1,3-Dipolar Character of Six-membered Aromatic Rings. Part 51.[1] Cycloadditions of 1-(β-Benzoylvinyl)-3-oxidopyridiniums and Subsequent Transformations

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β-*p*-Chloro-, β-*p*-bromo-, and β-2-chloro-5-nitrobenzoyl-vinyl chloride react with 3-hydroxypyridine to give quaternary salts which with base give the corresponding betaines. These betaines undergo thermal dimerisation and cycloadditions with mono- and di-enes at the 2,6- and 2,4-positions, respectively. The site-, regio-, and stereo-selectivity of these cycloadditions are discussed with reference to MO predictions. The β-aroylvinyl substituents in the adducts can be hydrolytically removed.

A MAJOR aim of the present series of papers has been to find an *N*-substituent derived from readily available starting materials, easily placed at the *N*-atom of the 3-oxidopyridinium ring, highly activating towards cycloadditions, and finally easily removed. 4,6-Dimethoxy-1,3,5-triazin-2-yl [2] was up until now the *N*-substituent most nearly meeting the above criteria. We now report β-aroylvinyl as a substituent which approaches the ideal and moreover shows a minimum of steric hindrance.

RESULTS AND DISCUSSION

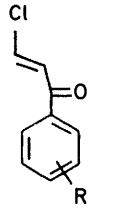
3-Hydroxypyridine is readily quaternised by *trans*-(4-chlorophenyl)- (1),[3a] *trans*-(4-bromophenyl)- (2),[3b] and *trans*-(2-chloro-5-nitrophenyl)-3-chloroprop-2-en-1-one (3) [3c] to yield the corresponding quaternary salts (4), (5), and (6), respectively, in quantitative yields. 3-Hydroxy-6-methylpyridine was also successfully quaternised using *trans*-(4-bromophenyl)-3-chloroprop-2-en-1-one (2) to yield the corresponding salt (7) but in only 65% yield, which probably reflects steric hindrance by the 6-methyl group. In the i.r. spectra, the salts (4)—(7) all displayed the characteristic H-bonded phenolic ν(O–H) at 2 500 and vinyl ν(C=O) at 1 650 cm^{-1}. Their ^{1}H n.m.r. spectra (Table 1) revealed multiplets for pyridine ring protons at δ 8.80, phenyl protons at δ *ca.* 7.50 and 8.05, and vinylic protons at δ 8.20.

TABLE 1

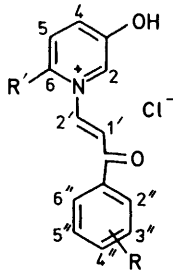
^{1}H N.m.r. spectra of salts [a,b]

Hydrogen	Salt (4)	(5)	(6)	(7)
(*a*) Chemical shifts (δ)				
2	8.92 [c]	9.08 [c]	8.96 [c]	7.75 [c]
4	8.20 [d]	8.40 [d]	8.40 [d]	7.75 [e]
5	8.10 [f]	8.15 [f]	8.30 [f]	8.15 [e]
6	9.00 [d]	9.20 [d]	9.02 [d]	
1′,2′	8.20 [d]	8.40 [d]	8.30 [d]	8.15 [d]
2″	7.50 [d]	7.80 [d]		7.75 [e]
3″	8.05 [d]	8.14 [d]	7.80 [d]	8.15 [e]
6″	7.50 [d]	7.80 [d]	8.56 [c]	7.75 [e]
Me				2.70 [c]
(*b*) Coupling constants (Hz)				
	(4)	(5)	(6)	(7)
$J_{2,4}$				2.0
$J_{4,5}$				
$J_{5,4}$				
$J_{2,6}$	1.5	2.0	2.0	
$J_{1',2'}$				
$J_{2'',3''}$	8.0	8.0		

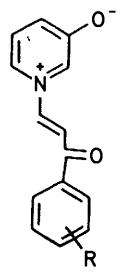
[a] $SiMe_4$ as internal standard. [b] In $(CD_3)_2SO$. [c] Singlet. [d] Doublet. [e] Multiplet. [f] Double doublet.



(1) R = 4-Cl
(2) R = 4-Br
(3) R = 2-Cl, 5-NO_2



(4) R = 4-Cl, R′ = H
(5) R = 4-Br, R′ = H
(6) R = 2-Cl, 5-NO_2, R′ = H
(7) R = 4-Br, R′ = Me



(8) R = 4-Cl
(9) R = 4-Br

Trimethylamine converted the salts (4) or (5) into the corresponding bright orange betaines (8) and (9) respectively (loss of 2 500 cm^{-1} absorption). These betaines are of low solubility, which hindered u.v. and ^{1}H n.m.r. studies. On keeping suspensions in acetonitrile at 20 °C for 12 h, the betaines undergo internal cycloadditions to the corresponding pale yellow thermal dimers (10) and (11). However, salts (6) and (7) with triethylamine in acetonitrile (or sodium hydrogencarbonate in water) give the corresponding thermal dimers (12) and (13) directly; that the corresponding betaines could not be isolated is probably due to their higher solubility which allows facile dimerisation. The

i.r. spectra of the thermal dimers each displayed characteristic [2] ν(C=O) at 1 720 and 1 680 cm^{-1} for the bicyclic ring system together with bands characteristic of the particular *N*-substituent.

^1H N.m.r. (Table 2) clearly confirmed the dimer

TABLE 2

^1H N.m.r. of the thermal dimers [a,b]

(*a*) Chemical shift (δ)

H	(10)	(11)	(13)
1	5.20 [c]	5.00 [c]	5.35 [d]
2	5.20 [c]	5.00 [c]	4.50 [d]
4	7.15 [d]	7.50 [d]	
5	5.20 [c]	5.00 [c]	4.95 [d]
6	3.25 [e]	3.30 [e]	3.05 [d]
7	5.20 [c]	5.00 [c]	
8	6.90 [f]	7.00 [f]	7.05 [d]
9	6.20 [e]	6.30 [e]	6.25 [d]
2′	7.80 [c]	7.70 [c]	7.70 [e]
1′	6.20 [d]	6.50 [d]	6.45 [d]
	6.40 [d]	6.30 [d]	6.00 [d]
2″,6″	7.80 [c]	7.70 [c]	7.70 [e]
3,5″	7.80 [c]	7.70 [c]	7.70 [e]
Me			1.80 [g]
			2.00 [g]

(*b*) Coupling constants (Hz)

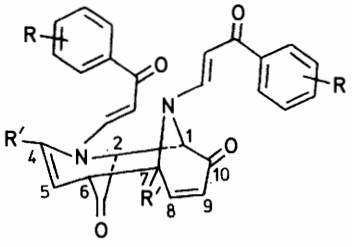
	(10)	(11)	(13)/(14)
$J_{1,2}$			2.0
$J_{2,6}$			2.0
$J_{6,5}$	6.0	6.0	8.0
$J_{8,9}$	8.0	8.0	10.0
$J_{4,5}$	8.0	8.0	
$J_{7,8}$	6.0	6.0	
$J_{1',2'}$	12.0	12.0	12.0

[a] $SiMe_4$ as internal standard. [b] In $(CD_3)_2SO$. [c] Overlapped with other signals. [d] Doublet. [e] Multiplet. [f] Double doublet. [g] Singlet.

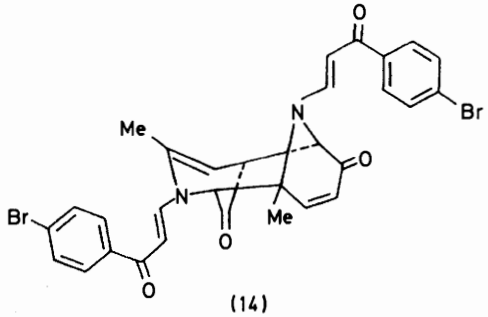
structure [2] but low solubility of dimers (10), (11), and (12) prevented the use of ^1H n.m.r. in the assignment of the regiochemistry. However, dimer (13) in $CDCl_3$ displays a clear ^1H n.m.r. spectrum; the doublet at δ 7.05 ($J_{8,9}$ 10.0 Hz) is assigned to 8-H because irradiation at δ 7.05 simplified the 9-H pattern (at δ 6.25) from a doublet to a singlet. The 5-H shows a broad doublet at δ 4.95 ($J_{5,6}$ 8.0 Hz), irradiation of which simplified the pattern of 6-H at δ 3.05. Irradiation at 6-H allowed identification of 2-H at δ 4.50 ($J_{2,6}$ 2.0 Hz) and 1-H at δ 5.35 ($J_{1,2}$ 2.0 Hz). The methyl groups appeared as singlets at δ 1.80 and 2.00. The chemical shift of 6-H (the bridgehead proton not α to a nitrogen atom) occurs at higher field than those of the other three bridgehead protons; this supports the *syn*-structure (13) against the *anti*-form (14). The 2-H–6-H coupling of 2.0 Hz demonstrates the *exo*-configuration for only here is the four-bond system connecting the two protons 2-H and 6-H close to the planar configuration necessary for W-type coupling; the system deviates sharply from coplanarity in the *endo*-form.

