{20}H_{22}N_4O_3S$ requires C, 60.3; H, 5.5; N, 14.1; S, 8.0%); $\nu_{max.}$ (Nujol) 1 720 cm^{-1} (saturated CO); $\lambda_{max.}$ ($CHCl_3$) 248 (log ε 4.21) and 290 nm (3.66); *m/e* 398 (25%).

3-Benzylideno-9-(4,6-dimethylpyrimidin-2-yl)-5-oxa-9-azatricyclo[5.2.1.$0^{4,8}$]*decan-2-one* (12b).—A solution of benzaldehyde (0.3 g, 0.002 8 mol) in EtOH (5 ml) was added to a solution of compound (10b) (0.5 g, 0.001 9 mol) and KOH (0.4 g, 0.007 mol) in a mixture of EtOH (20 ml) and H_2O (5 ml). After stirring at room temperature for 2 h, the yellow precipitate was filtered off and purified by preparative t.l.c. ($CHCl_3$) to give the *derivative* (12b) (0.35 g, 53%), as yellow prisms, m.p. 135—136 °C (Et_2O) (Found: C, 72.3; H, 6.1; N, 12.0. $C_{21}H_{21}N_3O_2$ requires C, 72.6; H, 6.1; N, 12.1%); $\nu_{max.}$ (Nujol) 1 695 cm^{-1} (unsaturated CO); $\lambda_{max.}$ ($CHCl_3$) 250 (log ε 4.21) and 295 nm (4.25); *m/e* 347 (100%).

6-endo-(*Acetoxymethyl*)-8-(*5-nitro-2-pyridyl*)-8-*azabicyclo*-[3.2.1]*oct-3-en-2-one* (17a).—The dimer (15a) (1 g, 0.002 3 mol) in allyl acetate (25 ml) was heated under reflux for 2 d and the reaction monitored by t.l.c. ($CHCl_3$). Excess of dipolarophile was removed *in vacuo*, and the residue purified by preparative t.l.c. [EtOAc–$CHCl_3$ (1 : 1)]. The *title compound* (17a) (0.394 g, 27%) was isolated as yellow prisms, m.p. 145—147 °C [EtOH–cyclohexane (50 : 1)] (Found: C, 56.6; H, 4.6; N, 13.3. $C_{15}H_{15}N_3O_5$ requires C, 56.8; H, 4.7; N, 13.2%); $\nu_{max.}$ (Nujol) 1 740 (ester CO) and 1 670 cm^{-1} (unsaturated CO); $\lambda_{max.}$ ($CHCl_3$) 350 nm (log ε 3.92); *m/e* 317 (46%).

t-Butyl 8-(3-p-*Bromophenyl-3-oxopropen-1-yl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*oct-3-ene*-6-exo-*carboxylate* (23d) *and* -6-endo-*carboxylate* (19d).—A solution of the betaine (13d) (0.5 g, 0.001 6 mol) and t-butyl acrylate (3 ml) in MeCN (20 ml) was refluxed gently for 3 d. The reaction was monitored by t.l.c. [EtOAc–light petroleum (1 : 1)]. The mixture was concentrated *in vacuo* and the pure isomers were separated by preparative t.l.c. [EtOAc–light petroleum (b.p. 40—60 °C) (1 : 1)]. The endo-*isomer* (19d) (0.11 g, 16%) was isolated as pinkish prisms, m.p. 190—191 °C (Et_2O) (Found: C, 58.7; H, 5.4; N, 3.1; Br, 18.2. $C_{21}H_{22}BrNO_4$ requires C, 58.3; H, 5.1; N, 3.2; Br, 18.5%); $\nu_{max.}$ (Nujol) 1 730 (ester CO) and 1 690 cm^{-1} (unsaturated CO); $\lambda_{max.}$ ($CHCl_3$) 265 (log ε 4.27) and 334 nm (4.43); *m/e* 432 (11%). The exo-*isomer* (23d) (115 mg, 17%) was isolated as pinkish prisms, m.p. 165—166 °C (Et_2O) (Found: C, 58.6; H, 5.4; N, 3.2; Br, 18.6%); $\nu_{max.}$ (Nujol) 1 720 (ester CO) and 1 690 cm^{-1} (unsaturated CO); $\lambda_{max.}$ ($CHCl_3$) 265 (log ε 4.23) and 334 nm (4.41); *m/e* 432 (8%).

