1,3-Dipolar Character of Six-membered Aromatic Rings. Part IX.[1] Rearrangement and Additions of 1-(2,4-Dinitrophenyl)-3-oxidopyridinium

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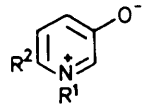
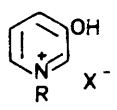
1-(2,4-Dinitrophenyl)-3-oxidopyridinium rearranges easily to 3-(2,4-dinitrophenoxy)pyridine. The betaine forms adducts with dipolarophiles by addition across the 2- and 6-positions.

In connection with studies on the 1,3-dipolar reactivity of 3-oxidopyridinium (1) and (2) and related betaines,[2-5] we required betaines with a strong electron acceptor at the pyridine nitrogen atom, which should be good precursors for tropolone synthesis.[3,5] Vompe *et al.*[6] claimed



(1) R^1=Me, R^2=H
(2) R^1=Ph, R^2=H
(3) R^1=2,4-$(O_2N)_2C_6H_3$, R^2=H
(4) R^1=2,4-$(O_2N)_2C_6H_3$, R^2=Me



(5) R=Me, X=I
(6) R=Ph, X=Cl
(7) R=2,4-$(O_2N)_2C_6H_3$, X=Cl

to have prepared 1-(2,4-dinitrophenyl)-3-oxidopyridinium (3) by treating the corresponding hydrochloride (7) (readily prepared from 3-hydroxypyridine and 1-chloro-2,4-dinitrobenzene) with sodium hydrogen carbonate. We obtained Vompe's compound but it failed to show 1,3-dipolar reactivity with various olefins which reacted with both 1-methyl-3-oxidopyridinium (1)[2,3] and 1-phenyl-3-oxidopyridinium (2).[7,8] This led us to re-examine the claimed synthesis of (3).

Vompe's compound possesses properties unusual for a betaine: it is soluble in organic solvents (*e.g.* chloroform), but insoluble in water, and its n.m.r. data differ from those of other betaines. However, the structure of the hydrochloride precursor (7) is supported by the similarity between the n.m.r. chemical shifts for the pyridinium protons of the three salts (5)—(7) (Table 1).

Suspecting that the conversion of (7) into the betaine (3) was followed by a rapid rearrangement to the ether (8), we followed the reaction of (7) with sodium hydrogen carbonate by the n.m.r. technique. The n.m.r. spectrum of (7) (in D_2O) measured immediately after sodium hydrogen carbonate was added (Table 1) differed completely from that of Vompe's compound and disclosed chemical shifts for the pyridine ring protons characteristic

[1] Part VIII, N. Dennis, A. R. Katritzky, and S. K. Parton, *J.C.S. Perkin I*, 1974, 750.
[2] A. R. Katritzky and Y. Takeuchi, *J. Amer. Chem. Soc.*, 1970, **92**, 4134.
[3] A. R. Katritzky and Y. Takeuchi, *J. Chem. Soc.* (*C*), 1971, 874.
[4] A. R. Katritzky and Y. Takeuchi, *J. Chem. Soc.* (*C*), 1971, 878.
[5] N. Dennis, A. R. Katritzky, and Y. Takeuchi, *J.C.S. Perkin I*, 1972, 2054.
[6] A. F. Vompe and N. F. Turitsyna, *Zhur. obshchei Khim.*, 1957, **27**, 3282 (*Chem. Abs.*, 1958, **52**, 9112*d*).
[7] Y. Takeuchi, N. Dennis, A. R. Katritzky, and I. Taulov, Third International Congress of Heterocyclic Chemistry, Sendai, Japan, 1971.
[8] N. Dennis, A. R. Katritzky, T. Matsuo, S. K. Parton, and Y. Takeuchi, *J.C.S. Perkin I*, 1974, 746.

of betaines. The solution later became coloured, with precipitate formation, and gave no sharp spectrum. Treatment of (7) with base thus initially gives the betaine

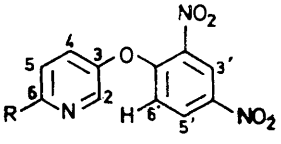
TABLE 1

Proton n.m.r. spectra (δ values) of betaines and halides [a]

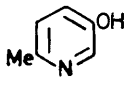
Proton(s)	(1) [b,c]	(2) [b,d]	(3) [b,c]	(5) [b,c]	(6) [b,d]	(7) [b,e]	(7) [e,i]	(7) [e,j]	Vompe's compound (8) [e,k]
2	7·30	7·50—7·65	7·4 *f*	8·63	8·91	9·00	8·73	7·93 *f*	8·53
4	6·90	7·08	7·3 *g*	8·16	8·35	8·45	8·39	7·76 *f*	7·50
5	7·21	7·40	7·0 *f*	8·16	8·08	8·20	8·24	7·76 *f*	7·45
6	7·35	7·50—7·65	7·4 *f*	8·63	8·78	9·00	8·73	7·93 *f*	8·60
3′			8·9 *h*			9·10	9·40	9·28	8·86
5′			8·65 *g*			8·96	8·98	8·87	8·35
6′			8·1 *h*			8·40	8·29	8·17	7·08
N-Me	3·73			4·48					
N-Ph		7·50—7·65		*ca.* 7·75					

[a] Me_4Si as internal standard. [b] In $(CD_3)_2SO$. [c] Ref. 3. [d] Ref. 8. [e] This study. [f] Centre of broad band. [g] Quartet. [h] Doublet. [i] In D_2O. [j] In D_2O + $NaHCO_3$. [k] In $CDCl_3$.