Thermal dimerisation of *N*-substituted-3-oxidopyridinium betaines is a function of the electronic nature of the *N*-substituent.[4] In terms of PMO—FMO theory, the activation of a betaine by the *N*-substituent mainly results from lowering of the LUMO energy while the HOMO energy level is largely maintained. Recent CNDO/2 energy and coefficient calculations [5] on 3-oxido-*N*-vinylformylpyridinium betaine showed that betaines (4)—(6) are of the same order of reactivity as the triazinyl betaines,[2] the most reactive of those previously studied. The thermal dimerisation can be considered as a concerted suprafacial $_\pi2 + _\pi4$ (or $_\pi4 + _\pi6$) addition between two molecules of the betaine. It should give the *syn*-dimer [as observed for (13)], since bonding at sites of largest coefficients (C-2 to C-2′ and C-4 to C-6′) gives rise to a larger stabilisation energy for the *syn*-transition state.[5] The *exo*-stereochemistry of (13) and of other thermal dimers is ascribed to a less crowded transition state as compared to that for *endo*-addition.[5]

Cycloaddition to 2π Electron Addends.—(i) *Olefinic dipolarophiles.* Betaines (4) and (6) are trapped by various dipolarophiles. These cycloadditions give good yields of the mixed *exo*- and *endo*-adducts with electron-deficient acrylic (15)—(22) and fumaric esters (28) and (29). With conjugated (styrene) [(23), (24)] and electron-rich (ethyl vinyl ether) (25) dipolarophiles only the



(10) R = 4-Cl, R′ = H
(11) R = 4-Br, R′ = H
(12) R = 2-Cl, 5-NO_2, R′ = H
(13) R = 4-Br, R′ = Me



(14)

endo-isomers were isolated, whilst with *N*-phenylmaleimide only the *exo*-adducts (26) and (27) were obtained.

In the ^1H n.m.r. studies (Table 3), 1-H and 5-H were used [2] as probes for the determination of the adduct configurations. *N*-Phenylmaleimide adducts (26) and (27) showed 1-H as a broadened singlet at δ *ca.* 5.00 and 5-H as a doublet at δ *ca.* 5.30, and both 6-H and 7-H gave doublets thus proving the *exo*-configuration. In the ^1H n.m.r. spectra of the acrylonitrile, methyl acrylate, styrene, and ethyl vinyl ether adducts (15)—(25), the 1-H signal appears as a doublet ($J_{1,7\text{-}exo}$ 8.0 Hz). The pattern for 5-H depends on the stereochemistry: it is a

TABLE 3

^{1}H N.m.r. of the 2,6-cycloadducts [a]

Hydrogen	(15) [b]	(16) [b]	(17) [b]	(18) [b]	(19) [b]	(20) [b]	(21) [b]	(22) [b]	(23) [b]	(24) [b]	(25) [b]	(26) [c]	(27) [c]	(28) [b]	(29) [b]	(30) [b]	(31) [b]	(36) [b]
(*a*) Chemical shifts (δ																		
1	4.32 *d*	4.44 *d*	4.38 *d*		4.32 *d*	4.42 *d*	4.25 *d*	4.38 *d*	4.35 *d*	4.40 d	4.24 *d*	5.06 *e*	4.64 *e*	4.90 *d*	4.60 *d*	5.20 *d*	5.00 *d*	4.64 *d*
2																		
3	6.15 *f*	5.92 *f*	5.95 *f*		6.02 *f*	5.98 *f*	5.98 *f*	5.96 *f*	5.95 *f*	6.05 *f*	6.10 *f*	6.05 *f*	5.92 *f*	6.19 *f*	6.00 *f*	5.82 *f*	5.52 *f*	6.20 *f*
			6.12 *e*															
4		7.12 *f*	6.90 *g*					7.20 *f*	6.69 *f*	6.78 *f*	7.12 *f*	7.12 *f*			7.20 *f*			7.12 *f*
5	4.70 *h*	4.72 *d*	4.70 *d*		4.70 *h*	4.82 *d*	4.70 *h*	4.80 *h*	4.59 *h*	4.66 *h*	4.64 *h*	5.28 *d*	4.82 *f*	5.04 *f*	4.80 *d*	5.80 *d*	5.08 *d*	4.84 *h*
6-*endo*		3.80 *f*	3.40 *g*			3.04 *f*		3.02 *f*						3.78 *d*	3.40 *d*			
6-*exo*	3.40 *g*		3.60 *g*				3.50 *i*		3.88 *j*	3.90 *j*	4.40 *j*							4.10 *g*
7-*endo*		2.45 *f*	2.50 *g*		2.18 *f*	2.16 *f*	2.10 *f*	2.10 *f*	2.00 *f*	2.04 *f*	1.62 *j*							
7-*exo*	2.94 *j*		2.80 *g*		2.76 *i*		2.72 *i*	2.80 *j*	2.84 *i*	2.86 *j*	2.80 *j*				4.00 *h*			3.60 *g*
1′	5.88 *d*	5.94 *d*	5.60 *d*		5.92 *d*	5.92 *d*	5.50 *d*	5.60 *d*	5.84 *d*	5.52 *d*	5.88 *d*	6.34 *d*	5.62 *d*	6.12 *d*	5.52 *d*	6.20 *d*	5.60 *d*	6.08 *d*
2′	7.48 *d*	5.58 *d*	7.35 *d*		7.60 *d*	7.64 *d*	7.45 *d*	7.38 *d*	7.60 *d*	7.49 *d*	7.60 *d*	7.74 *d*	7.25 *d*	7.79 *d*	7.45 *d*	7.80 *d*		7.85 *d*
2″,6″	7.28 *d*	7.30 *d*			7.36 *d*	7.36 *d*			5.84 *d*		7.36 *d*	7.46 *d*		7.55 *d*				7.54 *d*
3″,5″	7.70 *d*	7.72 *d*			7.82 *d*	7.78 *e*			7.70 *d*		7.80 *d*	7.90 *d*		7.96 *d*				7.99 *d*
3″,4″			7.45 *i*												7.40 *g*			
6″			8.10 *e*				8.12 *e*	8.12 *e*		8.20 *e*			7.40 *e*		8.12 *e*		8.12 *e*	
Me					4.70 *e*	3.76 *e*	1.20 *h*	1.20 *h*			1.20 *h*			1.45 *h*	1.25 *h*	4.06 *e*	1.22 *h*	
CH_2							4.10 *f*	4.18 *f*			3.50 *f*			4.38 *f*	4.10 *f*		4.20 *f*	
Ph									7.10 *g*	7.20 *g*		7.40 *g*	7.30 *g*					
9																		5.96 *g*
8																		5.64 *g*
10-*exo*																		2.60 *g*
10-*endo*																		2.15 *g*
(*b*) Coupling constants (Hz)																		
	(15)	(16)	(17)	(18)	(19)	(20)	(21)	(22)	(23)	(24)	(25)	(26)	(27)	(28)	(29)	(30)	(31)	(36)
$J_{1,3}$	2.0	2.0			2.0	1.5	2.0	2.0	2.0	1.5	2.0	1.5	1.5	2.0	2.0	1.5	1.5	2.0
$J_{1,7\text{-}exo}$	8.0	8.0			8.0	8.0	8.0	8.0	8.0	8.0	8.0			8.0	8.0			8.0
$J_{3,4}$	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	10.0	10.0
$J_{4,5}$	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
$J_{5,6\text{-}exo}$	6.0				6.0	6.0	6.0	6.0	6.0	6.0	6.0							6.0
$J_{6,7\text{-}exo}$	10.0	8.0			10.0	8.0	10.0	8.0	10.0	10.0	10.0				8.0			8.0
$J_{6,7\text{-}endo}$		10.0			8.0	10.0	8.0	10.0	8.0	8.0	8.0							
$J_{7\text{-}exo,7\text{-}endo}$	14.0	14.0			14.0	14.0	14.0	14.0	14.0	14.0	14.0							
$J_{1',2'}$	12.0	12.0	12.0		12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0
$J_{2'',3''}$	8.0	8.0			8.0	8.0												

[a] $SiMe_4$ as internal standared. [b] In $CDCl_3$. [c] In $(CD_3)_2SO$. [d] Doublet. [e] Singlet. [f] Double doublet. [g] Multiplet. [h] Triplet. [i] Overlapped with other signals. [j] Quartet of doublets.

doublet ($J_{4,5}$ 6.0 Hz) for the *exo*-isomers (16), (18), (20), and (22), and a triplet ($J_{4,5} = J_{5,6\text{-}exo}$ 6.0 Hz) for the *endo*-isomers (15), (17), (19), (21), and (23)—(25). In the *exo*-isomers, 6-*endo*-H appears as a double doublet ($J_{6\text{-}endo,7\text{-}exo}$ 8.0, $J_{6\text{-}endo,7\text{-}endo}$ 10.0 Hz) while for the *endo*-isomers, 6-*exo*-H gave a double triplet because of significant additional coupling ($J_{5,6\text{-}exo}$ 6.0 Hz). In the spectra of all eleven adducts, 7-*exo*-H appears as a quartet of doublets and 7-*endo*-H as a double doublet. The above assignments were all confirmed by exhaustive double resonance.

