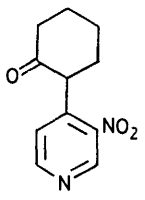
Polyhalogenoaromatic Compounds. Part 44.[1] Reactions of Enamines with Polyhalogenopyridines and their *N*-Oxides

By **Hans Suschitzky, Basil J. Wakefield,* and Jeffrey P. Whitten,** The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT

1-Dialkylaminocyclohexenes were readily *C*-arylated by pentafluoropyridine or 3,5-dichlorotrifluoropyridine but pentachloropyridine was much less reactive. The resulting (tetrahalogenopyridyl)enamines did not cyclise on heating except in the case of compound (10), which gave the heterocycle (16). 1-Dialkylaminocycloalkenes and other enamines were *C*-arylated by pentachloropyridine *N*-oxide. In the cases of the dialkylaminocyclo-hexenes and -heptenes the expected pyridylenamines were accompanied by 1-(tetrachloro-2-pyridyl)cyclo-pentene and -hexene, respectively. A mechanism for the ring-contraction leading to the pyridylcycloalkenes is proposed involving a novel elimination of an *N*-formyldialkylamine.

ENAMINES may be *C*-arylated by highly activated aryl halides such as 1-chloro-2,4-dinitrobenzene. On reaction with 1-pyrrolidinylcyclohexene, followed by hydrolysis, 4-chloro-3-nitropyridine gave the ketone (1), but 2-chloroquinoline required high temperature and gave only *N*-alkylation.[2] A special case involving activation by halogen alone was recently reported by Wakselman and Blazejewski, who observed that hexafluorobenzene arylated enamines to give intermediates (2), which on heating cyclised to give the carbazole derivatives (3), presumably with loss of fluoroalkane.[3] We now report that pentafluoropyridine (4) and 3,5-dichlorotrifluoropyridine (5) react with enamines in boiling benzene to give the pyridylenamines in high yields. The results are summarised in Table 1. The enamines (7)—(10) were extremely difficult to isolate and purify, owing to their susceptibility to hydrolysis. Since hydrolysis occurred during chromatography some of the fractions obtained were mixtures of the enamine and the corresponding ketone. Nevertheless, although they could not in all cases be purified for elemental analysis, their structures were established by their spectra, and by characterisation of the ketones (11) and (12) formed on hydrolysis. In particular, the position of substitution was established by ^{19}F n.m.r. spectroscopy.



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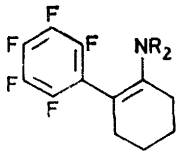

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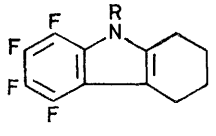

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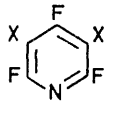

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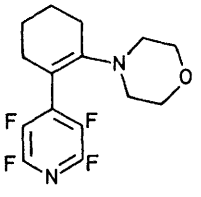
(5) X = Cl



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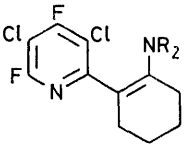


(8) R_2 =

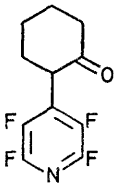
(9) R_2 =

(10) R = Et

Pentachloropyridine (13) failed to react with 1-morpholinocyclohexene or 1-diethylaminocyclohexene, but the more reactive 1-pyrrolidinylcyclohexene gave modest yields of the corresponding enamine (14) and ketone (15). The enamines (7) to (9) and (14) all failed to cyclise to carboline derivatives. Only the diethylamino-compound (10) gave the cyclised product (16).

The mechanism of the cyclisation observed by Wakselman[3] most likely involves intramolecular nucleophilic substitution into the polyhalogenoaromatic ring. This would be consistent with the known reluctance of polyhalogenopyridines to undergo cyclisation by nucleophilic substitution at the β-position.[4] An attempt to induce cyclisation of compound (9) photochemically (*cf.* refs. 5 and 6) gave only tars.

Since pentachloropyridine was relatively unreactive towards enamines, reactions of its *N*-oxide were investigated. Enamines have been reported to alkylate a number of pyridine *N*-oxides and related compounds, but only in the presence of acylating agents.[7] In the case of pentachloropyridine *N*-oxide, reaction occurred in the



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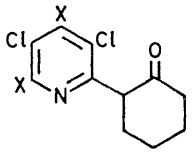
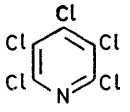


(12) X = F
(15) X = Cl



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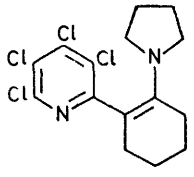

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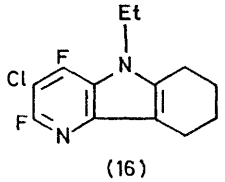
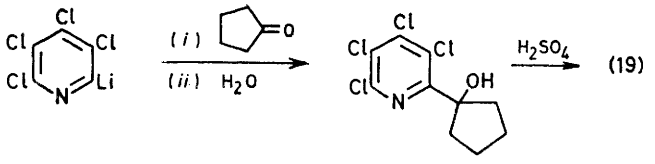


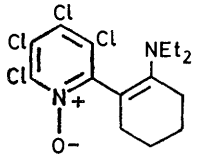
(16)

absence of acylating agents, to give the expected pyridylenamines, together with products of hydrolysis and deoxygenation. However, with certain enamines, highly unexpected products were also obtained.[8] For example, 2 mol equiv. of 1-diethylaminocyclohexene in boiling benzene gave a mixture (*ca.* 50%) of the enamine (17) and the ketone (18) together with 1-(tetrachloro-2-pyridyl)cyclopentene (19). The structure of the cyclopentene (19) was deduced from its spectra (see Experimental section), and confirmed by unambiguous synthesis from tetrachloro-2-pyridyl-lithium [9] as shown in Scheme 1.



