Photochemical Generation of 2-Arylbenzazetes from 1,2,3-Benzotriazines: Structure of 2-Arylbenzazete Dimers

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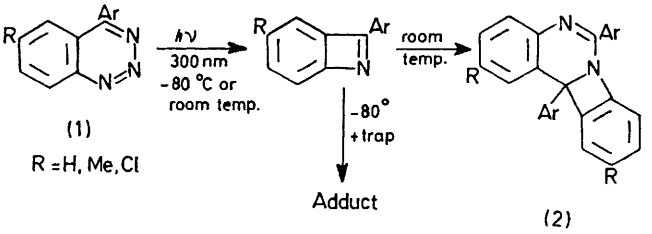
Summary 2-Arylbenzazetes are produced by photolysis of 4-arylbenzotriazines (**1**) and can be intercepted in cycloaddition reactions; the benzazetes dimerise thermally to give the angular dimers (**2**) and, in the presence of Lewis acids, the linear dimers (**5**).

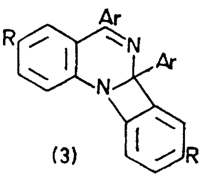
2-Arylbenzazetes can be generated by thermal extrusion of nitrogen from 4-aryl-1,2,3-benzotriazines at 450 °C and 0·1 Torr.[1] Disadvantages with this procedure are the high temperature required, the need for special although not sophisticated apparatus, the relatively small amounts of triazine (*ca.* 200 mg) which can be easily pyrolysed, and the formation of side products. While such problems are acceptable in exploratory work, there is a need for a simple, clean and potentially large-scale route to azetes.

We now report that preliminary studies on the photolysis of 4-aryl-1,2,3-benzotriazines indicate that photochemical generation of benzazetes is a viable alternative to the pyrolytic method. Photolysis (300 nm) of the arylbenzotriazines (**1**) (200 mg) in tetrahydrofuran (THF) (120 ml) in a Rayonet photochemical reactor at room temperature for 12—24 h gave the arylbenzazete dimers (**2**) identical with those obtained by the previously described pyrolytic route.[1] Photolysis of the triazines (1 g) in THF (120 ml) gave the dimers in somewhat lower percentage yields; however the overall conversion of triazine into benzazete dimer is a marked improvement over that from pyrolysis and the reaction is considerably cleaner, making isolation simpler.



Ar = Ph, R = H 73% (60%)
Ar = *p*-MeOC$_6$H$_4$, R = H 48% (24%)
Ar = Ph, R = Me 53% (30%)
Ar = Ph, R = Cl 30% (25%)

(Yields in parentheses for 1g scale)



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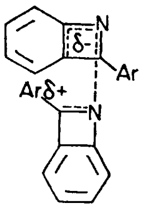

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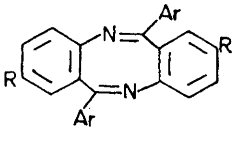

(5)

Thermal dimerisation of benzazetes is slow at −80 °C and irradiation of 4-phenylbenzotriazine (200 mg) in THF (40 ml) at −80 °C for 6 h gave a red solution containing 2-phenylbenzazete which reacted with a variety of reagents when these were added, in excess, after the irradiation was discontinued. Thus addition of *p*-nitrobenzonitrile oxide, tetraphenylcyclopentadienone, 1,3-diphenylisobenzofuran, and cyclopentadiene to the cold solution followed by warming to room temperature gave the previously reported products.[1,2] Absolute yields were rather low (22, 22, 17, and 16% respectively) but for conversion of the triazine into benzazete adducts were comparable to those obtained by the pyrolytic route.[1]

Appreciable loss of 2-phenylbenzazete occurs during the photochemical generation at low temperature. This appears to be the result of further photochemical transformations of the benzazete since the yield of dimer obtained by photolysis at −80 °C for 6 h followed by warming to room temperature is markedly lower (21%) than that obtained (43%) by photolysis at room temperature for the same time. Significantly the yields of dimer obtained by the former procedure are very similar to the yields of the products obtained when the more efficient azete traps were added at −80 °C after irradiation; in the presence of these traps *no* dimer was formed.

Because of the photolability of trapping agents such as those discussed above, *in situ* photolysis and interception of the azetes is unlikely to be generally applicable. However, *p*-nitrobenzonitrile oxide and cyclopentadiene did give the expected benz-1,3,5-oxadiazepine[2] (20%) and hydrated adduct[1] (23%) respectively. A further complication with this procedure was uncovered by the isolation from the latter experiment of a 1 : 1 photoadduct (37%) of the initial triazine and cyclopentadiene.

Originally the structures of the 2-arylbenzazete dimers were in some doubt because of the difficulty of clearly differentiating structure (**2**) from the three other posssible regioisomeric angular dimers *e.g.* (**3**). *X*-Ray crystallographic structure determination for the dimers from 2-phenyl- and 2-anisyl-benzazete has now unambiguously confirmed structure (**2**). Formation of the angular dimer (**2**) may be the result of a Diels–Alder reaction, *cf.* benzocyclobutadiene dimerisation;[3] the regioselectivity observed is that anticipated if the addition proceeds through a zwitterion or involves a transition state with appreciable polar character, (**4**). As is the case with benzocyclobutadiene,[3] the mode of dimerisation is sensitive to catalysis. Thus in the presence of $AlCl_3$, $AgBF_4$, or BF_3–Et_2O, 2-phenylbenzazete gives the linear dimer (**5**) (*ca.* 20%) in addition to the angular dimer (**2**) (*ca.* 20%).† Similarly, attempted hydrolysis of the benzazete from triazine (**1**; Ar = Ph, R = Me) with aqueous hydrochloric acid gave the expected *o*-aminobenzophenone together with some linear dimer (**5**, Ar = Ph, R = Me).

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† A trace of a benzazete trimer was also isolated from the experiment with BF_3–Et_2O.

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[2] C. W. Rees, R. Somanathan, R. C. Storr and A. D. Woolhouse *J.C.S. Chem. Comm.* 1975, 740.

[3] M. P. Cava and M. J. Mitchell, 'Cyclobutadiene and Related Compounds,' Academic Press, New York, 1967.