1,3-Dipolar Character of Six-membered Aromatic Rings. Part XXVI.[1] 3-Hydroxypyridine and 1-Benzyl-3-oxidopyridinium

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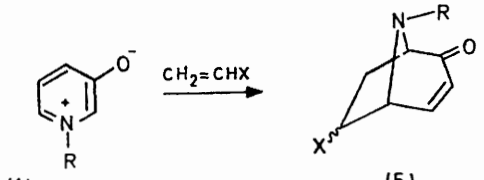
3-Hydroxypyridine undergoes successive 1,3-dipolar and Michael addition of acrylonitrile or methyl acrylate in high yield. These additions are thermally reversed, and 4-bromo-3-hydroxypyridine was prepared by adduct bromination followed by retro-addition.

1-Benzyl-3-oxidopyridinium undergoes various 1,3-dipolar additions.

THE *N*-substituent R in the pyridinium betaines (1) profoundly influences the ease of the cycloaddition



(1)

(2) R = CH_2CH_2CN

(3) R = $CH_2CH_2CO_2Me$

(4) R = CH_2Ph

(5)

reaction (1) ⟶ (5).[2] We now report our work with the betaines (1; R = H or $PhCH_2$).

Hydrogen as N-*Substituent.*—3-Hydroxypyridine (6) in solutions in polar solvents exists to a considerable extent [3] in the betaine form (7). We therefore studied its reactions with various dipolarophiles. Acrylonitrile gave a mixture of *endo*- (8) and *exo*- (11) cycloadducts (1 : 1) in 90% yield, from which the *exo*-isomer (11) could be separated as pale yellow needles, m.p. 72—73 °C. The structures were demonstrated by elemental analysis, i.r. and n.m.r.† spectral data, and the formation of the 2,4-dinitrophenylhydrazone (13), m.p. 215—219 °C (from the epimeric mixture). The stereochemistry of the cycloadducts was elucidated by n.m.r. spectroscopy. For both the *exo*-isomer (11) and the *endo*-isomer (8), the signal for the bridgehead proton H-1 appears as a doublet ($J_{1,7\text{-}exo}$ 7.5—8.0 Hz) irrespective of the

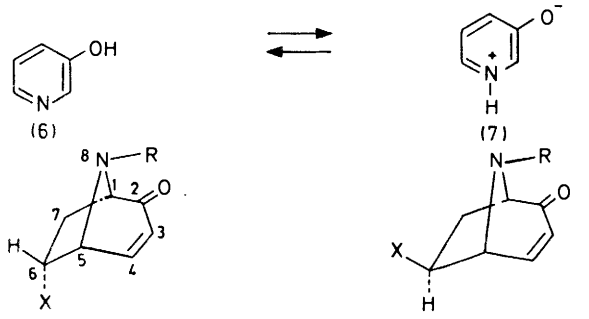
† N.m.r. data for compounds indicated in the Experimental section with an asterisk are given in the Supplementary Publication No. SUP 21797 (3 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1975, Index issue.

[1] Part XXV, N. Dennis, A. R. Katritzky, and R. Rittner, preceding paper.

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

[3] A. R. Katritzky and J. M. Lagowski, *Adv. Heterocyclic Chem.*, 1963, **1**, 353; J. Elguero, C. Marzin, A. R. Katritzky, and P. Linda, 'The Tautomerism of Heterocycles,' Academic Press, New York, 1976, p. 84.

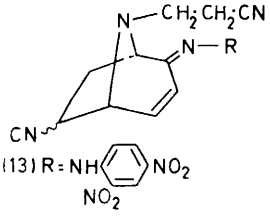
stereochemistry, and that of H-5 is a doublet ($J_{4,5}$ 5.0 Hz) for the *exo*-isomer (11) and a quartet ($J_{4,5}$ 5.0, $J_{5,6\text{-}exo}$ 6.0 Hz) for the *endo*-isomer (8). For the *exo*-isomer (11), the H-6-*endo* signal is a quartet ($J_{6\text{-}endo,7\text{-}exo}$ and $J_{6\text{-}endo,7\text{-}endo}$), but for the *endo*-isomer (8), the H-6-*exo* signal is a doublet of triplets because of significant additional coupling ($J_{5,6\text{-}exo}$ 6.0 Hz). In both isomers, the H-7-*exo* signal is an octet and that of H-7-*endo* a quartet. Each isomer displays a doublet of triplets assignable to the *N*-cyanoethyl protons.



