Metathesis of Heterocycles

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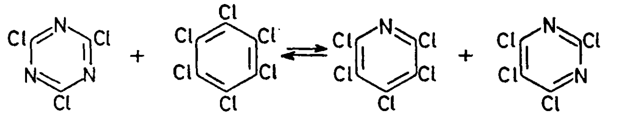
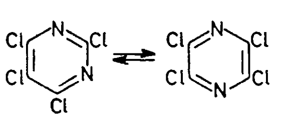
Summary The perchlorinated aromatic nitrogen heterocycles undergo metathesis and approach equilibrium compositions at *ca.* 600 °C in 3 h according to the equation $1,3,5\text{-}C_3Cl_3N_3 + C_6Cl_6 \rightleftharpoons C_4Cl_4N_2 + C_5Cl_5N$; $C_4Cl_4N_2$ consists of an equilibrium mixture of tetrachloropyrimidine and tetrachloropyrazine which interconvert by way of their cyanogen chloride Diels–Alder adducts.

A wide variety of aromatic homo- and hetero-cycles undergo transposition of skeletal atoms on photolysis or pyrolysis.[1] There is substantial evidence to implicate valence isomers of the starting material as intermediates, although the rigorous validity of that proposition has been challenged.[2] Other mechanisms have been suggested to accommodate specific observations but not seriously tested.[3] In every case, unimolecularity has been assumed. The following experiments suggest that the unimolecularity of the thermal rearrangements may be in doubt, at least as a general phenomenon.

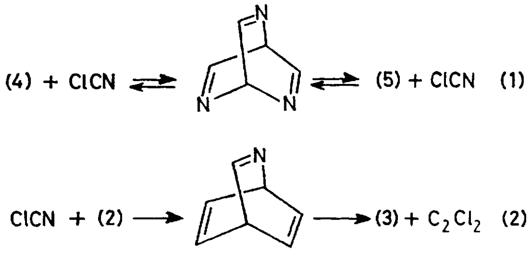
While trichloro-1,3,5-triazine (**1**) and hexachlorobenzene (**2**) were recovered without decomposition[4] when heated separately at 525 °C for 3 h in a sealed gold tube with an external pressure of 1 kbar, an equimolar mixture of (**1**) and (**2**) under the same conditions gave pentachloropyridine (**3**) tetrachloropyrimidine (**4**), and tetrachloropyrazine (**5**) in 91% yield and 14% conversion (see Table). This reaction attains equilibrium at 600 °C ($K_{\mathrm{eq}} = 2$) within 3 h as evidenced by the formation of the same product mixture starting with (**1**) and (**2**) as with (**4**) and (**3**).[5] At equilibrium, yields were 60%. By-products included decachlorobiphenyl, octachlorobipyridyl, carbon tetrachloride, tetrachloroethylene, and uncharacterized non-volatile material.


(1) (2) (3) (4)


(4) (5)

The diazines (**4**) and (**5**) equilibrate at 550 °C in 3 h (K_{eq}=0·05) with pyrimidine (**4**) strongly favoured over pyrazine (**5**).

Attainment of the pyrazine–pyrimidine equilibrium is strongly catalysed by cyanogen chloride (**6**) and not by (**1**) (see Table). This catalysis suggests that the (**4**)–(**5**) equilibration proceeds by fragmentation to cyanogen chloride followed by its Diels–Alder addition to starting material,† retro Diels–Alder cleavage to form the isomer, and regeneration of the cyanogen chloride catalyst [reaction (1), Scheme 1]. By analogy, the metathesis of the other chlorinated heterocycles is also expected to involve formation, reaction, and regeneration of (**6**). Support for this argument comes from the observation that the reaction of (**2**) to give (**3**) and (**4**) or (**5**) is faster with (**6**) than with (**1**). Further, under conditions of low conversion at 450 °C the reaction of (**2**) with (**6**) gives initially mainly (**3**), whereas reaction of (**2**) with (**1**) gives nearly equimolar proportions of (**4**) and (**3**). The former reaction is consistent with dienophilic attack of (**6**) on (**2**) [reaction (2), Scheme 1]. For the reaction of (**1**) with (**2**), we tentatively



Scheme 1. Chlorine atoms have been omitted for clarity.

Table

mmol of Reagents	T/°C	P/atm	Time/h	Products/mmol (1)	(5)	(4)	(3)	(2)
1(1) + 1(2)	525	1000	3	0·73	0·013	0·21	0·061	0·80
1(1) + 1(2)	600	1000	3	0·26	0·016	0·30	0·35	0·28
1(3) + 1(4)	600	1000	3	0·24	0·023	0·37	0·42	0·25
1(1) + 1(2)	450	4	672	0·90	0·000	0·0023	0·0020	0·89
1(2) + 3(6)	450	4	100	0·05	0·000	0·0012	0·0048	0·93
1(4)	550	1000	3	0·33	0·013	0·26	0·14	0·00
1(5)	550	1000	3	0·30	0·016	0·26	0·13	0·00
1(5)	450	2	264	0·000	1·00	0·000	0·000	0·000
1(5) + 1·5(6)	450	2	264	0·02	0·04	0·88	0·000	0·000
1(5) + 1·5(6)	450	2	20	0·005	0·86	0·010	0·000	0·000
1(5) + 0·5(1)	450	2	20	0·50	0·93	0·000	0·000	0·000

