Tetrahedron Letters No. 20, pp 1765 - 1768.   0040-4039/79/0508-1765$02.00/0
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REACTIONS OF QUINOLINIUM AND PYRIDINIUM N-IMINES WITH CYCLOPENTADIENONE DERIVATIVES

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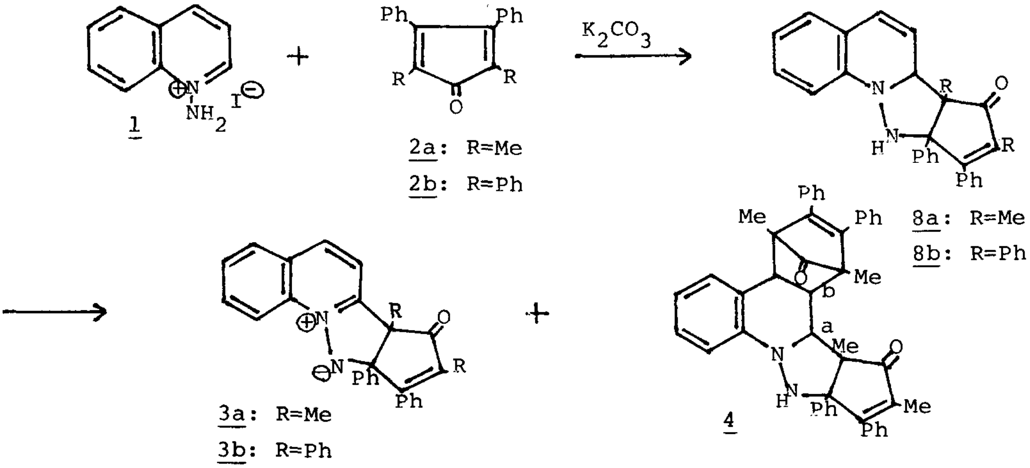
Summary : The novel reactions of quinolinium and pyridinium N-imines with cyclopentadienones are described.

The 1,3-dipolar addition reactions of pyridinium N-imines and related ylides with activated acetylenes provide a useful method to synthesize nitrogen-bridged heterocycles.[1] In recent years these reactions have been extended to cyclopropenones and yielded some interesting results.[2] For comparisons with cyclopropenones, we have investigated the reactions of quinolinium and pyridinium N-imines with cyclopentadienones and found novel reactions.

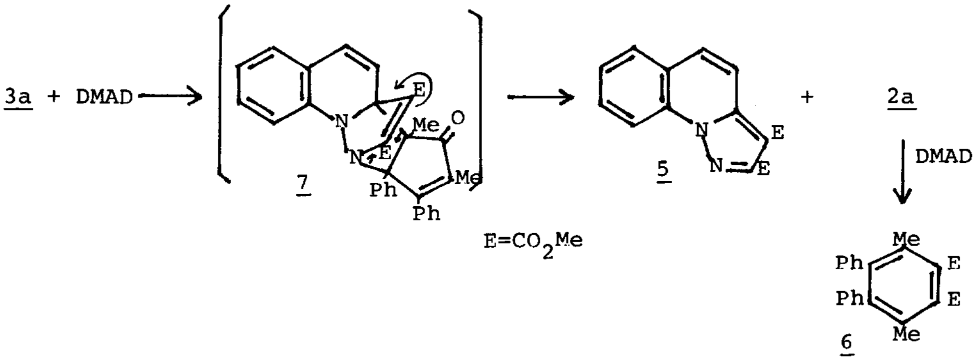
When a mixture of 1-aminoquinolinium iodide (1) and 2,5-dimethyl-3,4-diphenylcyclopentadienone (2a) (1.2:1 equiv) was heated in refluxing acetonitrile in the presence of potassium carbonate for 15 hr, orange crystals 3a (mp 190-192°C, 54%) and colorless crystals 4 (mp 204-205°C, 2%) were obtained.[3] The structures of these products were deduced on the basis of the spectroscopic data along with chemical evidence. 3a; νmax (KBr) 1690 cm^{-1}, δppm (60MHz, $CDCl_3$)



0.98 (s, 3H), 2.01 (s, 3H), 7.0-7.7 (m, 15H), 8.5-8.8 (m, 1H). 4; νmax (KBr) 3400, 1770, 1695 cm^{-1}, δppm (60MHz, CDCl$_3$) 0.59 (s, 3H), 1.22 (s, 3H), 1.35 (s, 3H), 1.48 (s, 3H), 3.09 (s, Ha), 3.25 (d, J=9.0 Hz), 3.50 (d, J=9.0), 4.72 (brs, NH), 5.8-6.0 (m, 2H), 6.6-7.8 (m, 22H).[4,5] The elemental analyses, NMR integration, and Mass spectra indicate that 3a is a dehydrogenation product of a 1:1 adduct and 4 is a 1:2 adduct. The ylide structure was suggested by the longer wavelength absorption maximum observed in the UV spectrum of 3a shown in Table 1 as well as no peak due to NH in its IR spectrum. Heating of 3a with dimethyl acetylenedicarboxylate (DMAD) in refluxing toluene gave pyrazolo[1,5-a]quinoline derivative 5 and o-terphenyl derivative 6 in 64% and 60% yields, respectively. The structures of 5 and 6 were established by direct comparisons with authentic samples.[1a, 6] An attractive pathway involves an initial 1,3-dipolar cycloaddition of the ylide 3a with DMAD to give a 1:1 adduct 7 which undergoes a retro-1,3-dipolar addition reaction to afford 5 and 2a. The cyclopentadienone 2a reacts with DMAD to give 6.[6] This reaction confirmed the structure of 3a. The formation of 3a can be explained by dehydrogenation of 1,3-dipolar cycloadduct 8a, while the formation of 4 can be explained by the Diels-Alder reaction of the cyclopentadienone 2a to 8a.[7] Although the intermediate 8a