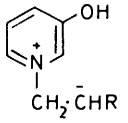
(6) (7)

(8) X = CN, R = CH_2CH_2CN
(9) X = CO_2Me, R = $CH_2CH_2CO_2Me$

(10) X = CN, R = Me
(11) X = CN, R = CH_2CH_2CN
(12) X = CO_2Me, R = $CH_2CH_2CO_2Me$



(13) R = NH(2,4-$(NO_2)_2$C$_6$H$_3$)



(14) R = CN
(15) R = CO_2Me

Similarly, reaction of 3-hydroxypyridine with methyl acrylate produced a mixture of *endo*- (9) and *exo*- (12) cycloadducts (1 : 1) in 86% yield. Although these stereoisomers could not be separated, their structures and stereochemistry were demonstrated by elemental analysis and i.r. and n.m.r. spectral data.

The *N*-(2-cyanoethyl)- [in (8) and (11)] and the *N*-(2-methoxycarbonylethyl) [in (9) and (12)] groups could have arisen by initial reaction of the zwitterion (7) to yield a cycloadduct (5; R = H) with an NH group which subsequently reacted with a further molecule of the addend by a Michael-type addition. Alternatively, the *N*-substituted betaines (2) and (3) could be the active intermediates resulting from direct reaction between the addend and the nitrogen atom of the substituted pyridine, with the initially formed zwitterions (14) and (15) undergoing tautomerisation to (2) and (3). Pyridine reacts with maleic acid,[4] with acetylenedicarboxylates,[5] and with *p*-benzoquinone [6] to produce zwitterions.

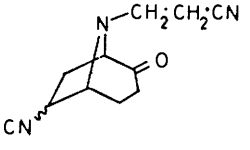
[4] O. Lutz, *Ber.*, 1910, **43**, 2636.
[5] R. M. Acheson, *Adv. Heterocyclic Chem.*, 1963, **1**, 125.
[6] E. de Barry Barnett, J. W. Cook, and E. P. Driscoll, *J. Chem. Soc.*, 1923, **123**, 503.
[7] N. Dennis, A. R. Katritzky, and M. Ramaiah, *J.C.S. Perkin I*, 1975, 1506.

However, our corresponding work in the phthalazinium series [7] indicates that the cycloadduct formation is probably the first step.

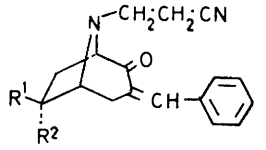
The reactions of 3-hydroxypyridine with methyl acrylate and acrylonitrile constitute simple, one-step, high-yield conversions into complex tropane-like compounds. Unfortunately, 3-hydroxypyridine is unreactive towards many other electron-deficient addends: *N*-phenylmaleimide, 2- and 4-vinylpyridine, diethyl maleate, fumarate, and azodiformate, phenyl vinyl and divinyl ketone, methyl cinnamate, styrene, crotononitrile, methacrylonitrile, methacrylaldehyde, phenyl propiolate, tetracyanoethylene, and fumaronitrile.

Reactions of 3-Hydroxypyridine Cycloadducts.—1,3-Dipolar cycloadditions are reversible thermally,[8] photochemically,[9] and by electron impact.[10] Both cycloadduct mixtures [(8) + (11) and (9) + (12)] undergo ready retro-1,3-dipolar cycloaddition reactions under thermal conditions [refluxing xylene (138 °C) or sublimation (120 °C at 1 mmHg)] to yield 3-hydroxypyridine. We have attempted to exploit such retroreactions for the synthesis of substituted pyridines. Hydrogenation of the isomeric cycloadducts (8) and (11) over Pd–C gave the saturated product (16), which readily formed the benzylidene derivatives (17) and (18) with benzaldehyde. We failed to convert the benzylidene derivatives (17) and (18) into 4-benzyl-3-hydroxypyridine (19) by thermally induced double-bond migration [to (22)] followed by retro-1,3-dipolar cycloaddition.

