CHEMISTRY LETTERS, pp. 489-492, 1983.

REACTION OF PYRIDINIUM PHENACYLIDES AND RELATED YLIDES WITH CYCLOPENTADIENONE DERIVATIVES

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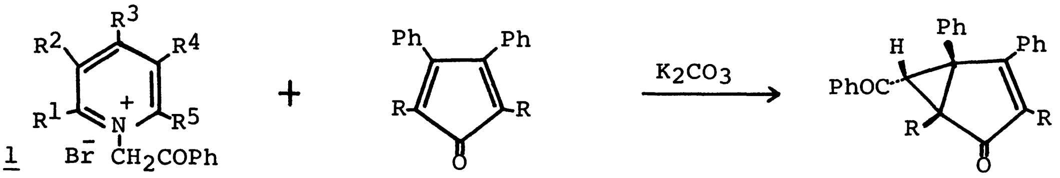
Reaction of pyridinium phenacylides with cyclopentadienone derivatives gave bicyclo[3.1.0]hex-3-en-2-one derivatives by the nucleophilic addition reaction followed by pyridine elimination. Isoquinolinium phenacylide underwent the 1,3-dipolar cycloaddition reaction with a cyclopentadienone.

Recently we have reported the novel reaction of pyridinium N-imines with cyclopentadienone derivatives giving new cyclic pyridinium N-imines.1) For comparisons with this novel reaction, we have investigated the reaction of pyridinium phenacylides and related ylides with cyclopentadienone derivatives.

When an acetonitrile solution of N-phenacylpyridinium bromide (1a) and 2,5-dimethyl-3,4-diphenylcyclopentadienone (2a) (1.2 : 1.0 equiv) was heated at reflux in the presence of potassium carbonate for 1h, colorless crystals 3a (mp 188-191 °C) was isolated in 10 % yield after separation by column chromatography on silica gel.2)



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a; $R^1=R^2=R^3=R^4=R^5=H$
b; $R^1=R^2=R^4=R^5=H$, $R^3=Me$
c; $R^1=R^3=R^5=H$, $R^2=R^4=Me$
d; $R^1=R^3=R^4=R^5=H$, $R^2=CN$
e; $R^1=R^3=R^5=Me$, $R^2=R^4=H$

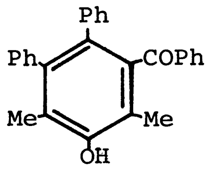
2

3

a; R=Me
b; R=Et
c; R=Ph

The structure of the product 3a was determined on the basis of the spectroscopic data along with chemical evidence. The elemental analysis and mass spectrum indicate that the product 3a is a pyridine-eliminated compound from a 1:1 adduct of pyridinium phenacylide and cyclopentadienone 2a. The UV spectrum of 3a indicates the presence of a conjugated system [λmax (EtOH) 221 nm (logε=4.31), 248 nm (logε=4.27),310 nm (logε=3.83)]. The IR spectrum exhibits peaks due to a conjugated carbonyl group in a five-membered ring and a benzoyl group [νmax (KBr) 1695, 1665 cm^{-1}]. The NMR spectrum is consistent with this structure. δppm ($CDCl_3$) 1.23 (s, Me), 1.88 (s, Me), 3.90 (s, 1H), 6.9-8.1 (m, 15H, Ph). Double irradiation of the methyl signal at δ1.23 resulted in both sharpening and enhancement (18 %) of the methine proton signal at δ3.90, establishing the stereochemistry of 3a. Furthermore, the structure of 3a was confirmed by the following photochemical reaction. Irradiation of a methanol solution of the product 3a with a 400W high pressure mercury lamp afforded the isomer 4 (mp 200-202 °C) in 80 % yield.[3,4] The structural assignment of 4 was based on the spectroscopic data. The IR spectrum (KBr) exhibits peaks due to a hydroxy group (3300 cm^{-1}) and a conjugated carbonyl group (1650 cm^{-1}), indicating 4 to be a hydroxybenzophenone derivative. The NMR spectrum is reasonably explained by this structure. δppm ($CDCl_3$) 2.08 (s, Me), 2.12 (s, Me), 5.15 (s, OH), 6.6-7.7 (m, 15H).

