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BICYCLIC AZIRIDINES AS INTERMEDIATES IN THE PHOTOLYSIS OF POLYCYCLIC AROMATIC AZIDES.

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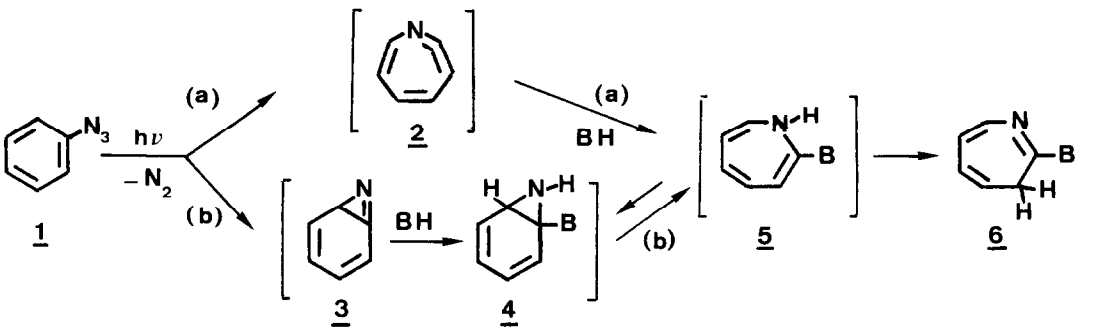
According to the subsequent treatment, azepines 16, 17, 19 or 1,2-dihydro derivatives 18 and 20 are obtained in the photolysis in basic medium of β-anthracenic azides 7b and 7c and provide strong evidence for the intermediate formation of bicyclic aziridines.

According to recent results [1] the photochemical conversion of phenyl azide 1 in the presence of bases to 2-substituted 3*H*-azepines 6 must proceed from 1-aza-1,2,4,6-cycloheptatetraene 2, which by nucleophilic trapping gives first the 1*H*-azepine 5 and then the 3*H*-azepine 6 (route a), rather than from the isomeric azirine 3, leading to an aziridine 4 which can afford the 1*H*-azepine by ring enlargement (route b).



This new pathway does not imply that in the polycyclic series the aziridine cannot be formed and behave as an intermediate, at least at low temperature, being favoured over its valence tautomer, the 1*H*-azepine, as a result of structural constraints [2]. Indeed we have shown previously [3] that the photolysis of 2-azidoanthracene 7a (or 2-azidonaphthalene) in a MeOH-MeOK/dioxane mixture goes through an intermediate which must be the methoxy-aziridine 8a as it affords the azepine 11 (via 10) after heating under reflux or the methoxy-amine 12 after immediate neutralization.

With respect to this problem it seemed worthwhile to investigate the photolytic decomposition of various 2-azidoanthracenes bearing a C-1 substituent which would be able to prevent the easy rearomatization of any transient aziridine. The results again provide strong evidence for the formation of such intermediates.

Two new β-anthracenic azides : 7b, $C_{20}H_{13}N_3$, pale-yellow cryst., m.p. 120°C, and 7c, $C_{15}H_{11}N_3O$, pale-yellow cryst., m.p. 100°C, have been studied. They were prepared from the corresponding 2-phenylazoanthracenes by the classical sequence of hydrogenolysis, diazotization and action of NaN_3 [4]. Irradiations were performed under N_2, with a high-pressure Hg

vapour lamp ("Philips" SP 500) equipped with "Sovirel" filters ($350 < \lambda < 410$ nm).

2-Azido-1-phenylanthracene 7b. The behaviour of this azide on irradiation under neutral conditions (dioxane/methanol : 1/1) recalls that of 2-azidobiphenyl [5], the predominant product being the naphthocarbazole 14 [6] (78 %), accompanied by traces of the symmetrical azo derivative 15 ($C_{40}H_{26}N_2$, orange cryst., m.p. 370°C, then 376°C).