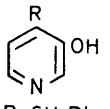
Treatment of the isomeric cycloadducts (8) and (11) with bromine in methylene chloride afforded the 3-bromo-derivatives (23) and (24) by bromination followed by dehydrobromination; the *exo*-isomer (24) was isolated. Sublimation of the *exo*-isomer (24) at 180 °C at 1 mmHg yielded 4-bromo-3-hydroxypyridine (20) as



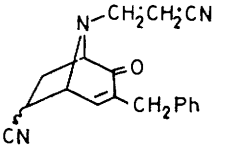
(16)



(17) R^1 = H, R^2 = CN
(18) R^1 = CN, R^2 = H



(19) R = CH_2Ph
(20) R = Br
(21) R = OH



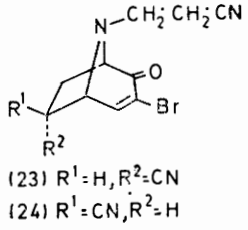
(22)

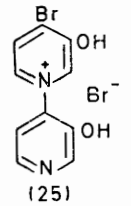
the quaternary salt (25) *via* a thermally induced retro-1,3-dipolar cycloaddition. However attempts to prepare 3,4-dihydroxypyridine (21) by treatment of the

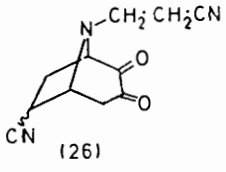
[8] R. Huisgen, H. Hauck, R. Grashey, and H. Seidl, *Chem. Ber.*, 1968, **101**, 2568.
[9] K. Burger and J. Fehn, *Tetrahedron Letters*, 1972, 1263.
[10] Y. Nomura, F. Furusaki, and Y. Takeuchi, *J. Org. Chem.*, 1972, **37**, 502.

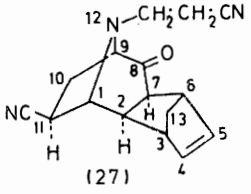
hydrogenated cycloadduct (16) with selenium dioxide failed to produce the key intermediate 1,2-dicarbonyl compound (26). The keto-group of the cycloadduct type (5) is unreactive towards traditional carbonyl reagents including Wittig and Grignard reagents, presumably because of steric hindrance by the N-CH_2·CH_2·CN group. Unreactivity of keto-groups in bicyclo[3.3.1]nonan-3-ones has been reported.[11] However, cyclopentadiene monomer underwent a Diels–Alder cycloaddition at the activated 3,4-double bond of the *exo*-adduct (11) to yield the adduct (27). N.m.r. spectroscopy indicates *exo*-addition of cyclopentadiene (the H-1 signal is a singlet).

1-*Benzyl*-3-*oxidopyridinium*.—Shapiro *et al.*[12] reported 1-benzyl-3-hydroxypyridinium bromide (28) and its conversion into the hydrated 1-benzyl-3-oxidopyridinium (4) with sodium in propan-1-ol–methanol, but no 1,3-dipolar additions have been described previously. We prepared 1-benzyl-3-oxidopyridinium (4) *in situ* from 1-benzyl-3-hydroxypyridinium bromide [12] (28) and triethylamine; with acrylonitrile it yielded the isomeric cycloadducts (29) and (30) (1 : 1) as shown by i.r. and n.m.r. The betaine (4) with the relatively unreactive [13] addend, styrene, produces both the 6-*endo*-cycloadduct





