A Novel Cleavage of Carbon-Carbon Triple Bond

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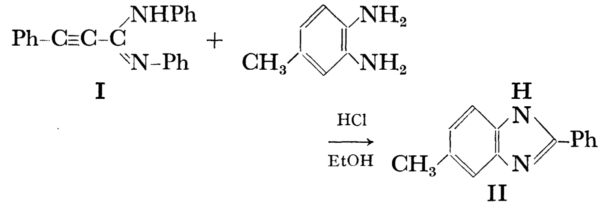
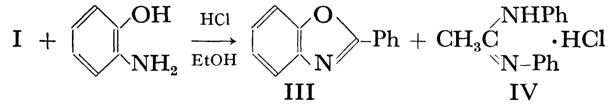
(Received December 25, 1971)

In our studies of phenylpropiolamidines, nucleophilic addition occurred predominantly at the β-carbon of the acetylenic bond in an acidic medium, and reactions with bifunctional nucleophiles (*e.g.* NH_2OH) afforded five membered heterocyclic compounds such as isoxazoles.[1]

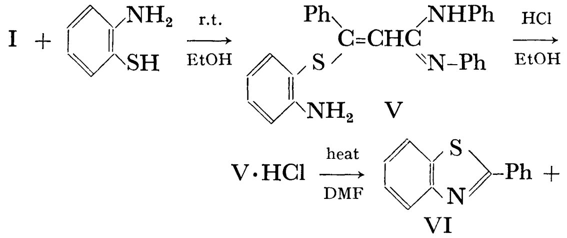
Although N,N'-diphenylphenylpropiolamidine (I) exhibited behavior similar to phenylpropiolate in the above cases, reaction of I with 4-methyl-*o*-phenylenediamine[2] in boiling ethanolic hydrogen chloride proceeded characteristically to furnish 5-methyl-2-phenylbenzimidazole (II; mp 248—248.5°C), as a result of cleavage of the acetylenic bond.



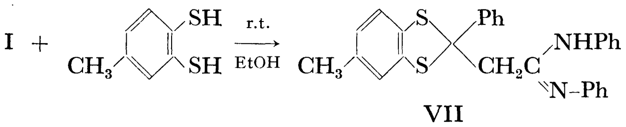


In the reaction of I with *o*-aminophenol in the presence of hydrogen chloride, N,N'-diphenylacetamidine was obtained as a hydrochloride (IV; mp 224—226°C), together with 2-phenylbenzoxazole (III; mp 103—104°C). The acetamidine formation indicated clearly that acetylenic bond fission had occurred.

o-Aminobenzenethiol reacted with I in ethanol to give 2-(*o*-aminophenylthio)-N,N'-diphenylcinnamamidine [V; mp 150—151°C. Found: C, 77.33; H, 5.62; N, 9.78; S, 7.66%. Calcd for $C_{27}H_{23}N_3S$: C, 76.93; H, 5.50; N, 9.97; S, 7.60%. NMR (δ in acetone-d_6): 5.54 (s, =CH–)]. Heating of V·HCl (mp 186.5—187°C) for a short time in dimethylformamide afforded 2-phenylbenzothiazole (VI; mp 114—115°C) and IV respectively, in good yields.

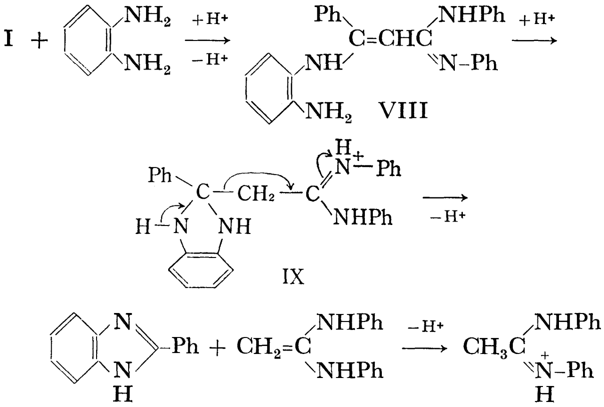


The reaction of I with toluene-3,4-dithiol gave 2-(N,N'-diphenylamidinomethyl)-5-methyl-2-phenyl-1,3-benzodithiol [VII; mp 139.5—141°C. Found: C, 74.61; H, 5.24; N, 6.22; S, 14.32%. Calcd for $C_{28}H_{24}N_2S_2$: C, 74.30; H, 5.34; N, 6.19; S, 14.17%. NMR (δ in $CDCl_3$): 3.52 (2H, s, CH_2). Mass (*m/e*): 452 (M^+), 243 (5-methyl-2-phenyl-1,3-benzodithiolium cation)].



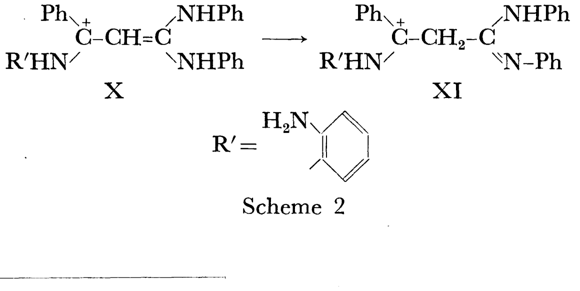
This reaction shows that a second nucleophilic attack can take place at the β-carbon of the acetylenic bond.

The mechanism of the cleavage of the triple bond followed by the formation of benzimidazole, benzoxazole, or benzothiazole can thus be considered as shown in Scheme 1.



Scheme 1

The smooth fission of the carbon-carbon triple bond in the protonated propiolamidine system under such mild reaction conditions might be explained by successive nucleophilic additions at the β-carbon of the acetylenic bond, followed by a fragmentation process, which would be due to the stronger electron withdrawing character of the protonated amidine group. Although the stereochemical aspects of this reaction are not clear, it is presumed that an activated enediamine form of protonated VIII (X in Scheme 2) readily undergoes prototropic change to XI, which is attacked predominantly at the β-carbon by the second nucleophilic function, as shown in Scheme 2.



Scheme 2

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[1] H. Fujita, R. Endo, A. Aoyama, and T. Ichii, This Bulletin, in press.

[2] For the reaction of diethyl acetylenedicarboxylate with 4-methyl-*o*-phenylenediamine, *cf.*, Y. Iwanami, *Nippon Kagaku Zasshi*, **83**, 161 (1962).