

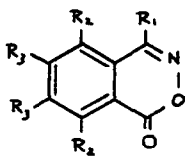
VAPOUR PHASE PYROLYSIS OF BENZOXAZINONES

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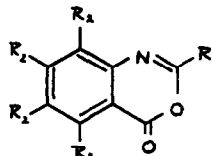
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The Communications of Rees *et al.* on the formation of 2-phenylbenzazate¹ and biphenylene² by the vapour phase pyrolysis of 4-phenylbenzo-1,2,3-triazine prompts us to record our closely related studies. By analogy with our work on the synthesis of biphenylenes by the pyrolysis of phthalic anhydrides³ we expected that benzoxazinones would undergo thermal fragmentation to give benzyne and thence biphenylenes. Our preliminary results show that this is so with 4-substituted 1H-2,3-Benzoxazin-1-ones (1) but not with 2-substituted 4H-3,1-Benzoxazin-4-ones (2).



(1)

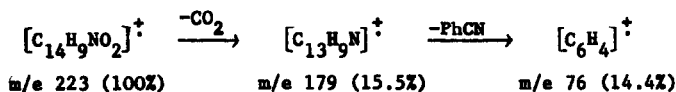
- a. R₁ = -Ph; R₂ = R₃ = H
- b. R₁ = -CH₃; R₂ = R₃ = H
- c. R₁ = -Ph; R₂ = H, R₃ = Cl
- d. R₁ = -Ph; R₂ = R₃ = Cl



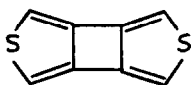
(2)

- a. R₁ = -Ph; R₂ = H
- b. R₁ = -CH₃; R₂ = H
- c. R₁ = -Ph; R₂ = Cl

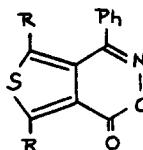
We have found that pyrolysis of the 4-phenyl compound (1a) at 700-720°/0.01 mm and of the 4-methyl compound (1b) at 840-860°/0.01 mm gave biphenylene in 35% and 25% yields respectively. Similarly the dichloro derivative (1c) at 700°/0.01 mm gave 2,3,6,7-tetrachlorobiphenylene (4%) and the tetrachloro derivative (1d) at 700°/0.05 mm gave octachlorobiphenylene (6%). The temperatures quoted are those which gave optimum yields of products. The thermal decomposition probably occurs stepwise, first by extrusion of carbon dioxide and then by loss of RCN to give a benzyne which dimerises to a biphenylene. In the pyrolysis of compounds (1a), (1c), and (1d) benzonitrile was detected in the pyrolysate. The thermal decomposition parallels the fragmentation which occurs in the mass-spectrometer, e.g. for compound (1a):



In contrast to 4-phenylbenzo-1,2,3-triazine which decomposes at 420-450° to give 2-phenyl benzasate and above 500° to give biphenylene,¹ the benzoxazin-1-one (1a) was recovered almost quantitatively after being passed through the apparatus at temperatures up to 560°. The isomeric benzoxazin-4-ones (2) are even more stable. Thus the compounds (2a), (2b), and (2c) were all recovered in over 90% yield after pyrolysis at temperatures up to 800°. If it is assumed that in the pyrolysis of benzotriazines and benzoxazinones the first bond to be broken is that between atoms 2 and 3 then the order of stability agrees with the order of the bond energies N-N < N-O < C-O.



(3)



(4) a. R=H; b. R=Cl

Our attempts to extend the synthesis of biphenylenes from benzoxazin-1-ones to the synthesis of the dithiophen analogue (3) of biphenylene were unsuccessful. The thia compounds (4a) and (4b) at 600° gave, as the only identifiable product, trace amounts of biphenylene. Presumably fragmentation of the oxazinone ring had occurred, with loss of carbon dioxide and benzonitrile, but the resulting thiophynes underwent decomposition or rearrangement rather than dimerisation to give (3) or its tetrachloro derivative. In separate experiments it was found that benzonitrile at 600° yields trace amounts of biphenylene. Previously it had been shown that pyrolysis of chlorobenzene at 690° likewise yields traces of biphenylene.⁴

The benzoxazin-1-ones (1a-1d) were prepared from the appropriate *o*-benzoyl (or acetyl) benzoic acid by reaction with hydroxylamine and cyclisation of the resultant oximes. The thiophen analogues (4a) and (4b) were prepared similarly.

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