

Reactions of Diazenediyl Compounds with Pyridones:
A Novel [4 + 2] Cycloaddition

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Low temperature cycloaddition of 1,4-phthalazinedione (**2**) and 4-phenyl-1,2,4-triazoline-3,5-dione (**10**) with a variety of *N*-substituted pyridones affording novel azabicyclic structures is described. The structures of these compounds were confirmed by spectral analyses and hydrogenation to their dihydro derivatives.

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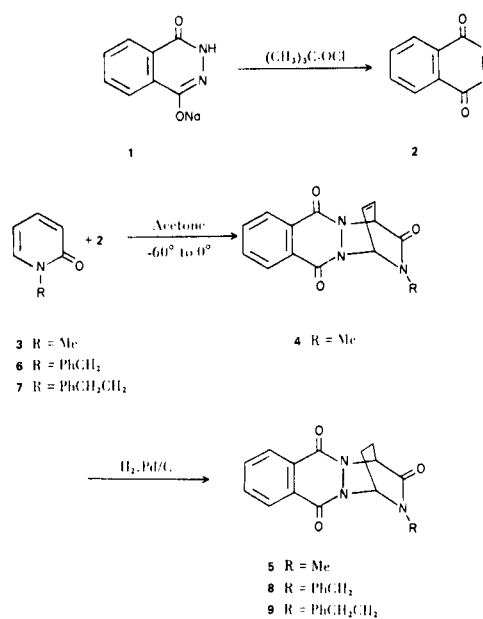
Sir:

Attempts to utilize *N*-methyl-2-pyridone (**3**) in cycloaddition reactions with dienophiles have been numerous (1a-d), but the isolation of the cycloadducts from the reaction with maleic anhydride and fumaronitrile represented the only reported successes for many years (2a-b). Interest has been renewed in this area as evidenced by recent publications describing the reaction of *N*-substituted pyridones with acetylenedicarboxylic acid methyl ester (**3**) and *N*-phenylmaleimide and maleimide (4a-b). Benzynes has also been reported to afford a cycloaddition product with **3** in 10% yield (5).

We became intrigued by the possibility of utilizing highly reactive -N=N- dienophiles (diazenediyls) in the reaction with pyridones to generate novel azabicyclic structures. We wish to report herein the successful utilization of these dienophiles in [4 + 2] cycloaddition reactions with pyridones.

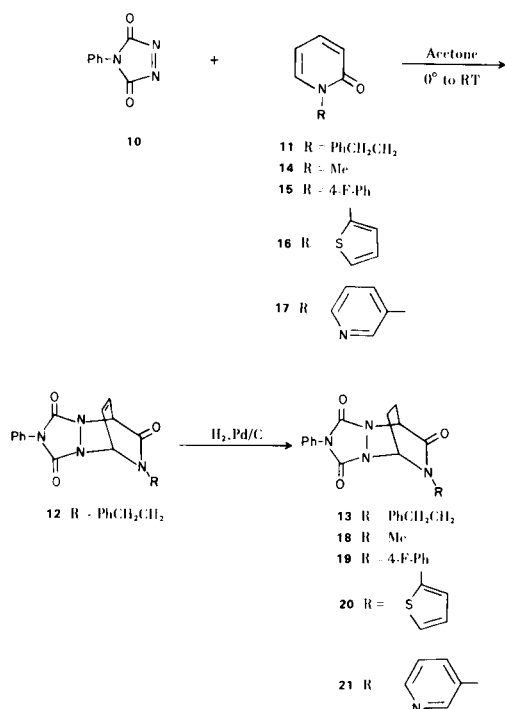
When 1,4-phthalazinedione (**2**) was generated from the sodium salt of phthalhydrazide (**1**) at -50 to -60° using *t*-butyl hypochlorite as an oxidizing agent (6), and a solution of **2** was treated with **3** at -60° for 1 hour followed by warming to 0°, we isolated a crystalline compound (7): C₁₄H₁₁N₃O₃; m.p. 188-192° dec.; nmr 2.99 (s, 3H, N-Me), 6.15 (m, 1H, bridgehead proton, -CO-CH-N-CO-), 7.12 (m, 2H, bridgehead proton, N-CH-N-CO- and -CH=CH-) and 8.1 (m, 5H, -CH=CH- and 4-Ar-H) δ. These data are consistent with the assignment of the [4 + 2] structure **4**. Hydrogenation of **4** with palladium/carbon in methylene chloride-methanol (1:1) afforded a crystalline solid in 17% overall yield (based on reacted phthalhydrazide): C₁₄H₁₃N₃O₃, M⁺ 271, m.p. 233-235°; nmr: 2.30 (m, 4H, -CH₂-CH₂-), 3.31 (s, 3H, N-Me), 5.78 (m, 1H, -CO-CH-),