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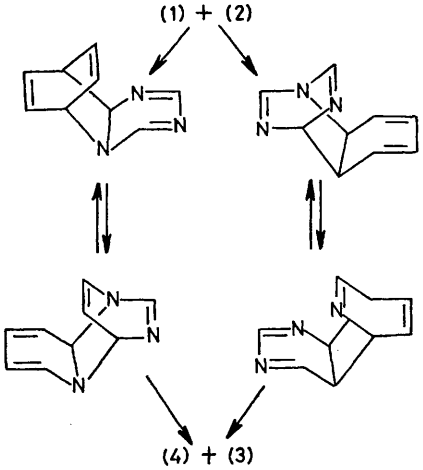
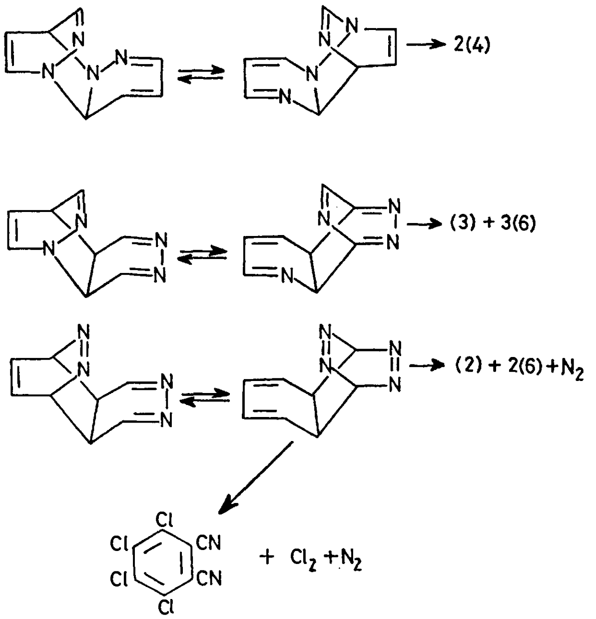
† (4 + 2)-Cycloadditions to pyrimidines (H. Neunhoffer and G. Werner, *Annalen*, **1974**, **1190**) and other heterocycles have been demonstrated under far milder conditions.

suggest a Diels–Alder adduct followed by internal Diels–Alder transfer of cyanogen chloride (or dichloroacetylene)‡ and retro Diels–Alder cleavage (Scheme 2).§



Scheme 2. Chlorine atoms have been omitted for clarity.

Such a process is more clearly indicated in the thermal decomposition of tetrachloropyridazine (**7**),¶ which shows a pressure dependence in the gas phrase. The half-life of (**7**) at 350 °C is 4 days at 1 atm and 20 days at 0·1 atm. Cyanogen chloride was not observed to have a catalytic effect. Diels–Alder dimers of (**7**) in several isomeric forms can account for the rearranged and disproportionated products while nitrogen extrusion from the dimer results in some of the more complex products (Scheme 3).



Scheme 3. Chlorine atoms have been omitted for clarity.

A hint that the unimolecularity of phototranspositions may also be brought into question comes from the photolysis of picolines wherein the metathesis products, lutidines and pyridine, are observed in addition to the rearrangement products.[6] All these could be accommodated readily by postulating a (2+2) photodimer intermediate undergoing Cope rearrangements prior to cleavage.

We urge that the extensive chemistry that has been developed in rearrangements of heterocycles be re-examined to ascertain the molecularity as broadly as possible. It is quite likely that examples of mono- and bi-molecular processes may be extant and that a change of mechanism dependent on pressure will be found.

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‡ The internal bridge transfer could occur either by a dissociation–recombination process or *via* tetracyclic, intramolecular cycloadducts.

§ Dissociation of (**2**) to dichloroacetylene and Diels–Alder addition to (**1**) must also be considered, particularly in view of the predominant formation of (**4**) and (**5**) at 525 °C.

¶ The flow pyrolysis of tetrachloropyridazine has been reported (R. D. Chambers, M. Clark, J. A. H. MacBride, W. K. R. Musgrave, and K. C. Srivastava, *J.C.S. Perkin I*, 1974, 125). We observed the same products in sealed tube experiments and in addition obtained a 6% yield of tetrachloropyrimidine. Rearrangement to pyrimidines is the major reaction of fluorinated pyridazines (R. D. Chambers, J. A. H. Macbride, and W. K. R. Musgrave, *J. Chem. Soc.* (*C*), 1971, 3384).

[1] L. Kaplan, K. E. Wilzbach, W. G. Brown and S. S. Yang, *J. Amer. Chem. Soc.*, 1965, **87**, 676; R. D. Chambers, W. K. R. Musgrave, and K. C. Srivastava, *J.C.S. Chem. Comm.*, 1971, 264; R. D. Chambers, M. Clark, J. R. Maslakiewicz, W. K. R. Musgrave, and P. G. Urben, *J.C.S. Perkin I*, 1974, 1513; M. G. Barlow, R. N. Haszeldine and M. J. Kershaw, *J.C.S. Perkin I*, 1974, 1736.

[2] J. A. Barltrop and A. C. Day, *J.C.S. Chem. Comm.*, 1975, 177.

[3] W. D. Crow and C. Wentrup, *Tetrahedron Letters*, 1968, **27**, 3115; J. M. Patterson, C. H. Issidorides, E. P. Papadopoulos, and W. T. Smith, Jr., *ibid.*, 1970, 1247.

[4] I. B. Johns, E. A. McElhill and J. O. Smith, *J. Chem. Eng. Data*, 1962, **7**, 277; E. K. Fields and S. Meyerson, *Amer. Chem. Soc. Petroleum Preprints*, 1973, **18**, 149.

[5] W. Mahler, U.S.P. 3,882,116 (1975).

[6] S. Caplain and A. Lablache-Combier, *Chem. Comm.*, 1970, 1247.