8-(4,6-Dimethylpyrimidin-2-yl)-6-endo-(4-pyridyl)-8-azabicyclo[3.2.1]*oct-3-en-2-one* (20b).—A solution of the salt (14b) (1 g, 0.004 2 mol), hydroquinone (200 mg), 4-vinylpyridine (5 ml), and Et_3N (4 ml) in MeCN (15 ml) was heated under reflux at 100 °C for 4 d. The mixture was concentrated *in vacuo* and filtered to remove precipitated Et_3N·HCl. The filtrate was evaporated to dryness *in vacuo* and the residue purified by preparative t.l.c. ($CHCl_3$). The *cycloadduct* (20b) (0.15 g, 12%) was isolated as prisms, m.p. 150 °C [EtOH–cyclohexane (1 : 1)] (Found: C, 70.4; H, 6.0; N, 18.2. $C_{18}H_{18}N_4O$ requires C, 70.6; H, 5.8; N, 18.3%); $\nu_{max.}$ (Nujol) 1 690 cm^{-1} (unsaturated CO); $\lambda_{max.}$ ($CHCl_3$) 254 (log ε 4.20) and 290 nm (3.59); *m/e* 306 (47%).

8-(4,6-Dimethylpyrimidin-2-yl)-6-endo-(2-pyridyl)-8-azabicyclo[3.2.1]*oct-3-en-2-one* (21b).—A mixture of the cycloadduct (36) (100 mg, 0.000 2 mol) in H_2O (5 ml) and KOH solution (200 mg, 0.003 5 mol in 5 ml water) was stirred at room temperature for 30 min. The precipitate was collected and washed with H_2O to give the *product* (21b) (55 mg, 90%) as prisms, m.p. 157—158 °C [EtOH–Et_2O (1 : 10)] (Found: C, 70.3; H, 6.0; N, 18.0. $C_{18}H_{18}N_4O$ requires C, 70.6; H, 5.9; N, 18.3%); $\nu_{max.}$ (Nujol) 1 685 cm^{-1} (unsaturated CO); $\lambda_{max.}$ ($CHCl_3$) 256 (log ε 4.20) and 293 nm (3.56); *m/e* 306 (55%).

Quaternization of Compound (21b).—A solution of (21b) (0.7 g, 0.002 2 mol) in EtOAc (50 ml) and MeI (25 ml) was refluxed for 7 d and the reaction monitored by t.l.c. ($CHCl_3$). When the starting material was consumed, the reaction mixture was evaporated *in vacuo* to give the *methiodide* (38) (0.6 g, 60%) as yellowish prisms, m.p. 172—173 °C (MeCN) (Found: C, 50.6; H, 4.8; N, 12.7; I, 28.2. $C_{19}H_{21}IN_4O$ requires C, 50.9; H, 4.7; N, 12.5; I, 28.3%); $\nu_{max.}$ (Nujol) 1 700 cm^{-1} (saturated CO); $\lambda_{max.}$ ($CHCl_3$) 248 nm (log ε 4.31).

8-Allyloxy-3,11-bis(4,6-dimethoxy-s-triazin-2-yl)-3,11-diazatricyclo[5.3.1.$1^{2,6}$]*dodecan-4-ene-10,12-dione* (24c).—Et_3N (1 ml) was added dropwise during 20 min to a well-stirred solution of salt (13c) (1 g, 0.003 7 mol) and allyl alcohol (1.6 g, 0.027 5 mol) in 1,2-dichloroethane (20 ml) at room temperature. After 2 h, the violet colour faded. The precipitated Et_3N·HCl was filtered off and the filtrate was concentrated *in vacuo*. The residue was purified by preparative t.l.c. [on silica gel ($CHCl_3$)] to yield the *cycloadduct* (24c) (0.486 g, 25%), as prisms, m.p. 185—186 °C [CH_2Cl_2–1,2-dichloroethane (1 : 2)] (Found: C, 52.0; H, 4.9; N, 21.2. $C_{23}H_{26}N_8O_7$ requires C, 52.5; H, 4.9; N, 21.3%); $\nu_{max.}$ (Nujol) 1 730 (saturated CO) and 1 550 cm^{-1} (C–N); $\lambda_{max.}$ ($CHCl_3$) 270 nm (log ε 4.2); *m/e* 526 (12%).

9-(4,6-Dimethylpyrimidin-2-yl)-5-oxa-9-azatricyclo-[5.2.1.$0^{4,8}$]*decan-2-one phenylhydrazone* (25).—Phenylhydrazine hydrochloride (0.7 g, 0.005 mol) and NaOAc (1 g, 0.001 2 mol) in H_2O (10 ml) were added to a well-stirred solution of the cycloadduct (10b) (0.4 g, 0.001 5 mol) in water (10 ml). After 2 h, the reaction mixture was diluted with H_2O (50 ml) and the precipitate collected by filtration. The crude product was washed with H_2O and crystallised from EtOH to give the *phenylhydrazone* (25) (0.5 g, 96%) as yellow prisms, m.p. 227—228 °C (Found: C, 68.4; H, 6.7; N, 19.7. $C_{20}H_{23}N_5O$ requires C, 68.7; H, 6.6; N, 20.0%); $\nu_{max.}$ (Nujol) 3 270 (NH) and 1 600 cm^{-1} (C–N); $\lambda_{max.}$ ($CHCl_3$) 348 nm (log ε 4.02); *m/e* 349 (100%).