The reaction of *N*-phenylmaleimide to form exclusively *exo*-adducts (26, 27) is contrary to the MO predictions for (2s + 4s) π processes which should proceed preferentially *via* the *endo*-transition state and it was found previously that the dinitrophenyl [6] and nitropyridyl [7] betaines do yield only the *endo*-adduct with *N*-phenylmaleimide. The long reaction time (2 d under reflux) in the preparation of (26) and (27) is suspected to isomerise the initially formed *endo*-adducts to more thermodynamically stable *exo*-adducts (*cf.* addition of furan to maleic anhydride [8]).

By contrast, ethyl vinyl ether and styrene gave exclusively the *endo*-adducts favoured by secondary orbital overlap [*cf.* (2s + 4s) π processes [8]]. Recent calculations [5] (utilising close models of the present betaine) have shown that the transition state leading to the *endo*-adduct is lower than its *exo*-counterpart by 0.25 and 0.61 eV, respectively (*cf.* styrene *exo*-approach 4.77 *vs. endo* 4.52 eV; ethyl vinyl ether *exo*-approach 3.94 *vs. endo* 3.33 eV).

The stereoselectivity is lost in the addition of the studied betaines (4) and (5) to acrylic esters and acrylonitrile, where weak secondary orbital overlap (favouring the *endo*-approach) is opposed to dipolar and steric interactions which would favour the *exo*-approach. Experimentally, most of these reactions gave the *endo*-adduct as the predominant isomer in qualitative agreement with the MO calculations [5] (methyl acrylate *endo*-addition 4.16 and *exo* 4.43 eV).

All the cycloadditions to monosubstituted dipolarophiles displayed high regioselectivity in the formation of the 6-substituted 2,6-adducts. MO calculations of the stabilisation energies of the transition states to the two possible regioisomers previously showed the 6-isomer to be the favoured [5] (*cf.* ethyl vinyl ether 6-*endo vs.* 7-*endo*, 3.33 *vs.* 4.48 eV; and 4.16 *vs.* 4.37 eV for the methyl acrylate isomers).

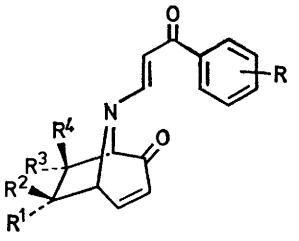
(ii) *Acetylenic dipolarophiles.* Dimethyl and diethyl acetylenedicarboxylate with betaines (4) and (5) yielded adducts (30) and (31); their structures were supported by the i.r. and ^{1}H n.m.r. spectra (Table 2).

Similar additions by dimethyl acetylenedicarboxylate and phenylacetylene to activated betaines [*e.g.* 1-(5-nitro-2-pyridyl)-3-oxidopyridinium] were previously observed [9] to give analogous adducts.

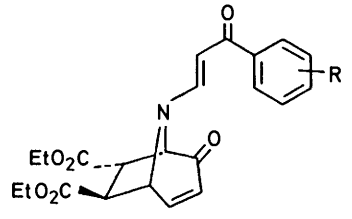
Cycloadditions to 4π-Electron Addends.—Cycloadditions of 2,3-dimethylbuta-1,3-diene across the 2,4-positions of the betaines (4), (6), and (7) gave exclusively the *endo*-isomers (32), (33), and (34). In contrast, cyclopentadiene on addition to betaine (4) gave the *exo*-2,4-adduct (35) together with the 2,6-adduct (36): the last resulting from the addition of cyclopentadiene as a 2π-system. It is now clear from the reactions of penta-1,3-diene [10] that the 2,4-addition of dienes yields initially the *exo*-isomer by kinetic control followed by

conformational isomerisation into the *endo*-isomer (*cf.* 2,3-dimethylbuta-1,3-diene adducts). It is only if such conformational isomerisation is prevented that the *exo*-isomer is isolated as for the addition of cyclopentadiene.

In the i.r. spectrum the 2,4-adducts display bands at 1 740 and 1 650 cm^{-1} characteristic of the bridgehead [2] and vinylic carbonyl [11] groups respectively. The ^1H n.m.r. spectra of these adducts (Table 4) show the characteristic low doublet for 8-H at δ *ca.* 4.84 [a singlet at δ 2.25 for the methyl group at C-8 in (34)], a double doublet for 9-H at δ 4.84 [a doublet at δ 4.65 for 9-H in

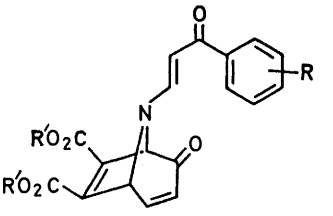


(15) R = 4-Cl, R^1 = CN, R^2 = R^3 = R^4 = H
(16) R = 4-Cl, R^1 = R^3 = R^4 = H, R^2 = CN
(17) R = 2-Cl,5-NO_2, R^1 = CN, R^2 = R^3 = R^4 = H
(18) R = 2-Cl,5-NO_2, R^1 = R^3 = R^4 = H, R^2 = CN
(19) R = 4-Cl, R^1 = CO_2Me, R^2 = R^3 = R^4 = H
(20) R = 4-Cl, R^1 = R^3 = R^4 = H, R^2 = CO_2Me
(21) R = 2-Cl,5-NO_2, R^1 = CO_2Et, R^2 = R^3 = R^4 = H
(22) R = 2-Cl,5-NO_2, R^1 = R^3 = R^4 = H, R^2 = CO_2Et
(23) R = 4-Cl, R^1 = Ph, R^2 = R^3 = R^4 = H
(24) R = 2-Cl,5-NO_2, R^1 = Ph, R^2 = R^3 = R^4 = H
(25) R = 4-Cl, R^1 = OEt, R^2 = R^3 = R^4 = H
(26) R = 4-Cl, R^1 = R^3 = H, R^2 – R^4 = CONPhCO
(27) R = 2-Cl,5-NO_2, R^1 = R^3 = H, R^2 – R^4 = CONPhCO

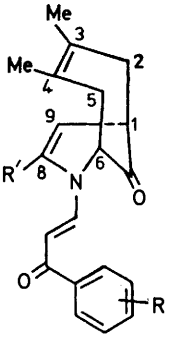


(28) R = 4-Cl
(29) R = 2-Cl,5-NO_2

(34)] and a doublet for 6-H at δ *ca.* 4.90. Double resonance techniques at 8-H, 9-H, and 6-H help assign 5-*endo*-H and 1-H at δ *ca.* 3.20 and 5-*exo*-H, 2-*exo*-H, and 2-*endo*-H at δ *ca.* 2.38 as a broad multiplet. The vinylic methyl groups appeared at δ *ca.* 1.80. The stereochemical integrity of these adducts was determined through the absence of coupling between 1-H and 2-*endo*-H or 6-H and 5-*endo*-H. It is only in the *endo*-structure (32)—(34) that the angle between 1-H and 2-*endo*-H ≈ that between 6-H and 5-*endo*-H ≈ 95° (no effective coupling) and the angle between 1-H and 2-*exo*-H = that between 6-H, and 5-*exo*-H ≈ 25° (little coupling). However in the *exo*-structures the corresponding angles



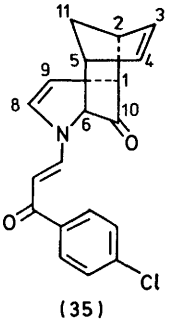
(30) R^1 = Me, R = 4-Cl
(31) R^1 = Et, R = 2-Cl,5-NO_2



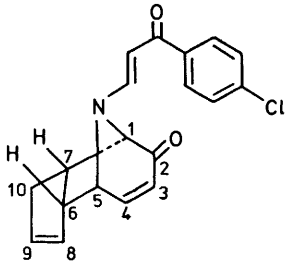
(32) R = 4-Cl, R^1 = H
(33) R = 2-Cl,5-NO_2, R^1 = H
(34) R = 4-Br, R^1 = Me

are 25 and 145° which would result in a large coupling constant for both the *exo*- and *endo*-protons.

The *exo*-configuration of the cyclopentadiene adduct (35) was established by the characteristic coupling between 1-H and 6-H with 5-H and 6-H respectively ($J_{5,6}$ 4.0 Hz), since in the corresponding *endo*-structure there should be no such coupling. The full structural assignment was supported by double resonance. Cycloaddition reactions of the betaine (8) with 1-acetoxybuta-1,3-diene and 1-(*NN*-dimethylamino)buta-1,3-diene were studied with the aim of forming adduct (37), a precursor to (39). However, unexpected products were isolated. The reaction with 1-acetoxybuta-1,3-diene yielded 4-chlorobenzophenone (40) which evidently arose by Diels–Alder addition of the diene to the *N*-substituent of the betaine (8), followed by elimination of acetic acid and 3-hydroxypyridine. By contrast, reaction of (8) with 1-(*NN*-dimethylamino)buta-1,3-diene



(35)



(36)

gave *trans*-1-(4-chlorophenyl)-3-(*NN*-dimethylamino)-prop-2-en-1-one probably by an addition–elimination reaction involving dimethylamine (from the diene) on the betaine.

