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META BRIDGING REACTIONS. II. THE FIRST REPORTED NUCLEOPHILIC ADDITIONS OF DIAZABICYCLONONENE.

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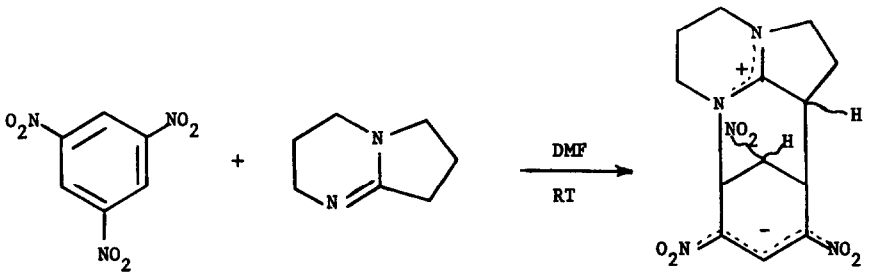
The synthetic utility of 1,5-diazabicyclo[4.3.0]nonene-5 (DBN) for dehydrohalogenations, cyclodehydrations, and other elimination reactions was the subject of a recent review.[1] The value of this reagent originates from its powerful basicity compared with other frequently used amine bases.[2] Although the literature contains numerous reports of the use of this base, nucleophilic reactivity of DBN in addition reactions has never been previously reported.

Attempts to employ DBN as a basic catalyst for meta bridging reactions[3] of trinitrobenzene (TNB) with N-cyanoacetylurethane resulted in complex mixtures containing TNB meta bridged with both N-cyanoacetylurethane and DBN moieties. This prompted us to investigate the reactivity of DBN alone with TNB.

Reaction of equimolar amounts of TNB and DBN in dry DMF at room temperature followed by extractive workup afforded 1 in 89% yield [m.p. >310°; vis, λ_{max}^{DMSO} 482 496 nm; analysis for $C_{13}H_{15}N_5O_6 \cdot 0.5$ MeOH (% theory, % found), C, 45.89, 46.14; H, 4.85, 4.52; N, 19.82, 19.64]. The nmr spectrum of 1 was consistent with a mixture of two isomers. These could easily arise from cyclization of either of



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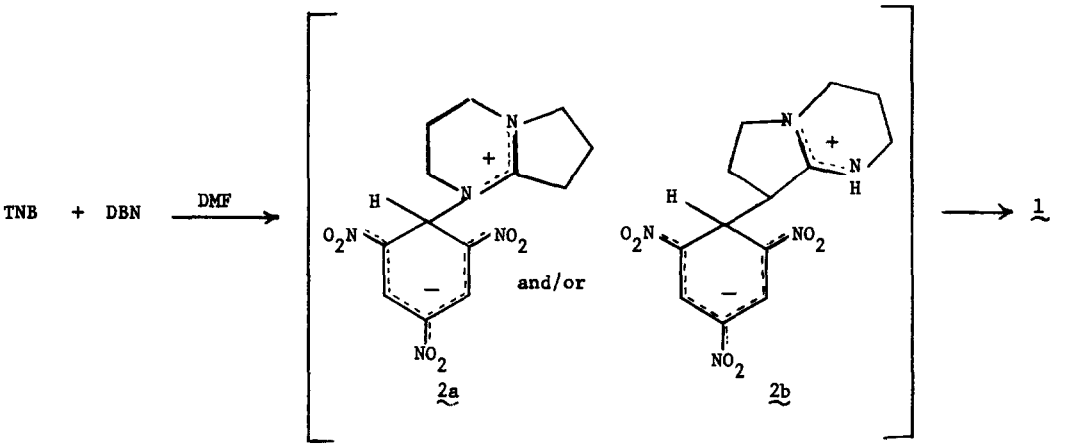
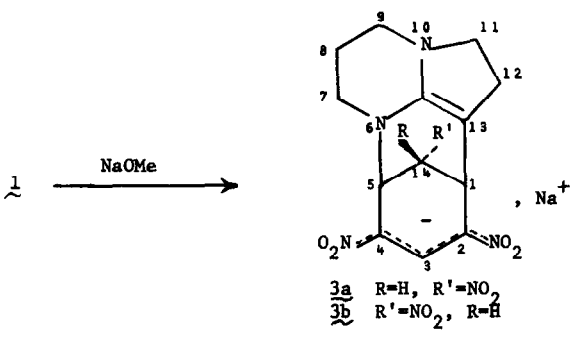
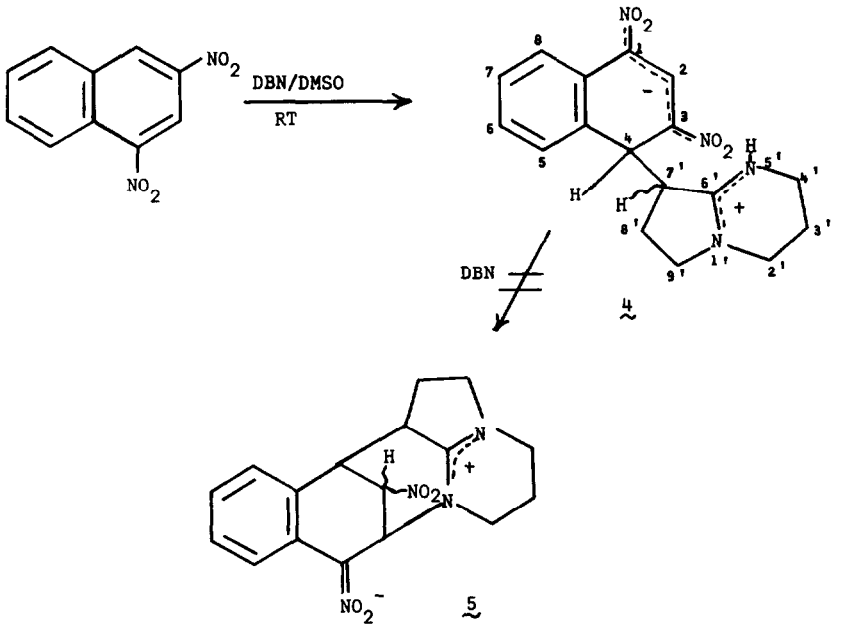
the initially formed addition complexes 2a or 2b. Following the reaction by uv-vis spectroscopy provided evidence for only one observed intermediate with maxima at 446 and 525 nm consistent with the C-N bonded σ complex 2a.[4,5] This presumably cyclizes to 1 which has maxima at 482, 496 nm. Attempts to observe the formation of 2a and/or 2b by pmr were unsuccessful. Addition of 0.303 mmoles DBN in DMSO-d_6 to 0.303 mmoles TNB in DMSO-d_6 resulted initially in a complex and