9-(4,6-Dimethylpyrimidin-2-yl)-2-morpholino-5-oxa-9-azatricyclo[5.2.1.$0^{4,8}$]*decan-2-ene* (26).—A mixture of the cyclo-

adduct (10b) (1 g, 0.003 8 mol), toluene-*p*-sulphonic acid (0.65 g, 0.003 mol), morpholine (3.5 g, 0.04 mol), and molecular sieves (4 Å, 4 g) in toluene (15 ml) was heated under reflux at 100 °C. The reaction was monitored by t.l.c. ($CHCl_3$). When all the starting cycloadduct was consumed, the reaction was cooled to room temperature and filtered. The filtrate was evaporated to dryness and the residue was purified by preparative t.l.c. ($CHCl_3$) to give the *adduct* (26) (200 mg, 16%) as prisms, m.p. 132—133 °C (cyclohexane) (Found: C, 65.8; H, 7.5; N, 16.8. $C_{18}H_{24}N_4O_2$ requires C, 65.9; H, 7.3; N, 16.8%); $\nu_{max.}$ (Nujol) 1 620 cm^{-1} (C=C–N); $\lambda_{max.}$ ($CHCl_3$) 250 nm (log ε 4.02); *m/e* 328 (100%).

9-(4,6-*Dimethylpyrimidin*-2-*yl*)-5-*oxa*-9-*azatricyclo*-[5.2.1.$0^{4,8}$]*decan*-2-*ol* (27).—A solution of the cycloadduct (10b) (0.5 g, 0.001 9 mol) in MeOH (25 ml) was treated with a solution of $NaBH_4$ (50 mg, in 2 ml of 0.2N NaOH) and stirred at room temperature for 1 h. The mixture was evaporated to dryness and extracted with Et_2O (4 × 10 ml). The extract was purified by preparative t.l.c. ($CHCl_3$) to yield the *alcohol* (27) (0.4 g, 81%) as prisms, m.p. 90—91 °C (Et_2O) (Found: C, 64.2; H, 7.6; N, 15.9. $C_{14}H_{19}N_3O_2$ requires C, 64.4; H, 7.3; N, 16.1%); $\nu_{max.}$ (Nujol) 3 380 cm^{-1} (OH); $\lambda_{max.}$ ($CHCl_3$) 256 (log ε 4.08) and 306 nm (3.52); *m/e* 261 (57%).

9-(5-*Bromo*-4,6-*dimethylpyrimidin*-2-*yl*)-5-*oxa*-9-*azatricyclo*[5.2.1.$0^{4,8}$]*decan*-2-*one* (28).—A solution of bromine (182 mg, 0.001 1 mol) in AcOH (5 ml) was added dropwise to a well-stirred solution of compound (10b) (0.45 g, 0.001 7 mol) in AcOH (7.5 ml). After 1 h the solution was basified with NH_4OH and extracted with $CHCl_3$. The combined extracts when concentrated *in vacuo* gave the crude product which was purified by preparative t.l.c. ($CHCl_3$). The desired *product* (28) (0.3 g, 76%) was obtained as prisms, m.p. 95—96 °C [EtOH–Et_2O (1 : 10)] (Found: C, 49.7; H, 4.9; N, 12.3; Br, 23.5. $C_{14}H_{16}BrN_3O_2$ requires C, 49.7; H, 4.7; N, 12.4; Br, 23.6%); $\nu_{max.}$ (Nujol) 1 725 cm^{-1} (saturated CO); $\lambda_{max.}$ ($CHCl_3$) 257 nm (log ε 4.38); *m/e* 337 (22%) and 339 (22%).