SCHEME 1

The formation of the cyclopentene (19) involves a ring-contraction accompanied by loss of a one-carbon fragment. The scope of this highly unusual rearrangement was investigated, and a possible mechanism is discussed.



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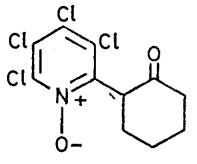

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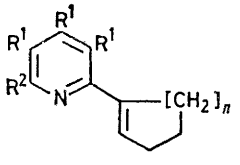
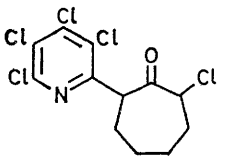


(19) $R^1=R^2=Cl, n=2$
(20) $R^1=R^2=Cl, n=3$
(28) $R^1=H, R^2=Cl, n=2$
(29) $R^1=R^2=H, n=2$



(21)

The experiments summarised in Table 2 indicated that optimum yields of the pyridylcyclopentene (19) required 2 mol equiv. of the enamine and temperatures over 100 °C, but that the nature of the 1-dialkylaminocyclohexene was not critical. A reaction with 1-pyrrolidinylcycloheptene gave 1-(tetrachloro-2-pyridyl)cyclohexene (20) in 11% yield. The only other pure product obtained from this reaction (apart from a trace of pentachloropyridine) was a ketone ($\nu_{max.}$ 1 705 cm^{-1}) with the molecular formula $C_{12}H_{10}Cl_5NO$. Its ^1H n.m.r. spectrum showed signals corresponding to *two* protons at δ *ca.* 5. We suggest that this compound is the chloroketone (21), but the route by which it is formed is obscure. Conceivably, the product enamine, or its *N*-oxide, is chlorinated (*cf.* ref. 10) by a reagent such as hypochlorous acid, formed by oxidation of hydrochloric acid by an *N*-oxide (*cf.* ref. 11).

TABLE 1

Arylation of enamines by pentahalogenopyridines

Pentahalogenopyridine (mmol)	Enamine (mmol)	Solvent (ml)	Enamine product (yield %)
Pentafluoro- (4) (30)	1-Morpholinocyclohexene (30)	Benzene (50)	(7) (55) [a]
3,5-Dichlorotrifluoro- (5) (24)	1-Morpholinocyclohexene (26)	Benzene (50)	(8) (85)
3,5-Dichlorotrifluoro- (5) (30)	1-Pyrrolidinylcyclohexene (30)	Benzene (50)	(9) (90)
3,5-Dichlorotrifluoro- (5) (20)	1-Diethylaminocyclohexene (23)	Benzene (50)	(10) (91) [b]
Pentachloro- (13) (16)	1-Pyrrolidinylcyclohexene (33)	Toluene (50)	(14) (33)

[a] Together with ketone (11) (24%). [b] Together with ketone (12) (9%).

TABLE 2

Formation of 1-(tetrachloro-2-pyridyl)cyclopentene (19)

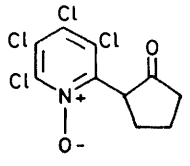
Enamine (mol. equiv.)	Solvent (reflux temperature)	Yield of (19) (%)
1-Diethylaminocyclohexene (2.3)	benzene (80 °C)	9
	toluene (110 °C)	46
1-Morpholinocyclohexene (2.1)	benzene [a]	0 [b]
	toluene (110 °C)	39
	xylene (*ca.* 140 °C)	43
(3.3)	toluene (110 °C)	38
(1.0) [c]	toluene (110 °C)	0 [d]

[a] Held at 55 °C. [b] Pentachloropyridine *N*-oxide recovered quantitatively. [c] Triethylamine (1.0 mol. equiv.) also present. [d] Pentachloropyridine (46%) obtained; remainder of product was complex mixture.

The only product identified from a reaction with 1-morpholinocyclopentene in boiling toluene was the cyclopentanone (22), the remainder of the product being a complex mixture with no evidence for the presence of a pyridylcyclobutene. Reactions in higher-boiling solvents gave only tarry mixtures. Reactions with 1-morpholinobut-1-ene and 5-pyrrolidinylnon-4-ene likewise gave only tars, in which no rearranged products could be detected. No reaction occurred with indole. With 1-pyrrolidinyl-indene and -dihydronaphthalene, no ring-contracted products were observed, but some di-substitution of the pyridine ring occurred. Thus, 1-pyrrolidinylindene gave the bis(enamine) (23) in 83% yield and 1-pyrrolidinyl-3,4-dihydronaphthalene (24) gave the di-substituted compound (25) as well as the tetralone (26). Presumably in the formation of compound (25) the dihydro-intermediate was oxidised to the naphthalene by *N*-oxide or during work-up. 2-Pyrrolidinyl-3,4-dihydronaphthalene gave only tars.

