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THE REACTION OF N,N-DIBENZYLCARBAMOYL CHLORIDE WITH N-NITROSOHYDROXYLAMINE

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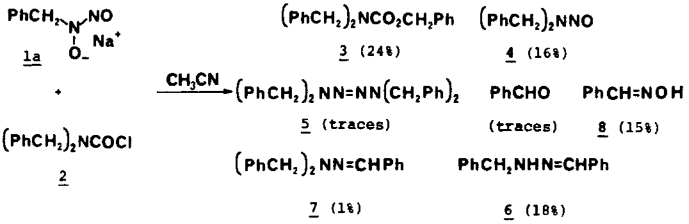
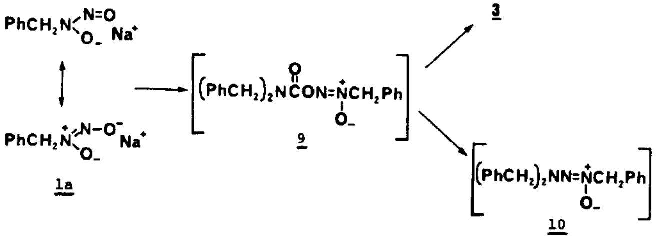
SUMMARY: *The action of N,N-dibenzylcarbamoyl chloride (2) on the sodium salt of N-nitrosohydroxylamines (1) in dry acetonitrile at reflux leads to products whose formation may be rationalized in terms of carbamoylation at either oxygen of the bidentate N-nitrosohydroxylamines.*

As a part of our investigation of the reaction of carbamoyl chlorides with nitrite ion and related species,[1] we studied the action of the sodium salt of N-nitroso-N-benzylhydroxylamine (1a) with N,N-dibenzylcarbamoyl chloride (2). Several products were characterized from the reaction carried out at reflux in acetonitrile (Eq. 1).

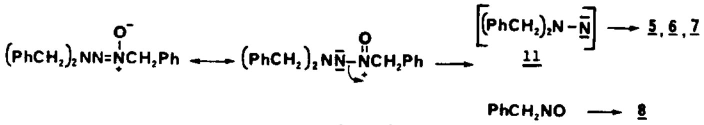


(1)

Carbamoylation of 1a at the nitroso oxygen to yield 9 (Scheme 1) may be used to rationalize the formation of all the products obtained. Thus, the generation of 3 may simply be explained by the loss of nitrous oxide from 9. There are ample precedents from the formation of esters by loss of nitrous oxide in related systems.[2] Alternatively, intermediate 9 could extrude carbon dioxide to yield the hitherto unknown alkyltriazene N-oxide 10.[3] Expulsion of ω-nitrosotoluene from 10 as depicted in Scheme 2, can account for the formation of benzaldoxime (8) while compounds 5, 6 and 7 are all known products of the subsequent decomposition of N-dibenzylaminonitrene (11).[4] The isomerization of 10 to

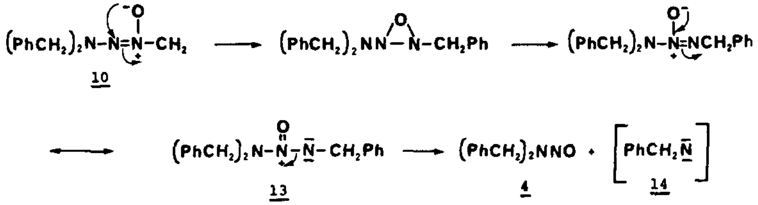


Scheme 1



Scheme 2

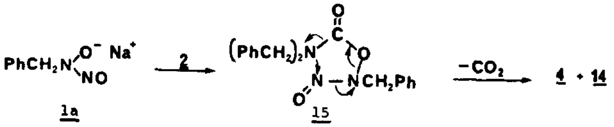
triazene N-oxide 13 (Eq. 2) provides an alternative route for the formation of 4; no attempt was made to detect the products that would be expected from 14,



(2)

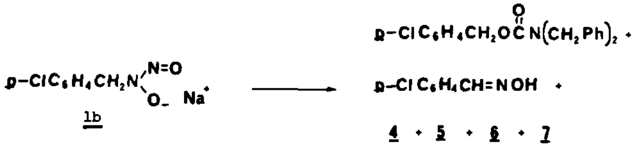
though benzaldehyde[5] could be detected in trace quantities by nmr.

The ambident nature of nitrosohydroxylamines however, would allow carbamoylation of 1a to occur at the hydroxy oxygen to yield 15; transnitrosation and concurrent expulsion of carbon dioxide would lead to 4 and 14 (Scheme 3). This path has the advantage that the participation of the unusual triazene N-oxide 13 need not be invoked. Even though the results obtained from the reaction of 1b and 2



Scheme 3

(Eq. 3) could not help establish which of the two oxygens is attacked, they did confirm the N-nitrene path for the formation of 5, 6 and 7.



(3)

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† Postdoctoral Research Associate

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4. G. Koga and J.-P. Anselme, J. Am. Chem. Soc., 91, 4323 (1969); so far we have not been able to detect bibenzyl in the reaction mixture. While compound 6 is the *expected* product of the *diazene-hydrazone* rearrangement, the mode of formation of dibenzylhydrazone (7) is somewhat obscure.
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