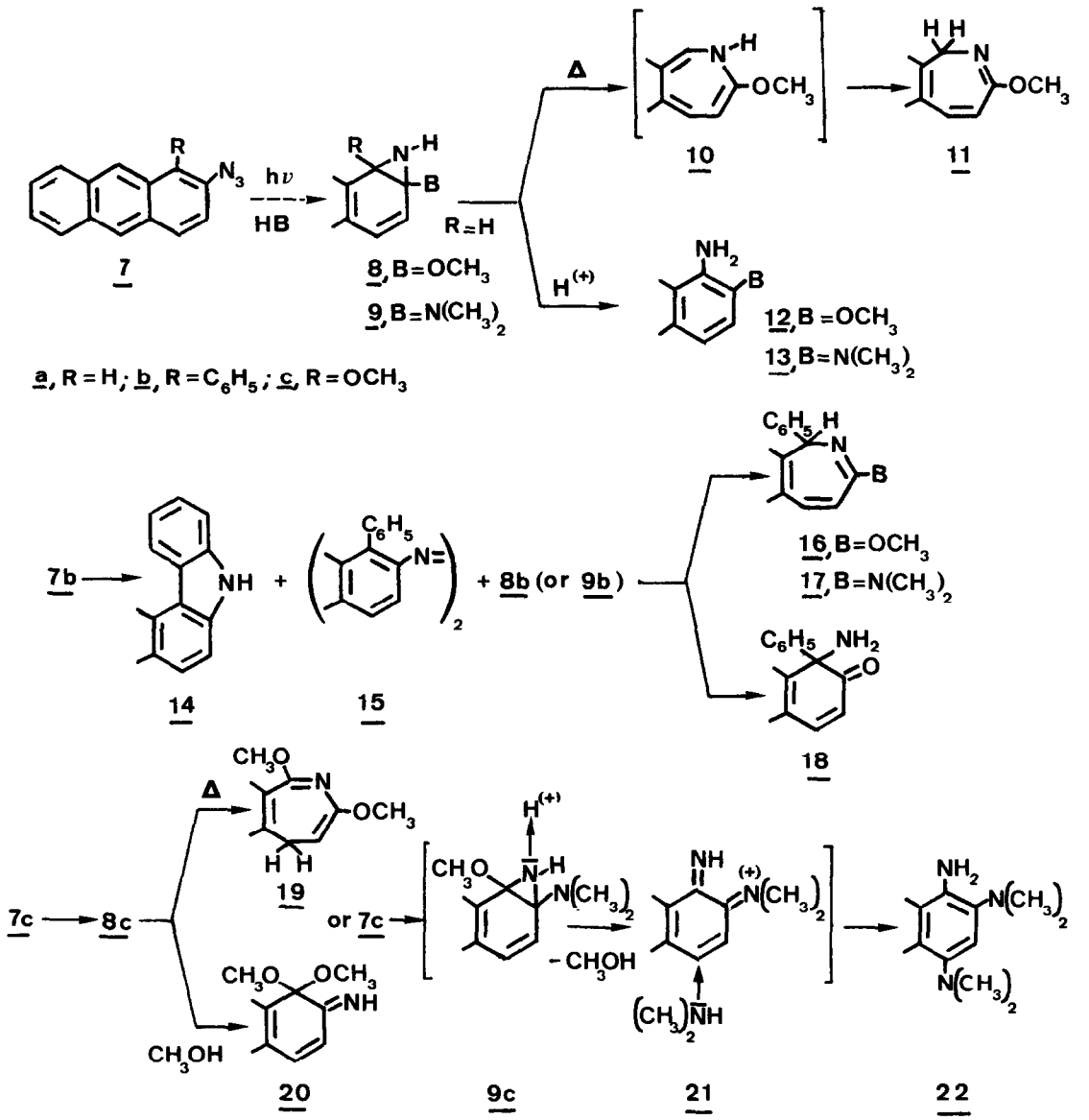
Formation of 14 cannot be completely avoided but it is minimized by working in the presence of base. As a matter of fact, if the irradiation is carried out in dioxane/MeOH-MeOK, two new compounds can be obtained as main products : 3-methoxy-1-phenyl-1*H*-naphth[2,3-*c*]azepine, 16, $C_{21}H_{17}NO$, colourless cryst., m.p. 139°C [^{1}H-NMR ($CDCl_3$) δ ppm (δ_{TMS}=0) : 3.77 (3H, OCH_3), 5.37 (1H at C_1), 6.37 (1H at C_4 or C_5, d, J=12 Hz), 7.00-7.87 (12H)]or 1-amino-1-phenyl-1,2-dihydroanthracen-2-one, 18, $C_{20}H_{15}NO$, colourless cryst., m.p. 118°C. One can see from Table I that the outcome of the reaction essentially depends on the treatment which follows photolysis. It seems most probable that irradiation under these conditions leads to the aziridine 8b which can give the azepine 16 by ring opening and prototropic migration, or the amino-ketone 18 by acid hydrolysis.