In order to ascertain whether the fully halogenated

pyridine ring was essential to the ring-contraction, reactions of enamines with the *N*-oxides of pyridine, 2-chloropyridine, 2,6-dichloropyridine, and 4-nitropyridine



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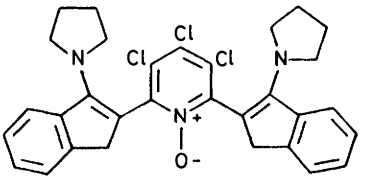
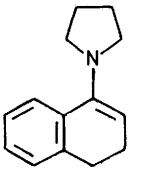


(23)

were tried. Little or no reaction occurred with pyridine *N*-oxide and 2,6-dichloropyridine *N*-oxide. 4-Nitropyridine *N*-oxide gave a complex mixture, from which only the enol (27) was isolated, as lustrous purple-black crystals (*cf.* ref. 2). The reaction between 1-pyrrolidinylcyclohexene and 2-chloropyridine *N*-oxide gave two oils, which were too unstable to purify adequately. However, both showed n.m.r. signals at δ *ca.* 6; one of them showed signals for *three* pyridyl ring protons and the other for *four* pyridyl ring protons including one at δ 8.2, corresponding to an α-proton. These spectra suggest that the products were the pyridylcyclopentenes (28)



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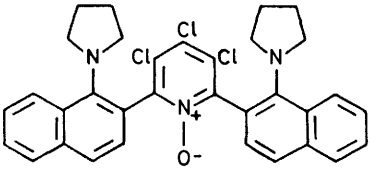
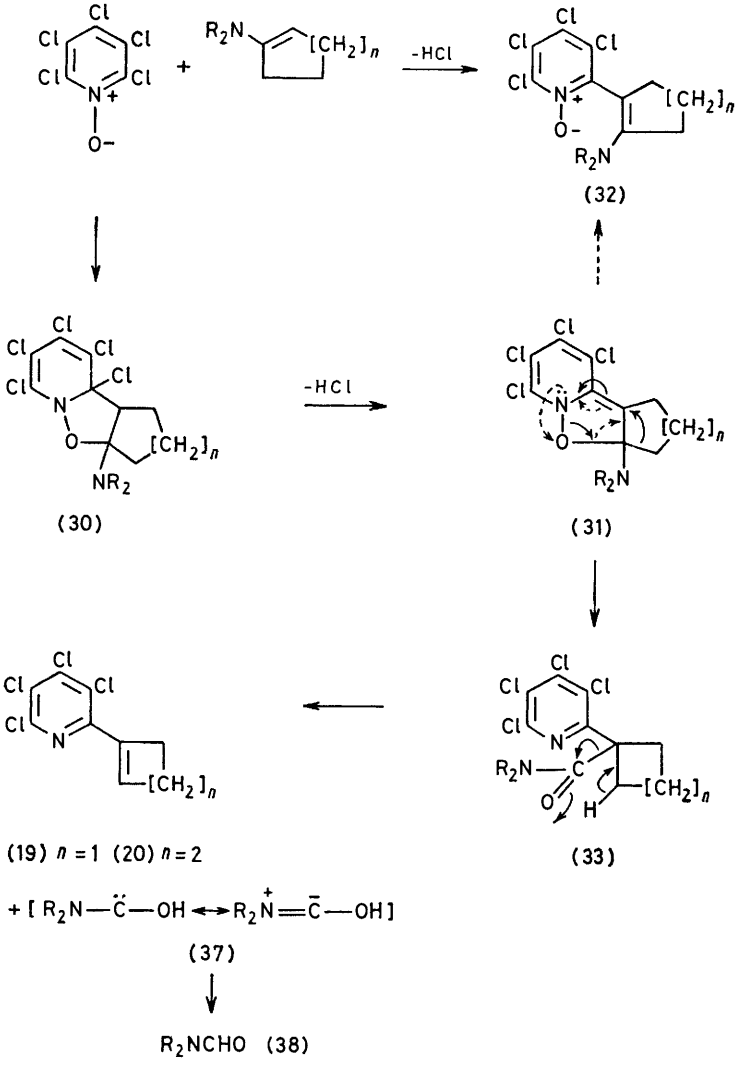


(25)

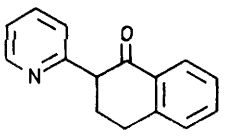
and (29), formed by ring-contraction following attack at the unsubstituted and chlorine-substituted α-positions, respectively.