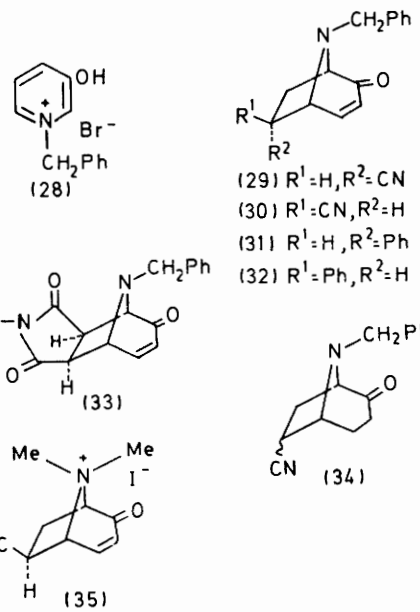




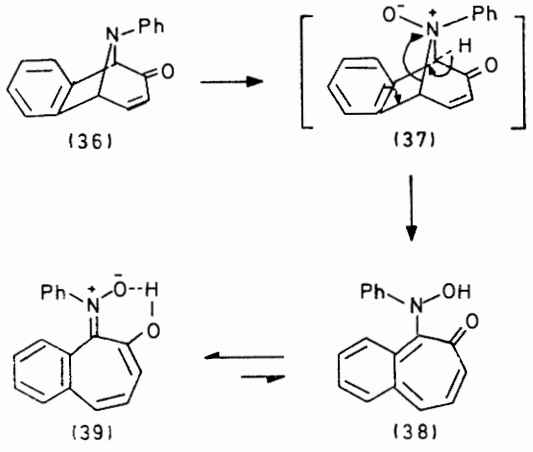
(31) [the *endo*-stereochemistry follows from the H-5,-H-6 coupling (6.0 Hz)] and the 6-*exo*-cycloadduct (32) [$J_{5.6}$ 0 Hz]. N-Phenylmaleimide reacts with the betaine (4) to form exclusively the *exo*-cycloadduct (33) ($J_{1.7} = J_{5.6} = 0$ Hz).

The cycloadduct mixture [(29) and (30)] was hydrogenated to the saturated compounds (34). Quaternisation of the isomeric mixture [(29) and (30)] unexpectedly yielded (35), by dissociation of the benzyl iodide from the initial product followed by further methylation of (10).

We have previously shown [14] that 3-hydroxypyridine reacts with benzyne (prepared [15] by diazotisation of anthranilic acid) to form 5,9-dihydro-10-phenyl-5,9-iminobenzocyclohepten-6-one (36). The adduct (36) with *m*-chloroperbenzoic acid yields compound (38) ⇌ (39), m.p. 137—138 °C, for which i.r. and n.m.r. spectral



data indicate the nitrone tautomeric structure (39). This reaction presumably proceeds *via* the intermediate N-oxide (37), which suffers cleavage of the C(5)–N bond (Scheme).



SCHEME

EXPERIMENTAL

M.p.s were determined with a Reichert apparatus. Spectra were recorded with a Perkin-Elmer 257 grating i.r. spectrophotometer, a Hitachi–Perkin-Elmer RMU-6E mass spectrometer, a Unicam SP 800A u.v. spectrophotometer, and a Varian HA-100 n.m.r. spectrometer. Compounds were purified until they were observed as single spots by t.l.c. on silica gel GF 254.

8-(2-*Cyanoethyl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-exo- *and* -6-endo-*carbonitrile*, (11) * *and* (8) *.—3-Hydroxy-

[11] T. Momose, S. Atarashi, and O. Muraoka, *Tetrahedron Letters*, 1974, 3697.

[12] S. L. Shapiro, K. Weinberg, and L. Freedman, *J. Amer. Chem. Soc.*, 1959, **81**, 5141.

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

[14] N. Dennis, A. R. Katritzky, and S. K. Parton, *J.C.S. Perkin I*, 1976, 2285.

[15] L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, 1963, **85**, 1549.

pyridine (9.5 g, 0.1 mol), acrylonitrile (90 ml), and hydroquinone (20 mg) were heated under reflux for 25 h. The excess of acrylonitrile was removed (40 °C at 5 mmHg), and the cooled residue twice chromatographed [aluminium oxide, type H; CH_2Cl_2–light petroleum (b.p. 40—60 °C) (3 : 1) and then CH_2Cl_2] to give a yellow viscous oil (18.1 g, 90%) (n.m.r. shows *endo* : *exo* ratio 50 : 50).

The mixed adducts (0.30 g) in Et_2O (170 ml) after a few days at 0 °C deposited the exo-*cycloadduct* (11) as pale yellow needles (0.092 g, 30%), m.p. 72—73 °C (from Et_2O) (Found: C, 65.8; H, 5.5; N, 20.7. $C_{11}H_{11}N_3O$ requires C, 65.7; H, 5.5; N, 20.9%); $\nu_{max.}$ (Nujol) 2 244 (C≡N) and 1 690 cm^{-1} (α,β-unsat. ketone C=O); $\lambda_{max.}$ (EtOH) 222 nm (log ε 2.95); *m/e* 201. Attempts to isolate the pure *endo*-cycloadduct (8) from the mother liquors failed, but gave an enriched mixture (n.m.r. *endo* : *exo* ratio 60 : 40) which was used for the n.m.r. study.

