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UNEXPECTED REACTIONS OF 1,4-DIAZA-1,3-DIENES UNDER ACYLATING CONDITIONS. A NEW CYCLIZATION TO NON-ACYLATED IMIDAZOLE DERIVATIVES

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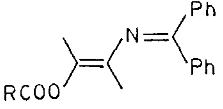
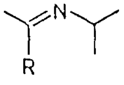
Summary: The reaction of anions from 1,2-bisimines with acid chlorides gives unacylated 2*H*-imidazoles. The unprecedented reactivity of these anions is interpreted by cyclization of the radical generated by electron transfer from the anion to the acid chloride.

Previously we have reported the efficient synthesis of 2-azabuta-1,3-dienes (1) by routes involving the double aroylation of anions of imines (2a)[1] or by the more flexible path for *O*-acylation of the anions of mono imines (2b) of 1,2-dicarbonyl compounds.[2] Our interest in these compounds (1) arose from the observation that the photochemistry of some heavily arylated derivatives is dominated apparently by an electron transfer from nitrogen to the acyl group leading to a novel 1,2-acyl migration followed by cyclization to afford derivatives of dihydro-oxazole.[3] As an extension of this study we have sought a synthetic route to the corresponding amides by an analogous reaction path with surprising results.

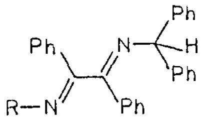


(1)



(2)

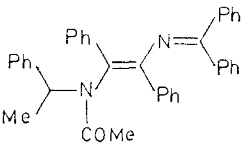
2a: R=H
2b: R=COR



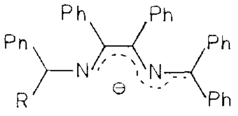
(3)

3a: R=PhCHMe
3b: R=(Ph)$_2$CH
3c: R=Ph

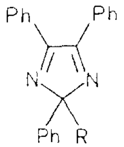
The route adopted for the synthesis of the amides involved the readily accessible 1,2-bisimines (3) obtainable from benzil.[4] Treatment of (3a) under the normal conditions used for the production of such anions[2] led to the generation of a coloured solution indicative of anion formation. This was quenched by the addition of acetyl chloride[5] and worked up in the conventional manner to afford recovered bisimine (3a, 49%) and a mixture of three products in 38, 9, and 9% yield respectively. One of the minor products was a yellow oil with spectral characteristics compatible with the azadiene (4)[6] presumably formed by the acylation of one of the anions (5a) which can be formed from (3a). The other two products were colourless and crystalline and from mass spectroscopic examination it was clear that these compounds were neither isomeric with starting material nor had they undergone acylation. The simplicity of the spectra[7] of these products indicated that they were probably the cyclic compounds (6a) and (6b) respectively and this was verified by comparison with authentic data.[8] It is clear from the formation of the azadiene (4) and from the fact that treatment of the solution of the anion from (3a) with water reforms starting material that the anion (or anions) are not cyclic. Indeed there are very few literature precedents for anion cyclization in such systems. The one exception is the synthesis of amarine (7) from the cyclization of anion (8).[9] Thus there is a dilemma as to the identity of the species which effects the cyclization of bisimine (3a). In view of the foregoing a radical appears to be the most likely identity of this intermediate. Indeed, although not in highly conjugated systems such as (3a), there seems to be a preference, in some instances, for radicals to undergo five membered ring formation while anions do not.[10] Thus it seems likely, in order to propose a cyclization in the reaction of bisimine (3a), that a radical has to be produced from the anions (5). This could arise by electron transfer to a suitable acceptor such as the acid chloride. However, acid chloride is not essential for the process if nitrobenzene or cyanobenzene, known electron acceptors,[11] are used. Under these conditions the cyclic products (6) are formed again confirming the postulate that an electron transfer yielding a radical is involved (Scheme). The cyclization process is not restricted to bisimine (3a) as can be shown by treatment of bisimine (3b) under the same conditions with acetyl chloride. In this case no diene analogous to (4) is obtained and the sole product is the 2*H*-imidazole (6a, 26%) apart from recovered starting material. In this experiment there is no evidence for acylation of the anion. To account for these unprecedented cyclizations we propose that the route to the cyclic products is as illustrated in the scheme for the cyclization of bisimine (3b). What is not clear at this stage is at what point the electron transfer occurs. It could be, however, that the acyclic anion undergoes electron transfer to afford an acyclic radical as shown in the scheme. This would then cyclise to a cyclic radical (scheme). There is ample evidence in the literature that such cyclic radicals do not readily ring open.[12] This radical would then expel a leaving group to afford the isolated product.