Cycloadduct Transformations.—The transformation reactions of interest in our work were aimed at the synthesis of tropones and tropolones from the olefin cycloadducts, substituted pyridines from the keten cycloadducts, and heteroannulenes from the diene adducts.

Transformation reactions of 2,6-adducts. These transformations fall into two classes: (*i*) modification of the 2,6-adducts with the bridgehead nitrogen substituent, and (*ii*) removal of the *N*-substituent to obtain a free bridgehead nitrogen suitable for further modifications.

TABLE 4

^{1}H N.m.r. of the 2,4-cycloadducts [a]

(*a*) Chemical shift (δ)

H	(32) [b]	(33) [b]	(34) [b]	(35) [b]
1	3.02 [c]	2.80 [d]	3.25 [d]	3.20 [d]
2-*exo*	2.38 [d]	2.10 [d]	2.40 [d]	3.20 [d]
2-*endo*	2.38 [d]	2.10 [d]	2.40 [d]	
3				6.46 [e]
4				
5-*exo*	3.02 [d]	2.80 [d]	3.25 [d]	3.76 [e]
5-*endo*	2.38 [d]	2.10 [d]	2.40 [d]	
6	4.32 [f]	4.18 [f]	4.90 [f]	4.32 [f]
8	6.39 [f]	6.20 [f]		6.80 [f]
9	4.84 [c]	4.78 [c]	4.65 [f]	5.26 [c]
11-*exo*				1.90 [e]
11-*endo*				2.66 [f]
1′	6.04 [f]	5.60 [f]	6.25 [f]	6.26 [f]
2′	7.70 [f]	7.35 [f]	8.20 [f]	7.86 [f]
2″,6″	7.40 [f]		7.70 [f]	7.56 [f]
3″,5″	7.84 [f]		8.00 [f]	8.02 [f]
3″,4″		7.40 [c]		
6″		8.18 [f]		
Me	1.72 [g]	1.60 [g]	1.90 [g]	
			2.25 [g]	

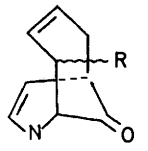
(*b*) Coupling constants (Hz)

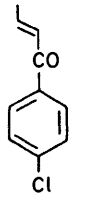
	(32)	(33)	(34)	(35)
$J_{1,2\text{-}exo}$	8.0	8.0		6.0
$J_{2\text{-}exo,2\text{-}endo}$				
$J_{5\text{-}exo,5\text{-}endo}$				
$J_{5\text{-}exo,6}$	8.0	8.0	6.0	4.0
$J_{6,8}$	2.0	2.0	6.0	
$J_{8,9}$	8.0	8.0		8.0
$J_{11\text{-}exo,11\text{-}endo}$				12.0
$J_{2'',3''}$	8.0	8.0	8.0	8.0
$J_{1',2'}$	12.0	12.0	12.0	12.0

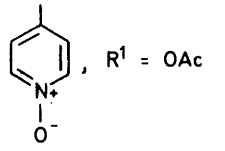
[a] $SiMe_4$ as internal standard. [b] In $CDCl_3$. [c] Double doublet. [d] Overlapped with other signals. [e] Multiplet. [f] Doublet. [g] Singlet.

Attempted quaternisation of the bridgehead nitrogen of adduct (23) (the first step in the tropone synthesis) failed using methyl iodide, tosylate, perchlorate, or trifluoromethanesulphonate, probably owing to steric hindrance and the adverse induction effect. Planarity at the bridgehead nitrogen would involve considerable strain, and this probably prevents quaternisation at the carbonyl oxygen (Scheme 1). Recent ^{13}C n.m.r. studies [12] show that the *N*-substituent lies over the cyclic αβ-unsaturated carbonyl system again indicating lack of planarity at the nitrogen atom.

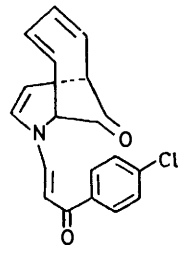
Acid hydrolysis of the *N*-substituent in (23) was achieved to yield (43). This dimer (43), which was first prepared by the analogous acid hydrolysis of the styrene



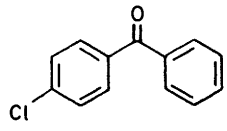
(37) R =  R^1 = OAc or NMe_2



(38) R = , R^1 = OAc



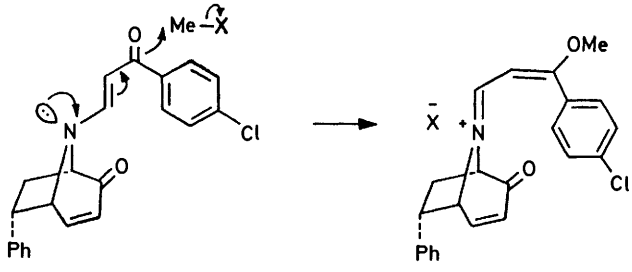
(39)



(40)

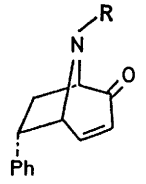
adduct in the triazine series,[2] was the result of a double Michael addition reaction involving two monomers (41). Such a dimer was still seen as a possible precursor to phenyltropone through a double Hoffmann degradation. The first of these would yield 8-methyl-6-*endo*-phenyl-8-azabicyclo[3.2.1]oct-3-en-2-one (42), which would then be converted to the desired tropone. Although the dimer was successfully dimethylated to (44), base degradation of (44) to adduct (42) failed, yielding the dimer (43) by demethylation.

It was planned that the transformation of adducts containing β-2-chloro-5-nitrobenzoylvinyl (3) as an *N*-substituent would proceed either spontaneously through ring-closure to the quinolinium derivative (46) (Scheme 2) or on initial treatment with a primary amine to give an intermediate (47) which would undergo internal cyclisation to a 4-quinoline with the displacement of the NH-

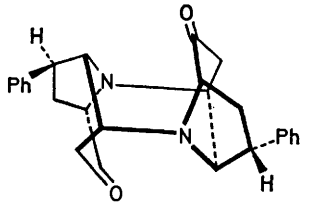


SCHEME 1

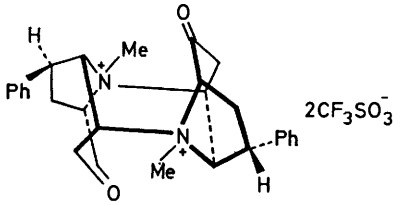
form of the cycloadduct (Scheme 3). The first approach failed under a variety of reaction conditions, possibly due to a high energy barrier for the geometrical isomerisation of the original *trans* to the *cis* cycloadduct required for



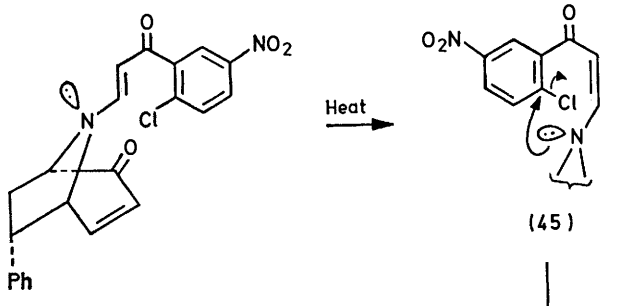
(41) R = H
(42) R = Me



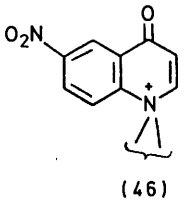
(43)



(44)



(45)



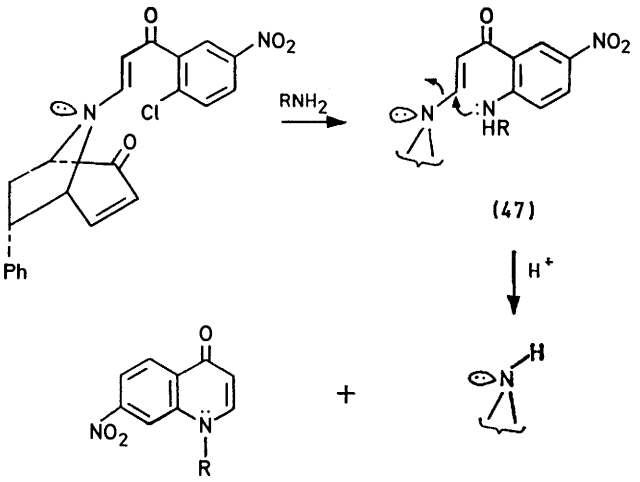
(46)

SCHEME 2

the formation of (45). The second approach succeeded in forming (47) using either benzyl- or t-butyl-amine, but subsequently cyclisation failed: perhaps the attacking nitrogen is too weakly nucleophilic (Scheme 3).