The reaction giving the bicyclo[3.1.0]hexenone derivative 3a is a new type of a cyclopropanation reaction. The formation of 3a can be explained by the nucleophilic addition reaction to give an intermediate 5 followed by pyridine elimination. Therefore, the reaction was expected to be dependent on the substituent effects. In fact, the yield of the product 3a increased when the methyl groups were substituted. The reaction of the methyl derivatives 1b and 1c with cyclopentadienone 2a under the same conditions as that of 1a gave the product 3a in 15 and 22 % yields, respectively. In contrast, neither a cyano derivative 1d nor pyridinium dicyanomethylide (6) reacted with cyclopentadienone 2a at all. This result can be attributed to the electron donating property of the methyl substituents which increase



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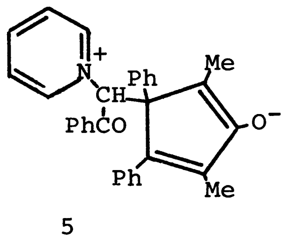

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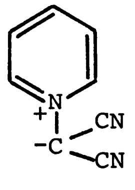

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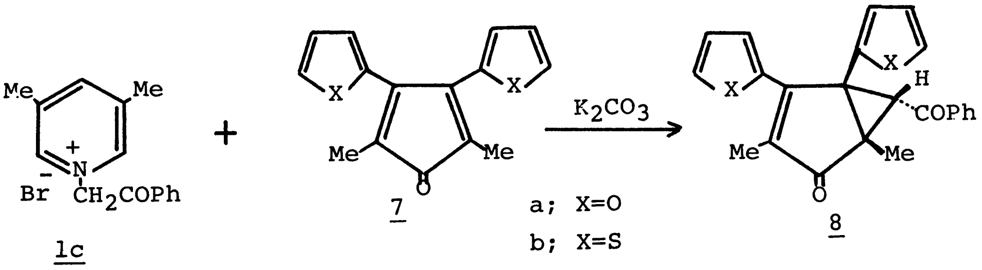
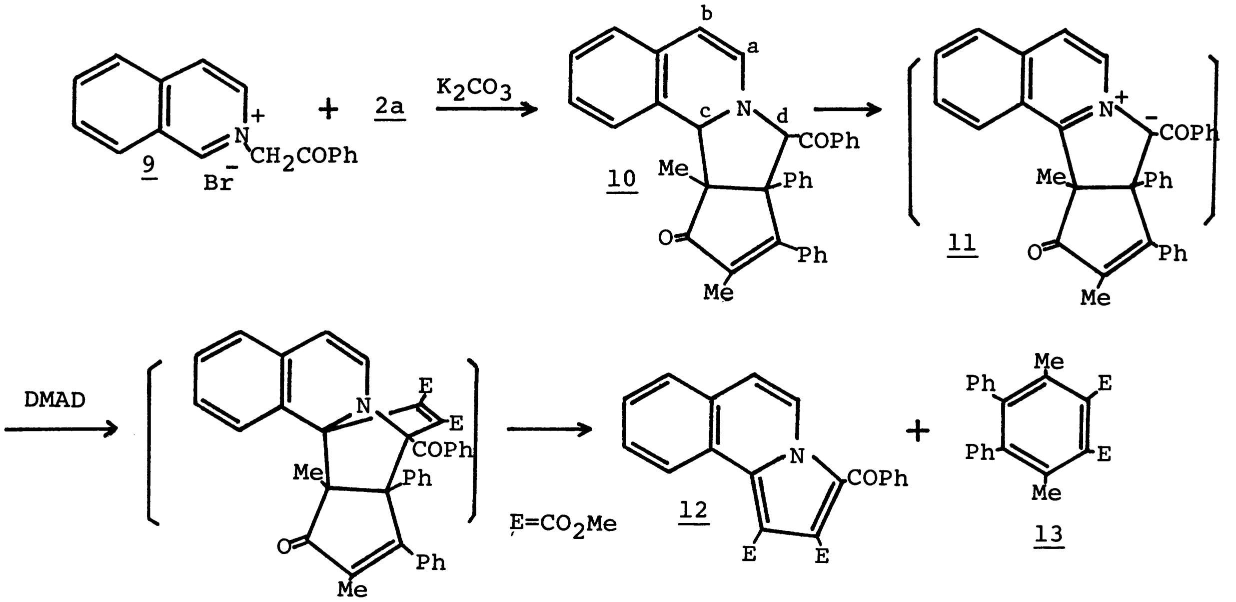
the nucleophilicity of pyridinium phenacylides. On the other hand, the trimethyl derivative 1e did not react with cyclopentadienone 2a at all probably due to steric hindrance. The best yield of 3a (83 %) was achieved when a mixture of bromide 1c, cyclopentadienone 2a, and potassium carbonate (1.2 : 1.0 : 1.5 equiv) was heated in hexamethylphosphoramide (HMPA) at 110 °C for 4h. Under the same conditions, the reaction of the bromide 1c and 2,5-diethyl-3,4-diphenylcyclopentadienone (2b) afforded the bicyclo[3.1.0]hexenone derivative 3b (mp 121-123 °C) in 44 % yield. Similarly, the tetraphenyl derivative 3c (mp 230-232 °C) was obtained in 27 % yield in the reaction of 1c with 2c. The lower yield of 3c can be attributed to the steric hindrance of the phenyl substituents. Furthermore, this reaction could be extended to the cyclopentadienones possessing heterocyclic substituents.[5] When the bromide 1c and cyclopentadienone 7a,b were reacted with potassium carbonate in HMPA at 110 °C for 3h, the similar reaction occured to give the bicyclo[3.1.0]hexenone derivatives 8a (mp 150-152 °C, 13 %) and 8b (mp 168-172 °C, 17 %).



