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THE OXIDATIVE FRAGMENTATION OF 1-AMINO-1,3,4-TRIAZOLES TO NITROGEN AND NITRILES[1]

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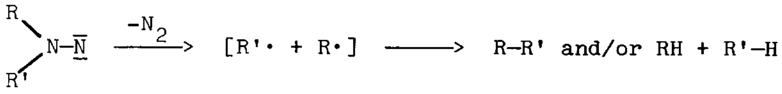
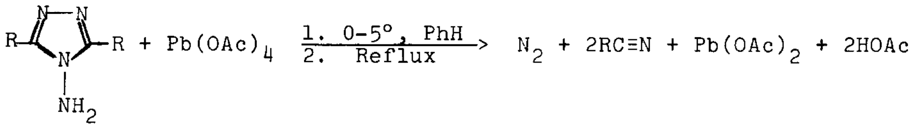
The elimination of elemental nitrogen is now a well-established path for a number of reactions which presumably proceed via a common N-nitrene intermediate.[3] The extrusion of nitrogen is usually accompanied by coupling and/or disproportionation of the resulting fragments. However, it has also been shown that these fragments may undergo further breakdown when a low energy path to such fragmentation is available.[4,5,6]



I

In striking contrast to the lability of these non-aromatic systems, the corresponding pyrrole derivatives are extremely stable. For example, the sodium salt of N-tosylamino pyrrole did not decompose until 275°; pyrrole (∿ 10%) was the only product identified.[5] The results of Lemal and his students were amply confirmed by Carpino.[7] The stability of N-amino pyrroles and their derivatives has been ascribed to the inability of the pair of electrons of the pyrrole nitrogen to help in the stabilization of N-nitrene intermediates.[5] Carpino has suggested other factors which may be important in this respect.[7] However, these considerations did not appear wholly compelling to us. It seemed that the strength of the "backbone" bond (the 3-4 bond) might be the single most important factor in determining whether fragmentation takes place or not. In order to test this hypothesis, the oxidation of 1-amino-1,3,4-triazoles(II) was investigated and we should like to briefly report our results at this time.

When a benzene solution of 1-amino-1,3,4-triazole(IIa) was treated with an equivalent amount of lead tetraacetate (LTA) at 0°, vigorous evolution of gas was observed. The evolved gases were passed through a wash bottle containing a large excess of concentrated ammonium hydroxide and the untrapped gas (nitrogen) measured volumetrically, amounted to 55% of theory. Titration of the ammonium hydroxide with a solution of 0.1N silver nitrate[8] showed an 88% yield of hydrogen cyanide. Similarly, the action of LTA on 1-amino-2,5-dimethyl- and 1-amino-2,5-diphenyl-1,3,4-triazoles(IIb and IIc) gave nitrogen and the corresponding nitriles in high yields (88-90%). Work up and distillation gave acetonitrile and benzonitrile, identified by their refractive indexes and by comparison of the vpc retention times and their infrared spectra with those of authentic samples.

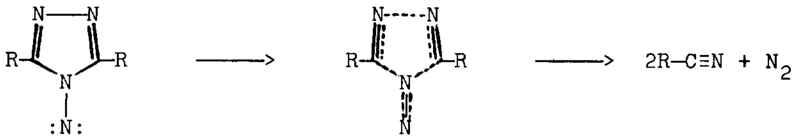


$$\text{II} + Pb(OAc)_4 \xrightarrow[\text{2. Reflux}]{\text{1. 0-5°, PhH}} N_2 + 2RC{\equiv}N + Pb(OAc)_2 + 2HOAc$$

II a) R=H b) $R=CH_3$ c) R=Ph

In order to compare our results with those previously reported,[5,7] N-aminocarbazole[5] and N-amino-2,5-diphenylpyrrole were treated with LTA under identical conditions. In complete accord with Lemal, Rave and McGregor's results,[5] a 73% yield of carbazole identical to an authentic sample, was obtained. A similar oxidation of N-amino-2,5-diphenylpyrrole[7] resulted in the formation (in apparently high yield) of a yellow crystalline solid,[9] mp. 171-172.5° (dec.) which upon pyrolysis at 200° gave a 70% yield of 2,5-diphenylpyrrole, identical in all respects to an authentic sample.[6]

Both nitrogen elimination and tetrazene formation can be viewed as arising <u>via</u> the N-nitrene intermediate (I). As previously indicated, the failure of the N-amino pyrrole derivatives to eliminate nitrogen[5,7] has been rationalized through the unavailability of the pair of electrons of the pyrrole nitrogen for stabilization of the N-nitrene intermediate; with this type of stabilization lacking, the N-nitrenes are presumably not likely to be generated.[5] However, the results of the oxidations of N-amino pyrroles coupled with those of Rees and his group[10] and of Koga and Anselme[11] support the involvement of I as a direct precursor of the tetrazenes. If the not unreasonable assumption that all other factors are comparable between the pyrrole and 1,3,4-triazole ring systems, the only difference is that the N—N bond is weaker than the C—C bond by ∿ 40 kcal/mole. Our results would seem to support our original hypothesis that in equivalent systems, the strength of 3-4 bond and the energy available to break it will control the path of the reaction. Although no definite conclusions can be reached at the present time, the fragmentation may be viewed as occurring in a concerted fashion.



The results of this type of fragmentation may become useful in sorting out the nature of transition states and the importance of and balance between resonance effects and bond strengths. In addition, the ease and the high yields of the reaction suggest that it may provide a clean and direct entry into difficultly accessible systems containing the —C≡N function. Both of these aspects are currently under investigation in our laboratories.

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2. Fellow of the Alfred P. Sloan Foundation. To whom inquiries should be

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