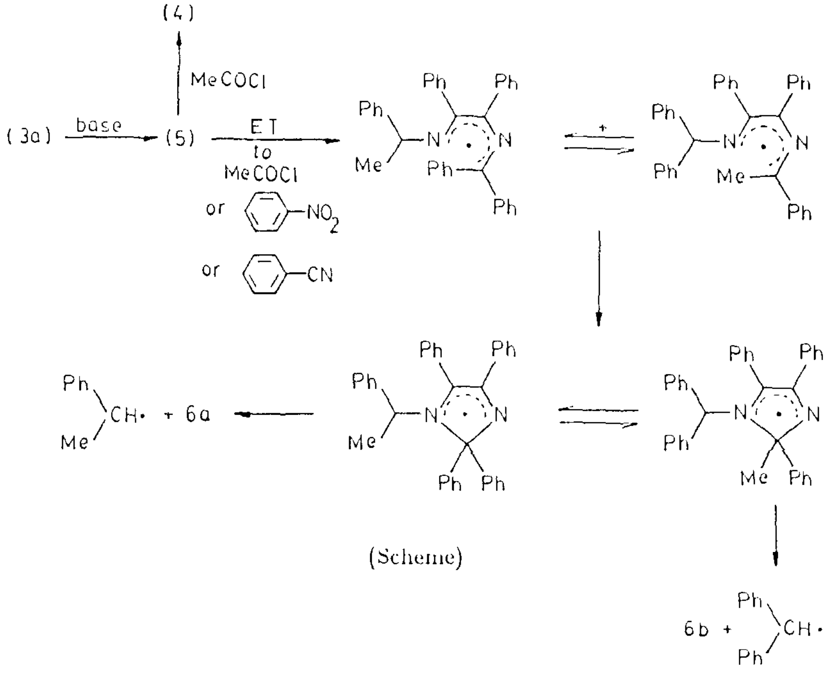
(4)



(5)
5a: R=Me
5b: R=Ph

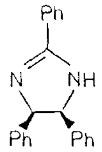


(6)
6a: R:Ph
6b R:Me

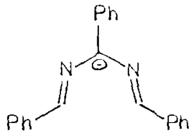


(Scheme)

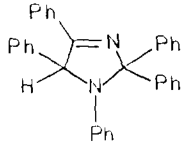
Cyclization is also the preferred route to product for bisimine (3c). Under the standard conditions the product formed is the 2,5-dihydro-imidazole (9, 54%).[13] In this case cyclization to a radical such as (10) cannot be followed by expulsion of a leaving group but instead hydrogen is abstracted to yield (9).



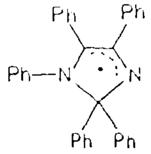
(7)



(8)



(9)



(10)

As far as we are aware this is the first example where an electron transfer process appears to be involved in the cyclization of such molecules. It is conceivable that there are many more examples in the literature of similar electron transfer reactions, as yet unrecognised as such. Further research will inevitably uncover more.