The mixed cycloadducts (0.94 g, 0.004 7 mol), 2,4-dinitrophenylhydrazine (0.92 g, 0.004 7 mol), EtOH–tetrahydrofuran (2 : 5, 70 ml), and conc. HCl (2 drops) were stirred at room temp. for 10 h. The solid was washed with EtOH (5 ml) and purified by preparative thick-layer chromatography (Kieselgel PF 254; tetrahydrofuran) to give orange needles (1.4 g, 80%) of the 2,4-*dinitrophenylhydrazone* (13) (from EtOH), m.p. 215—219 °C (decomp.) (Found: C, 53.3; H, 4.2; N, 25.7. $C_{17}H_{15}N_7O_4$ requires C, 53.5; H, 4.0; N, 25.7%); *m/e* 381.

Methyl 8-(2-*Methoxycarbonylethyl*)-2-*oxo*-8-*azabicyclo*-[3.2.1]*oct*-3-*ene*-6-exo- *and* -6-endo-*carboxylate*, (12) * *and* (9).*—3-Hydroxypyridine (9.5 g, 0.1 mol), methyl acrylate (80 ml), and hydroquinone (20 mg) were heated under reflux for 18 h. The excess of methyl acrylate was removed (40 °C at 5 mmHg) and the residue chromatographed [aluminium oxide, type H; light petroleum (b.p. 60—80 °C) CH_2Cl_2 (2 : 3)] to yield a yellow viscous oil (23.1 g, 86.5%) containing the mixed (50 : 50) exo- and endo-*cycloadducts* (12) and (9) (Found: C, 58.4; H, 6.3; N. 5.4. $C_{13}H_{17}NO_5$ requires C, 58.4; H, 6.4; N, 5.2%); $\nu_{max.}$ (film) 1 725 (ester C=O) and 1 685 cm^{-1} (α,β-unsat. ketone C=O); *m/e* 267.

Retro-1,3-*dipolar Cycloadditions*.—(i) The mixed 8-(2-cyanoethyl)-2-oxo-8-azabicyclo[3.2.1]oct-3-ene-6-*exo*- and -6-*endo*-carbonitriles (11) and (8) (50 : 50) (0.25 g, 1.3 × 10^{-3} mol) were heated (120 °C at 1 mmHg). 3-Hydroxypyridine (0.12 g, 98%) collected on the cold finger as plates, m.p. 129 °C (mixed m.p. 129 °C).

(ii) The mixed methyl 8-(2-methoxycarbonylethyl)-2-oxo-8-azabicyclo[3.2.1]oct-3-ene-6-*exo*- and -6-*endo*-carboxylates (12) and (9) (50 : 50) (0.4 g, 1.5 × 10^{-3} mol) were heated (140 °C at 0.2 mmHg) as above to yield 3-hydroxypyridine (0.13 g, 95%).

8-(2-*Cyanoethyl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*octane*-6-exo- *and* -6-endo-*carbonitrile* (16).—The isomeric cycloadducts (8) and (11) (2.01 g, 0.01 mol) in EtOAc (250 ml) were shaken under hydrogen at 20 °C over Pd–C (10%; 100 mg) for 3 h. The solution was evaporated to yield the *isomeric mixture* (16) as a viscous oil (1.88 g, 90%) which did not crystallise and decomposed on distillation (Found: N, 20.7. $C_{11}H_{13}N_3O$ requires N, 20.7%); $\nu_{max.}$ (film) 2 238 (C≡N) and 1 725 cm^{-1} (sat. ketone C=O); *m/e* 203.

