THE SYNTHESIS OF ACENAPHTHO[1,2-c][1,2,3]THIADIAZOLE AND PHENANTHRO[9,10-c][1,2,3]THIADIAZOLE

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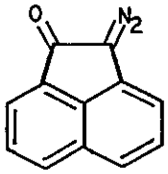
Acenaphtho[1,2-c][1,2,3]thiadiazole 3 and phenanthro[9,10-c][1,2,3]thiadiazole 4 have been synthesized by the direct reaction of Lawesson's reagent 5 with the respective α-diazoketones 1 and 2.

Although 1,2,3-benzothiadiazoles are well known and readily available by conventional synthetic routes,[1,2] relatively little is known about the higher ring-fused aromatic 1,2,3-thiadiazoles. Jacobson first prepared naphtho[1,2-c][1,2,3]thiadiazole by diazotization of 2-aminonaphthalene-1-thiol.[3,4] Later Bamberger prepared the same thiadiazole from the 2-diazo-1-naphthenone and P_4S_{10} in 40% yield.[5] Hurd and Mori discovered that carbethoxyhydrazones cyclized with thionyl chloride to 1,2,3-thiadiazoles. By the application of this method, 4-carbethoxyhydrazonothiochroman-1-dioxide was readily converted to 4-H-thiadiazolo[5,4-c]benzothiopyran-5-dioxide.[6] In an alternative approach, Fries and Reitz successfully elaborated amino-1,2,3-benzothiadiazoles to thiadiazoloquinolines and thiadiazophenazines.[7,8]

We wish to report the preparation of several hitherto unknown condensed aromatic thiadiazoles, 3 and 4, by a greatly improved variation on the Bamberger technique in which Lawesson's reagent 5 is employed as the thionating agent.[9,10] Thus, 10-diazo-9-phenanthrone 2 was reacted with 1.1 equivalents of Lawesson's reagent in refluxing methylene chloride until all the diazoketone was consumed (TLC). The reaction product was isolated by chromatography on silica followed by crystallization (benzene/pet. ether) to give thiadiazole 4, m.p. 185° C, in 87% yield.[11]

The thionation of 2-diazo-1-acenaphthenone 1 followed a more complex course. The best results were obtained using 1.1 equivalents of Lawesson's reagent and 2 equivalents of HMPA in refluxing benzene. Chromatography of the products on silica (benzene/pet. ether) and crystallization from the same solvent afforded thiadiazole 3, m.p. 116° C, in 48% yield.[11] Recovered by-product included acenaphthenone 6 (13%), biacephthenone 7 (17%), and diacenaphthothiophene 8, (12%), all of which are presumably derived from the decomposition of the diazo ketone to an α-ketocarbene prior to thionation.

The attempted thionation of azibenzil 9 afforded a complex mixture which contained none of the desired thiadiazole 10 as shown by TLC. It would appear that a rigid cis-diazoketone



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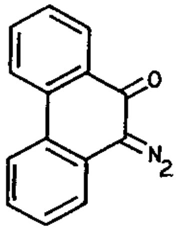

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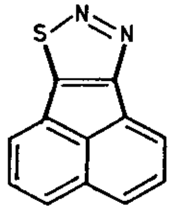

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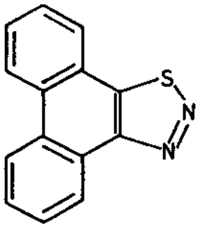

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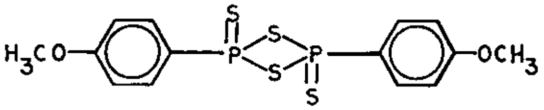

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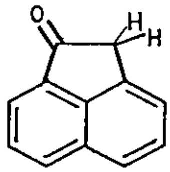

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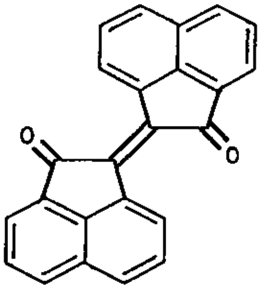

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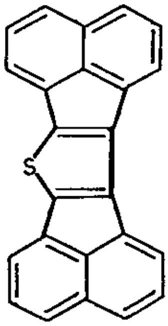

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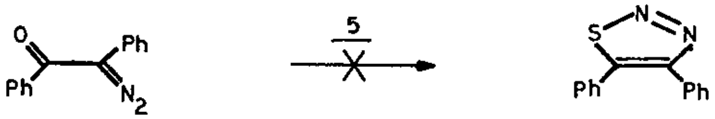

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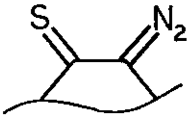

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structure such as that present in 1 and 2 is necessary for the formation of the thiadiazole system. This result is not unexpected if a highly unstable α-diazothioketone of the type 11 is formed as the reaction intermediate.

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