Reactions of Enamines with Pentachloropyridine *N*-Oxide; a Novel Ring Contraction

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Summary The reaction of 1-dialkylaminocycloalkenes with pentachloropyridine *N*-oxide gave tetrachloro-*N*-oxido-2-pyridylenamines (**6**) accompanied, in the cases of the cyclohexenyl and cycloheptenyl derivatives, by tetrachloro-2-pyridylcyclo-pentene (**10**) and -hexene (**11**), respectively.

STUDIES on some reactions of enamines with polyhalogenopyridines revealed marked differences from those recently described for hexafluorobenzene, which was reported to give tetrafluorotetrahydrocarbazoles on reaction with 1-dialkylaminocyclohexenes.[1] Pentachloropyridine did not react with the enamines (**1**)—(**4**) in boiling benzene or toluene, but the more reactive *N*-oxide (**5**) did so. Azatetrahydrocarbazole derivatives were not obtained. The expected intermediate pyridylenamines (**6**) were formed, together with products of hydrolysis and deoxygenation (**7**)—(**9**). However, in the cases of the cyclohexenyl and cycloheptenyl derivatives, they were accompanied by unexpected products whose i.r., mass, and ^1H and ^{13}C n.m.r. spectra and elemental analyses indicated that they were the 1-(tetrachloro-2-pyridyl)cycloalkenes (**10**) and (**11**). The structure of compound (**10**) was confirmed by unambiguous synthesis *via* the reaction of tetrachloro-2-pyridyl-lithium with cyclopentanone, followed by dehydration.

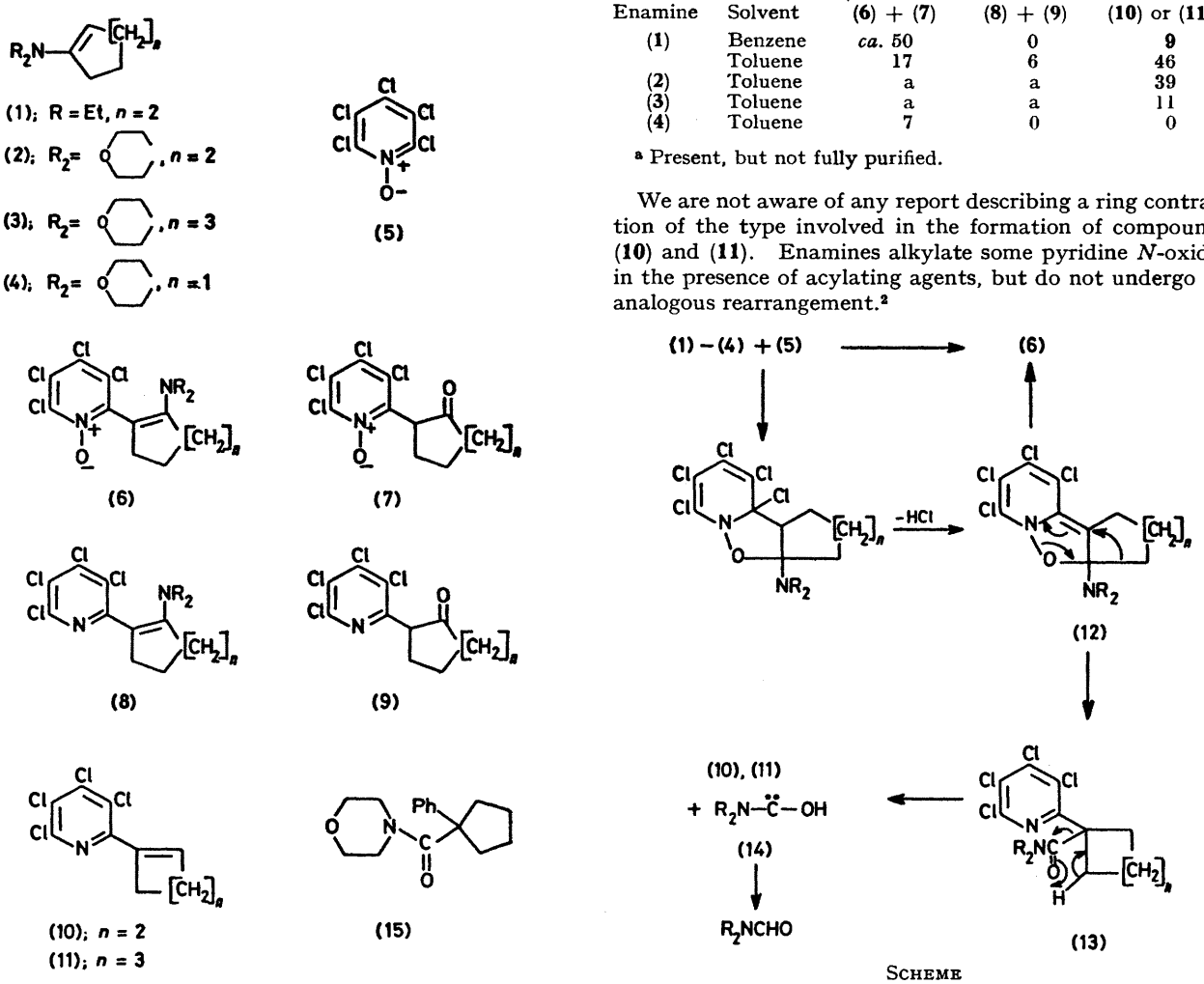
The products obtained from some reactions between the enamines (2 equiv.) and pentachloropyridine *N*-oxide in boiling benzene or toluene (*ca.* 16 h) are listed in the Table.

TABLE. Reactions of enamines with pentachloropyridine *N*-oxide

		Product (Yield/%)		
Enamine	Solvent	(**6**) + (**7**)	(**8**) + (**9**)	(**10**) or (**11**)
(**1**)	Benzene	*ca.* 50	0	**9**
	Toluene	17	6	46
(**2**)	Toluene	a	a	39
(**3**)	Toluene	a	a	11
(**4**)	Toluene	7	0	0

[a] Present, but not fully purified.

We are not aware of any report describing a ring contraction of the type involved in the formation of compounds (**10**) and (**11**). Enamines alkylate some pyridine *N*-oxides in the presence of acylating agents, but do not undergo an analogous rearrangement.[2]



SCHEME

A possible pathway for the ring contraction is shown in the Scheme. Dipolar cycloaddition of the enamine to the *N*-oxide, followed by loss of HCl, could give the isoxazoline (**12**); the reaction of enamines with nitrones provides an analogy for the cycloaddition.[3] The arylated enamine (**6**) could be formed directly or by ring-opening of the intermediate (**12**). The enamine (**6**) is apparently not the precursor of (**12**) since it did not undergo the ring contraction on heating in toluene. Some evidence for the elimination from the amide (**13**) was obtained from examination of the products by i.r. spectroscopy and g.l.c. coupled with mass spectrometry. Absorption at 1640 cm^{-1} and a peak with the appropriate retention time and molecular ion at *m/e* 115 were consistent with the presence of *N*-formylmorpholine. Examination of models showed that the amide (**13**) is overcrowded but that the conformation required for *syn*-elimination to the carbene (**14**) or a related species is relatively favourable. The carbene (**14**) can rearrange to the formamide by migration of hydrogen from oxygen to carbon. Hydroxy(methyl)carbene rearranges to acetaldehyde by a similar migration.[4] The amide (**15**), prepared as a model for compounds (**13**), is relatively stable, but on heating at 400 °C it gives a low yield of phenylcyclopentene.

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