Transformation reactions of the 2,4-*adducts.* After acid treatment of the diene adduct (32), none of the corresponding NH-compound (48) could be isolated probably due to further reactions at the enamine group.

However, 3-oxido-1-(1-oxido-4-pyridyl)pyridinium reacted successfully with 1-acetoxybuta-1,3-diene to yield

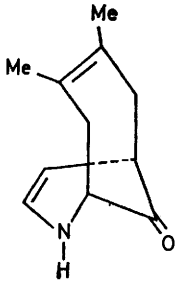


(47)

SCHEME 3

adduct (38).[13] Further transformation reactions are under investigation.

General Conclusions.—The β-aroylvinyl group meets all the conditions originally prescribed [14] for the ideal *N*-substituent: available, easy to attach, activating, and easy to remove. However, because of the tendency of the NH-cycloadducts to dimerise (for 2,6-adducts) or to be unstable (for 2,4-adducts), it has not been possible to



(48)

develop convenient and high-yield procedures except for the keten reactions which take place at the *O*,2-position and are useful precursors to 2-benzyl-3-hydroxypyridines.[15]

EXPERIMENTAL

The m.p.s were determined with a Reichert apparatus. Spectra were recorded with a Perkin-Elmer 257 grating i.r. spectrophotometer, a Unicam SP 800 u.v. spectrophotometer, a Hitachi–Perkin-Elmer RMU-6E mass spectrometer, and a Varian HA 100-MHz n.m.r. spectrometer. Compounds were purified until they were observed as single spots on thin-layer chromatography using Kieselgel GF254 (type 60). Unless otherwise indicated, all cycloadducts were recrystallised from EtOAc–light petroleum (60—80 °C).

1-[trans-3-(4-*Chlorophenyl*)-3-*oxoprop*-1-*enyl*]-3-*hydroxy*-

pyridinium Chloride (4).—3-Hydroxypyridine (2 g, 0.02 mol) was added slowly to *trans*-1-(4-chlorophenyl)-3-chloroprop-2-en-1-one (1) (4.2 g, 0.02 mol) in dry tetrahydrofuran (25 ml) with stirring at 20 °C. After 3 h, the *salt* (4) (5.95 g, 95.7%) separated; it crystallised from EtOH as cream prisms, m.p. 212—213 °C (Found: C, 57.0; H, 4.0; N, 4.7. $C_{14}H_{11}Cl_2NO_2$ requires C, 56.8; H, 3.7; N, 4.7%); $\nu_{max.}$ (Nujol) 1 675 (unsaturated C=O), 3 070 (Ar–H), and 2 500 cm^{-1} (O–H); $\lambda_{max.}$ (EtOH) 270 nm (log ε 4.32); *m/e* 259 (55%).

1-[trans-3-(4-*Bromophenyl*)-3-*oxoprop*-1-*enyl*]-3-*hydroxypyridinium chloride* (5) (93.4%) was prepared similarly from *trans*-1-(4-bromophenyl)-3-chloroprop-2-en-1-one (2); it crystallised from EtOH as cream prisms, m.p. 224—225 °C Found: C, 49.1; H, 3.5; N, 4.1. $C_{14}H_{11}BrClNO_2$ requires C, 49.4; H, 3.2; N, 4.1%); $\nu_{max.}$ (Nujol) 1 680 (unsaturated C=O), 3 080 (Ar–H), and 2 500 cm^{-1} (O–H); $\lambda_{max.}$ (EtOH) 280 nm (log ε 4.38); *m/e* 304 (60%).

1-[trans-3-(2-*Chloro*-5-*nitrophenyl*)-3-*oxoprop*-1-*enyl*]-3-*hydroxypyridinium Chloride* (6).—3-Hydroxypyridine (1.2 g, 0.01 mol) and *trans*-1-(2-chloro-5-nitrophenyl)-3-chloroprop-2-en-1-one (3) (3 g, 0.01 mol) similarly gave the *salt* (6) (4.01 g, 98%) as cream prisms. The *picrate* crystallised from EtOH as yellow prisms, m.p. 168—170 °C (Found: C, 45.2; H, 2.5; N, 12.9. $C_{20}H_{13}ClN_5O_{11}$ requires C, 44.9; H, 2.4; N, 13.1%); $\nu_{max.}$ (Nujol) 1 690 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ (EtOH) 262 nm (log ε 4.53); *m/e* 305 (30%).

1-[trans-3-(4-*Bromophenyl*)-3-*oxoprop*-1-*enyl*]-3-*hydroxy*-6-*methylpyridinium Chloride* (7).—3-Hydroxy-6-methylpyridine (1.1 g, 0.01 mol) and the bromovinyl ketone (2) (2.6 g, 0.01 mol) similarly gave the *salt* (7) (2.3 g, 65%) which crystallised from EtOH as needles, m.p. 149—150 °C (Found: C, 49.6; H, 4.0; N, 3.9. $C_{15}H_{13}BrClNO_2 \cdot 0.5H_2O$ requires C, 49.5; H, 3.9; N, 3.9%); $\nu_{max.}$ (Nujol) 1 665 (unsaturated C=O), 2 600 (O–H), 3 400 (H_2O), and 1 580 cm^{-1} (Ar, C=C); $\lambda_{max.}$ (EtOH) 280 (log ε 4.34) and 230 nm (4.38); *m/e* 318 (7%).

1-[trans-3-(4-*Chlorophenyl*)-3-*oxoprop*-1-*enyl*]-3-*oxidopyridinium* (8).—NEt_3 (1.5 ml) was added dropwise to the salt (4) (5 g, 0.01 mol) in MeCN (15 ml) with vigorous agitation until all the solid changed to orange. The *betaine* (8) (4.1 g, 94%) was collected as orange prisms, washed with MeCN, and air-dried, m.p. 124—125 °C (Found: C, 64.7; H, 4.0; N, 5.6. $C_{14}H_{10}ClNO_2$ requires C, 64.7; H, 3.9; N, 5.4%); $\nu_{max.}$ (Nujol) 1 680 cm^{-1} (unsaturated C=O); *m/e* 94 (100%).

1-[trans-3-(4-*Bromophenyl*)-3-*oxoprop*-1-*enyl*]-3-*oxidopyridinium* (9).—Salt (5) (1 g, 0.003 mol) in MeCN (10 ml) with NEt_3 (0.5 ml) gave as above the *betaine* (9) (0.82 g, 92%) as orange prisms, m.p. 144—145 °C (Found: C, 54.9; H, 3.5; N, 4.6. $C_{14}H_{10}BrNO_2$ requires C, 55.3; H, 3.3; N, 4.6%); $\nu_{max.}$ (Nujol) 1 680 cm^{-1} (unsaturated C=O); *m/e* 94 (100%).

3,11-*Bis*-[trans-3-(4-*chlorophenyl*)-3-*oxoprop*-1-*enyl*]-3,11-*diazatricyclo*[5.3.1.$1^{2,6}$]*dodeca*-4,8-*diene*-10,12-*dione* (10).—The betaine (8) (0.5 g, 0.002 mol) was stirred under MeCN (10 ml) at 40—50 °C for 3 h, to give the *dimer* (10) (0.42 g, 85%) which crystallised from MeCN as yellow prisms, m.p. 176—178 °C [Found: C, 64.4; H, 4.0; N, 5.4. $(C_{14}H_{10}ClNO_2)_2$ requires C, 64.7; H, 3.9; N, 5.4%]; $\nu_{max.}$ ($CHBr_3$) 1 740 (saturated C=O), 1 680 (unsaturated C=O), and 1 650 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ (MeCN) 330 (log ε 4.61), 254 (4.43), and 215 nm (4.50); *m/e* 259 (36%).

3,11-*Bis*-[trans-3-(4-*bromophenyl*)-3-*oxoprop*-1-*enyl*]-3,11-*diazatricyclo*[5.3.1.$1^{2,6}$]*dodeca*-4,8-*diene*-10,12-*dione* (11).—By the procedure for dimer (10), betaine (9) (0.5 g, 0.002 mol) and MeCN (10 ml) at 40—50 °C for 3 h gave the *dimer* (11) (0.41 g, 84%) which crystallised from MeCN as prisms, m.p. 159—160 °C [Found: C, 54.9; H, 3.3; N, 4.4. $(C_{14}H_{10}BrNO_2)_2$ requires C, 55.3; H, 3.3; N, 4.6%]; $\nu_{max.}$ ($CHBr_3$ film) 1 740 (saturated C=O), 1 690 (unsaturated C=O), and 1 650 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ (MeCN) 339 (log ε 4.46), 259 (4.38), and 215 nm (4.41); *m/e* 304 (40%).