9-(5-*Bromo*-4,6-*dimethylpyrimidin*-2-*yl*)-3,3-*dibromo*-5-*oxa*-9-*azatricyclo*[5.2.1.$0^{4,8}$]*decan*-2-*one* (29).—A solution of bromine (0.23 g, 0.001 4 mol) in pyridine (5 ml) was added dropwise during 1 h to a well-stirred solution of the cycloadduct (10b) (0.5 g, 0.001 9 mol) in pyridine (10 ml). The reaction mixture was evaporated to dryness *in vacuo* at 100 °C, and the residue obtained was treated with light petroleum (25 ml) (b.p. 40—60 °C) to remove unreacted bromine. The crude mixture was purified by preparative t.l.c. ($CHCl_3$) to give the *bromo-derivative* (29) (0.35 g, 37%) as prisms, m.p. 206—207 °C (1,2-dichloroethane) (Found: C, 33.7; H, 3.0; N, 8.3; Br, 48.4. $C_{14}H_{14}Br_3N_3O_2$ requires C, 33.9; H, 2.8; N, 8.5; Br, 48.4%); $\nu_{max.}$ (Nujol) 1 740 cm^{-1} (saturated CO); $\lambda_{max.}$ ($CHCl_3$) 253 nm (log ε 4.22).

3,3-*Dibromo*-9-(5-*nitro*-2-*pyridyl*)-5-*oxa*-9-*azatricyclo*-[5.2.1.$0^{4,8}$]*decan*-2-*one* (30) *and* 9-(3-*Bromo*-5-*nitro*-2-*pyridyl*)-3,3-*dibromo*-5-*oxa*-9-*azatricyclo*[5.2.1.$0^{4,8}$]*decan*-2-*one* (31).—Bromine was added dropwise to a solution of the cycloadduct (10a) (0.6 g, 0.002 1 mol) in pyridine (40 ml) until the colour of bromine remained. After stirring at room temperature for 1 h, pyridine was removed *in vacuo* at 100 °C, and the residue obtained was extracted with portions of 1,2-dichloroethane (2 × 10 ml). The crude extracts were purified by preparative t.l.c. ($CHCl_3$) to give the *dibromo-derivative* (30) (0.45 g, 51%), yellow prisms, m.p. 225—226 °C (1,2-dichloroethane) (Found: C, 34.1; H, 2.7; N, 9.8; Br, 38.0. $C_{12}H_{11}Br_2N_3O_4$ requires C, 34.2; H, 2.6; N, 10.0; Br, 38.0%); $\nu_{max.}$(Nujol) 1 750 cm^{-1} (saturated CO); $\lambda_{max.}$ ($CHCl_3$) 355 (log ε 4.31) nm. The *compound* (31) (0.117 g, 11%) was recrystallised from 1,2-dichloroethane as yellow prisms, m.p. 215—216 °C (Found: C, 28.7; H, 2.3; N, 8.3; Br, 47.9. $C_{12}H_{10}Br_3N_3O_4$ requires C, 28.8; H, 2.0; N, 8.4; Br, 48.0%); $\nu_{max.}$ (Nujol) 1 740 cm^{-1} (saturated CO); $\lambda_{max.}$ ($CHCl_3$) 355 nm (log ε 4.11).

Preparation of Compound (32).—A solution of the cycloadduct (10b) (0.5 g, 0.001 9 mol), benzofuroxan (0.6 g, 0.004 5 mol), and KOH (0.56 g, 0.01 mol) in EtOH (40 ml) was heated under reflux. When all the starting cycloadduct had been consumed (t.l.c., $CHCl_3$), the solution was cooled and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by preparative t.l.c. ($CHCl_3$). The pure *compound* (32) (150 mg, 20%) was obtained as orange prisms, m.p. 215—216 °C [EtOH–Et_2O (1 : 1)] (Found: C, 63.5; H, 5.3; N, 18.3. $C_{20}H_{19}N_5O_3$ requires C, 63.7; H, 5.0; N, 18.6%); $\nu_{max.}$ (Nujol) 1 570 and 1 370 cm^{-1} (N–O); $\lambda_{max.}$ ($CHCl_3$) 248 (log ε 3.82) and 270 nm (3.87); *m/e* 377 (8%).

Preparation of Compound (33).—Potassium borohydride (0.5 g, 0.006 mol) was added in small portions to a stirred solution of compound (32) (50 mg, 0.000 1 mol) and KOH (5 ml of 10% solution) in MeOH (10 ml). After 1 h, the reaction mixture was gently refluxed until no more colour fading was observed (orange to pale yellow). The reaction mixture was neutralised (glacial AcOH) and evaporated to dryness *in vacuo*. The residue was diluted with H_2O and extracted with $CHCl_3$ (2 × 10 ml). The $CHCl_3$ extracts were purified by preparative t.l.c. ($CHCl_3$) to give *compound* (33) (25 mg, 69%) as yellow prisms, m.p. 215—216 °C (Et_2O) (Found: C, 66.6; H, 5.3; N, 19.6. $C_{20}H_{19}N_5O_2$ requires C, 66.5; H, 5.3; N, 19.4%); $\nu_{max.}$ (Nujol) 1 580 and 1 360 (N–O) cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 253 nm (log ε 4.39); *m/e* 361 (68%).