3-*Benzylidene*-8-(2-*cyanoethyl*)-8-*azabicyclo*[3.2.1]*octane*-6-exo- *and* -6-endo-*carbonitrile*, (18) * *and* (17).*—NaOH solution (0.5 ml; 5N) was added dropwise to the cycloadduct (16) (1.0 g, 0.005 mol), and freshly distilled benzaldehyde (0.53 g, 0.005 mol) in absolute EtOH (50 ml) was stirred in at 17—20 °C. After 2 h, the EtOH was evaporated off. The residue was taken up in $CHCl_3$ (50 ml) and the solution washed with water (30 ml), dried (Na_2SO_4), and evaporated. The residual thick viscous oil (1.16 g, 80%; *endo* : *exo* 1 : 1 by n.m.r.) was separated by preparative t.l.c. [Kieselgel PF 254; benzene–EtOAc (1 : 1)]. The exo-*nitrile* (18) was obtained as yellow crystals, m.p. 107—108 °C (0.58 g, 50%) (EtOH) (Found: C, 73.8; H, 5.8; N, 14.2. $C_{18}H_{17}N_3O$ requires C, 74.2; H, 5.9; N, 14.4%); $\nu_{max.}$ ($CHBr_3$) 2 239 (C≡N), 1 700 (αβ-unsat. ketone C=O), and 1 600 cm^{-1} (C=C); $\lambda_{max.}$ (EtOH) 208 (log ε 3.204), 227 (3.398), 231 (3.380), and 301 nm (3.875); *m/e* 291. The endo-*nitrile* (17) formed a viscous gum (0.46 g, 40%); $\nu_{max.}$ ($CHBr_3$) 2 240 (C≡N), 1 700 (αβ-unsat. ketone C=O), and 1 598 cm^{-1} (C=C); $\lambda_{max.}$ (EtOH) 209 (log ε 3.69), 225 (3.68), and 300 nm (3.99); *m/e* 291.

4-*Bromo*-8-(2-*cyanoethyl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-exo- *and* -6-endo-*carbonitrile* (24) * *and* (23).—Bromine (2.6 ml, 5.1 × 10^{-2} mol) in CH_2Cl_2 (100 ml) was added dropwise at 17 °C to the mixed adducts (11) and (8) (10.05 g, 0.05 mol) in CH_2Cl_2 (400 ml). The solution was stirred at 17—20 °C for 4 h, and more bromine (2.6 ml) in CH_2Cl_2 (100 ml) was then added. After 8 h, the solution was decanted and the orange gum dissolved in $CHCl_3$ (500 ml); this solution was washed with $NaHCO_3$–H_2O, dried (Na_2SO_4), and concentrated (to 50 ml). The yellow precipitate was crystallised from EtOH to give the exo-*bromo-derivative* (24) (2.8 g, 20%), as pale yellow needles, m.p. 130 °C (Found: C, 46.8; H, 3.8; N, 15.1; Br, 28.5. $C_{11}H_{10}BrN_3O$ requires C, 47.1; H, 3.6; N, 15.0; Br, 28.6%); $\nu_{max.}$ (Nujol) 2 240 (C≡N), 1 700 (αβ-unsat. ketone C=O), and 1 585 cm^{-1} (C=C); $\lambda_{max.}$ (EtOH) 250 nm (log ε 3.95); *m/e* 280.

The endo-*bromo-derivative* (23) could not be separated.

Reaction of 8-(2-*Cyanoethyl*)-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-exo-*carbonitrile* (11) *with Cyclopentadiene*.—The cycloadduct (11) (1.0 g, 2.6 × 10^{-3} mol) and an excess of cyclopentadiene (monomer) (5 × 10^{-3} mol) in tetrahydrofuran (20 ml) were stirred for 14 days at room temp. The tetrahydrofuran was removed under vacuum (50 °C at 12 mmHg). The yellow gum was purified by thick-layer chromatography [Kieselgel PF 254; benzene–EtOAc (3 : 1)] to give 12-(2-*cyanoethyl*)-8-*oxo*-12-*azatetracyclo*-[7.2.1^{3,6}.0^{2,7}]*tridec*-4-*ene*-11-*carbonitrile* (27) * (0.34 g, 50%) as prisms, m.p. 140—144 °C (from EtOH) (Found: C, 71.6; H, 6.3; N, 15.4. $C_{16}H_{17}N_3O$ requires C, 71.9; H, 6.4; N, 15.7%); $\nu_{max.}$ ($CHBr_3$) 2 230 (C≡N) and 1 715 cm^{-1} (sat. ketone C=O); *m/e* 267.