SCHEME 2

In our preliminary communication, we suggested that the ring-contraction might take place by the pathway shown in Scheme 2.[8] Although the evidence for this route remains sparse, it is simple and accounts for all the

observations. Cycloaddition of the *N*-oxide to the enamine to give the isoxazolidine (30) is analogous to the known cycloaddition of nitrones to enamines.[12] If, as calculations indicate, carbon–carbon bond formation leads carbon–oxygen bond formation in such cycloadditions, except with electron-poor dipolarophiles, the



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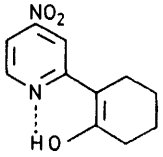
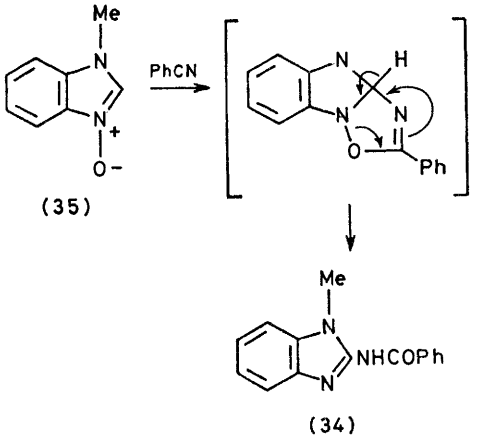


(27)

regioisomer shown (30) would be the one predicted.[13] Base-induced dehydrohalogenation to the isoxazoline (31) could be followed by fission of the weak N–O bond to give the pyridylenamine (32) (dotted arrows in Scheme 2), which could alternatively be formed by direct arylation of the enamine. The pyridylenamine (32) is evidently not the precursor of the isoxazoline (31), since it did not give the cyclopentene (19) when it was heated in toluene. Fission of the nitrogen–oxygen bond in (31) could alternatively lead to rearrangement to the amide (33). This rearrangement regains the aromatic pyridine ring and forms a carbonyl group; there is some analogy in the formation of the amide (34) from the benzimidazole *N*-oxide (35) and benzonitrile as shown in Scheme 3.[14] Inspection of models shows that the isoxazoline (31) is very strained and that conversion to the amide (33), although it is itself overcrowded, does offer some relief from strain.

Amides are in general very thermally stable, although at high temperatures pyrolysis of *N*-alkylamides can result in Chugaev-type elimination to give an alkene.[15] We are aware of no precedent for the type of elimination, (33) to (19) or (20), shown in Scheme 2. However, at

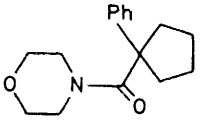


(35) (34)

SCHEME 3

400 °C the model amide (36) underwent a clean elimination to 1-phenylcyclopentene, albeit in only *ca.* 1% conversion; at higher temperatures complex mixtures were obtained, probably because alternative modes of decomposition involving the morpholino-group ensued. The thermal instability of the tetrachloropyridyl analogue (33) may be attributed to steric strain; inspection of models suggests that the conformation required for the *syn*-elimination is relatively favoured. Assistance by the ring nitrogen might also play a part.

As written in Scheme 2, the elimination from the amide (33) gives the carbene (37). This might possess some stabilisation involving mesomerism of the type shown, but would probably rapidly rearrange to the formamide (38), by analogy with the rearrangement of hydroxy(methyl)carbene to acetaldehyde.[16] We were unable to isolate *N*-formylmorpholine [38, $R^2 = -CH_2CH_2OCH_2CH_2-$] from the reaction of pentachloropyridine *N*-oxide with 1-morpholinocyclohexene, but gas-chromatography of the reaction mixture showed a peak with the same retention time as an authentic specimen, with the appropriate mass spectrum (M^+ at *m/e* 115). Moreover, the i.r. spectrum of the crude reaction mixture showed a peak at 1 640 cm^{-1}, present in *N*-formylmorpholine but not in the other identified products of the



(36)

reaction; comparison of the height of this peak with that for a standard solution indicated that *N*-formylmorpholine had been formed in *ca.* 45% yield, *i.e.* in approximately the same yield as the cyclopentene (19).

EXPERIMENTAL

Infrared data are for liquid films or Nujol mulls. Hydrogen-1 and ^{13}C n.m.r. spectra were recorded with tetramethylsilane as internal standard in deuteriochloroform unless otherwise stated; ^{19}F n.m.r. spectra were recorded with trifluoroacetic acid as external standard and the chemical shifts referred to trichlorofluoromethane.[17] Calculated *m/e* values for mass spectra are given for ions containing only ^{35}Cl; the appropriate patterns of isotope peaks were observed. Light petroleum refers to the fraction of b.p. 60—80 °C. The pentahalogenopyridines were gifts from I.C.I. Ltd., Mond Division; pyridine *N*-oxide and 4-nitropyridine *N*-oxide were commercial materials; 2-chloropyridine *N*-oxide was obtained from a commercial sample of its hydrochloride; pentachloropyridine *N*-oxide [18] and 2,6-dichloropyridine *N*-oxide [19] were prepared from the pyridines according to the references cited, as were the enamines as follows: 1-morpholinocyclohexene, 1-morpholinocyclopentene, 1-pyrrolidinylcyclohexene, and 1-pyrrolidinylcycloheptene;[20] 1-diethylaminocyclohexene and 5-pyrrolidinylnon-4-ene;[21] 1-morpholinobut-1-ene;[22] 1- and 2-pyrrolidinyl-3,4-dihydronaphthalene;[23] and 1-pyrrolidinylindene.[24]

Reactions of Enamines with Pentahalogenopyridines.—*General procedure.* The enamine and the pentahalogenopyridine were dissolved in the solvent and the solution was refluxed during 14 h. The solvent was evaporated, and the products were obtained from the residue by chromatography on alumina (gradient elution with light petroleum–chloro-

form). The details of the experiments are given in Table 1 and the properties of the products are recorded in Table 3.