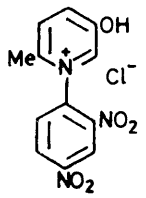
(3), but this rapidly rearranges: for example treatment with ion-exchange resin IRA-401 (OH^-) [3,5] formed Vompe's compound (insoluble in water).



(8) R = H
(9) R = Me



(10)



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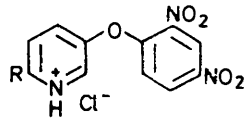
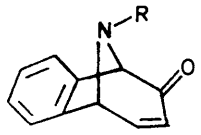


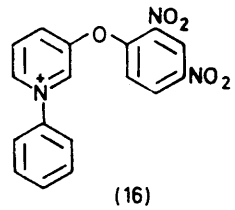
(12) R = H
(13) R = Me

The ether (8) has previously been synthesised from 3-hydroxypyridine and 1-chloro-2,4-dinitrobenzene in the presence of methanolic potassium hydroxide,[9] and also by the direct nitration of 3-phenoxypyridine.[10] We repeated the syntheses given in references 6 and 9 and thus proved the identity of the ether (8) with Vompe's compound.*

That Vompe's compound is the ether (8) was confirmed by a shift reagent study. The plot of the lanthanide induced shift (LIS) [11,12] [by $Eu(fod)_3$ or $Pr(fod)_3$] [13] against the molar ratio of the shift reagent (Figure 1), confirms the pyridine nitrogen atom as the complexation site. The enhanced LIS for 6′-H suggests that the 2,4-dinitrophenyl ring has the conformation illustrated in (8). Treatment of the ether (8) with hydrogen chloride yielded a hydrochloride (12) which differed from the betaine hydrochloride (7) in colour, m.p., and i.r. and n.m.r. spectra.

The 2,4-dinitrophenyl betaine derived from 3-hydroxy-6-methylpyridine (10) is even more difficult to isolate than (3): treatment of (10) with 2,4-dinitrochlorobenzene gave a mixture of the hydrochloride of (10) and 3-(2,4-dinitrophenoxy)-6-methylpyridine (9), but no 1-(2,4-dinitrophenyl)pyridinium salt (11). The ether (9) readily forms the hydrochloride (13) when treated with hydrochloric acid. The structure (9) was confirmed by conventional spectroscopic measurements as well as by an





(14) R = Ph
(15) R = 2,4-$(O_2N)_2C_6H_3$

(16)

LIS study in which the 6-methyl protons showed large paramagnetic shifts (Figure 2).

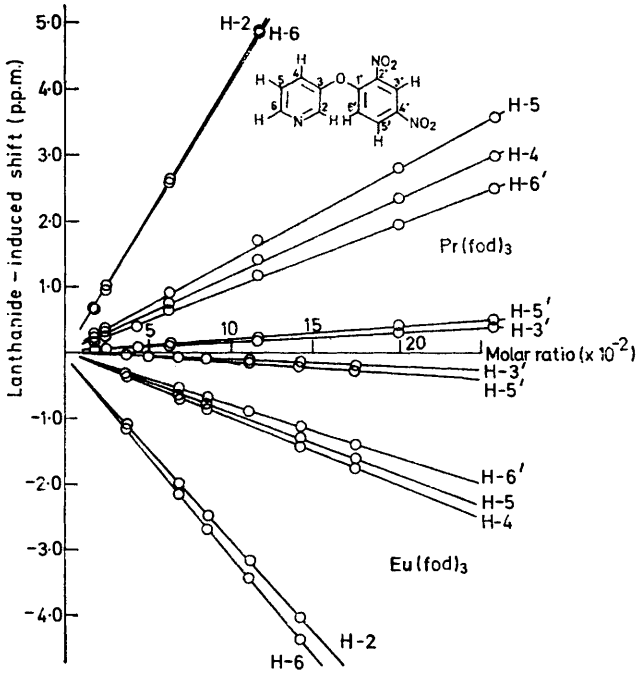


FIGURE 1 δΔ *vs.* molar ratio of lanthanide to substrate for 3-(2,4-dinitrophenoxy)pyridine (8)

Recently we reported [14] that the reaction of Vompe's compound with benzyne gave the cycloadduct (14)

* K. Undheim and P. E. Hansen (*Org. Mass Spectrometry*, 1973, **7**, 635) have recently reported the mass spectral fragmentation of the betaine (3). In view of our present results, it is unlikely that they ever isolated the betaine (3) but were in fact studying the ether (8). Similarly, their reported *N*-(4-nitrophenyl)pyridinium-3-oxide is probably also the corresponding rearranged ether. We are at present investigating the mass spectral fragmentations of betaines and related compounds.