Table I : Irradiation of azide 7b (30 min for 0.1 g)

Treatment after photolysis	In dioxane/MeOH-MeOK.3M:1/1			In dioxane/aq $HN(CH_3)_2$ 25%:5/1		
	% 14	% 16	% 18	% 14	% 17	% 18
Short reflux	19	63	-	15	46	6
Immediate neutralization	17	-	61	15	21	47

The stabilization of the intermediate aziridine provided by the phenyl substituent at C-1 is further illustrated by photolysis in the presence of $HN(CH_3)_2$ (see Table I). Whereas irradiation of the azide 7a in the presence of such a base only leads to the aromatic diamine 13, after irradiations of 7b and subsequent heating, we can observe the formation, in moderate yields, of the dimethylamino-azepine 17, $C_{22}H_{20}N_2$, colourless cryst., m.p. 157°C [^{1}H-NMR ($CDCl_3$) δ ppm (δ_{TMS}=0) : 2.93 (6H, $N(CH_3)_2$), 5.23 (1H at C_1), 6.53 (1H at C_4 or C_5, d, J=12 Hz), 6.73-7.83 (12H)].

2-Azido-1-methoxyanthracene 7c. In this case, aromatization of the potential aziridine intermediate 8c is no more possible as for 8b, but, owing to the presence of the methoxy substituent at C_1, heterolytic cleavage of the N-C_1 bond should be particularly easy. In fact irradiations in dioxane/methanol : 1/1 afford as sole product the imino-ketal 20, $C_{16}H_{15}NO_2$, colourless cryst., m.p. 94°C (yield 77 %).



This easy solvolysis is without any doubt related to the proton-donor ability of methanol towards 8c ; indeed when the molarity of MeOK in MeOH is increased to 3M, and the mixture heated briefly after irradiation, one obtains increasing proportions of the 1,3-dimethoxy-5*H*-naphth[2,3-*c*]azepine 19, $C_{16}H_{15}NO_2$, colourless cryst., m.p. 76°C [^{1}H-NMR ($CDCl_3$) δ ppm (δ_{TMS}=0) : 3.17 (2H, CH_2 at C_5, d, J=7 Hz), 3.53 (3H, OCH_3), 4.03 (3H, OCH_3). 4.50 (1H, H at C_4, t, J=7 Hz), 7.17-8.20 (6H arom.)] (see Table II). It is likely that the strongly basic methanolate stabilizes the intermediate aziridine 8c which is then able to undergo the ring expansion ending in 19.

Table II : Irradiation of azide 7c in dioxane/MeOH-MeOK : 1/1 followed by short reflux

MeOK concentration in MeOH	% 19	% 20
0.	0	77
0.1 M	0	77
1 M	28	55
3 M	54	16

Unexpectedly, photolyses in dioxane/$HN(CH_3)_2$ give good yields of 1-amino-2,4-bis (dimethylamino)anthracene, 22, (51 %), orange-yellow cryst., m.p. 90-95°C [acetyl derivative $C_{20}H_{23}N_3O$, yellow cryst., m.p. 162°C]. However, this new reaction may be easily understood in terms of the intermediate aziridine 9c, which may undergo proton-catalyzed opening of the three-membering ring leading to the iminium ion 21 which by conjugate addition of $HN(CH_3)_2$ at C_4 and prototropy affords 22.

From all the above transformations, it is clear that the bicyclic aziridines, although not isolated as such, are present in solutions after photolysis. The ready electrocyclic ring opening they undergo on heating, which is not found for the oxygenated analogs like naphthalene 1,2-oxide [7], is in keeping with differences in valence tautomerism between monocyclic *oxa*- and *aza*-tropilidenes : bicyclic isomers appear to exist only in the oxygen series.

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