Enamine (7) hydrolysed on standing to 2-(*tetrafluoro*-4-*pyridyl*)*cyclohexanone* (11), m.p. 70—71 °C (from hexane); $\nu_{max.}$ 1 710 cm^{-1}; δ_H 1.7—2.7 (8 H, br m) and 4.1 (1 H, t, Ar–C*H*); δ_F 84.5 (2 F, dd, F-2 and F-6) and 136.5 (2 F, dd, F-3 and F-5) (Found: C, 53.3; H, 3.6; N, 5.7%; M^+, 247. $C_{11}H_9F_4NO$ requires C, 53.4; H, 3.7; N, 5.7%; *M*, 247).

Enamines (8), (9), and (10) were hydrolysed by dilute acid to 2-(3,5-*dichloro*-4,6-*difluoro*-2-*pyridyl*)*cyclohexanone* (12), m.p. 106—107 °C (from hexane); $\nu_{max.}$ 1 700 cm^{-1}; δ_H 1.7—2.6 (8 H, br m) and 4.2 (1 H, t, Ar–C*H*); δ_F 69.0 (1 F, d, F-6) and 97.0 (1 F, d, F-4) (Found: C, 47.5; H, 3.3; N, 5.2%; M^+, 279. $C_{11}H_9Cl_2F_2NO$ requires C, 47.2; H, 3.2; N, 5.0%; *M*, 279). Enamine (14) was hydrolysed by dilute acid to 2-(*tetrachloro*-2-*pyridyl*)*cyclohexanone* (15), m.p. 128—129 °C (from hexane); $\nu_{max.}$ 1 685 cm^{-1}; δ_H 1.7—2.7 (8 H, br m) and 4.1 (1 H, t, Ar–C*H*); δ_C 24.7 (C-4), 27.2 (C-5), 31.1 (C-3), 42.2 (C-6), 56.1 (C-2), 128.5 (pyridyl C-3), 130.6 (pyridyl C-5), 142.8 (pyridyl C-4), 147.0 (pyridyl C-6), and 154.9 (pyridyl C-2) (Found: C, 42.3; H, 3.0; N, 4.5%; M^+, 311. $C_{11}H_9Cl_4NO$ requires C, 42.2; H, 2.9; N, 4.5; M^+, 311).

Thermolysis of the (*Tetrahalogenopyridyl*)*enamines*.—The enamines were heated in bulb-to-bulb distillation apparatus at low pressure. Enamines (7), (9), and (14) gave only tars and/or starting materials. Enamine (8) gave a distillate containing starting material and, probably, 3,5-dichloro-4,6-difluoro-2-morpholinopyridine.[24] Enamine (10) after 4 h at 110 °C rising to 145 °C, at 1 Torr, gave a distillate from which chromatography (alumina, gradient elution with hexane–chloroform) separated 3-*chloro*-5-*ethyl*-2,4-*difluoro*-6,7,8,9-*tetrahydropyrido*[3,2-b]*indole* (16) (0.5 g, 23%), m.p. 145—146 °C (from chloroform–hexane); δ_H 1.3 (3 H, t, Me), 1.8 (4 H, m, $-CH_2CH_2CH_2CH_2-$), 2.65—2.9 (4 H, m, =CCH_2-), and 4.2 (2 H, q, NCH_2) ; δ_F 86.2 (1 F, d, F-2) and 98.0 (1 F, d, F-4) [Found: C, 57.5; H, 4.8; N, 10.6%; M^+, 270. $C_{13}H_{13}ClF_2N_2$ requires C, 57.7; H, 4.8; N, 10.4%; *M*, 270].

Reactions of Enamines with Pyridine N-*Oxides*.—*General procedure*. The *N*-oxide (*ca.* 20 mmol) and the enamine were dissolved in the solvent (*ca.* 40 ml) and the solution was refluxed during 18 h. The solution was cooled, shaken with dilute acid, and the mixture extracted with chloroform. The products were isolated by conventional work-up followed by chromatography on silica (gradient elution

