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# DIRECTING EFFECT OF BASES ON THE PHOTO-REACTIONS OF POLYCYCLIC AROMATIC AZIDES. SYNTHESIS OF "ORTHO-FUSED" AZEPINES IN THE ANTHRACENE AND NAPHTHALENE SERIES.

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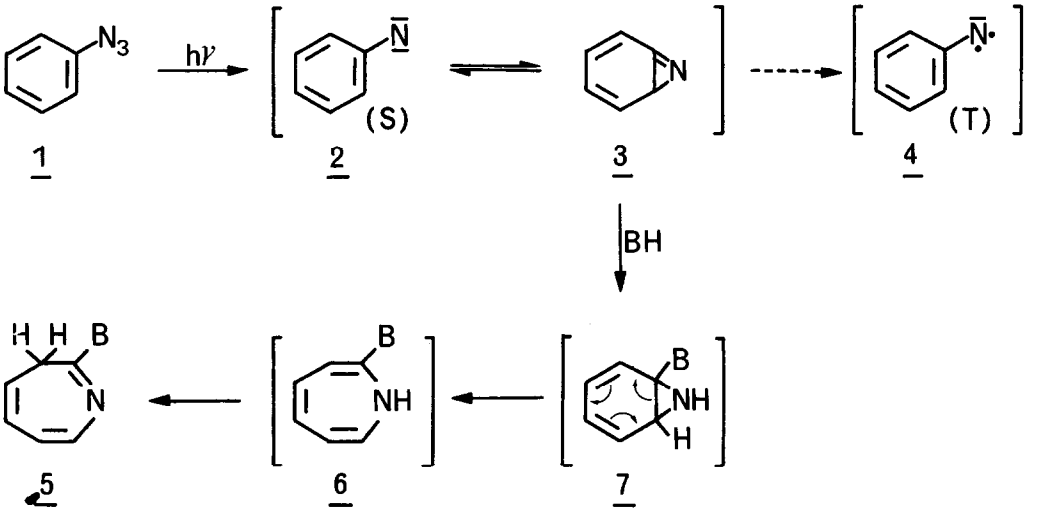
Photolytic decomposition of benzenic azides 1 in primary and secondary amines is well known to afford essentially 2-amino-3*H*-azepines 5 (B=$NR_2$) [1] and further studies have shown that azepine formation arises by loss of nitrogen from the azide to form a singlet nitrene 2 which is in equilibrium with the azirine 3. Addition of amine to the azirine which prevents conversion of 2 into the triplet state 4, leads to the aziridine 7. Electrocyclic ring expansion of 7 gives the unstable 1*H*-azepine 6 [2], which by prototropic migration yields finally the 3*H*-tautomer 5. Photolysis in alcohols, which are evidently much poorer "traps" for the intermediate 3 than are amines, affords only low yields of 2-alkoxy-3*H*-azepines 5 (B=OR) [3], except for ortho-substituted azides, bearing various carbonylated groups [4].



The possibility to extend this synthetic transformation to polycyclic aromatic azides looks fairly restricted according to the results obtained recently with diethylamine in the naphthalene [5] and benzo[*b*]thiophene [6] series. When the azido group is in the α position of the fused ring, as in α-naphthyl azide or in 4-azidobenzo[*b*] thiophene, interception of the azirine intermediate does not occur and the products are those expected from a triplet nitrene, whereas when the azido group is in the β position, as in β-naphthyl azide or in 5-azidobenzo[*b*]thiophene, the amino-aziridines seem to be formed but the derived products are diamines with unchanged skeleton, such as 1-amino-2-diethylaminonaphthalene ; only certain 6-azidobenzo [*b*] thiophenes, irradiated in an excess of diethylamine, have led to 8*H*-thieno [2,3-*c*] azepines in limited yields [7].

We have shown with two azides of the second type (β-position) that photolysis in the presence of concentrated potassium methoxide in methanol solution leads to a stabilized aziridine, allowing a subsequent ring expansion and the obtainment of methoxy-azepine in excellent yields.

The irradiations are conducted, under nitrogen, with a high pressure mercury vapour lamp ("Philips SP.500") through filters,between 10 and 20°C.

