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FLASH PYROLYSIS OF 4-METHYLENE-1,2,3-BENZOTRIAZINES

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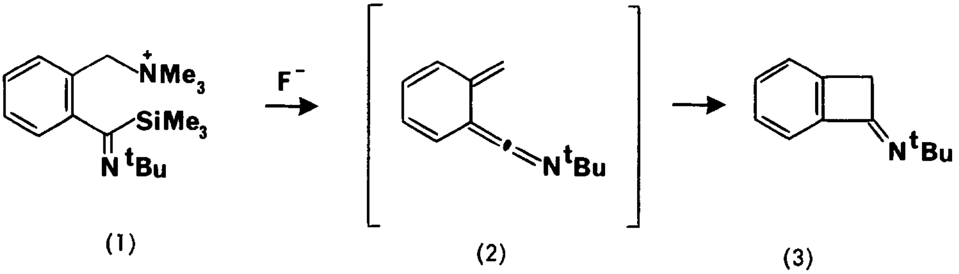
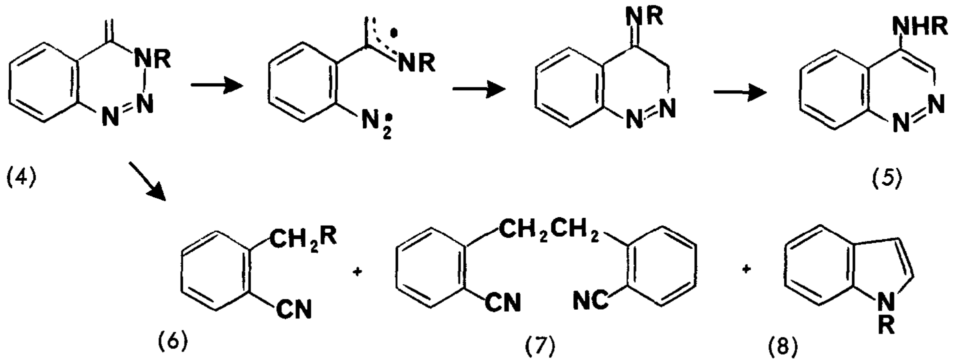
Summary: Flash vacuum pyrolysis of 3-alkyl-4-methylene-1,2,3-benzotriazines gives products derived from benzocyclobutane N-alkylimines and to a lesser extent from 2-methylene-benzazetidines. Benzocyclobutane N-phenylimine is formed in high yield by flash pyrolytic elimination of HCl from N-phenyl-2-methyl benzimidoyl chloride.

Saegusa and his coworkers have recently reported the formation of the iminoxylylene (2) in the fluoride ion induced 1,4-elimination of fluorotrimethylsilane and trimethylamine from the quaternary salt (1).[1] The reactive xylylene (2) was trapped in Diels-Alder reactions or cyclised to the iminobenzocyclobutane (3). In view of this report we now describe our observations on the flash vacuum pyrolysis of 4-methylene-1,2,3-benzotriazines (4) where thermal extrusion of nitrogen could also lead to iminobenzocyclobutanes or the isomeric and, as yet unknown, 2-methylenebenzazetidines (10).



The methylene triazines (4; R = Me, Et) were prepared by the method of Vaughan and Fong[2] or by the action of MeMgI on 3-methyl and 3-ethyl-1,2,3-benzotriazinones.[3] On F.V.P. at 400°C/2 x 10^{-2} torr, the methyl derivative (4; R = Me) gave 4-methylaminocinnoline (5; R = Me)[4] (40%) together with 2-ethylbenzonitrile (6; R = Me)[5] (30%). At 600°C, no methylaminocinnoline was observed but the yield of nitrile rose to 70%. At 600°C, the ethyl derivative (4; R = Et) gave 2-n-propylbenzonitrile (6; R = Et) (60%) together with N-ethylindole (8; R = Et) (5%)[6] and the dinitrile (7) (17%).[7] Surprisingly no ethylaminocinnoline was found when the pyrolysis of the ethyl methylenetriazine was carried out at 400°C.

