Photochemical Cyclisation of Substituted Polyhalogenopyridines

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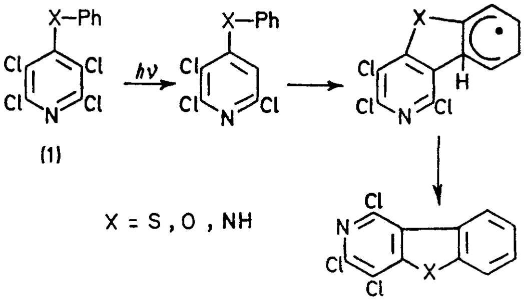
Summary Irradiation of appropriately substituted polyhalogenopyridines affords a practicable synthesis to fused polyhalogeno-heterocycles.

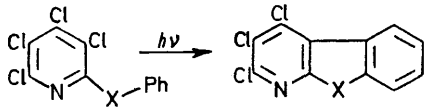
We have recently found that the 3-chlorine–carbon bond in pentachloropyridine is photolabile[1] yielding 2,3,4,6-tetrachloropyridine on irradiation. On the likely assumption that this reductive dechlorination involves a 3-pyridyl radical, a suitably 2- or 4-substituted polychloropyridine could undergo cyclisation by an intramolecular arylation process, *e.g.* (**1**) → (**2**). It was indeed found that photolysis of 2- or 4-thiophenoxy-, phenoxy-, and anilino-tetrachloropyridines caused cyclisation with loss of HCl to give the polychlorotricyclic systems (**2** or **4**; X = S, O, or NH) in practicable yields (*cf.* Table). Irradiation was carried out with immersion type medium-pressure lamp (type Q81, Quarz Lampen GMBH, Hanau) with Pyrex envelope in ethanol as solvent except in the case of the 2-phenoxy- and the 2-anilino-tetrachloropyridine (**3**; X = O or NH) when tetrahydrofuran proved the only efficacious medium. Internuclear cyclisation also occurred with the chlorofluoropyridines (**5**; R^1 = R^2 = Cl or R^1 = F, R^2 = Cl) to give the corresponding benzothienopyridines (**6**; R^1 = Cl or F, respectively). The trifluoro-compound (**6**; R^1 = F) could not be obtained from the tetrafluorothiophenoxy-compound (**5**; R^1 = R^2 = F) by irradiation with a quartz or Pyrex filter which reflects the much higher C–F bond energy.

The 2,6-dithiophenoxy- (**7**) and the 2,4,6-trithiophenoxypyridine (**9**) could only be made to cyclise once, (**7**) → (**8**) and (**9**) → (**10**). The exclusive formation of compound (**10**) whose structure was confirmed by its identity with the product obtained from (**2**; X = S) and excess of thiophenol, indicates the higher reactivity of the 4-substituent towards arylation. Attempts to cyclise the tetrachloropyridyl-4-diphenylphosphine or its oxide[2] in a similar way resulted in tar formation. This failure is in keeping with the observation that phenylphosphines suffer rapid photo-homolysis of the C–P bond.[3]

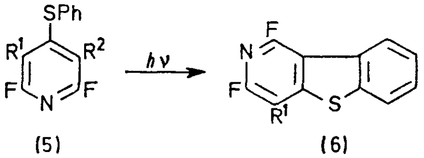
The successful examples demonstrate a convenient route to polyhalogeno-substituted systems containing fused furan, thiophen, and pyrrole rings which could not be made from the parent 3-ring system by conventional halogenation. To our knowledge the photocyclisation of decachlorodi-



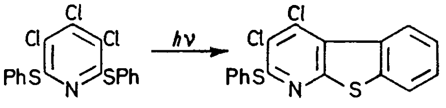
(1)
X = S, O, NH
(2)



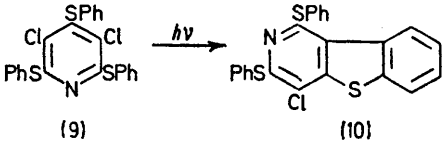
(3) X = S, O, NH (4)



(5) (6)



(7) (8)



(9) (10)

Products from the photolysis of polyhalogenopyridines in ethanol

Pyridine	Reaction time (h)	Product Type	Yield (%)	M.p.(°)
(**1**; X = S)	24	(**2**; X = S)	68	185
(**1**; X = O)	24	(**2**; X = O	54	130
(**1**; X = NH)	24	(**2**; X = NH)	79	239
(**3**; X = S)	24	(**4**; X = S)	87	215
(**3**; X = O)[a]	5	(**4**; X = O)	38	95
(**3**; X = NH)[a]	24	(**4**; X = NH)	12	304
(**5**; R^1 = R^2 = Cl)	24	(**6**; R^1 = R^2 = Cl)	83	159
(**5**; R^1 = F, R^2 = Cl)	20	(**6**; R^1 = F, R^2 = Cl)	46	154
(**7**)	24	(**8**)	26	222
(**9**)	24	(**10**)	30	118

[a] The solvent used in these cases was tetrahydrofuran.

phenyl sulphide[4] with loss of chlorine to give perchlorodibenzothiophen is the only reported case so far of utilising polyhalogenoarenes in photocyclisation. Till recently the C–Cl bond in aromatic chloro-compounds had been regarded as photochemically unreactive.[5]

The synthesis of the starting materials and the chemistry of the new heterocyclic products as well as analytical and spectral data on which the orientation of all new compounds were based will be published elsewhere.

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