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2-Alkylbenzazetes

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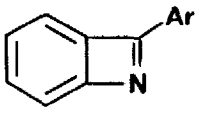
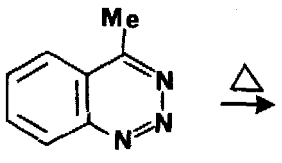
We have reported the formation of a number of 2-arylbenzazetes (1) by pyrolysis and photolysis of 4-arylbenzotriazines.[1,2] These benzazetes are reactive dienophiles and dipolarophiles and their cycloadditions have led to several new reactions of potential synthetic application.[1,3] The generation of 2-alkylbenzazetes is therefore of interest in order to establish the scope of such cycloadditions and also to probe the effect of substituents on the antiaromatic azete ring.

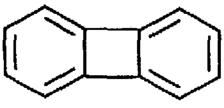
Pyrolysis of 4-methyl-1,2,3-benzotriazine[1] (2) at 450°/0.1 Torr as described for the 4-arylbenzotriazines[2] and condensation of the pyrolysate at -90°C or -197°C, followed by warming to room temperature gave a complex mixture from which the only identified products were biphenylene (3) and 9-methylacridine, (4). Transient red colouration, characteristic of 2-arylbenzazetes, was not observed and the only evidence for the formation of a 2-methylbenzazete dimer came from the observation



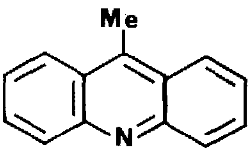
(1)



(2)



(3)



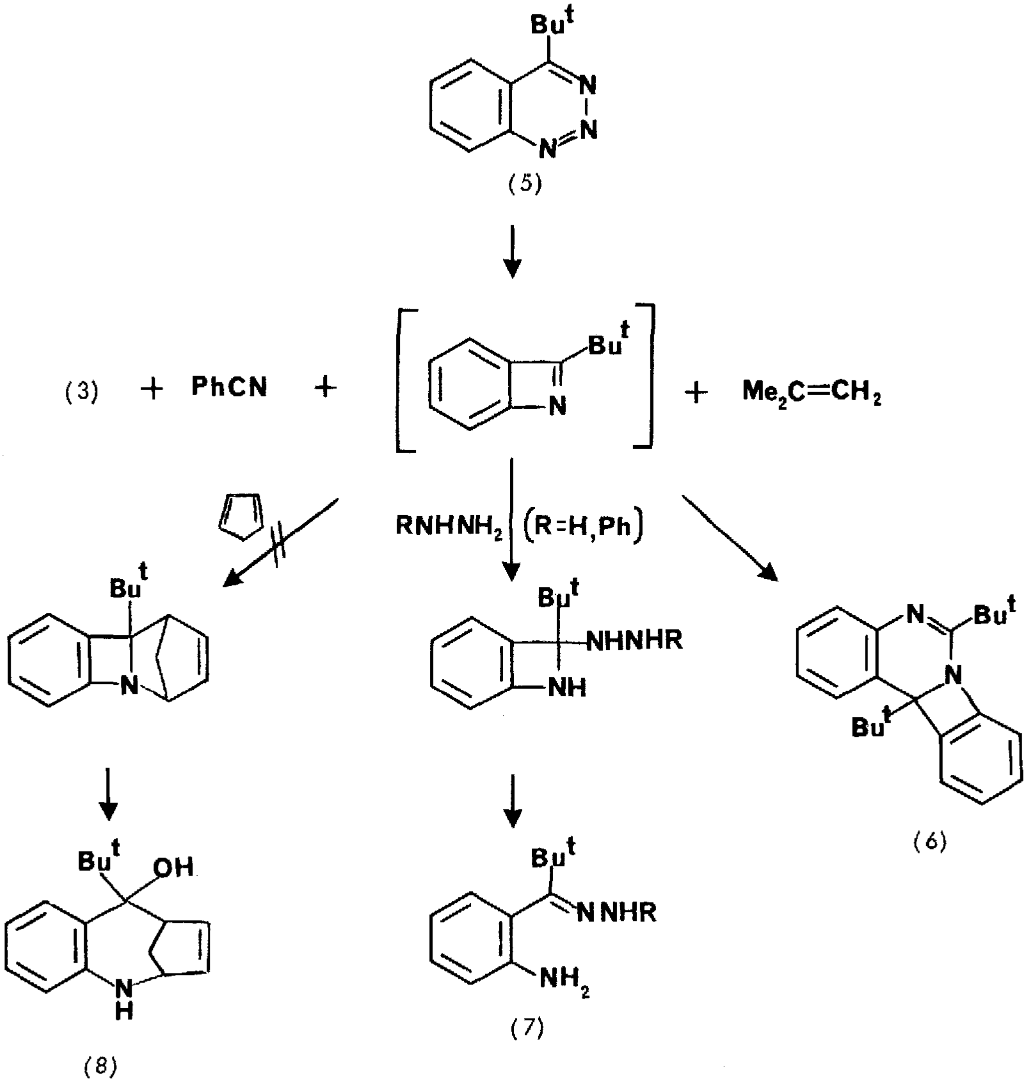
(4)

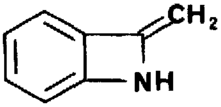
of a peak, m/e 234, in the mass spectrum of a minor chromatographic fraction. No recognisable benzazete products could be isolated when cyclopentadiene or tetraphenylcyclopentadienone was added to the cold pyrolysate. Photolysis of 4-methylbenzo-1,2,3-triazine alone or in the presence of cyclopentadiene also gave very complex mixtures from which none of the anticipated benzazete dimer (6, Me for Bu^t) or hydrated adduct (8, Me for Bu^t) could be isolated. There is thus no evidence for the formation of 2-methylbenzazete in significant amounts.