[9] F. Yoneda, *Yakugaku Zasshi*, 1957, **77**, 944.
[10] T. Takahashi and J. Shibasaki, *Chem. and Pharm. Bull. (Japan)*, 1953, **1**, 70.
[11] B. C. Mayo, *Chem. Soc. Rev.*, 1973, **2**, 49.
[12] R. von Ammon and R. D. Fischer, *Angew. Chem. Internat. Edn.*, 1972, **11**, 675.
[13] R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 1971, **93**, 1522.
[14] N. Dennis, A. R. Katritzky, S. K. Parton, and Y. Takeuchi, *J.C.S. Chem. Comm.*, 1972, 707.

instead of the compound (15), which was at that time expected on the basis of structure (3) rather than (8) for the starting material. We postulated a displacement reaction of the 2,4-dinitrophenyl residue by benzyne.[14]

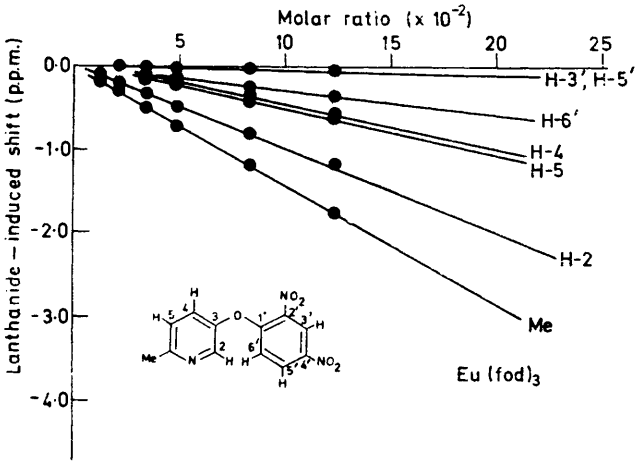
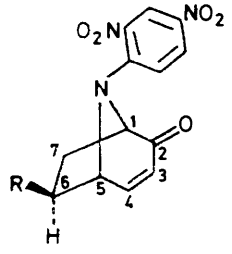


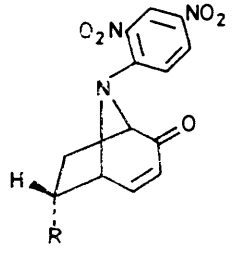
FIGURE 2 $\delta\Delta$ *vs.* molar ratio of lanthanide to substrate for 3-(2,4-dinitrophenoxy)-6-methylpyridine (9)

We now believe that initial attack of benzyne at the pyridine nitrogen atom of (8) yields (16) which is hydrolysed to the betaine (2) by water or alcohols in the reaction mixture. A second molecule of benzyne then reacts as dipolarophile with (2) in the normal way. Authentic (2) is known to give the cycloadduct (14) with benzyne.[14]

The authentic 2,4-dinitrophenyl betaine (3) was isolated by treating a suspension of 1-(2,4-dinitrophenyl)-3-hydroxypyridinium chloride (7) in acetonitrile with triethylamine. It reacts with *N*-phenylmaleimide, acrylonitrile, and methyl acrylate to give the expected cycloadducts as mixtures of *endo*- and *exo*-isomers [(17)—(20) and (22)] in high yields. In all the reactions of the betaine (3) with dipolarophiles, 3-(2,4-dinitrophenoxy)-pyridine (8) is formed as a by-product. However, isolation of the betaine is not necessary; liberation of (3) in



(17) R = CO_2Me
(18) R = CN



(19) R = CO_2Me
(20) R = CN
(21) R = Ph

the presence of a dipolarophile allows the 1,3-dipolar cycloaddition to compete favourably with the rearrangement in solution and gives adducts with numerous dipolarophiles.

The structures of the cycloadducts were confirmed by i.r., mass, and n.m.r. spectra. A characteristic pattern is observed for H-3 and H-4 [for numbering see (17)] in the n.m.r. spectra (Table 2) of all the *N*-methyl,[2,3] *N*-phenyl,[8] and *N*-(2,4-dinitrophenyl) cycloadducts investigated: H-4 [δ 6·8—7·0 for *N*-methyl, 7·2—7·6 for *N*-phenyl, and 6·68—7·53 for *N*-(2,4-dinitrophenyl)] gives rise to a quartet with $J_{3,4}$ 10·0 and $J_{4,5}$ 5·0 Hz, and H-3 [δ 6·06—6·15 for *N*-methyl, 6·0—6·1 for *N*-phenyl, and 5·94—6·32 for *N*-(2,4-dinitrophenyl)] gives a doublet of doublets with $J_{3,4}$ 10·0 and $J_{1,3}$ 1·4 Hz. The H-4 quartet for the *N*-phenyl [8] derivatives overlaps with the aromatic signals but this characteristic quartet is readily observable in the spectra of all *N*-(2,4-dinitrophenyl) derivatives.