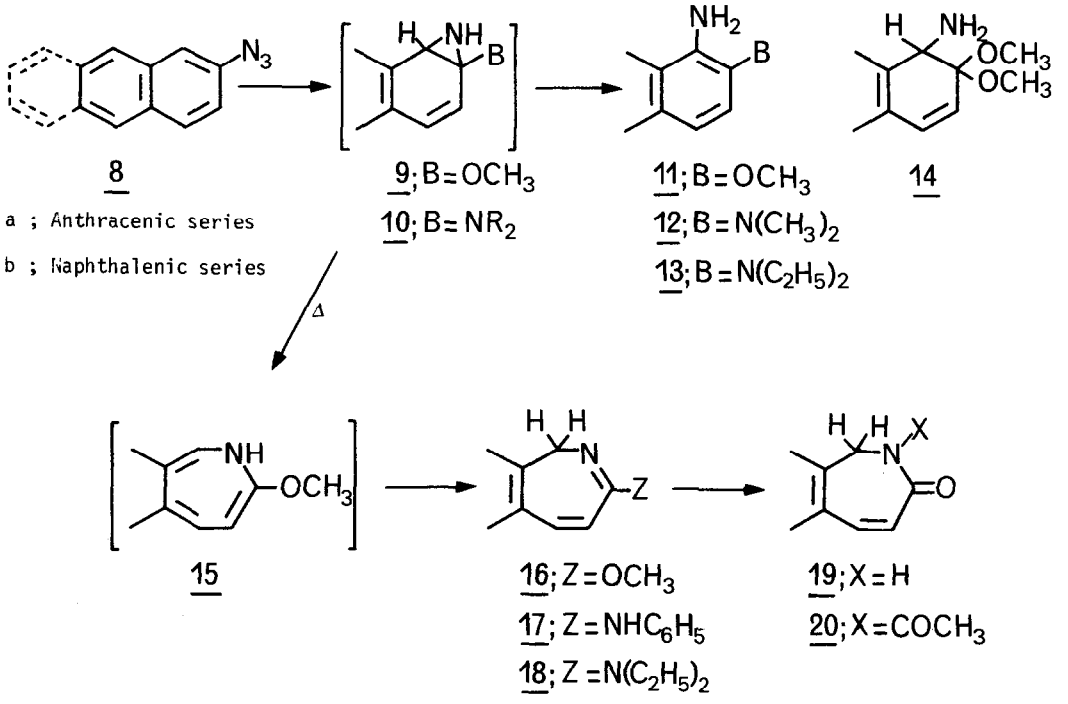
The most illustrative example is afforded by 2-azidoanthracene, 8a, $C_{14}H_9N_3$, pale-yellow cryst., m.p. 174°C (70%),obtained by treating with $NaN_3$ a diazotized acetic solution of 2-aminoanthracene fluoroborate. Azide 8a is irradiated [350<λ<410nm ;30min for 0.1g ]in a 1-1 mixture of dioxane and MeOK (3M) in MeOH and the resulting solution is refluxed briefly (15min)or left overnight at room temperature ; neutralization and further treatment give in nearly quantitative yield 3-methoxy-1*H*-naphtho [2,3-*c*] azepine, 16a, $C_{15}H_{13}ON$, colorless cryst., m.p.160°C (hexane) ; $^1$H-NMR ($C_6D_6$) $\delta_{TMS}$=0 : δ=4.48(2H at 1) ; δ=6.20 and 6.86, J=12Hz (AB system, 2H at 4 and 5). In contrast, if the solution is neutralized immediately after irradiation, the naphthazepine 16a is no longer obtained, but one gets instead 1-amino-2-methoxyanthracene, 11a, $C_{15}H_{13}ON$, yellow cryst., m.p. 120°C ($^i$PrOH) (60%).

These results suggest that the irradiated solution contains a unique intermediate, most probably the methoxy-aziridine 9a, which can undergo the two kinds of transformations. Its stability in this highly basic medium could be explained on one side by the acid-catalysed nature of the isomerization leading to 11a, and on the other side, by the increased amount of energy required in this series for the electrocyclic opening to the transient 2*H*-naphthazepine 15a, since it implies the loss of aromaticity of the lateral naphthalene nucleus. In fact, the irradiated solution shows a UV spectrum distinct from that of 16a and characteristic of a 1,2-dihydroanthracenic compound [λmax nm(logε) : 351(3.13) ; 342(2.98) ; 334(3.12) ; 311(3.98); 298(4.06) ; 288(3.96)] such as 9a.