TABLE 3

(Tetrahalogenopyridyl)enamines

Compound	M.p. (°C) (Recrystallisation solvent)	$\nu_{max.}$/cm^{-1}	δ_H	Molecular formula	Found (required) C(%)	H(%)	N(%)	M^+
1-Morpholino-2-(tetrafluoro-4-pyridyl)cyclohexene (7)	Oil	1 650	1.8—2.3 (8 H, m), 2.6 (4 H, t, NCH_2), 3.4 (4 H, t, OCH_2)	$C_{15}H_{16}F_4N_2O$		*a*		316 (316)
1-(3,5-Dichloro-4,6-difluoro-2-pyridyl)-2-morpholinocyclohexene (8)	Oil	1 600	1.8—2.2 (8 H, m), 2.6 (4 H, t, NCH_2), 3.45 (4 H, t, OCH_2)	$C_{15}H_{16}Cl_2F_2N_2O$		*a*		348 (348)
1-(3,5-*Dichloro*-4,6-*difluoro*-2-*pyridyl*)-2-*pyrrolidinyl*-*cyclohexene* (9)	59—61 (hexane)	1 620	1.7—2.5 (12 H, m), 2.85 (4 H, t, NCH_2)	$C_{15}H_{16}Cl_2F_2N_2$	54.1 (54.1)	5.0 (4.8)	8.6 (8.4)	332 (332)
1-(3,5-*Dichloro*-4,6-*difluoro*-2-*pyridyl*)-2-*diethylamino*-*cyclohexene* (10)	88 [b]	1 620	0.9—2.9 (8 H, m), 2.7 (4 H, q, NCH_2)	$C_{15}H_{18}Cl_2F_2N_2$	53.9 (53.8)	5.6 (5.4)	8.6 (8.4)	334 (334)
1-*Pyrrolidinyl*-2-(*tetrachloro*-2-*pyridyl*)*cyclohexene* (14)	121—122 (hexane)	1 620	1.2—2.6 (12 H, m), 2.8 (4 H, t, NCH_2)	$C_{15}H_{16}Cl_4N_2$	49.2 (49.2)	4.5 (4.4)	7.7 (7.6)	364 (364)

[a] Could not be adequately purified. [b] B.p. at 1.5 Torr.

TABLE 4

Reactions of enamines with pyridine *N*-oxides [a]

Pyridine *N*-oxide [c]	Enamine [b] (mol. equiv.)	Solvent	Products (yield), in order of elution
Pentachloro-	1-Morpholinocyclopentene (2.2)	Toluene [d]	Pentachloropyridine (1%); mixture; 2-(tetrachloro-*N*-oxido-2-pyridyl)cyclopentanone (22) (6%)
Pentachloro-	1-Pyrrolidinylcycloheptene (2.2)	Toluene	(13) (trace); 1-(tetrachloro-2-pyridyl)cyclohexene (20) (11%); 2-chloro-7-(tetrachloro-2-pyridyl)cycloheptanone (21) (5%); mixture
Pentachloro-	1-Pyrrolidinylindene (4.2)	Toluene	Indan-1-one (53%); 2,6-di(1-pyrrolidinylinden-2-yl)-3,4,5-trichloropyridine *N*-oxide (23) (83%)
Pentachloro-	1-Pyrrolidinyl-3,4-dihydronaphthalene (24) (3.2)	Toluene	Mixture; 2,6-di(1-pyrrolidinyl-2-naphthyl)-3,4,5-trichloropyridine *N*-oxide (25) (8%); mixture; 2-(tetrachloro-2-pyridyl)-3,4-dihydronaphthalen-1(2*H*)-one (26) (30%)
2-Chloro-	1-Pyrrolidinylcyclohexene (2.3)	Toluene	Oil [possibly 1-(2-pyridyl)cyclopentene (29)]; oil [possibly 1-(6-chloro-2-pyridyl)cyclopentene (28)]
2,6-Dichloro-	1-Morpholinocyclohexene (2.3)	Toluene	2,6-Dichloropyridine (61%); 2,6-dichloropyridine *N*-oxide (25%)
4-Nitro-	1-Morpholinocyclohexene	Toluene	4-Nitropyridine (28%); 1-hydroxy-2-(4-nitro-2-pyridyl)cyclohexene (27) (4%)

[a] See also Table 2. Tars were also obtained from the reactions listed here and in Table 2. [b] 1-Morpholinobut-1-ene, 5-pyrrolidinylnon-4-ene, and 2-pyrrolidinyl-3,4-dihydronaphthalene gave only tarry mixtures. Indole gave only starting materials. [c] No identifiable products were obtained from pyridine *N*-oxide itself. [d] A similar experiment in decahydronaphthalene gave only an intractable mixture.