10-*Allylamino*-3,11-*bis*(4,6-*dimethylpyrimidin*-2-*yl*)-3,11-*diazatricyclo*[5.3.1.$1^{2,6}$]*dodecan*-4-*ene*-8,12-*dione* (34).—A solution of the dimer (16b) (0.5 g, 0.001 2 mol), allylamine (15 ml), and toluene (10 ml) was heated under reflux at 100 °C for 2 d. The course of the reaction was monitored by t.l.c. (EtOAc). The reaction mixture was evaporated to dryness *in vacuo* and the residue purified by preparative t.l.c. on silica gel [EtOAc–$CHCl_3$ (1 : 1)]. The *title compound* (34) (0.247 g, 22%), was isolated as yellowish prisms, m.p. 150 °C [EtOH–Et_2O (2 : 1)] (Found: C, 65.5; H, 6.5; N, 21.0. $C_{25}H_{29}N_7O_2$ requires C, 65.4; H, 6.3; N, 21.4%); $\nu_{max.}$ (Nujol) 1 720 (saturated CO) and 1 640 cm^{-1} (C=C–N); $\lambda_{max.}$ ($CHCl_3$) 250 (log ε 4.33) and 278 nm (4.29); *m/e* 459 (29%).

9-(5-*Nitro*-2-*pyridyl*)-5-*oxa*-9-*azatricyclo*[5.2.1.$0^{4,8}$]*decane*-2,6-*dione* (35a).—A solution of the dimer (15a) (0.8 g, 0.003 8 mol betaine) and triethylammonium acrylate (2 g) in MeCN–H_2O (1 : 1) was refluxed for 7 d. The precipitate was collected and washed several times with MeCN (4 × 5 ml). The dark brown solid was recrystallised from MeCN–H_2O to give *compound* (35a) as brown prisms (0.48 g, 44%), m.p. 265—266 °C (Found: C, 53.7; H, 3.6; N, 14.3. $C_{13}H_{11}N_3O_5$ requires C, 54.0; H, 3.8; N, 14.5%); $\nu_{max.}$ (Nujol) 1 770 (lactone CO) and 1 720 cm^{-1} (saturated CO); *m/e* 289 (15%).

9-(4,6-*Dimethylpyrimidin*-2-*yl*)-5-*oxa*-9-*azatricyclo*-[5.2.1.$0^{4,8}$]*decane*-2,6-*dione* (35b).—A solution of the salt (13b) (1 g, 0.004 2 mol), triethylammonium acrylate (2 g), and Et_3N (10 ml) in MeCN (15 ml) was heated under reflux

for 2 d. The course of the reaction was followed by t.l.c. ($CHCl_3$). The reaction mixture was evaporated *in vacuo* and the residue treated with CH_2Cl_2. The precipitate was discarded and the filtrate was concentrated *in vacuo*. The concentrate was purified by preparative t.l.c. ($CHCl_3$) to give the *adduct* (35b) (0.6 g, 52%) as prisms, m.p. 136—137 °C (Et_2O) (Found: C, 61.4; H, 5.5; N, 15.0. $C_{14}H_{15}N_3O_3$ requires C, 61.5; H, 5.5; N, 15.4%); $\nu_{max.}$ (Nujol) 1 780 (lactone CO) and 1 720 cm^{-1} (saturated CO); $\lambda_{max.}$ ($CHCl_3$) 247 (log ε 4.31) and 287 nm (3.67); *m/e* 273 (45%).

Preparation of Cycloadducts (36) *and* (37).—A solution of the salt (13b) (0.9 g, 0.003 7 mol), hydroquinone (200 mg), water (1 ml), 2-vinylpyridine (5 ml), and Et_3N (4 ml), in MeCN (20 ml) was heated under reflux at 100 °C for 3 d. The course of the reaction was monitored by t.l.c. ($CHCl_3$). The reaction was cooled and the Et_3N·HCl removed. The filtrate was evaporated *in vacuo* and the brown gum was triturated with 1,2-dichloroethane (15 ml) and cooled (0 °C). The *cycloadduct* (36) was precipitated as prisms (0.7 g, 55%), m.p. 235—236 °C [1,2-dichloroethane–EtOH (10 : 1)] (Found: C, 62.8; H, 5.7; N, 16.1; Cl, 10.5. $C_{18}H_{19}ClN_4O$ requires C, 63.1; H, 5.5; N, 16.4; Cl, 10.4%); $\nu_{max.}$ (Nujol) 1 720 cm^{-1} (saturated CO); $\lambda_{max.}$ ($CHCl_3$) 246 (log ε 4.27) and 270 nm (log ε 4.11); *m/e* 342.5 (37%). The filtrate was evaporated to dryness and chromatographed (preparative t.l.c., $CHCl_3$) to give 8-(4,6-*dimethylpyrimidin*-2-*yl*)-6-exo-(2-*pyridyl*)-8-*azabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (37) (0.1 g, 9%) as yellowish prisms, m.p. 105—106 °C [Et_2O–EtOH (10 : 1)] (Found: C, 70.4; H, 6.0; N, 18.2. $C_{18}H_{18}N_4O$ requires C, 70.6; H, 5.9; N, 18.3%); $\nu_{max.}$ (Nujol) 1 680 cm^{-1} (unsaturated CO); $\lambda_{max.}$ ($CHCl_3$) 250 (log ε 4.28) and 293 nm (3.63); *m/e* 306 (40%).