3,11-*Bis*-[trans-3-(2-*chloro*-5-*nitrophenyl*)-3-*oxoprop*-1-*enyl*]-3,11-*diazatricyclo*[5.3.1.$1^{2,6}$]*dodeca*-4,8-*diene*-10,12-*dione* (12).—(*A*) The salt (6) (1 g, 0.003 mol) in MeCN (5—10 ml) was stirred with NEt_3 (0.5 ml) for 10 min. The *dimer* (12) (0.8 g, 87%) crystallised from MeCN as yellow flakes, m.p. 186—188 °C (Found: C, 54.8; H, 3.3; N, 9.4. $C_{18}H_{18}Cl_2N_4O_8$ requires C, 55.2; H, 3.0; N, 9.2%); $\nu_{max.}$ ($CHBr_3$ film) 1 740 (saturated C=O), 1 690 (unsaturated C=O), and 1 670 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ (MeCN) 343 (log ε 4.46), 292 (4.74), and 220 nm (4.61); *m/e* 305 (30%).

(*B*) Sodium hydrogencarbonate (0.25 g, 0.003 mol) was slowly added to a stirred suspension of the salt (6) (1 g, 0.003 mol) in water to give a yellow dimer (0.55 g, 60%) with spectral and physical properties similar to that from procedure (*A*).

3,11-*Bis*-[trans-3-(4-*bromophenyl*)-3-*oxoprop*-1-*enyl*]-3,11-*diazatricyclo*[5.3.1.$1^{2,6}$]*dodeca*-4,7-*dimethyl*-4,8-*diene*-10,12-*dione* (13).—NEt_3 (3 ml) added dropwise to a suspension of the salt (7) (1 g, 0.002 mol) in MeCN (10 ml) gave *dimer* (13) (0.4 g, 67%) which recrystallised from MeCN as yellowish prisms, m.p. 135—137 °C [Found: C, 56.2; H, 4.0; N, 4.3. $(C_{15}H_{12}BrNO_2)_2$ requires C, 56.6; H, 3.8; N, 4.4%]; $\nu_{max.}$ ($CHBr_3$ film) 1 740 (saturated C=O), 1 680 (unsaturated C=O), 1 660 (N–C=C–*C=O*), and 1 580 cm^{-1} (Ar, C=C); $\lambda_{max.}$ ($CHCl_3$) 325 (log ε 4.50) and 270 nm (4.43); *m/e* 318 (40%).

8-[trans-3-(4-*Chlorophenyl*)-3-*oxoprop*-1-*enyl*]-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo- *and* -6-exo-*carbonitrile* (15) *and* (16).—The betaine (8) (0.5 g, 0.002 mol), acrylonitrile (15—20 ml), and hydroquinone (100 mg) were heated for 24 h at 50—60 °C. The reaction mixture was evaporated to dryness at 20 mmHg to yield a mixture of (15) and (16) as a brown gum which was purified by preparative t.l.c. [light petroleum (60—80 °C)–EtOAc (1 : 1)]. The endo-*adduct* (15) (50 mg, 8.0%) was isolated as yellow prisms, m.p. 224—225 °C (Found: C, 65.1; H, 4.3; N, 8.8. $C_{17}H_{13}ClN_2O_2$ requires C, 65.3; H, 4.2; N, 8.9%); $\nu_{max.}$ ($CHBr_3$ film) 2 225 (C≡N), 1 680 (unsaturated C=O), and 1 645 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ ($CHCl_3$) 330 (log ε 4.32) and 270 nm (4.13); *m/e* 259 (31%). The exo-*adduct* (16) (30 mg, 4.8%) crystallised as cream prisms, m.p. 218—220 °C (Found: C, 65.0; H, 4.3; N, 8.8. $C_{17}H_{13}ClN_2O_2$ requires C, 65.3; H, 4.2; N, 8.9%); $\nu_{max.}$ ($CHBr_3$ film) 2 220 (C≡N), 1 680 (unsaturated C=O), and 1 640 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ ($CHCl_3$) 325 (log ε 4.42) and 265 nm (3.91); *m/e* 259 (21%).

8-[trans-3-(2-*Chloro*-5-*nitrophenyl*)-3-*oxoprop*-1-*enyl*]-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo- *and* -6-exo-*carbonitrile* (17) *and* (18).—The dimer (12) (0.5 g), chlorobenzene (15 ml), tetrahydrofuran (5 ml), hydroquinone (100 mg), and acrylonitrile (5 ml) were heated at 110—130 °C for 2 d. The reaction mixture was evaporated to dryness at 20 mmHg to yield a black gum which was purified by t.l.c. on silica gel [EtOAc–light petroleum (60—80 °C) (3 : 2)] to give a mixture of *endo*- and *exo*-adducts which was difficult to separate. The *isomeric mixture* (200 mg, 35%) crystallised as yellow plates, m.p. 118—124 °C (Found: C, 57.1;

H, 3.8; N, 12.0. $C_{17}H_{12}ClN_3O_4$ requires C, 57.1; H, 3.4; N, 11.7%); $\nu_{max.}$ ($CHBr_3$ film) 2 245 (C≡N), 1 690 (unsaturated C=O), and 1 630 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ ($CHCl_3$) 290 (log ε 4.38) and 245 nm (4.20); *m/e* 52 (90%).

Methyl 8-[trans-3-(4-*Chlorophenyl*)-3-*oxoprop*-1-*enyl*]-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo- *and* -exo-*carboxylate* (19) *and* (20).—Betaine (8) (0.5 g, 0.002 mol), hydroquinone (100 mg), and methyl acrylate (20—25 ml) were heated at 50—60 °C for 24 h. The mixture was evaporated to dryness at 20 mmHg to yield a mixture of (19) and (20) which was separated by preparative t.l.c. on silica gel [EtOAc–light petroleum (60—80 °C) (1 : 1)]. The endo-*adduct* (19) (100 mg, 14.4%) formed yellow prisms, m.p. 168—170 °C (Found: C, 62.3; H, 4.6; N, 4.2. $C_{18}H_{16}ClNO_4$ requires C, 62.5; H, 4.7; N, 4.0%); $\nu_{max.}$ ($CHBr_3$ film) 1 748 (MeO–C=O), 1 680 (unsaturated C=O), and 1 648 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ ($CHCl_3$) 330 (log ε 4.36) and 263 nm (4.11); *m/e* 259 (81.5%). The exo-*adduct* (20) (150 mg, 21.7%) was obtained as hygroscopic yellow needles, m.p. 132 °C (Found: C, 62.1; H, 4.6; N, 4.4. $C_{18}H_{16}ClNO_4$ requires C, 62.5; H, 4.7; N, 4.0%); $\nu_{max.}$ ($CHBr_3$ film) 1 730 (MeO–C=O), 1 680 (unsaturated C=O), and 1 635 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ ($CHCl_3$) 332 (log ε 4.43) and 262 nm (4.20); *m/e* 259 (53%).

Ethyl 8-[trans-3-(2-*Chloro*-5-*nitrophenyl*)-3-*oxoprop*-1-*enyl*]-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo- and -exo-*carboxylate* (21) *and* (22).—Dimer (12) (0.5 g), ethyl acrylate (5 ml), and hydroquinone (100 mg) in MeCN (10—15 ml) were heated at 80—90 °C for 3 d, and then evaporated to dryness at 20 mmHg and 100 °C. The resulting gum was separated by preparative t.l.c. on silica gel [light petroleum (60—80 °C)–EtOAc (1 : 1)] into the endo-*adduct* (21) (250 mg, 39%), pale yellow prisms, m.p. 182—184 °C (Found: C, 56.3; H, 4.2; N, 7.2. $C_{19}H_{17}ClN_2O_6$ requires C, 56.4; H, 4.2; N, 6.9%); $\nu_{max.}$ ($CHBr_3$) 1 730 (saturated C=O), 1 690 (unsaturated C=O), and 1 650 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ ($CHCl_3$) 307 (log ε 4.16) and 228 nm (4.13); *m/e* 305 (68%): and the exo-*adduct* (22) (200 mg, 31%) as cream prisms, m.p. 148—150 °C (Found: C, 56.5; H, 4.4; N, 6.8. $C_{19}H_{17}ClN_2O_6$ requires C, 56.4; H, 4.2; N, 6.9%); $\nu_{max.}$ ($CHBr_3$ film) 1 730 (saturated C=O), 1 690 (unsaturated C=O), and 1 645 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ ($CHCl_3$) 303 (log ε 4.66) and 250 nm (4.39); *m/e* 304 (50%).

8-[trans-3-(4-*Chlorophenyl*)-3-*oxoprop*-1-*enyl*]-6-endo-*phenyl*-8-*azabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (23).—Betaine (8) (0.5 g, 0.002 mol) was heated for 3 d at 60 °C with styrene (5 ml), MeCN (15—20 ml), and hydroquinone (100 mg). Evaporation at 20 mmHg and purification by preparative t.l.c. on silica gel [light petroleum (60—80 °C)–EtOAc (2 : 1)] gave the endo-*adduct* (23) (200 mg, 27.6%) as yellow prisms, m.p. 206—208 °C (Found: C, 72.5; H, 5.1; N, 3.8. $C_{22}H_{18}ClNO_2$ requires C, 72.6; H, 5.0; N, 3.8%); $\nu_{max.}$ ($CHBr_3$ film) 1 690 (unsaturated C=O) and 1 640 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ ($CHCl_3$) 336 (log ε 4.72) and 258 nm (4.32); *m/e* 259 (100%).

