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THE UNUSUAL CYCLIZATION OF BENZIL MONOHYDRAZONES TO 4,5-DIPHENYLIMIDAZOLES

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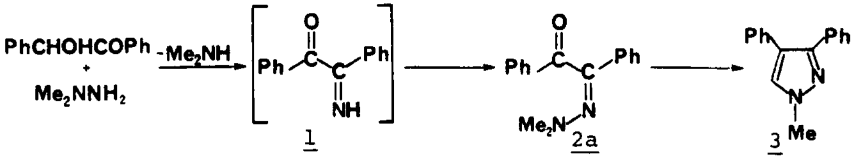
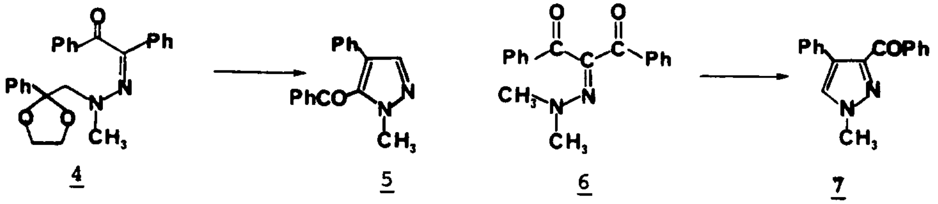
SUMMARY *Benzil monodisubstituted hydrazones (2) have been shown to undergo cyclodehydration to the corresponding imidazoles (10) and not to pyrazoles as previously reported.*

As a part of our investigation of the action of sodium hydroxide upon 1,1-dimethyl-1-phenacylhydrazinium bromide,[1] we attempted to prepare the monodimethylhydrazone of benzoin by the action of 1,1-dimethylhydrazine on benzoin. However, the product isolated, mp. 158-159°, was devoid of oxygen and corresponded to the formula $C_{16}H_{14}N_2$. Examination of the literature revealed that a Russian group had isolated a compound of similar mp. to which they had assigned the structure of 3,4-diphenyl-1-methylpyrazole (3).[2] Since the purported pyrazole was obtained from the cyclization of benzil monodimethylhydrazone (2a), it seemed reasonable that after initial oxidation of benzoin to benzil monoimine (1) by 1,1-dimethylhydrazine, condensation of the latter with a second molecule of 1,1-dimethylhydrazine should lead to the hydrazone 2a thence to the pyrazole as described by the Russian workers. Our desire to exploit this reaction as a facile, convenient and versatile route to pyrazoles led us to investigate its scope.[3] We now describe the startling preliminary results of this investigation.



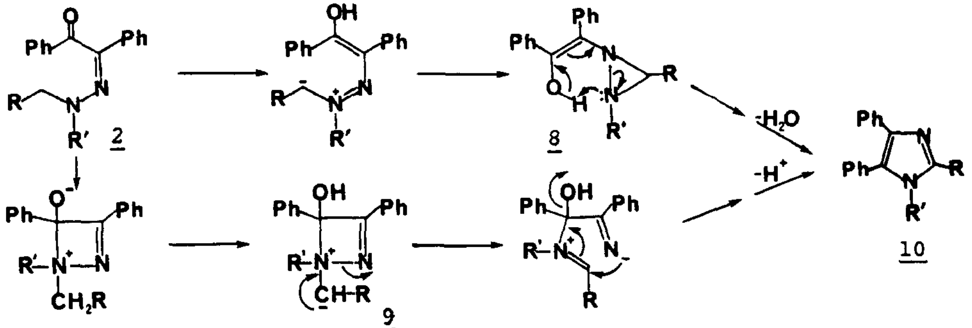
(1)

The product of the cyclodehydration of benzil monodimethylhydrazone (α-form, mp. 99°) was prepared[1] and was shown to be identical to our product, mp. 158-159°, obtained from benzoin and 1,1-dimethylhydrazine.[4] This result seemed to support the scheme shown in Eq. 1 and the



Scheme 1

successful cyclization of hydrazones 4 and 6 to the corresponding pyrazoles 5 and 7 (Scheme 1) initially appeared to be in complete accord with the results described above.[2] However, further exploration of this reaction using simple monodialkylhydrazones of benzil revealed that the cyclized products were not pyrazoles but instead the corresponding imidazoles (10). The products were identified as imidazoles by comparison of their spectral data, mps and the tlc behavior with those of authentic samples. An authentic 10a was obtained from the methylation of 4,5-diphenylimidazole[5] and authentic 10b and 10c were prepared by methylation and benzylation of lophine respectively;[6] a literature procedure was followed for the obtention of authentic 10d.[7] An authentic sample of 3,4-diphenyl-1-methylpyrazole (3), mp. 58-61°, prepared by the cycloaddition of N-methylsydnone to tolan and by oxidation of 3,4-diphenyl-1-methyl-2-pyrazoline, was totally different from 10a in every respect. While sufficient data is not yet available to permit the elaboration of a definite mechanism, it is clear that the N-N bond of the hydrazine is cleaved. It might be speculated that the reorganiation of the N-N-C to the N-C-N arrangement required by the imidazole structure of the products passes through a diaziridine intermediate (8) or through the four-membered ring ylid (9).



a) R = H, R' = CH_3 b) R = Ph, R' = CH_3 c) R = Ph, R' = $PhCH_2$ d) R = H, R' = Ph

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† Taken in part from the M. Sc. Thesis of W. L. Collibee, Univ. of Massachusetts at Boston, June 1985.

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