7-(5-*Nitro*-2-*pyridyl*)-7-*azabicyclo*[4.3.1]*deca*-3,8-*dien*-10-*one* (56a).—A solution of the dimer (15a) (0.7 g, 0.001 6 mol betaine), hydroquinone (200 mg), and liquid butadiene (10 ml) in 1,2-dichloroethane (10 ml) was heated in a Carius tube for 4 d at 80 °C. The solvent was removed *in vacuo* and the residue extracted with benzene. The extract was purified by preparative t.l.c. ($CHCl_3$) to give the *adduct* (56a) (0.36 g, 83%) as yellow needles, m.p. 139—140 °C (EtOH) (Found: C, 61.8; H, 4.8; N, 15.4. $C_{14}H_{13}N_3O_3$ requires C, 61.9; H, 4.8; N, 15.5%); $\nu_{max.}$ (Nujol) 1 733 cm^{-1} (saturated CO); $\lambda_{max.}$ ($CHCl_3$) 386 nm (log ε 4.52); *m/e* 271 (40%).

7-(4,6-*Dimethylpyrimidin*-2-*yl*)-7-*azabicyclo*[4.3.1]*deca*-3,8-*dien*-10-*one* (56b).—A solution of the dimer (16b) (2.5 g, 0.006 mol betaine), hydroquinone (200 mg), and liquid butadiene (10 ml) in 1,2-dichloroethane (10 ml) was heated in a Carius tube for 3 d at 80 °C. The solvent was evaporated off *in vacuo* and the residue extracted with benzene. The extract was purified by preparative t.l.c. ($CHCl_3$) to give the *adduct* (56b) (0.94 g, 62%), as prisms, m.p. 100—101 °C (EtOH) (Found: C, 70.5; H, 6.7; N, 16.4. $C_{15}H_{17}N_3O$ requires C, 70.6; H, 6.7; N, 16.4%); $\nu_{max.}$ (Nujol) 1 725 cm^{-1} (saturated CO); $\lambda_{max.}$ ($CHCl_3$) 277 nm (log ε 4.50); *m/e* 255 (33%).

9-*Bromo*-7-(5-*nitro*-2-*pyridyl*)-7-*azabicyclo*[4.3.1]*deca*-3,8-*dien*-10-*one* (57a).—Bromine (0.05 g, 0.000 3 mol) in CH_2Cl_2 (5 ml) was added dropwise during 20 min to a well-stirred solution of the cycloadduct (56a) (160 mg, 0.000 6 mol) in a mixture of CH_2Cl_2 (5 ml) and CCl_4 (10 ml) at 0—5 °C. The precipitate was collected and purified by preparative t.l.c. ($CHCl_3$) to give the *bromo-derivative* (57a) (0.189 g, 91%) as yellow prisms, m.p. 143—144 °C [EtOH–CH_2Cl_2 (1 : 1)] (Found: C, 47.7; H, 3.6; N, 11.7; Br, 23.2. $C_{14}H_{12}BrN_3O_3$ requires C, 48.0; H, 3.5; N, 12.0; Br, 22.8%); $\nu_{max.}$ (Nujol) 1 725 cm^{-1} (saturated CO); $\lambda_{max.}$ ($CHCl_3$) 350 nm (log ε 3.92); *m/e* 349 (42%) and 351 (42%).