6.46 (m, 1H, HC-N-Me), 7.33 (m, 2H, Ar-H) and 8.36 (m, 2H, Ar-H) δ. These results confirm the novel triazabicyclic structure **5**. Treatment of *N*-benzyl-2-pyridone (**6**) (**8**) and *N*-phenethyl-2-pyridone (**7**) by the same sequence of reactions afforded the corresponding cycloaddition products **8** and **9**.



Encouraged by our results we next attempted to extend the scope of the reaction by utilizing 4-phenyl-1,2,4-triazoline-3,5-dione (**10**) (**9**) as the dienophile in the reaction (10). Treatment of an acetone solution of **10** at 0° with **11** (in acetone) followed by warming to room temperature gave the cycloadduct **12** in 68% yield, m.p. 128-130°; nmr:

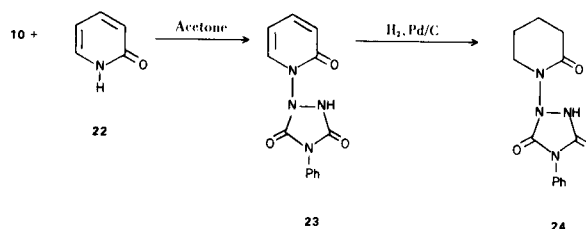
2.92 (d of d, 2H, CH₂-Ph), 3.72 (m, 2H, N-CH₂-CH₂-Ph), 5.19 (d of d, 1H, N-CH-CO-), 5.62 (d of d, 1H, -N-CH-N-), 6.5 (m, 2H, CH=CH), 7.2 (broad s, 5H, Ar-H), 7.38 (s, 5H, Ar-H) δ . Hydrogenation of **12** as described for **4** afforded the ethano-bridged derivative **13** in 59% yield, C₂₁H₂₀N₄O₃, M⁺ 376, m.p. 155-156°; nmr: 1.95 (m, 4H, -CH₂-CH₂-), 2.9 (m, 2H, Ph-CH₂-), 3.6 (m, 2H, Ph-CH₂-CH₂-), 4.7 (m, 1H, -CO-CH-), 5.4 (m, 1H, N-CH-N-), 7.2 (s, 5H, Ar-H), and 7.32 (s, 5H, Ar-H) δ . These data confirm the [4 + 2] nature of **13**. In a similar fashion, the tetra-bicyclic products **18-21** were obtained by hydrogenation of the initially formed [4 + 2] cycloaddition products



which were prepared by the reaction of **10** with pyridones **14-17**.

Although diethyl azodicarboxylate and dibenzyl azodicarboxylate react with several conjugated dienes in a [4 + 2] fashion, we observed no reaction (tlc, nmr) upon treatment with **3** in refluxing benzene or xylene for 18 hours. However, when **10** was reacted with 2-pyridone (**22**) in acetone as described above, the only product isolated was the adduct **23** in 17% yield. This is in accord with the results obtained in the reaction of **22** with hexafluorobutyne, and indicates that 1,2 addition is faster than

the cycloaddition process (11a-b). Hydrogenation of **23** afforded the expected substituted piperidone (**24**).



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