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3. D. Armesto, M.J. Ortiz, R. Perez-Ossorio, and W.M. Horspool, *J. Chem. Soc., Perkin Trans. 1*, 1986, 623.
4. D. Armesto, P. Bosch, M.G. Gallego, J.F. Martin, M.J. Ortiz, R. Perez-Ossorio, and A. Ramos, *OPPI*, in press.
5. The conditions used for the synthesis and the trapping are the same as those reported previously by us. D. Armesto, M.G. Gallego, W.M. Horspool, M.J. Ortiz, and R. Perez-Ossorio, *Synthesis*, in press, 1987.
6. Spectroscopic data for azadiene (4): ν_{max} (liq. film) 1640 (C=O) cm^{-1}; ^{1}H n.m.r. (CDCl$_3$) δ 1.1 (3H, S, CH$_3$), 2.2 (3H, s, CH$_3$CO), 4.3 (1H, q, CH), 6.7-7.8 (25H, m, aryl); m/z (rel. intensity, %) 520 (M^+, 2), 372 (100), 297 (7), 269 (4), 165 (43), 105 (22), 77 (10), 43 (24); UV (CH$_2$Cl$_2$) λ_{max} 259 (ε 7 300).
7. Spectroscopic data for 2*H*-imidazoles:

   Imidazole (6a): m.p. 198-200°C (lit.[14] m.p. 202°C); ν_{max} (KBr) 1620 (C=N) cm^{-1}; ^{1}H n.m.r. (CDCl$_3$) δ 7.1-7.9 (20H, m, aryl); ^{13}C n.m.r. (CDCl$_3$) δ 108.4, 127.5-141.4 (aryl) 165.0 (C=N); m/z (rel. intensity, %) 372 (M^+, 12), 269 (100), 165 (65), 101 (4), 89 (4), 43 (6); UV (CH$_2$Cl$_2$) λ_{max} 274 nm (ε 12 000).

   Imidazole (6b): m.p. 82-84°C (lit.[15] m.p. 80-82°C); ν_{max} (KBr) 1600 (C=N) cm^{-1}; ^{1}H n.m.r.(CDCl$_3$) δ 1.9 (3H, s, CH$_3$), 6.9-8.0 (15H, m, aryl); ^{13}C n.m.r. n.m.r. (CDCl$_3$) δ 27.4 (CH$_3$),104.7, 126.8-140.4 (aryl), 164.1 (C=N); m/z (rel. intensity, %) 310, (M^+, 65), 207 (100), 166 (40), 104 (80), 89 (18) 78 (42), 63 (11), 51 (12); UV (CH$_2$Cl$_2$) λ_{max} 270 nm (ε 15 300).

274 nm (ε 12 000).

Imidazole (6b): m.p. 82-84°C (lit.[15] m.p. 80-82°C); ν_{max} (KBr) 1600 (C=N) cm^{-1}; ^{1}H n.m.r.(CDCl$_3$) δ 1.9 (3H, s, CH$_3$), 6.9-8.0 (15H, m, aryl); ^{13}C n.m.r. n.m.r. (CDCl$_3$) δ 27.4 (CH$_3$),104.7, 126.8-140.4 (aryl), 164.1 (C=N); m/z (rel. intensity, %) 310, (M^+, 65), 207 (100), 166 (40), 104 (80), 89 (18) 78 (42), 63 (11), 51 (12); UV (CH$_2$Cl$_2$) λ_{max} 270 nm (ε 15 300).

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11. P.S. Mariano and J.L. Stavinoha in "Synthetic Organic Photochemistry", Ed. W.M. Horspool, Plenum Press, 1984, 145.
12. D.R. Arnold, V.Y. Abraitys, and D. McLeod, jun., *Can. J. Chem.* , 1971, **49**, 923.
13. Spectroscopic data for 2,5-dihydro-imidazole (9): m.p. 188-190°C; ν_{max} (KBr) 1635 (C=N) cm^{-1}; ^{1}H n.m.r. (CDCl$_3$) δ 6.3 (1H, s, CH), 6.5-7.5 (21H, m, aryl), 6.3 (1H, s, CH), 6.5-7.5 (21H, m, aryl); 7.6-7.9 (4H, m, 7.6-7.9 (4H, m, aryl); ^{13}C n.m.r. (CDCl$_3$) δ 73.6 (CH), 100.0, 127.6-143.8 (aryl), 166.2 (C=N); m/z(rel. intensity, %) 372 (M^+-78, 7), 346 (1), 269 (100), 225 (3), 195 (4), 180 (4), 165 (63), 105 (2), 77 (9); UV (CH$_2$Cl$_2$) λ_{max} 260 nm (ε 18 600).

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