9-*Bromo*-7-(4,6-*dimethylpyrimidin*-2-*yl*)-7-*azabicyclo*[4.3.1]*deca*-3,8-*dien*-10-*one* (57b).—Bromine was added dropwise to a stirred solution of the cycloadduct (56b) (0.5 g, 0.001 9 mol) in CCl_4 (25 ml) at 0 °C until the bromine was no longer consumed (30 min). After 30 min, the yellow precipitate was filtered, washed with CCl_4, and purified by preparative t.l.c. ($CHCl_3$) to give the *bromo-derivative* (57b) (0.3 g, 47%), as prisms, m.p. 150—151 °C (EtOH) (Found: C, 53.5; H, 5.0; N, 12.3; Br, 23.6. $C_{15}H_{16}BrN_3O$ requires C, 53.7; H, 4.8; N, 12.5; Br, 24.0%); $\nu_{max.}$ (Nujol) 1 725 cm^{-1} (saturated CO); $\lambda_{max.}$ ($CHCl_3$) 287 nm (log ε 4.24); *m/e* 333 (21%) and 335 (21%).

7-(4,6-*Dimethylpyrimidin*-2-*yl*)-7-*azabicyclo*[4.3.1]*deca*-3,8-*dien*-10-*one Oxime* (58b).—A solution of the cycloadduct (56b) (0.5 g, 0.001 9 mol) in EtOH (75 ml) was mixed with hydroxylamine solution (1 g, 0.143 mol NH_2OH·HCl in 4 ml 10% NaOH) and heated under reflux for 2 h. The solution was concentrated *in vacuo* and extracted with $CHCl_3$ (2 × 10 ml). The crude product obtained was recrystallised from $CHCl_3$ to give the *oxime* (58b) (0.36 g, 70%) as prisms, m.p. 170—171 °C (Found: C, 65.5; H, 6.7; N, 20.7. $C_{15}H_{18}N_4O$ requires C, 65.6; H, 6.7; N, 20.8%); $\nu_{max.}$ (Nujol) 3 380 and 3 160 cm^{-1} (OH stretch); $\lambda_{max.}$ ($CHCl_3$) 246 nm (log ε 4.04); *m/e* 270 (55%).

7-(5-*Nitro*-2-*pyridyl*)-7-*azabicyclo*[4.3.1]*deca*-3,8-*dien*-10-*one Phenylhydrazone* (59a).—A solution of the cycloadduct (56a) (150 mg, 0.000 5 mol) in EtOH (20 ml) was mixed with a clear solution of $PhNHNH_2$·HCl (0.5 g, 0.003 mol) and NaOAc (1.0 g, 0.01 mol) in H_2O (25 ml). The precipitate formed after stirring the mixture for 1 h at room temperature was collected and washed with H_2O to give the crude *phenylhydrazone* (59a) (174 mg, 96%), as yellow prisms, m.p. 197—198 °C (EtOH) (Found: C, 66.3; H, 5.1. $C_{20}H_{19}N_5O_2$ requires C, 66.5; H, 5.3%); $\nu_{max.}$ (Nujol) 3 350 (NH) and 1 600 cm^{-1} (C–N); $\lambda_{max.}$ ($CHCl_3$) 345 nm (log ε 3.70); *m/e* 361 (16%).

7-(4,6-*Dimethylpyrimidin*-2-*yl*)-7-*azabicyclo*[4.3.1]*deca*-3,8-*dien*-10-*ol* (60b).—(*a*) A solution of $NaBH_4$ (30 mg) in NaOH solution (20 ml, 0.2N) was added dropwise to a solution of the cycloadduct (56b) (0.5 g, 0.001 9 mol) in MeOH (25 ml). The reaction mixture was stirred at room temperature for 15 min and then evaporated to dryness. The residue was extracted with Et_2O (3 × 5 ml) to give the *alcohol* (60b) (0.3 g, 61%) as prisms, m.p. 149—150 °C (EtOH) (Found: C, 69.9; H, 7.5; N, 16.2. $C_{15}H_{19}N_3O$ requires C, 70.0; H, 7.4; N, 16.4%); $\nu_{max.}$ (Nujol) 3 330 cm^{-1} (OH); $\lambda_{max.}$ ($CHCl_3$) 279 nm (log ε 4.32); *m/e* 257 (48%).

(*b*) A solution of the cycloadduct (56b) (0.5 g, 0.001 9 mol) and NaOH (5 g) in a mixture of EtOH (40 ml) and H_2O (25 ml) was heated under reflux until the cycloadduct was completely consumed (t.l.c., $CHCl_3$). The solution was then neutralised with glacial AcOH and extracted with $CHCl_3$ (2 × 10 ml). The $CHCl_3$ extracts were evaporated to dryness *in vacuo* and the crude product purified by preparative t.l.c. ($CHCl_3$) to give the *alcohol* (60b) (0.3 g, 61%) as prisms, m.p. 149—150 °C (EtOH).