Treatment of the betaine (3) with *N*-phenylmaleimide afforded only the *endo*-adduct (22), in the n.m.r. spectrum of which H-1 gives a broadened doublet ($J_{1,7\text{-}exo}$ 8·2, $J_{1,3}$ 1·1 Hz) and H-5 a doublet of doublets ($J_{4,5}$ 5·1 and $J_{5,6\,exo}$ 7·0 Hz). Both H-6 and H-7 of the *exo*-adduct (22) give a doublet of doublets.

TABLE 2

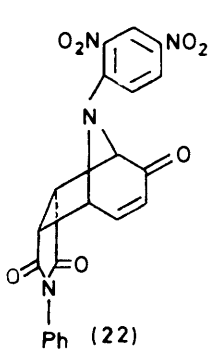
Proton n.m.r. spectra of cycloadducts [a]

Proton(s)	(17) [b]	(18) [c]	(19) [b]	(20) [b]	(21) [b]	(22) [c]	(23) [c]
	δ Values						
1	4·50 *d*	4·55 *d*	4·33 *d*	4·30 *d*	4·50 *d*	4·87 *d*	4·69 *d*
3	6·08 *d*	5·94 *d*	6·05 *d*	6·11 *d*	6·12 *d*	6·32 *d*	6·0 *d*
4	7·26 *d*	7·28 *d*	7·08 *d*	7·04 *d*	6·68 *d*	7·53 *d*	7·45 *d*
5	4·83 *e*	5·05 *e*	4·70 *d*	4·62 *d*	4·54 *d*	5·49 *d*	4·72 *d*
6-*exo*			3·80 *g*	3·58 *g*	4·19 *g*	4·26 *d*	2·64 *f*
6-*endo*	3·15 *d*	3·57 *d*					2·06 *d*
7-*exo*	3·15 *f*	2·76 *f*	2·90 *f*	3·01 *f*	3·08 *g*	4·42 *d*	4·04 *f*
7-*endo*	2·10 *d*	2·29 *d*	2·2 *d*	2·07 *d*	2·17 *d*		
3′	8·67 *e*	8·56 *e*	8·65 *e*	8·60 *e*	8·71 *e*	8·71 *e*	8·50 *e*
5′	8·20 *d*	8·25 *d*	8·20 *d*	8·13 *d*	8·24 *d*	8·35 *d*	8·16 *d*
6′	6·95 *e*	7·13 *e*	6·86 *e*	6·74 *e*	6·92 *e*	7·09 *e*	7·11 *e*
CO_2Me	3·84		3·73				
Ph					7·30 *h*	7·45 *g*	
Coupling	*J*/Hz						
1,3					1·5	1·1	
1,7-*endo*	0·0	0·0	0·0	0·0	1·1		
1,7-*exo*	8·0	8·0	8·5	8·5	8·3	8·2	7·5
3,4	10·0	9·5	10·0	10·0	9·9	10·0	10·0
4,5	5·5	5·5	5·0	6·0	5·0	5·1	5·5
5,6-*endo*	0·0	0·0					0·0
5,6-*exo*			6·0	6·0	5·8	7·0	6·0
6-*exo*,6-*endo*							13·0
6-*exo*,7-*endo*			7·0	6·0	7·1		
6-*exo*,7-*exo*			11·0	10·5	9·5	9·0	10·5
6-*endo*,7-*endo*	10·0	9·5					
6-*endo*-7-*exo*		4·0					4·0
7-*exo*,7-*endo*	14·5	14·0	14·0	14·0	14·0		
3′,5′	2·5	2·5	2·5	2·5	2·5	2·6	2·5
5′,6′	9·5	9·5	9·5	9·5	9·5	9·3	9·5

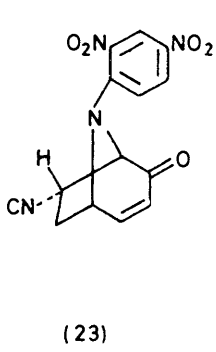
[a] Me_4Si as internal standard. [b] In $CDCl_3$. [c] In $(CD_3)_2SO$. [d] Doublet of doublets. [e] Doublet. [f] Octet. [g] Doublet of triplets. [h] Complex.

