Sensitisation of Thermal Aromatic Rearrangements

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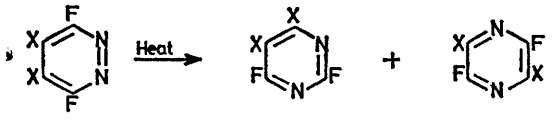
Summary Rearrangement of perfluoro-4,5-di-isopropylpyridazine (**1**) or tetrafluoropyridazine (**3**) occurs in the presence of perfluoro-4,5-di-s-butylpyridazine (**2**), under conditions where (**1**) and (**3**) are relatively unchanged when heated alone; a mechanism is advanced for this case of thermal sensitisation.

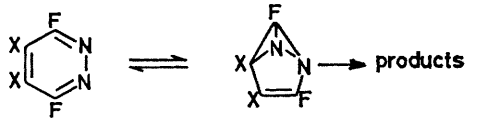
IN the previous communication,[1] we described experiments that ruled out cross-over products in the thermal rearrangement of the pyridazine derivatives (**1**) and (**2**) to the corresponding products (**1a**) and (**2a**,**b**). However, in conducting these experiments we made the intriguing observation that rearrangement of perfluoro-4,5-di-isopropylpyridazine (**1**) is sensitised by the presence of perfluoro-4,5-di-s-butylpyridazine (**2**). This was confirmed by heating a (1 : 1) mixture of (**1**) with (**2**) at 300 °C in a sealed tube. When heated alone under these conditions, only 8% of compound (**1**) is converted into (**1a**) while (**2**) is quantitatively converted into (**2a**) and (**2b**). From the mixture the product contained approximately equal amounts of (**1a**) and (**2a**,**b**), in each case *ca.* 90% conversion.



(1), X = $CF(CF_3)_2$ (1a)
(2), X = $CF(CF_3)C_2F_5$ (2a) + (2b)
(3), X = F (3a)

However, an even more spectacular example of sensitisation occurs with tetrafluoropyridazine (**3**). In a sealed tube, alone, at 300 °C there was *no* detectable rearrangement of (**3**) but, in the presence of (**2**) rearrangement of (**3**) to (**3a**) occurred. The amount of (**3a**) produced increased with the amount of (**2**) added but, with comparable amounts of (**2**)

and (**3**) in the starting mixture, more (**2a**,**b**) was obtained than (**3a**). At the other extreme, however, with a 10:1 molar ratio excess of (**3**) over (**2**), a greater total amount of (**3a**) was produced (21% conversion of **3**) than (**2a**,**b**). Three points emerge from these experiments: (i) Without doubt, (**2**) sensitises the rearrangement of (**1**) and (**3**). (ii) Rearrangement of (**2**) is partly *inhibited* by added (**1**) or (**3**). (iii) More than one molar proportion of (**3**) is rearranged, for every molar proportion of (**2**) converted, when (**3**) is in excess at the beginning of the experiment.



(**2**), X = $CF(CF_3)C_2F_5$ (**4**)

We are unaware of any other example of sensitisation of a thermal aromatic rearrangement and the mechanism of this process is of considerable interest. It has been argued elsewhere[2] that only the formation and rearrangement of intermediate diazabenzvalene derivatives will account for the highly specific results of substituent labelling experiments. Therefore, we suggest that the much easier rearrangement of (**2**) than (**1**), and especially easier than (**3**) stems from a higher initial-state energy for (**2**), due to the larger steric requirements of the perfluoro-s-butyl group.[3] Therefore, it is probable that at *e.g.* 300 °C, (**2**) is in equilibrium with its valence isomer (**4**). This has some precedent in the results of Haszeldine and his co-workers,[4] who showed that perfluorohexaethylbenzene, $C_6(C_2F_5)_6$, is converted into its *para*-bonded isomer at 400 °C.[4] We suggest, therefore, that the basis of the new sensitisation process described here is the collision of valence isomer (**4**) with, for example, (**3**), transferring in the process the normal Boltzmann energy, plus an additional amount corresponding to reversion of (**4**) to its initial-state (**2**), or products (**2a**) and (**2b**). A general description of the process, for two molecules A and B may be outlined as shown in the Scheme.

$$A \rightleftharpoons (A)_{V.I.} \qquad (V.I. = \text{valence isomer})$$

$$B + (A)_{V.I.} \rightarrow (B)_{V.I.} + A \text{ or products}$$

$$(B)_{V.I.} \rightarrow \text{products}$$

SCHEME

An alternative explanation could, in principle,[5] be the formation of a triplet state of molecule A, followed by intersystem crossing with molecule B. However, we have not observed products of the type described here, in various attempted triplet sensitised photolyses of fluorinated pyridazines.

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