7-(4,6-*Dimethylpyrimidin*-2-*yl*)-10-*phenyl*-7-*azabicyclo*[4.3.1]*deca*-3,8-*dien*-10-*ol* (61b).—A mixture of a few crystals of iodine and magnesium powder (190 mg, 0.007 9 mol) in anhydrous Et_2O was heated under reflux. Dry bromo-

benzene (1.23 g, 0.007 8 mol) was added dropwise during 1 h. Then a solution of the cycloadduct (56b) (1 g, 0.003 9 mol) in Et_2O (10 ml) was added dropwise. The reaction mixture was heated under reflux for a further 30 min. Ice (10 g) was added to the cooled reaction mixture. The precipitate was removed by filtration and the filtrate extracted with $CHCl_3$. The extract was purified by t.l.c. ($CHCl_3$) to give the *alcohol* (61b) (1 g, 77%) as needles, m.p. 145—146 °C (EtOH) (Found: C, 75.2; H, 7.1; N, 12.6. $C_{21}H_{23}N_3O$ requires C, 75.1; H, 7.0; N, 12.6%); $\nu_{max.}$ (Nujol) 3 330 cm^{-1} (OH stretch); $\lambda_{max.}$ ($CHCl_3$) 279 nm (log ε 4.49); *m/e* 333 (94%).

7-(4,6-*Dimethylpyrimidin*-2-*yl*)-7-*azabicyclo*[4.3.1]*decan*-10-*one* (62b).—A solution of the cycloadduct (56b) (0.5 g, 0.001 9 mol) in EtOH (200 ml) was hydrogenated over palladium–charcoal (100 mg) under 30 lb in^{-2} hydrogen pressure at room temperature for 2 days. The course of the reaction was followed by t.l.c. ($CHCl_3$). On complete hydrogenation, the catalyst was filtered off and the filtrate evaporated *in vacuo*. The residue was purified by preparative t.l.c. ($CHCl_3$) to give the *adduct* (62b) (0.36 g, 73%) as prisms, m.p. 89—90 °C (EtOH) (Found: C, 69.4; H, 8.2; N, 16.1. $C_{15}H_{21}N_3O$ requires C, 69.5; H, 8.1; N, 16.2%); $\nu_{max.}$ (Nujol) 1 711 cm^{-1} (saturated CO); $\lambda_{max.}$ ($CHCl_3$) 275 nm (log ε 3.63); *m/e* 259 (65%).

7-(4,6-*Dimethylpyrimidin*-2-*yl*)-7-*azabicyclo*[4.3.1]*decan*-10-*one Oxime* (63b).—A solution of compound (62b) (0.5 g, 0.001 9 mol) in EtOH (50 ml) was mixed with a solution of $NH_2OH{\cdot}HCl$ (1 g, 0.001 4 mol) and NaOAc (2 g, 0.23 mol) in H_2O (25 ml). The reaction mixture was heated under reflux for 2 h. Then the solution was concentrated *in vacuo* and extracted with $CHCl_3$ (2 × 10 ml) to give the *oxime* (63b) (0.35 g, 68%) as prisms, m.p. 170—171 °C (EtOH) (Found: C, 65.4; H, 8.4; N, 20.5. $C_{15}H_{22}N_4O$ requires C, 65.7; H, 8.0; N, 20.4%); $\nu_{max.}$ (Nujol) 3 280 and 3 360 cm^{-1} (OH stretch); $\lambda_{max.}$ ($CHCl_3$) 246 nm (log ε 4.15); *m/e* 274 (50%).

7-(4,6-*Dimethylpyrimidin*-2-*yl*)-7-*azabicyclo*[4.3.1]*decan*-10-*ol* (64b).—An ethanolic solution of compound (62b) (0.5 g, 0.001 9 mol in 50 ml EtOH) was mixed with NaOH solution (3 g, in 25 ml H_2O) and heated under reflux at 100 °C. The course of the reaction was followed by t.l.c. ($CHCl_3$) and when all the starting material was consumed the reaction mixture was neutralised (dilute HCl) and extracted with $CHCl_3$ (2 × 10 ml). The crude product obtained from the $CHCl_3$ extracts was purified by preparative t.l.c. ($CHCl_3$) to give the *alcohol* (64b) (0.3 g, 60%) as prisms, m.p. 139—140 °C [EtOH–Et_2O (1 : 1)] (Found: C, 66.7; H, 9.0; N, 13.6. $C_{15}H_{23}N_3O$ requires C, 66.9; H, 8.9; N, 13.8%); $\nu_{max.}$ (Nujol) 3 280 cm^{-1} (OH stretch); $\lambda_{max.}$ ($CHCl_3$) 255 nm (log ε 3.95); *m/e* 261 (98%).

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