For the acrylonitrile and methyl acrylate cycloadducts (17)—(20), the H-1 signal appears as a doublet ($J_{1,7\text{-}exo}$ 8·0—8·5 Hz), and that of H-5 as a doublet ($J_{4,5}$ 5·0—6·0 Hz) for the *exo*-isomer and a quartet ($J_{4,5}$ 5·0—6·0, $J_{5,6\text{-}exo}$ 6·0 Hz) for the *endo*-isomers. For the *exo*-isomers (17) and (18), H-6-*endo* gives a quartet ($J_{6\text{-}endo,7\text{-}exo}$ and $J_{6\text{-}endo,7\text{-}endo}$), but for the *endo*-isomers (19) and (20), H-6-*exo* gives a doublet of triplets because of significant additional coupling ($J_{5,6\text{-}exo}$ 6·0 Hz). In the spectra of all four isomers (17)—(20), H-7-*exo* gives an octet and H-7-*endo* a quartet. All these assignments were confirmed by exhaustive n.m.r. double-resonance techniques involving all ring protons, *e.g.* irradiation at the frequency of H-5 caused the H-4 quartet to collapse to a doublet in every case.

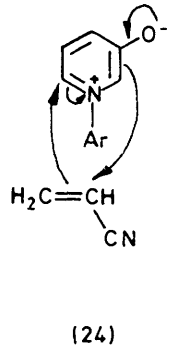
All the cycloadducts (17)—(23) showed the expected characteristic n.m.r. pattern for the *N*-(2,4-dinitrophenyl) group (Table 2).



(22)



(23)



(24)

The reaction of the betaine (3) with acrylonitrile yielded, in addition to the two products (18) and (20), expected on the basis of previous results,[2,3,5,8] a third cycloadduct [15] (23), m.p. 204—206°, identified from its n.m.r. spectrum (Table 2): H-4 gives a quartet (coupling to H-3 and H-5), H-3 forms a doublet (coupling with H-4) further split by W-type long-range coupling with H-1. The signals for the bridgehead H-5 and H-1 again appear as a doublet of doublets and as a doublet with fine splitting due to long-range coupling with H-3, respectively. Thus the cyano-group must have the *endo*-configuration either at C-6 or C-7. As the isomer (23) is different from the known 6-*endo*-isomer (20), it must have structure (23). In agreement, H-5 is coupled to H-6-*exo* with *J* 6·0 Hz, and H-6-*exo* is in turn coupled geminally to H-6-*endo* with *J* 13 Hz, as expected for a 7-*endo*-cyano-group. The structural assignment was confirmed by double-resonance experiments, *e.g.* on irradiation at the frequency of H-1, the low-field (deshielded by the cyano-group) octet of H-7-*exo* collapsed to four lines.

The formation of the adduct (23) indicates that activation by the cyano-group is not needed for the cycloaddition reaction to proceed [see (24)]. Indeed, the reaction of the betaine (3) with the relatively unreactive dipolarophile [16] styrene produced the *endo*-cycloadduct (21), m.p. 188—190°, in high yield (50%). The 6-*endo*-configuration of the phenyl group was confirmed by the n.m.r. spectrum in which the H-5 signal appears as a quartet ($J_{4,5}$ 5·0, $J_{5,6\text{-}exo}$ 5·8 Hz).

All attempts to quaternise the cycloadducts (17)—(23) with methyl iodide failed, presumably owing to the steric requirements of the *N*-(2,4-dinitrophenyl) group and the decreased basicity of the nitrogen atom. Conversion of these cycloadducts into tropones and tropolones by other methods is in progress.

EXPERIMENTAL

M.p.s were determined with a Reichert apparatus. Spectra were recorded with a Perkin-Elmer 257 grating spectrophotometer (i.r.), a Unicam SP 800 spectrophotometer (u.v.), a Hitachi–Perkin-Elmer RMU-6E mass spectrometer, and a Varian HA-100 (100 MHz) n.m.r. spectrometer. Compounds were purified until they were observed as single spots on t.l.c. [Kieselgel GF254 (type 60); $CHCl_3$–EtOAc (50 : 50) as eluant].

1-(2,4-*Dinitrophenyl*)-3-*hydroxypyridinium Chloride* (7).—3-Hydroxypyridine (20 g, 0·2 mol) and 1-chloro-2,4-dinitrobenzene (40 g, 0·2 mol) were heated under reflux in tetrahydrofuran (150 ml) at 100° for 24 h to give the salt (7) (40 g, 75%) as buff plates (from EtOH–Et_2O), m.p. 205—206° (lit.,[6] 193—194°); $\lambda_{max.}$ (EtOH) 213 (log ε 4·34), 225 (4·35), and 302 (4·1) nm; $\nu_{max.}$ (Nujol) 3600—3300 (OH), 1610 (benzene, C=C), 1540 (antisym. NO_2), and 1340 (sym. NO_2) cm^{-1}.