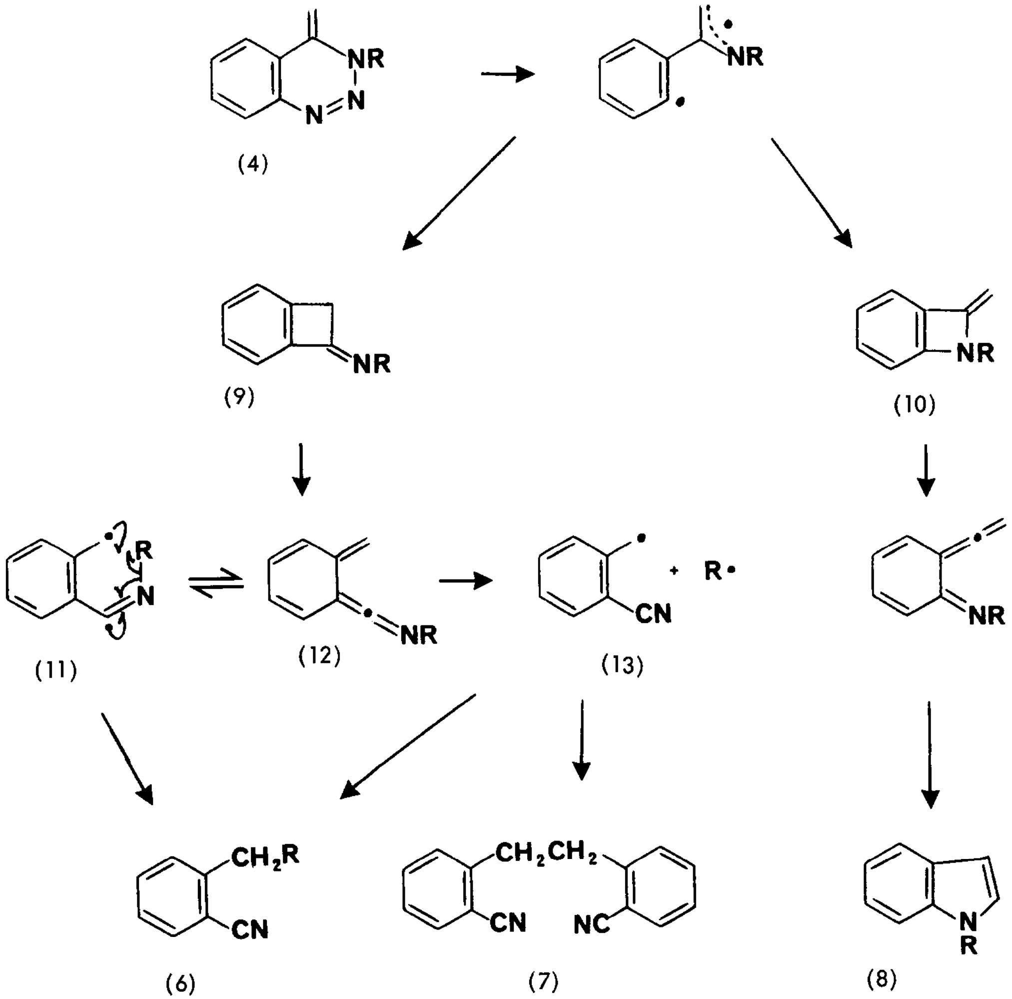


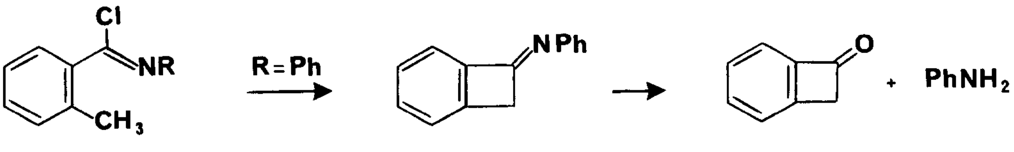
Formation of the methylaminocinnoline (5; R = Me) can be explained by a Dimroth type of rearrangement resulting from $N_2 - N_3$ bond cleavage and recyclisation on carbon. The same rearrangement has been observed, but in lower yield, under acidic conditions.[8]

Formation of the 2-alkylbenzonitriles (6; R = Me, Et) is more interesting since it strongly implicates iminobenzocyclobutanes (9) as intermediates formed by loss of N_2 and ring closure. Under the F.V.P. conditions cleavage of the iminobenzocyclobutanes to the iminoxylylenes (12) is reasonable and subsequent alkyl migration would lead to the observed products (6). Although the migration is formally an allowed 1,5-sigmatropic shift the geometry of the iminoxylylene is not compatible with the transition state for such a process. However, at the elevated temperatures involved the iminoxylylene and diradical (11) may well be readily interconvertible and the relaxation of geometry in the latter would allow the shift to occur as an intramolecular S_R2 process as shown. Formation of the dinitrile (7) from the ethyl methylenebenzotriazine (4; R = Et) indicates that some cleavage of the iminoxylylene (12) or diradical (11) to give the stable 2-cyanobenzyl radical (13) (which dimerises) and an ethyl radical also occurs. This raises the possibility of a dissociation - recombination mechanism for formation of the 2-alkylbenzonitriles and further studies are necessary to elucidate the mechanism.

Isolation of N-ethylindole from the pyrolysis of the ethyl methylenetriazine (4; R = Et) is also significant since it provides evidence for a minor pathway involving loss of nitrogen and closure to the 2-methylenebenzazetidine (10; R = Et). Ring opening of this species under the reaction conditions would give the methylene azaxylylene (14) for which cyclisation to the indole (8), possibly via 2-ethylaminophenylacetylene, seems very reasonable.

An alternative approach to the iminoxylylenes (12) is flash pyrolytic 1,4-elimination of HCl from the imidochlorides (15). 2-Methylbenzoyl chloride undergoes such an elimination to give benzocyclobutanone via the analogous ketoxylylene (12; O for NR)[10]. However our attempts to produce the xylylenes (12; R = Me and Et) from imidochlorides (15; R = Me and Et) failed because facile von Braun degradation leads only to 2-methylbenzonitrile.[11] In contrast the imidochloride (15; R = Ph) underwent clean 1,4-elimination on F.V.P. ($650^{\circ}C/2 \times 10^{-2}$ torr) to give a pyrolysate in which methylene ^{1}H m.r. absorptions at δ 4.50 and 4.55 (ratio 1:3) can be attributed to the geometrical isomers of benzocyclobutane N-phenylimine. Hydrolysis of this pyrolysate with aqueous sodium bicarbonate gave a 1:1 mixture of aniline and benzocyclobutanone.[12] Thus aryl migration does not occur with (12; R = Ph) but ring closure is observed as reported by Saegusa and his coworkers for the t-butyl analogue (12; R = ^{t}Bu) produced in solution at lower temperature.[1]


(4) (9) (10) (11) (12) (13) (14) (6) (7) (8)


(15) (16) (17)

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Acknowledgements

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