TABLE 5

Properties of new compounds from experiments summarised in Tables 2 and 4

Compound	M.p., °C (recrystallisation solvent)	$\nu_{max.}$/cm^{-1}	δ	Molecular formula	Found (required) C, %	H, %	N, %	M^+
1-(Tetrachloro-2-pyridyl)-cyclopentene (19)	73—74 (methanol)	3 100, 1 600	^{1}H, 1.95 (2 H, q, $CH_2CH_2CH_2$), 2.6 (2 H, m, =CHCH_2), 2.8 (2 H, m, Ar-CCH_2), 6.75 (1 H, m, =CH–) ^{13}C, 22.8 (C,4), 34.4 (C-3), 35.3 (C-5), 127.0 (pyridyl C-5), 127.8 (pyridyl C-3), 138.5 (C-2), 143.3 (pyridyl C-4), 146.4 (pyridyl C-6), 151.8 pyridyl C-2)	$C_{10}H_7Cl_4N$	42.0 (42.4)	2.5 (2.5)	5.05 (4.95)	281 (281)
1-Diethylamino-2-(tetrachloro-*N*-oxido-2-pyridyl)-cyclohexene (17)	Oil	1 640	^{1}H, 1.1 (6 H, t, Me), 1.5—2.5 (8 H, br, m), 2.9 (4 H, q, NCH_2)	$C_{15}H_{18}Cl_4N_2O$		*a*, *b*		382 (382)
2-(Tetrachloro-*N*-oxido-2-pyridyl)cyclopentanone (22)	143—145 (ethanol)	1 740	^{1}H, 1.8—2.9 (6 H, br, m), 6.0 (1 H, t, Ar-C*H*) ^{13}C, 21.3 (C-3), 24.2 (C,4), 36.6 (C-5), 50.2 (C-2), 129.3 (pyridyl C-3, -5), 140.6 (pyridyl C-4, C-6), 148.5 (pyridyl C-2)	$C_{10}H_7Cl_4NO$	39.2 (39.1)	2.2 (2.2)	4.4 (4.4)	313 (313)
1-(Tetrachloro-2-pyridyl)-cyclohexene (20)	39—40 [c]	1 540	^{1}H, 1.5—2.5 (8 H, br m), 6.1 (1 H, m, =C*H*) ^{13}C, 21.4 (C-4), 22.2 (C-5), 25.1 (C-3), 27.1 (C-6), 127.4 and 127.8 (pyridyl C-3 and -5), 134.8 (C-1), 143.1 (pyridyl C-4), 146.5 (pyridyl C-6), 157.2 (pyridyl C-2)	$C_{11}H_9Cl_4N$	44.5 (44.5)	3.2 (3.1)	4.9 (4.7)	295 (295)
2-Chloro-7-(tetrachloro-2-pyridyl)cycloheptanone (21)	96—97 (carbon tetrachloride–hexane)	1 705	^{1}H, 1.7—2.7 (8 H, broad m), 4.7—5.2 (2 H, m, CHCl and Ar-C*H*)	$C_{12}H_{10}Cl_5NO$	39.5 (39.9)	2.4 (2.8)	3.9 (3.9)	358.9217 (358.9204)
2,6-Di(1-pyrrolidinyl-inden-2-yl)-3,4,5-trichloro-pyridine (23)	196 (chloroform–hexane)	1 600, 1 570	^{1}H, 2.4 (4 H, m, NCH_2CH_2), 4.1 (4 H, m, NCH_2), 4.8 (2 H, m, Ar-C*H*), 8.0—8.5 (4 H, m, Ar-H)	$C_{31}H_{28}Cl_3N_3O$	65.8 (65.9)	4.9 (5.0)	7.2 (7.4)	563 (563)
2,6-Di(1-pyrrolidinyl-2-naphthyl)-3,4,5-trichloro-pyridine (25)	212 (chloroform)	1 590, 1 540	^{1}H, 2.0 (4 H, m, NCH_2CH_2), 3.75 (4 H, m, NCH_2), 7.2—7.55 (6 H, m, naphthyl H-3, -6, -7), 7.75 (2 H, m, naphthyl H-5) 8.0 (2 H, d, naphthyl H-4), 8.4 (2 H, m, naphthyl H-8) ^{13}C, 25.7 (N–C–*C*), 50.9 (NC), 113.3, 116.6, 117.4, 123.0, 125.1, 125.7 and 126.8 (naphthyl), 127.2 (pyridyl C-3, -5), 150.6 (pyridyl C-4), 154.6 (pyridyl C-2, -6)	$C_{33}H_{28}Cl_3N_3O$	67.3 (67.3)	4.7 (4.8)	7.2 (7.1)	391 [d] (587)
1-(2-Pyridyl)cyclopentene (29) [e]	Oil	3 040, 1 700, 1 590, 1 580	^{1}H, 2.1 (2 H, m, $CH_2CH_2CH_2$), 3.3—3.5 (4 H, m, =CCH_2), 5.9 (1 H, m, =CH), 6.3—7.8 (3 H, m, pyridyl H-3, -4, -5), 8.2 (1 H, m, pyridyl H-6)				*a*	

TABLE 5 (*continued*)

Compound	M.p., °C (recrystallisation solvent)	$\nu_{max.}$/cm^{-1}	δ	Molecular formula	Found (required) C, %	H, %	N, %	M^+
1-(6-Chloro-2-pyridyl)cyclopentene [e] (28)	Oil	3 050, 1 700, 1 600	^{1}H, 2.1 (2 H, m, $CH_2CH_2CH_2$), 3.3—3.6 (4 H, m, $=CCH_2$), 6.0 (1 H, m, =CH), 6.4—7.8 (3 H, m, pyridyl H)				*a*	
1-Hydroxy-2-(4-nitro-2-pyridyl)cyclohexene (27)	131—132 (ethanol)	1 620, 1 590	^{1}H, 1.7 (4 H, m, $CH_2CH_2CH_2CH_2$), 2.2 (4 H, m, $=CCH_2$), 7.7 (2 H, m, pyridyl H-2, -5), 8.5 (1 H, d, pyridyl H-6), 15 (1 H, broad, exchangeable, OH)	$C_{11}H_{13}N_2O_3$	59.7 (59.7)	5.9 (5.9)	13.1 (12.7)	203 [f] (221)

[a] Could not be adequately purified. [b] Treatment with phosphorus trichloride followed by dilute acid gave 2-(tetrachloro-2-pyridyl)cyclohexanone (15), identical to the material described in Table 3. [c] Distilled at 73° C and 1 Torr. [d] $M^+ - (C_{10}H_6 \cdot NC_4H_8)$. [e] Tentative identification. [f] $M^+ - H_2O$.

with hexane–chloroform). A typical experiment is described. The experiments involving reactions of pentachloropyridine *N*-oxide with 1-dialkylaminocyclohexenes are summarised in Table 2. The other experiments are summarised in Table 4. The properties of the products are recorded in Table 5.