A possible explanation for this difference between aryl- and methyl-benzotriazines and benzazetes lies in the presence of reactive α-hydrogens in the methyl derivative. This could lead to complicating tautomerism in the starting triazine or in the azete; for example 2-methylbenzazete may rapidly isomerise to the less stable tautomer (9). Such a complication is not possible in 2-t-butylbenzazete and, in view of the marked stabilising effect of t-butyl groups in cyclobutadienes,[4] one might anticipate that 2-t-butylbenzazete would be particularly stable.

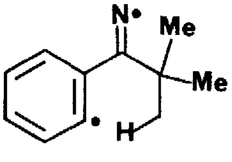
4-t-Butyl-1,2,3-benzotriazine (5), m.p. 112-113°, was readily obtained from 2-aminopivalophenone.[5] Pyrolysis at 450°/0.1 Torr gave starting triazine (4%), biphenylene (21%), benzonitrile (54%), and a dimer of 2-t-butylbenzazete (12%), m.p. 142-143°. The t-butyl groups in this dimer were non-equivalent, consistent with structure (6), analogous with that of 2-arylbenzazete dimers.[2] The formation of benzonitrile as the major product can be rationalised by elimination of isobutene from an intermediate such as (10) in the extrusion of nitrogen from the triazine. Indeed isobutene (43%)[6] was condensed in a second cold trap when the pyrolysate was allowed to warm up from -197° to room temperature.

No red colouration was observed in the pyrolysate even at -197°. Addition of cyclopentadiene to the pyrolysate at -197° gave no adduct or hydrated adduct (8) and the yield of dimer was unaffected. With p-chlorobenzonitrile oxide again none of the expected benzazete adduct was formed but the yield of dimer was considerably depressed. With hydrazine and phenylhydrazine, dimer formation was completely suppressed and the corresponding hydrazones (7, R=H,Ph) were formed in yields very close to that of dimer in their absence. These hydrazones could be formed by nucleophilic addition to 2-t-butylbenzazete or by reaction with unchanged 4-t-butylbenzotriazine.[1] However under pyrolytic conditions where virtually no triazine ($<$ 4%) is recovered,[7] the phenyl hydrazones can still be isolated in significant yield (13%).


Bu^t
(5)
(3) + PhCN +
+ Me2C=CH2
RNHNH2 (R=H,Ph)
NHNHR
NH
N
Bu^t
OH
NNHR
NH2
H
(6)
(7)
(8)



(9)



(10)

Photolysis (300 nm) of 4-t-butylbenzotriazine also gave the dimer (6) (14%). Photolysis in the presence of cyclopentadiene gave the hydrated 1:1-adduct (8) (4%) in addition to dimer (4%) and to benzotriazine-cyclopentadiene adducts.[2] In the presence of p-nitrobenzonitrile oxide no adduct was isolated but significantly dimer formation was suppressed.

In conclusion, we have evidence for the formation of a 2-alkylbenzazete only from the 4-t-butyltriazine. Even this benzazete is produced in low yield owing to a competing process involving fragmentation of the t-alkyl group. If the t-butylbenzazete is involved it differs significantly from the 2-arylbenzazetes both in colour and reactivity. Whilst one could minimise the problems of α-H lability and, possibly, of β-elimination with 2-adamantylbenzazete it is clear from these initial results that the chemistry of 2-arylbenzazetes cannot, at present, be usefully extrapolated to 2-alkylbenzazetes generally.

References and Notes.

1. B.M. Adger, C.W. Rees and R.C. Storr, J.C.S. Perkin I, 1975, 45.
2. C.W. Rees, R.C. Storr and P.J. Whittle, J.C.S. Chem.Comm., 1976, 411.
3. C.W. Rees, R. Somanathan, R.C. Storr and A.D. Woolhouse, J.C.S. Chem.Comm., 1975, 740; C.W. Rees, R. Somanathan, R.C. Storr and A.D. Woolhouse, ibid., 1976, 125.
4. G. Maier, Angew.Chem.Intern.Ed., 1974, 13, 425.
5. Obtained by reaction of t-butylmagnesium chloride with 2-methyl-3,1-benzoxazin-4-one and hydrolysis of the resulting amide.
6. Characterised as the dibromide.
7. 4-t-Butylbenzotriazine is recovered (> 80% yield) from treatment with phenylhydrazine under these conditions.