The high tendency to acid-catalysed heterolytic cleavage of the N-$C_2$ bond in aziridine 9a, which is the first step of the isomerization leading to 11a, is further demonstrated by the third route which is followed when one reduces to 0.5 M the potassium methoxide concentration in the methanol solution and leaves the photolysed mixture at room temperature, or lower, to limit the thermal rearrangement.Under these conditions, formation of a new compound,1-amino-2,2-dimethoxy-1,2-dihydroanthracene, 14a, $C_{16}H_{17}O_2N$, colorless cryst., m.p. 118°C, competes with those of azepine 16a and methoxy-amine 11a (After 4 days at -15°C, one gets only 24% of

14a and 40% of 11a). This third reaction parallels that observed in the photolysis of 1-azido-3,4-dihydronaphthalene [8] and is justified by the relative stability of the amino-acetal 14a, which needs heating in a diluted ethereal solution of acetic acid to give the amine 11a.

Heterolysis of the N-$C_2$ bond must be easier with an amino-aziridine, such as 10a, than with the methoxy analogue 9a, and it is not surprising that irradiations of 2-azidoanthracene, 8a, in solutions of aliphatic secondary amines, much less basic than the preceeding mixture, give exclusively anthracenic diamines and no corresponding naphthazepines. We obtained in this way, with dimethylamine in aqueous dioxane, 1-amino-2-dimethylaminoanthracene, 12a, $C_{16}H_{16}N_2$, yellow cryst., m.p. 140°C (methanol) (76%), and with diethylamine in benzene, 1-amino-2-diethylaminoanthracene, 13a, $C_{18}H_{20}N_2$, yellow cryst., m.p. 95°C (methanol) (50%).




This behaviour, using amines as nucleophilic reagents, is identical to that already reported for 2-azidonaphthalene, 8b, [5] but here too, photolysis[$\lambda$>270nm ;30min for 0.1g] in a 1-1 mixture of [MeOH-MeOK (3M) -dioxane], accompanied or followed by a reflux in methanol, leads in high yield (84%) to 3-methoxy-1*H*-benzo[*c*]azepine, 16b, liquid, analogous to 16a in

NMR, [picrate : $C_{17}H_{14}O_8N_4$, m.p. 146°C (ethanol)], whereas immediate neutralization after irradiation at room temperature gives only 1-amino-2-methoxynaphthalene, 11b [9], (50%).

The amino-azepines which are not obtainable directly by photolysis can readily be prepared from the methoxy-azepines, by a more or less extended heating in amines. Thus, we prepared from 16a, using aniline, 3-anilino-1*H*-naphtho[2,3-*c*] azepine, 17a, $C_{20}H_{16}N_2$, pale-yellow cryst., m.p. 159°C (cyclohexane) (62%), and, using diethylamine with 16% added acetic acid, 3-diethylamino-1*H*-naphtho[2,3-*c*] azepine, 18a, $C_{18}H_{20}N_2$, colorless cryst., m.p. 112°C (42%). Moreover, the methoxy-azepines 16a and 16b are hydrolysed slowly in a refluxing aqueous dioxane solution (1-1) into the corresponding lactams : 2,3-dihydro-1*H*-naphtho[2,3-*c*] azepin-3-one, 19a, $C_{14}H_{11}ON$, colorless cryst., m.p. 293°C (ethanol) (74%) [N-acetyl der. 20a, $C_{16}H_{13}O_2N$ colorless cryst., m.p. 157°C (methanol) (88%)], and 2,3-dihydro-1*H*-benzo[*c*] azepin-3-one, 19b, $C_{10}H_9ON$, colorless cryst., m.p. 185°C (benzene) (66%).

Further investigations in progress indicate that this stabilization procedure, allowing a synthesis of polycyclic ortho-fused azepines, is very promising in other series where the intermediate aziridines are actually formed but where the trend to aromatization is very high

All the new compounds present analytical and spectral data (UV, IR, NMR) in accordance with their assigned structures and the anthracenic and naphthalenic amines have been identifi by independent synthesis.

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