The reaction of pentachloropyridine *N*-oxide (4.5 g, 17 mmol) with 1-diethylaminocyclohexene (6.3 g, 40 mmol) in benzene (40 ml) gave, in order of elution: (*i*) 1-(tetrachloro-2-pyridyl)cyclopentene (19) (0.4 g, 9%): (*ii*) 2-(tetrachloro-2-pyridyl)cyclohexanone (15) (1.05 g, 19%): (*iii*) impure 1-diethylamino-2-(tetrachloro-*N*-oxido-2-pyridyl)cyclohexene (17) (0.65 g, 3%): and (*iv*) a mixture (1.9 g) of 1-diethylamino-2-(tetrachloro-*N*-oxido-2-pyridyl)-cyclohexene and 2-(tetrachloro-*N*-oxido-2-pyridyl)cyclohexanone (18).

1-(*Tetrachloro-2-pyridyl*)*cyclopentene*.—1.6M n-Butyllithium in hexane (20 ml) was added to a suspension of pentachloropyridine (7.5 g, 30 mmol) in methylcyclohexane (100 ml) at −78 °C. The solution was stirred for 20 min and cyclopentanone (6.0 g) was then added. The solution was stirred for 10 min and allowed to warm to room temperature. Hydrolysis, conventional work-up, and chromatography (silica, gradient elution with hexane–dichloromethane) gave (*i*) pentachloropyridine (2.7 g, 36%): (*ii*) a mixture (0.78 g): and (*iii*) 1-(*tetrachloro-2-pyridyl*)*cyclopentanol* (3.5 g, 39%), m.p. 82—84 °C (from hexane); $\nu_{max.}$ 3 450 cm^{-1}; δ_H 1.8—2.7 (8 H, br m) and 4.2 (1 H, s, exchangeable, OH) (Found: C, 40.0; H, 3.2; N, 4.6. $C_{10}H_9Cl_4NO$ requires C, 39.9; H, 3.0; N, 4.65%).

The cyclopentanol (0.5 g, 1.7 mmol) was dissolved in concentrated sulphuric acid (5 ml). After 30 min the solution was added to ice (100 g) and the mixture was extracted with chloroform. The organic layer was dried and evaporated, to yield 1-(tetrachloro-2-pyridyl)cyclopentene (0.4 g, 78%), m.p. 73 °C (from methanol), identical to the material described in Table 5.

Identification of N-*Formylmorpholine*.—Preparation of an authentic specimen: a mixture of morpholine (8.7 g), formic acid (4.6 g), and water (40 ml) was refluxed for 1.5 h and then distilled. The fraction of b.p. 236 °C was collected $\nu_{max.}$ 1 640 cm^{-1}; δ 3.3—3.8 (8 H, m) and 8.1 (1 H, s, CHO).

The crude product from the reaction of pentachloropyridine *N*-oxide with 1-morpholinocyclohexene was subjected to g.l.c. (3-ft × 0.25-in 10% Carbowax 20M on Chromosorb WW 100/120, 45 ml min^{-1} N_2, 160 °C). The mass spectrum of a peak, which was enhanced by the admixture of *N*-formylmorpholine, showed M^+ at *m/e* 115, as required for $C_5H_9NO_2$.

Preparation and Pyrolysis of N-(1-*Phenylcyclopentylcarbonyl*)*morpholine*.—Thionyl chloride (3.0 g) was added to 1-phenylcyclopentanecarboxylic acid (1.0 g) and the mixture was refluxed during 20 min. The excess of thionyl chloride was distilled off, and ether (100 ml) and morpholine (20 g) were added. The resulting mixture was washed with dilute hydrochloric acid, and the ether layer was dried and evaporated to yield N-(1-*phenylcyclopentylcarbonyl*)*morpholine* (36) (0.7 g, 52%), m.p. 75—77 °C (from benzene–hexane); $\nu_{max.}$ 1 630 cm^{-1}; δ_H 1.7—2.2 (8 H, m), 3.2 (8 H, br s, morpholino), and 7.25 (5 H, m, Ar–H) (Found: C, 74.3; H, 8.2; N, 5.6. $C_{16}H_{21}NO_2$ requires C, 74.1; H, 8.2; N, 5.4%).

The amide was evaporated in a stream of nitrogen, which was passed through a 60-cm × 3-cm column packed with glass helices and heated to 400 °C. The effluent from the column was passed through a trap cooled in liquid nitrogen. G.l.c. of the material from the trap showed only starting material (almost quantitative) and 1-phenylcyclopentene, both identified by comparison with authentic specimens.

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