3-(2,4-*Dinitrophenoxy*)*pyridine* (8).—(i) *Vompe's procedure.*[6] The hydrochloride (7) (10 g, 0·034 mol) and aqueous $NaHCO_3$ (150 ml, 10%) were kept for 3 days at 0° to give the ether (8) (3·1 g, 34%), which crystallised from EtOH–Et_2O as pale yellow plates, m.p. 128—130° (lit.,[6] 128°; lit.,[9] 130°) (Found: C, 50·6; H, 3·1; N, 16·1. Calc. for $C_{11}H_7N_3O_5$: C, 50·6; H, 2·8; N, 16·1%); $\nu_{max.}$ (Nujol) 1600 (benzene, C=C), 1520 (antisym. NO_2), 1340 (sym. NO_2), and 1270 (Ar–O–Ar, C–O) cm^{-1}; $\lambda_{max.}$ (EtOH) 218 (log ε 4·16) and 273 (4·09) nm; *m/e* 261.

(ii) *Yoneda's procedure.*[9] 3-Hydroxypyridine (2·5 g, 0·0264 mol), 1-chloro-2,4-dinitrobenzene (5·0 g, 0·025 mol), KOH (1·5 g, 0·026 mol), and MeOH (15 ml) were heated under reflux for 1 h, and cooled. The ether (8) precipitated and after recrystallisation from MeOH (yield 3·8 g, 58·5%) had m.p. 128—130°, not depressed by admixture with the sample prepared by method (i).

3-(2,4-*Dinitrophenoxy*)*pyridinium Hydrochloride* (12).—Obtained by treatment of the ether (8) in Me_2CO with 12N-HCl, this compound separated as *needles* (4·3 g, 100%) from EtOH–Et_2O, m.p. 114—115° (Found: C, 42·7; H, 2·9; Cl, 11·5; N, 13·7. $C_{11}H_8ClN_3O_5$,0·5H_2O requires C, 42·7; H, 2·9; Cl, 11·5; N, 13·6%); $\nu_{max.}$ (Nujol) 3600—3300 (H_2O), 2800—2200 ($\overset{+}{\geq}NH$), 1600 (benzene, C=C), 1530 (antisym. NO_2), 1340 (sym. NO_2), and 1260 (Ar–O–Ar, C–O) cm^{-1}; $\lambda_{max.}$ (EtOH) 218 (log ε 4·14) and 272 (4·06) nm.

Reaction of 3-*Hydroxy*-6-*methylpyridine* (10) *with* 1-*Chloro*-2,4-*dinitrobenzene.*— 3-Hydroxy-6-methylpyridine (10) (3·0 g, 0·0275 mol) and 1-chloro-2,4-dinitrobenzene (5·6 g, 0·0275 mol) were fused at 120° for 6 h. The cooled mixture was extracted with $CHCl_3$ and then with water. The $CHCl_3$ layer was evaporated and the residue was chromatographed on alumina (B.D.H. aluminium oxide, neutral; $CHCl_3$) to give 3-(2,4-*dinitrophenoxy*)-6-*methylpyridine* (9) as yellow prisms (2·5 g, 68%), m.p. 78° (from Et_2O) (Found: C, 52·4; H, 3·5; N, 15·0. $C_{12}H_9N_3O_5$ requires C, 52·4; H, 3·3; N, 15·2%); $\nu_{max.}$ (Nujol) 1600 (benzene, C=C), 1520 (antisym. NO_2), 1340 (sym. NO_2), and 1270 (Ar–O–Ar, C–O) cm^{-1}; $\lambda_{max.}$ (EtOH) 219 (log ε 4·26) and 278 (4·19) nm; *m/e* 275.

The aqueous layer was evaporated to give 3-*hydroxy*-6-*methylpyridinium hydrochloride*, which formed needles (1·5 g, 75·0%), m.p. 156° (from EtOH–Et_2O) (Found: C, 66·5; H, 6·3; N, 12·6. C_6H_8ClNO requires C, 66·1; H, 6·4; N, 12·8%), converted into 3-hydroxy-6-methylpyridine (10) (m.p. 169°) upon treatment with aqueous $NaHCO_3$ (20%).

1-(2,4-*Dinitrophenyl*)-3-*oxidopyridinium* (3).—1-(2,4-Dinitrophenyl)-3-hydroxypyridinium chloride (7) (6 g, 0·02

[15] N. Dennis, B. Ibrahim, A. R. Katritzky, and Y. Takeuchi, *J.C.S. Chem. Comm.*, 1973, 292.

[16] R. Huisgen, R. Grashey, and J. Sauer, in ' The Chemistry of Alkenes,' in the series ' The Chemistry of Functional Groups,' ed. S. Patai, Interscience, London, 1964, p. 865.

mol) was suspended in MeCN (75 ml) and Et_3N (2 g, 0·02 mol) was added at room temperature. The mixture which soon became homogeneous, was quickly filtered and the filtrate was set aside for 5 min. The orange crystalline solid which precipitated was collected and washed well with $CHCl_3$ (100 ml) until the filtrate gave a negative test for chloride. The *betaine* (3) (4·5 g, 85·5%) crystallised as orange prisms from MeCN and had m.p. 112° (Found: C, 50·3; H, 2·9; N, 16·2. $C_{11}H_7N_3O_5$ requires C, 50·5; H, 2·8; N, 16·1%); $\nu_{max.}$ (Nujol) 1615, 1590 (benzene, C=C), 1510 (antisym. NO_2), 1540 (C–O^-), and 1340 (sym. NO_2) cm^{-1}; $\lambda_{max.}$ (EtOH) 213 (log ε 4·3), 225 (4·37), 255 (4·22), and 300 (3·85) nm; *m/e* 261.