Retro-1,3-*dipolar Cycloaddition of Compounds* (23) *and* (24).—A mixture of cycloadducts (23) and (24) (1.39 g, 4.96 × 10^{-3} mol) when heated (180 °C at 1 mmHg), gave, on the cold finger, the *salt* (25) (needles from water) (0.43 g, 50%), m.p. 295 °C (decomp; sealed tube) (Found: C, 33.8; H, 2.3; Br, 44.9; N, 8.1. $C_{10}H_8Br_2N_2O_2$ requires C, 34.5; H, 2.3; Br, 46.0; N, 8.1%); δ (D_2O) 7.7 (2H, d, *J* 7 Hz), 8.60 (2 H, d, *J* 7 Hz), 8.64 (1 H, d, H-2′, *J* 1 Hz), and 8.68 (1 H, d, H-2, *J* 1 Hz); *m/e* 186 (no M^+).

8-*Benzyl*-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo- *and* -6-exo-*carbonitrile*, (29) * *and* (30).*—*N*-Benzyl-3-hydroxypyridinium bromide [12] (28) (7.98 g, 0.03 mol), hydroquinone (0.05 g), and Et_3N (3.13 g, 0.031 mol) in acrylonitrile (60 ml) were heated under reflux for 16 h. After cooling, the Et_3N,HCl was filtered off and discarded. The filtrate was evaporated to dryness and the resultant gum chromatographed (alumina; CH_2Cl_2) to give the mixed endo- and exo-*cycloadducts* (1 : 1) (29) and (30) (5.7 g, 80%) which

could not be separated or crystallised (Found: C, 75.3; H, 5.9; N, 11.4. $C_{15}H_{14}N_2O$ requires C, 75.6; H, 5.9; N, 11.8%); $\nu_{max.}$ (Nujol) 2 230 (C≡N), 1 692 (αβ-unsat. ketone C=O), 1 490, 1 455, 730, and 695 cm^{-1} (arom. C=C); $\lambda_{max.}$ (EtOH) 218 nm (log ε 4.049); *m/e* 238.

8-*Benzyl*-6-endo- *and* -6-exo-*phenyl*-8-*azabicyclo*[3.2.1]-*oct*-3-*en*-2-*one*, (31) * *and* (32).*—*N*-Benzyl-3-hydroxypyridinium bromide (28) (3.0 g, 0.011 mol), hydroquinone (0.05 g), styrene (37 g, 0.3 mol), and Et_3N (3 ml) in tetrahydrofuran (60 ml) were heated under reflux for 48 h. The filtrate was evaporated (40 °C at 12 mmHg) and the residue was chromatographed on alumina [Brockmann grade 1, neutral (100 g); toluene–EtOAc (2 : 1)]. The eluate was evaporated and the resultant yellow gum (1.8 g, 80%) separated by preparative t.l.c. [Kieselgel PF 254; benzene–EtOAc (9 : 1)]. The exo-6-*phenyl cycloadduct* (32) (0.1 g, 3.3%) was isolated as yellow needles, m.p. 104—106 °C (from EtOH) (Found: C, 82.5; H, 6.5; N, 4.8. $C_{20}H_{19}NO$ requires C, 83.0; H, 6.6; N, 4.8%); $\nu_{max.}$ ($CHBr_3$) 1 679 (αβ-unsat. ketone C=O), 1 600, and 1 500 cm^{-1} (benzene C=C); $\lambda_{max.}$ (EtOH) 218 nm (log ε 3.97); *m/e* 289. The endo-6-*phenyl cycloadduct* (31) (1.1 g, 36%) was isolated as a wax-like solid, m.p. 50 °C; $\nu_{max.}$ ($CHBr_3$) 1 680 (αβ-unsat. ketone C=O), 1601, and 1 499 cm^{-1} (benzene C=C); $\lambda_{max.}$ (EtOH) 218 nm (log ε 4.017); *m/e* 289; *picrate*, m.p. 156 °C (decomp.) (from EtOH) (Found: C, 59.4; H, 4.2; N, 10.8; $C_{26}H_{22}N_4O_8$ requires C, 60.2; H, 4.3; N, 10.8%); $\nu_{max.}$ ($CHBr_3$) 3 380 (phenol O–H) and 1 705 cm^{-1} (αβ-unsat. ketone C=O).