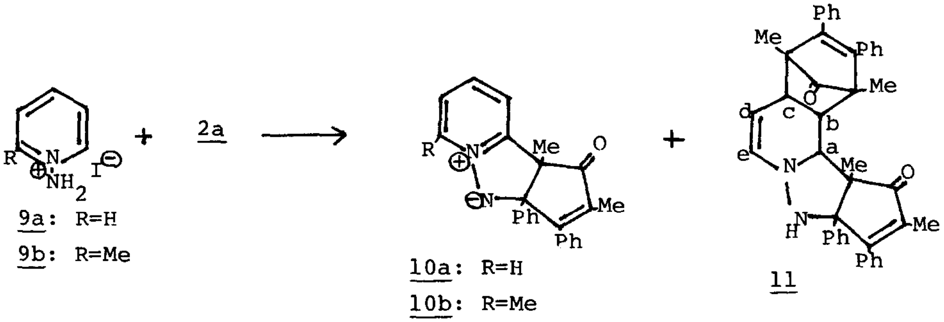
Table 1. Uv spectra of the ylides 3, 10, and the amine 8b

compds	λ max nm, (log ε) in ethanol			
3a	208(4.58)	225(4.57)	268(4.20)	445(3.51)
3b	205(4.73)	225(4.70)	278(4.33)	450(3.93)
10a	206(4.41)	278(4.12)	340(3.96)	430sh(3.45)
10b	206(4.39)	276(4.13)	330(3.98)	430sh(3.46)
8b	205(4.70)	231(4.67)	269sh(4.21)	317sh(4.02)



could not be isolated, the tetraphenyl derivative 8b was isolated in the reaction of the salt 1 with tetracyclone (2b). Upon heating 1 with 2b in refluxing acetonitrile in the presence of potassium carbonate for 30 min, the 1,3-dipolar cycloadduct 8b, mp 189-190°C, was obtained in 74% yield.[3] Treating of 8b with 10% Pd-C in refluxing toluene gave the ylide 3b in 80% yield.[3] The formation of the ylide 3b was confirmed by the comparison of their UV spectra shown in Table 1.

For comparison, the reactions of pyridinium N-imines were investigated. When a mixture of 1-aminopyridinium iodide (9a) and 2,5-dimethyl-3,4-diphenylcyclopentadienone (2a) (1.3:1 equiv) was heated in refluxing acetonitrile in the presence of potassium carbonate for 3 hr, a ylide 10a (mp 201-202°C, 32%) and a 1:2 adduct 11 (mp 185-187°C, 3%) was obtained.[3] Similarly, the reaction of salt 9b with 2a under the same conditions as above afforded the ylide 10b, (mp 213-215°C, 21%) although a 1:2 adduct such as 11 could not be obtained. The structures of these products were determined in a similar manner as those of 3a and 4. 10a; νmax (KBr) 1690 cm^{-1}, δppm (60 MHz, $CDCl_3$) 0.90 (s. 3H), 2.05 (s, 3H), 6.55(ddd, 1H, J=7.5, 7.0, 1.5 Hz), 6.8-7.6 (m, 12H), 7.80 (d, 1H, J= 7.0). 11; νmax (KBr) 3400, 1760, 1690 cm^{-1}, δppm (60MHz, $CDCl_3$) 0.72 (s, 3H), 1.22 (s, 3H), 1.35 (s, 3H), 1.88 (s, 3H), 2.52 (dd, Hc, J=9.0, 4.0 Hz), 3.15 (s, Ha), 3.16 (d, Hb J=9.0),[4] 4.56 (dd, Hd, J=8.0, 4.0), 4.79 (brs, NH), 6.25 (d, He, J=8.0), 7.0-7.8 (m, 20H).[5] The UV spectra of 10 characteristic of the ylide structure are shown in Table 1. The reaction of 10a with DMAD in refluxing toluene gave the o-terphenyl derivative 6 in 32% yield although a pyrazolo[1,5-a]pyridine derivative corresponding to 5 could not be obtained.



9a: R=H
9b: R=Me

10a: R=H
10b: R=Me

11

To our best knowledge, the ylides 3 and 10 are first examples of stable N-(alkylimino)quinolinium and pyridinium ylides. This property may be attributed to the fact that the ylides are constructed in a five-membered ring and surrounded by bulky substituents. This point, however, remains equivocal. Further studies are in progress to investigate the reactivities of these novel ylides involving photochemical behaviors.

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3. Satisfactory elemental analyses were obtained for all new compounds.
4. The coupling constant between Ha and Hb is nearly zero.
5. The stereochemistry of the 1:2 adducts 4 and 11 is not clear.
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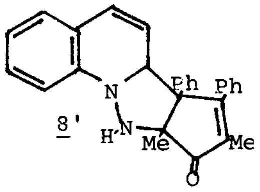
7. The possibility of 1,3-adduct 8' instead of 8 can be denied by the following reason. There are a number of reports concerning the nucleophilic attack of the pyridinium ylides[8] and the reactions of the pyridinium ylides with acrylonitrile[9] and monosubstituted acetylenes[10] give the 1,3-dipolar cycloadducts in which the anion part of the ylides attacks the β-position of the substituted olefins. Furthermore, The methyl signals (δ 0.98, 2.01) in the nmr spectrum of 3a are located in the lower field compared to those (δ 0.83, 1.76) of 8a, which was observed when the reaction of 1 with 2a was performed for 1 hr, supporting that 8a is the correct structure because the methyl signals of the ylide formed from 8' can be expected to be in the higher field than those of 8'.



8'

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(Received in Japan 29 January 1979)