Methyl 8-(2,4-*Dinitrophenyl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo- *and* -6-exo-*carboxylate* [(19) *and* (17)].—A well stirred suspension of 1-(2,4-dinitrophenyl)-3-hydroxypyridinium chloride (7) (6·0 g, 0·02 mol) in an excess of methyl acrylate (200 ml) was heated to reflux. Et_3N (2 g, 0·02 mol) in methyl acrylate (20 ml) was added dropwise during 1 h. The mixture was heated under reflux for a further 12 h then filtered. The filtrate was evaporated (50° at 10 mmHg) and the residue was chromatographed on alumina [B.D.H. aluminium oxide, neutral (100 g); benzene]. The eluate was evaporated and the residue (3·55 g, 50%) gradually solidified (three components by t.l.c.).

The mixture was separated by preparative t.l.c. on silica gel (Kieselgel PF254; $CHCl_3$). 3-(2,4-Dinitrophenoxy)-pyridine (8) was separated as pale yellow plates, m.p. 128—130°. The endo-6-*carboxylate* (19) was isolated as yellow prisms (1·75 g, 25%), m.p. 171° (from $[CH_2]_4O$–H_2O) (Found: C, 51·5; H, 3·8; N, 12·1. $C_{15}H_{13}N_3O_7$ requires C, 51·9; H, 3·8; N, 12·1%); $\nu_{max.}$ (Nujol) 1730 (ester, C=O) 1690 (αβ-unsaturated ketone, C=O), 1610 (C=C), 1515 (antisym. NO_2), and 1340 (sym. NO_2) cm^{-1}; $\lambda_{max.}$ (EtOH) 223 (log ε 4·48) and 347 (4·27) nm; *m/e* 347. The exo-*isomer* (17) was isolated as yellow prisms (1·75 g, 25%), m.p. 170—172° (from $[CH_2]_4O$–H_2O) (Found: C, 52·3; H, 4·0; N, 11·6%); $\nu_{max.}$ (Nujol) 1735 (ester, C=O), 1690 (αβ-unsaturated ketone, C=O), 1610 (C=C), 1515 (antisym. NO_2), and 1340 (sym. NO_2) cm^{-1}; $\lambda_{max.}$ (EtOH) 224 (log ε 4·42) and 347 (4·21) nm; *m/e* 347.

8-(2,4-*Dinitrophenyl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo- *and* -6-exo-*carbonitrile* [(20) *and* (18)] *and* 8-(2,4-*Dinitrophenyl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-7-endo-*carbonitrile* (23).—A well-stirred suspension of 1-(2,4-dinitrophenyl)-3-hydroxypyridinium chloride (7) (6 g, 0·02 mol) in an excess of acrylonitrile (100 ml) was heated to reflux. Et_3N (2 g, 0·02 mol) in acrylonitrile (10 ml) was added dropwise during 1 h. The mixture was heated under reflux for a further 6 h. The precipitated salt was filtered off and the filtrate evaporated (40° at 12 mmHg). The solid residue was chromatographed on alumina [B.D.H. aluminium oxide, neutral (120 g); benzene]. The eluate was evaporated and the residue solidified (four components by t.l.c.). The mixture was separated by preparative t.l.c. on silica gel [Kieselgel PF254; EtOAc—$CHCl_3$ (50 : 50)]. 3-(2,4-Dinitrophenoxy)pyridine (8) was separated as pale yellow plates, m.p. 128—130°. The endo-6-*carbonitrile* (20) (1·8 g, 28%) was isolated as yellow prisms, m.p. 193° (from $[CH_2]_4O$–H_2O) (Found: C, 53·7; H, 3·4; N, 17·4. $C_{14}H_{10}N_4O_5$ requires C, 53·5; H, 3·2; N, 17·8%); $\nu_{max.}$ (Nujol) 2260 (C≡N), 1690 (αβ-unsaturated ketone, C=O), 1610 (C=C), 1600, 1520 (antisym. NO_2), and 1335 (sym. NO_2) cm^{-1}; $\lambda_{max.}$ (EtOH) 222 (log ε 4·32) and 344 (4·13) nm; *m/e* 314. The exo-6-*carbonitrile* (18) was isolated as yellow prisms (2·3 g, 37%), m.p. 221—223° (from $[CH_2]_4O$–H_2O) (Found: C, 53·3; H, 3·5; N, 17·6%); $\nu_{max.}$ (Nujol) 2260 (C≡N), 1690 (αβ-unsaturated ketone, C=O), 1610 (C=C), 1600, 1520 (antisym. NO_2), and 1335 (sym. NO_2) cm^{-1}; $\lambda_{max.}$ (EtOH) 223 (log ε 4·69) and 340 (4·46) nm; *m/e* 314. The endo-7-*carbonitrile* (23) was separated as yellow prisms (0·63 g, 10%), m.p. 204—206° (from $[CH_2]_4O$–EtOH) (Found: C, 53·4; H, 3·3; N, 17·5%); $\nu_{max.}$ (Nujol) 225 (C≡N), 1690 (αβ-unsaturated ketone, C=O), 1615, 1605, 1590 (C=C), 1510 (antisym. NO_2), and 1340 (sym. NO_2) cm^{-1}; $\lambda_{max.}$ (EtOH) 222 (log ε 4·35) and 344 (4·15) nm; *m/e* 314.

