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



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 [λ max (EtOH) 221 nm (log ϵ =4.31), 248 nm (log ϵ = 4.27),310 nm (log ε =3.83)]. The IR spectrum exhibits peaks due to a conjugated carbonyl group in a five-membered ring and a benzoyl group [vmax (KBr) 1695, 1665 cm⁻¹]. The NMR spectrum is consistent with this structure. δppm (CDCl₃) 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 δ 1.23 resulted in both sharpening and enhancement (18 %) of the methine proton signal at δ 3.90, 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 (CDCl₃) 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 <u>3a</u> is a new type of a cyclopropanation reaction. The formation of <u>3a</u> can be explained by the nucleophilic addition reaction to give an intermediate <u>5</u> followed by pyridine elimination. Therefore, the reaction was expected to be dependent on the substituent effects. In fact, the yield of the product <u>3a</u> increased when the methyl groups were substituted. The reaction of the methyl derivatives <u>1b</u> and <u>1c</u> with cyclopentadienone <u>2a</u> under the same conditions as that of <u>1a</u> gave the product <u>3a</u> in 15 and 22 % yields, respectively. In contrast, neither a cyano derivative <u>1d</u> nor pyridinium dicyanomethylide (<u>6</u>) reacted with cyclopentadienone <u>2a</u> at all. This result can be attributed to the electron donating property of the methyl substituents which increase



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the nucleophilicity of pyridinium phenacylides. On the other hand, the trimethyl derivative <u>le</u> did not react with cyclopentadienone <u>2a</u> at all probably due to steric hindrance. The best yield of <u>3a</u> (83 %) was achieved when a mixture of bromide <u>lc</u>, cyclopentadienone <u>2a</u>, 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 <u>lc</u> and 2,5-diethyl-3,4-diphenylcyclopentadienone (<u>2b</u>) afforded the bicyclo[3.1.0]hexenone derivative <u>3b</u> (mp 121-123 °C) in 44 % yield. Similarly, the tetraphenyl derivative <u>3c</u> (mp 230-232 °C) was obtained in 27 % yield in the reaction of <u>lc</u> with <u>2c</u>. The lower yield of <u>3c</u> 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 <u>lc</u> and cyclopentadienone <u>7a</u>,<u>b</u> 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 $\underline{2a}$ at all. On the other hand, when a mixture of N-phenacylisoquinolinium bromide ($\underline{9}$), cyclopentadienone $\underline{2a}$, and potassium carbonate (1.2 : 1.0 : 1.5 equiv) was heated in refluxing acetonitrile for 20h, orange crystals $\underline{10a}$ (mp 126-130 °C) and yellow crystals $\underline{10b}$ (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 $\underline{2a}$. The adducts $\underline{10a,b}$ could not afford stable cyclic ylides $\underline{11}$ by dehydrogenation with Pd-C or DDQ in contrast to the corresponding pyridinium N-imines.¹⁾ However, the reaction of the adducts $\underline{10a,b}$ with dimethyl acetylenedicarboxylate (DMAD) gave pyrrolo[2.1-a]isoquinoline derivative $\underline{12}$ and o-terphenyl derivative $\underline{13}$. The structures of $\underline{12}$ and $\underline{13}$ 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 <u>11</u> 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

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- 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-3en-2-ones.⁴⁾ The photochemical reaction found here gives a typical example.
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- 6) The stereochemistry of the adducts <u>10a,b</u> could not be unequivocally determined. Their NMR spectra are as follows. <u>10a</u>; δppm (CDCl₃) 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).
 <u>10b</u>; δppm (CDCl₃) 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).
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