In contrast to the reaction described above, N-phenacylquinolinium bromide did not react with cyclopentadienone 2a at all. On the other hand, when a mixture of N-phenacylisoquinolinium bromide (9), cyclopentadienone 2a, and potassium carbonate (1.2 : 1.0 : 1.5 equiv) was heated in refluxing acetonitrile for 20h, orange crystals 10a (mp 126-130 °C) and yellow crystals 10b (mp 174-177 °C) were obtained in 42 and 30 % yields, respectively, after separation by fractional crystallization.[2,6] Their spectroscopic data indicate that they are isomeric 1,3-dipolar cycloadducts of isoquinolinium phenacylide and cyclopentadienone 2a. The adducts 10a,b could not afford stable cyclic ylides 11 by dehydrogenation with Pd-C or DDQ in contrast to the corresponding pyridinium N-imines.[1] However, the reaction of the adducts 10a,b with dimethyl acetylenedicarboxylate (DMAD) gave pyrrolo[2.1-a]isoquinoline derivative 12 and o-terphenyl derivative 13. The structures of 12 and 13 were confirmed by direct comparisons with authentic samples.[7,8] Their formation can be explained by the 1,3-dipolar cycloaddition reaction of the initially formed ylide 11 with DMAD followed by a retro-Diels-Alder reaction.[1,9] Thus, this reaction proves the presence of the cyclic ylide 11 as an intermediate.



References

1) Y. Yamashita and M. Masumura, Tetrahedron Lett., 20, 1765 (1979).

2) All new compounds obtained here showed satisfactory elemental analyses and spectral data.

3) Much attention has been focused on the photochemistry of bicyclo[3.1.0]hex-3-en-2-ones.[4] The photochemical reaction found here gives a typical example.

4) P. J. Kropp, "Organic Photochemistry", ed by O. L. Chapman, Marcel Dekker INC., New York (1967), Vol. 1, p. 1.

5) Y. Yamashita and M. Masumura, Heterocycles, 14, 29 (1980).

6) The stereochemistry of the adducts 10a,b could not be unequivocally determined. Their NMR spectra are as follows. 10a; δppm (CDCl$_3$) 0.55 (s, Me), 2.03 (s, Me), 4.80 (d, Hb, J=7.5 Hz), 5.04 (s, Hc), 5.90 (d, Ha, J=7.5), 6.3-8.3 (m, 20H). 10b; δppm (CDCl$_3$) 1.60 (s, Me), 1.68 (s, Me), 5.09 (s, Hc), 5.21 (d, Hb, J=7.5), 5.40 (s, Hd), 6.14 (d, Ha, J=8.0), 6.5-8.0 (m, 19H).

7) C. A. Henrick, E. Ritchie, and W. C. Taylor, Aust. J. Chem. 20, 2467 (1967).

8) C. F. H. Allen and J. A. VanAllan, J. Am. Chem. Soc., 64, 1260 (1942).

9) Y. Yamashita, T. Hayashi, and M. Masumura, Chem. Lett., 1980, 1123.

(Received January 26, 1983)