8-(2,4-*Dinitrophenyl*)-endo-6-*phenyl*-8-*azabicyclo*[3.2.1]*oct*-3-*en*-2-*one* (21).—A well-stirred suspension of 1-(2,4-dinitrophenyl)-3-hydroxypyridinium chloride (1 g, 3·3 mmol) in an excess of styrene (100 ml) was heated to reflux. Et_3N (0·33 g, 3·3 mmol) in styrene (20 ml) was added dropwise during 1 h. After filtration, the solution was evaporated (50°; 10 mmHg) and the residue was chromatographed on alumina (B.D.H. aluminium oxide, neutral; $CHCl_3$). The eluate was evaporated to give a solid (0·73 g), which was recrystallised from $[CH_2]_4O$–EtOH to give the endo-6-*phenyl cycloadduct* (21) (0·5 g, 50%), as yellow prisms, m.p. 188—190° (Found: C, 62·5; H, 4·3; N, 11·3. $C_{19}H_{15}N_3O_5$ requires C, 62·5; H, 4·1; N, 11·5%); $\nu_{max.}$ (Nujol) 1685 (αβ-unsaturated ketone, C=O), 1610, 1590 (benzene, C=C), 1515 (antisym. NO_2), and 1340 (sym. NO_2) cm^{-1}; $\lambda_{max.}$ (EtOH) 220·5 (log ε 4·69), 207·5 (4·78), and 353 (4·29) nm; *m/e* 365.

8-(2,4-*Dinitrophenyl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6,7-endo-*dicarboxylic* N-*Phenylimide* (22).—A well stirred solution of 1-(2,4-dinitrophenyl)-3-oxidopyridinium (1·8 g, 0·0069 mol) and *N*-phenylmaleimide (1·19 g, 0·0069 mol) in MeCN (40 ml) was heated under reflux for 2 h. On cooling, the excess of MeCN was removed under vacuum to leave a dark gum which was dissolved in hot EtOH (10 ml). After 1 h, the yellow crystalline solid which separated was filtered off and washed with Me_2CO (10 ml). Recrystallisation from dioxan–EtOH gave the endo-*cycloadduct* (22) (1·7 g, 57%) as yellow prisms, m.p. 247° (Found: C, 57·5; H, 3·4; N, 12·8. $C_{21}H_{14}N_4O_7$ requires C, 58·1; H, 3·2; N, 12·9%); $\nu_{max.}$ (Nujol) 1710 (amide, C=O), 1605, 1590 (benzene, C=C), 1510 (antisym. NO_2), and 1340 (sym. NO_2) cm^{-1}; $\lambda_{max.}$ (EtOH) 208 (log ε 4·55), 220·5 (4·49), and 343 (4·12) nm.

Reaction of Benzyne with 3-(2,4-*Dinitrophenoxy*)*pyridine*.—3-(2,4-Dinitrophenoxy)pyridine (9 g, 0·034 mol), n-pentyl nitrite (7·94 g, 0·068 mol), and 1,2-dichloroethane (200 ml) were heated to reflux (76°) with stirring. Anthranilic acid (9·3 g, 0·068 mol) in bis-(2-methoxyethyl) ether (40 ml) was added dropwise to the refluxing solution during 2 h. This was then heated under reflux for a further 3 h. Water (100 ml) was then added and the mixture extracted with $CHCl_3$. The extract was dried (Na_2SO_4) and evaporated *in vacuo* and the residue was chromatographed on silica gel (200 g). Elution with $CHCl_3$ gave a yellow product which was further purified by preparative thick-layer chromatography [Kieselgel PF254; $CHCl_3$]. The product crystallised from Et_2O to give 5,9-dihydro-10-phenyl-5,9-epiminobenzocyclohepten-6-one (14) as yellow prisms (3 g, 35%), m.p. 192° (lit.,[8] 192—193°).

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