Methylation of 8-*Benzyl*-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-endo- *and* -6-exo-*carbonitrile*, (29) *and* (30).—The isomeric mixture (29) and (30) (1 g, 0.004 mol) in MeCN (20 ml) was treated with MeI (10 ml) at 20 °C for 30 days. The quaternary salt (35) was obtained as yellow *needles* (200 mg, 12.5%), m.p. 150 °C (from MeCN) (Found: C, 39.7; H, 4.7; N, 9.0; I, 37.6. $C_{10}H_{13}IN_2O$ requires C, 39.5; H, 4.3; N, 9.2; I, 41.7%); $\nu_{max.}$ (Nujol) 2 240 (C≡N) and 1 710 cm^{-1} (αβ-unsat. ketone C=O).

8-*Benzyl*-2-*oxo*-8-*azabicyclo*[3.2.1]*octane*-6-exo- *and* -6-endo-*carbonitrile* (34).—The cycloadduct mixture (29) and (30) (1.19 g, 0.05 mol) in absolute EtOH (50 ml) was hydrogenated at 20 °C over Pd–C (10%; 50 mg) for 3 h. The solution was evaporated to yield the *hydrogenated compounds* (34) as a pale yellow viscous oil (0.94 g, 79%) which could not be crystallised (Found: C, 74.0; H, 6.8; N, 11.4. $C_{15}H_{16}N_2O$ requires C, 75.0; H, 6.7; N, 11.7%); $\nu_{max.}$ (film) 2 230 (C≡N), 1 725 (sat. ketone C=O), 1 490, 1 450, and 695 cm^{-1} (arom. C=C); *m/e* 240.

8-*Benzyl*-2-*oxo*-8-*azabicyclo*[3.2.1]*oct*-3-*ene*-6-exo,7-exo-*N*-*phenyldicarboximide* (33).*—*N*-Benzyl-3-hydroxypyridinium bromide (28) (2.66 g, 0.01 mol), *N*-phenylmaleimide (1.9 g, 0.011 mol), and Et_3N (1.11 g, 0.011 mol) in tetrahydrofuran (20 ml) were heated under reflux for 47 h. The filtrate was concentrated (40 °C at 12 mmHg) and the residue (2.35 g, 65.5%) was separated by thick-layer chromatography [Kieselgel PF 254; benzene–EtOAc (4 : 1) (two developments)]. The exo-*cycloadduct* (33) was isolated as pale yellow needles, m.p. 134 °C (from EtOH) (Found: C, 73.3; H, 5.0; N, 8.0. $C_{22}H_{18}N_2O_3$ requires C, 73.7; H, 5.1; N, 7.8%); $\nu_{max.}$ ($CHBr_3$) 1 715 (imide C=O), 1 675 (αβ-unsat. ketone C=O), 1 600, and 1 500 cm^{-1} (benzene C=C); $\lambda_{max.}$ (EtOH) 218 nm (log ε 4.006); *m/e* 358.

Reaction of 5,9-*Dihydro*-10-*phenyl*-5,9-*iminobenzocycloheptene*-6-*one* (36) *with* m-*Chloroperbenzoic Acid*.—The cycloadduct (36) (1.3 g, 5.2×10^{-3} mol) and *m*-chloroperbenzoic acid (0.91 g, 6.6×10^{-3} mol) in CH_2Cl_2 (100 ml) were stirred at 22 °C for 30 min. The mixture was washed with 5% $NaHCO_3$ (20 ml) followed by water (20 ml), dried (Na_2SO_4), and evaporated, and the residual red oil was chromatographed (alumina; CH_2Cl_2) to give *compound* (39) (0.58 g, 42%) as orange plates, m.p. 137—138 °C (from MeOH) (Found: C, 78.1; H, 4.8; N, 5.3. $C_{17}H_{13}NO_2$ requires C, 77.6; H, 5.0; N, 5.3%).

We thank Dr. E. Lunt (May and Baker, Dagenham) for discussions. We are grateful to the Chinoin Pharmaceutical and Chemical Works Ltd., Budapest, Hungary, and Takeda Chemical Industries Ltd., Osaka, Japan, for leave of absence to J. F. and T. M., respectively.

[5/2476 *Received*, 18*th December*, 1975]