8-[trans-3-(2-*Chloro*-5-*nitrophenyl*)-3-*oxoprop*-1-*enyl*]-6-endo-*phenyl*-8-*azabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (24).—Dimer (12) (0.5 g), MeCN (10—15 ml), hydroquinone (100 mg), and styrene (2—3 ml) were heated at 80—90 °C for 2 days. Evaporation at 20 mmHg and preparative t.l.c. on silica gel [light petroleum (60—80 °C)–EtOAc (2 : 1)] yielded the endo-*adduct* (24) (150 mg, 23%), as yellow prisms, m.p. 118—120 °C (Pr^iOH) (Found: C, 61.5; H, 4.7; N, 6.8. $C_{22}H_{17}ClN_2O_4$ requires C, 61.9; H, 4.5; N, 6.6%); $\nu_{max.}$ ($CHBr_3$ film) 1 690 (unsaturated C=O), 1 640 (N–C=C–*C–O*), and 3 300 cm^{-1} (H_2O); $\lambda_{max.}$ ($CHCl_3$) 305 (log ε 4.08) and 250 nm (4.36); *m/e* 304 (100%).

8-[trans-3-(4-*Chlorophenyl*)-3-*oxoprop*-1-*enyl*]-6-endo-*ethoxy*-8-*azabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (25).—Betaine (8) (0.5 g, 0.002 mol), hydroquinone (100 mg), and ethyl vinyl ether (10—15 ml) were heated in a sealed tube at 70 °C for 7 d. The mixture was evaporated at 20 mmHg and the crude solid purified by preparative t.l.c. on silica gel [light petroleum (60—80 °C)–EtOAc (1 : 1)] to give the endo-*adduct* (25) (200 mg, 30%) as cream prisms, m.p. 146—148 °C (Found: C, 64.7; H, 5.5; N, 4.5. $C_{18}H_{18}ClNO_3$ requires C, 65.1; H, 5.5; N, 4.2%); $\nu_{max.}$ 1 690 (unsaturated C=O) and 1 640 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ ($CHCl_3$) 335 (log ε 4.31) and 260 nm (4.14); *m/e* 259 (100%).

N-*Phenyl*-8-[trans-3-(4-*chlorophenyl*)-3-*oxoprop*-1-*enyl*]-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6,7-exo-*dicarboximide* (26).—Betaine (8) (0.5 g, 0.002 mol) and *N*-phenylmaleimide (0.33 g, 0.002 mol) in MeCN (15—20 ml) were heated at 80 °C for 3 d, and then evaporated to dryness at 20 mmHg. The product was purified by preparative t.l.c. on silica gel [light petroleum (60—80 °C)–EtOAc (1 : 1)] to give the exo-*adduct* (100 mg, 11.6%), as white needles, m.p. 282—284 °C (EtOAc) (Found: C, 66.2; H, 4.1; N, 6.7. $C_{24}H_{17}ClN_2O_4$ requires C, 66.6; H, 3.9; N, 6.5%); $\nu_{max.}$ ($CHBr_3$ film) 1 700br (C=O) and 1 640 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ ($CHCl_3$) 319 (log ε 3.66) and 265 nm (3.49); *m/e* 173 (50%).

N-*Phenyl*-8-[trans-3-(2-*chloro*-5-*nitrophenyl*)-3-*oxoprop*-1-*enyl*]-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6,7-exo-*dicarboximide* (27).—A mixture of dimer (12) (0.5 g), chlorobenzene (15 ml), tetrahydrofuran (5 ml), hydroquinone (100 mg), and *N*-phenylmaleimide (280 mg) was heated at 130 °C for 2 d. Evaporation at 20 mmHg gave a brown gum which was purified by preparative t.l.c. on silica gel [EtOAc–light petroleum (60—80 °C) (1 : 2)] to give the exo-*adduct* (27) (100 mg, 13%) as brown prisms, m.p. 174—175 °C (Found: C, 60.6; H, 3.6. $C_{24}H_{16}ClN_3O_6$ requires C, 60.3; H, 3.4%); $\nu_{max.}$ ($CHBr_3$ film) 1 730br (C=O) and 1 630 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ ($CHCl_3$) 280 (log ε 4.04) and 230 nm (4.20); *m/e* 173 (32%).

Diethyl 8-[trans-3-(4-*Chlorophenyl*)-3-*oxoprop*-1-*enyl*]-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-exo,7-endo-*dicarboxylate* (28).—The betaine (8) (0.5 g, 0.002 mol), diethyl fumarate (5 ml), hydroquinone (100 mg), and MeCN (15—20 ml) were heated at 60 °C for 2 d. Evaporation at 20 mmHg gave a brown gum which was purified by preparative t.l.c. on silica gel [light petroleum (60—80 °C)–EtOAc (2 : 1)] to give the *adduct* (28) (120 mg, 13.9%), as cream needles, m.p. 143—144 °C (Found: C, 60.9; H, 5.3; N, 3.5. $C_{22}H_{22}ClNO_6$ requires C, 61.2; H, 5.1; N, 3.2%); $\nu_{max.}$ ($CHBr_3$ film) 1 740 (EtO–*C=O*), 1 680 (unsaturated C=O), and 1 640 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ ($CHCl_3$) 327 (log ε 4.43) and 263 nm (4.14); *m/e* 259 (27.5%).

Diethyl 8-[trans-3-(2-*Chloro*-5-*nitrophenyl*)-3-*oxoprop*-1-*enyl*]-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-exo,7-endo-*dicarboxylate* (29).—Dimer (12) (0.5 g), chlorobenzene (15 ml), tetrahydrofuran (5 ml), hydroquinone (100 mg), and diethyl fumarate (2 ml) were refluxed for 24 h, then evaporated at 20 mmHg. The residue was purified by preparative t.l.c. on silica gel [light petroleum (60—80 °C)–EtOAc (1 : 1)] to yield *adduct* (29) (0.3 g, 33%) as a gum which resisted recrystallisation; $\nu_{max.}$ ($CHBr_3$ film) 1 735 (EtO–*C=O*), 1 690 (unsaturated C=O), and 1 620 cm^{-1} (N–C=C–*C=O*); *m/e* 304 (90%).

Dimethyl 8-[trans-3-(4-*Chlorophenyl*)-3-*oxoprop*-1-*enyl*]-2-

oxo-8-*azabicyclo*[3.2.1]*octa*-3,6-*diene*-6,7-*dicarboxylate* (30).—Betaine (8) (0.5 g, 0.002 mol), dimethyl acetylenedicarboxylate (2 ml), hydroquinone (100 mg), and MeCN (15—20 ml) were heated at 50—60 °C for 4 h, and then evaporated at 20 mmHg. Purification by preparative t.l.c. [multiple developments on silica gel [light petroleum (60—80 °C)–EtOAc (1 : 1)] gave *adduct* (30) (150 mg, 18.7%) as brownish yellow prisms, m.p. 143—144 °C (Found: C, 59.8; H, 4.3; N, 3.4. $C_{20}H_{16}ClNO_6$ requires C, 59.8; H, 4.0; N, 3.5%); $\nu_{max.}$ ($CHBr_3$ film) 1 730br (saturated C=O) and 1 650 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ ($CHCl_3$) 325 (log ε 4.47) and 265 nm (4.28); *m/e* 259 (98%).

Diethyl 8-[trans-3-(2-*Chloro*-5-*nitrophenyl*)-3-*oxoprop*-1-*enyl*]-2-*oxo*-8-*azabicyclo*[3.2.1]*octa*-3,6-*diene*-6,7-*dicarboxylate* (31).—Dimer (12) (0.5 g), diethyl acetylenedicarboxylate (2 ml), hydroquinone (100 mg), chlorobenzene (15 ml), and tetrahydrofuran (5 ml) were heated at 140 °C for 24 h, and evaporated at 20 mmHg. Purification of the residue by t.l.c. on silica gel [light petroleum (60—80 °C)–EtOAc (2 : 1)] yielded compound (31) (250 mg, 33%) as brownish orange prisms, m.p. 90—92 °C (Pr^{i}OH) (Found: C, 54.0; H, 4.4; N, 5.2. $C_{22}H_{19}ClN_2O_8 \cdot H_2O$ requires C, 53.6; H, 4.3; N, 5.5%); $\nu_{max.}$ ($CHBr_3$ film) 1 730br (C=O ester), 1 670 (unsaturated C=O), 1 620 (N–C=C–*C=O*), and 3 400 cm^{-1} (H_2O); $\lambda_{max.}$ ($CHCl_3$) 345 (log ε 4.00) and 275 nm (4.20); *m/e* 236 (100%).