poorly resolved spectrum. In 48 hours this was transformed into a spectrum essentially identical with that of the isolated adduct 1. Although the two components in this mixture could not be separated and their stereochemistry has not been determined, further evidence in support of 1 was obtained by converting it to ca. 50/50 mixture of 3a and 3b, epimeric at C-14 [m.p. 166-70° dec.; vis, λ_{max}^{DMSO} 500 nm; analysis for $C_{13}H_{14}N_5O_6Na$ (% theory, % found), C, 43.46, 43.25; H, 3.93, 4.12; N, 19.49, 1950; nmr (δ, DMSO-d_6), 8.73 (s, 1H, H_3), 8.40 (s, 1H, H_3), 5.73 (s, bd, 2H), 4.90, 4.75 (m, 4H), 3.40 (m, 12H), 2.0 (m, 8H)].



The less reactive aromatic 1,3-dinitronaphthalene (DNN) on reaction with DBN led to a surprisingly different result. The only product, isolated in 83% yield, from reaction of equimolar amounts of DNN and DBN was the addition product 4 [m.p. 158-9°; vis, λ_{max}^{DMSO} 359, 367, 548 nm; analysis for $C_{17}H_{18}N_4O_4$ (% theory, % found), C, 59.64, 59.41; H, 5.30, 5.28; N, 16.37, 16.19; nmr (δ, DMSO-d_6), 8.92 (s, 1H, H_2), 8.75 (dd, 1H, H_8, $J_{7,8}$ = 6Hz, $J_{6,8}$ = 2Hz), 7.30 (m, 3H, H_5, H_6, H_7), 4.98 (d, 1H, H_4, $J_{4,7'}$ = 3Hz), 4.50 (s, bd, +NH), 3.40 (m, 7H, $H_{2'}$, $H_{4'}$, $H_{7'}$, $H_{9'}$), 1.90 (m, 4H, $H_{3'}$, $H_{8'}$)]. This adduct does not cyclize to 5 even in the presence of excess amidine. In fact 4 can be obtained in 96% yield from reaction of one



equivalent of DNN with two equivalents of DBN. It is interesting to note that 4 is the result of carbon attack on DNN and not nitrogen attack.[5] It is possible that the product of nitrogen attack, either at C-2 or C-4 of DNN is formed first and rapidly isomerizes to the more stable 4. Such a process could not be detected by uv-vis or pmr spectroscopy, and if it does occur, it must be very rapid.

These observations shed new light on the mechanism by which amidines bridge electron deficient aromatics. We are re-examining aspects of our recently report work on amidine additions to electron deficient aromatics[5] in order to more fully understand the structural features of amidine and aromatic which favor initial carbon or nitrogen attack.

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References

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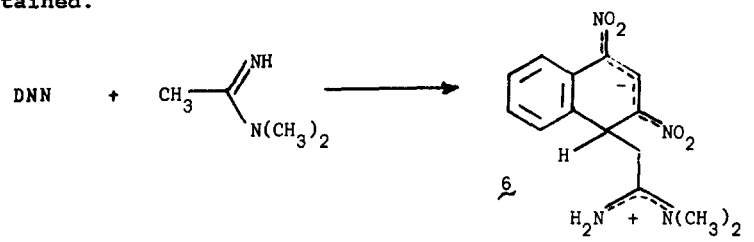
We have shown that reaction of DNN with N,N-dimethylacetamidine yields 6 (λ_{max}^{DMSO} 358, 368, 545 nm) which is stable to cyclization even in the presence of excess amidine, whereas with α-phenyl-N,N-dimethylacetamidine a cyclized product is obtained.[5]



We are further investigating the various modes of addition using deuterium labelled substrates.