7,8-*Dimethyl*-2-[trans-3-(4-*chlorophenyl*)-3-*oxoprop*-1-*enyl*]-endo-2-*azabicyclo*[4.3.1]*deca*-3,7-*dien*-10-*one* (32).—Betaine (8) (0.5 g, 0.002 mol), 2,3-dimethylbuta-1,3-diene (3 ml), hydroquinone (100 mg), and MeCN (15—20 ml) were refluxed for 2 d. Evaporation at 20 mmHg and purification of the residue by preparative t.l.c. on silica gel [light petroleum (60—80 °C)–EtOAc (6 : 1)] yielded the *adduct* (32) (100 mg, 14%) as yellow prisms, m.p. 196—198 °C (EtOAc) (Found: C, 70.0; H, 6.1; N, 4.5. $C_{20}H_{20}ClNO_2$ requires C, 70.3; H, 5.9; N, 4.1%); $\nu_{max.}$ ($CHBr_3$ film) 1 720 (saturated C=O) and 1 630 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ ($CHCl_3$) 360 (log ε 4.60) and 263 nm (4.39); *m/e* 259 (100%).

7,8-*Dimethyl*-2-[trans-3-(2-*chloro*-5-*nitrophenyl*)-3-*oxoprop*-1-*enyl*]-endo-2-*azabicyclo*[4.3.1]*deca*-3,7-*dien*-10-*one* (33).—Dimer (12) (0.5 g), 2,3-dimethylbuta-1,3-diene (3 ml), chlorobenzene (15 ml), tetrahydrofuran (5 ml), and hydroquinone (100 mg) were heated at 130 °C for 24 h and evaporated at 20 mmHg. The brown gum was purified by t.l.c. on silica gel [light petroleum (60—80 °C)–EtOAc (2 : 1)] to give the *adduct* (33) (300 mg, 48%) as yellow-brown prisms, m.p. 110—112 °C (Pr^{i}OH) (Found: C, 59.3; H, 4.8; N, 6.5. $C_{20}H_{19}ClN_2O_4 \cdot H_2O$ requires C, 59.3; H, 5.2; N, 6.9%); $\nu_{max.}$ ($CHBr_3$ film) 1 735 (saturated C=O), 1 640 (N–C=C–*C=O*), and 3 300 cm^{-1} (H_2O); $\lambda_{max.}$ ($CHCl_3$) 340 (log ε 4.08) and 265 nm (4.30); *m/e* 304 (100%).

3,7,8-*Trimethyl*-2-[trans-3-(4-*bromophenyl*)-3-*oxoprop*-1-*enyl*]-3-endo-2-*azabicyclo*[4.3.1]*deca*-3,7-*dien*-10-*one* (34).—Dimer (13) (0.3 g, 0.8 mmol), 2,3-dimethylbuta-1,3-diene (2—3 ml), hydroquinone (100 mg), and MeCN (20—25 ml) were heated at 70 °C for 8 h, and evaporated at 20 mmHg. The gum was purified by preparative t.l.c. on silica gel [EtOAc–light petroleum (60—80 °C) (1 : 3)] to give *compound* (34) (0.2 g, 25%) as yellow needles, m.p. 210—211 °C (EtOAc) (Found: C, 63.0; H, 5.7; N, 3.4. $C_{21}H_{22}BrNO_2$ requires C, 63.0; H, 5.5; N, 3.5%); $\nu_{max.}$ ($CHBr_3$ film) 1 720 (saturated C=O), 1 660 (N–C=C–*C–O*), and 1 580 cm^{-1} (Ar, C=C); $\lambda_{max.}$ ($CHCl_3$) 360 (log ε 4.60) and 265 nm (4.39); *m/e* 318 (100%).

Reaction of the Betaine (8) *with Cyclopentadiene*.—Betaine (8) (0.5 g, 0.002 mol), freshly distilled cyclopentadiene (2 ml), hydroquinone (100 mg), and MeCN (15—20 ml) were stirred at 20 °C for 2 d, and evaporated at 20 mmHg. The residue was purified by t.l.c. on silica gel [light petroleum (60—80 °C)–EtOAc (2 : 1)] to give 7-[trans-3-(4-*chlorophenyl*)-3-*oxoprop*-1-*enyl*]-exo-7-*azabicyclo*[4.3.1.1^{2,5}]*undeca*-3,8-*dien*-10-*one* (35) (150 mg, 23%) as cream prisms, m.p. 156—158 °C (Found: C, 70.0; H, 5.0; N, 4.4. $C_{19}H_{16}ClNO_2$ requires C, 70.0; H, 4.9; N, 4.3%); $\nu_{max.}$ ($CHBr_3$ film) 1 740 (saturated C=O) and 1 640 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ ($CHCl_3$) 358 (log ε 4.56) and 262 nm (4.30); *m/e* 66 (100%), 259 (30%); and 11-[trans-3-(4-*chlorophenyl*)-3-*oxoprop*-1-*enyl*]-11-endo-11-*azatricyclo*[5.3.1.0^{2,6}]*undeca*-3,9-*dien*-8-*one* (36) (100 mg, 15.9%) as prisms, m.p. 164—166 °C (Found: C, 69.8; H, 5.0; N, 4.3. $C_{19}H_{16}ClNO_2$ requires C, 70.0; H, 4.9; N, 4.3%); $\nu_{max.}$ ($CHBr_3$ film) 1 680 (unsaturated C=O) and 1 640 cm^{-1} (N–C=C–*C=O*); $\lambda_{max.}$ ($CHCl_3$) 340 (log ε 4.28) and 260 nm (4.18); *m/e* 259 (45%).

4,12-*Diphenyl*-2,10-*diazapentacyclo*[9.5.0.0^{2,6}.0^{3,9}.0^{10,14}]*hexadecane*-7,15-*dione* (43).—Adduct (23) (300 mg), EtOH (10 ml), and concentrated HCl (10 ml) were refluxed for 4 h. The mixture was extracted with $CHCl_3$ and the water layer was then evaporated to dryness at 20 mmHg. The residue was taken up in water, neutralised with $NaHCO_3$, then extracted with $CHCl_3$. The combined $CHCl_3$ extracts (dried over $MgSO_4$) were evaporated (20 mmHg). The resultant gum was treated with H_2O to give *compound* (43) (160 mg, 49%) which crystallised from EtOH as flakes, m.p. 296—298 °C (lit.,[2] m.p. >280 °C).

2,10-*Dimethyl Bistrifluoromethanesulphonate Salt* (44) *of* (43).—Dimer (43) (50 mg, 0.12 mmol) in CH_2Cl_2 (10 ml) and methyl trifluoromethanesulphonate were stirred at 60 °C for 5 min. The cream solid *salt* (44) (60 mg, 66%) which precipitated after 15 min was recrystallised from aqueous EtOH as white prisms, m.p. 208—210 °C; $\nu_{max.}$ ($CHBr_3$ film) 1 700 cm^{-1} (saturated C=O); *m/e* 726.626 5; $C_{30}H_{32}F_6N_2O_8$ requires 726.71.

The Reaction of Betaine (8) *and* 1-*Acetoxybuta*-1,3-*diene*.—Betaine (8) (0.5 g, 0.002 mol), acetonitrile (10—15 ml), hydroquinone (100 mg), and 1-acetoxybuta-1,3-diene [16] (2 ml) were stirred at 50 °C for 12 h. Evaporation at 20 mmHg yielded a brown gum, which was purified by preparative t.l.c. on silica gel [light petroleum (60—80 °C)–EtOAc (1 : 1)] to yield *p*-chlorobenzophenone (200 mg, 46%) which crystallised from EtOH as yellow prisms, m.p. 77 °C (lit.,[17] 77—78 °C); $\nu_{max.}$ ($CHBr_3$ film) 1 740 (OAc), 1 680 (αβ-unsaturated C=O), and 1 590, 1 500 cm^{-1} (Ar, C···C); δ($CDCl_3$) 7.40 (5 H, m), 7.35 (2 H, d), and 7.75 (2 H, d).

The Reaction of Betaine (8) *and* NN-*Dimethylaminobuta*-1,3-*diene*.—Betaine (8) (0.5 g, 0.002 mol), MeCN (10—15 ml), hydroquinone (100 ml), and *NN*-dimethylaminobuta-1,3-diene [18] (2 ml) were stirred at 50 °C for 24 h. Evaporation at 20 mmHg gave a brown gum which was purified by preparative t.l.c. on silica gel [light petroleum (60—80 °C)–EtOAc (2 : 1)] to give trans-1-(4-*chlorophenyl*)-3-(*NN*-*dimethylamino*)*prop*-2-*en*-1-*one* (150 mg, 35%) which resisted recrystallisation; $\nu_{max.}$ ($CHBr_3$ film) 1 675 (αβ-unsaturated C=O), 1 580 and 1 550 cm^{-1} (Ar, C···C); δ($CDCl_3$) 3.00 (6 H, s), 5.62 (1 H, d), 7.35 (2 H, d), 7.80 (1 H, d), and 7.85 (2 H, d).

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