Six-membered N-Heterocyclic Ring Formation *via* Photocyclization: Photocyclization of 2-Haloarenes

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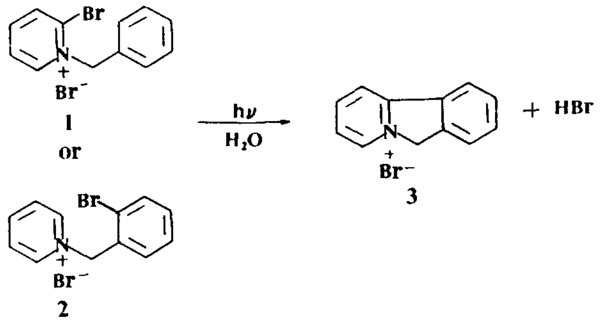
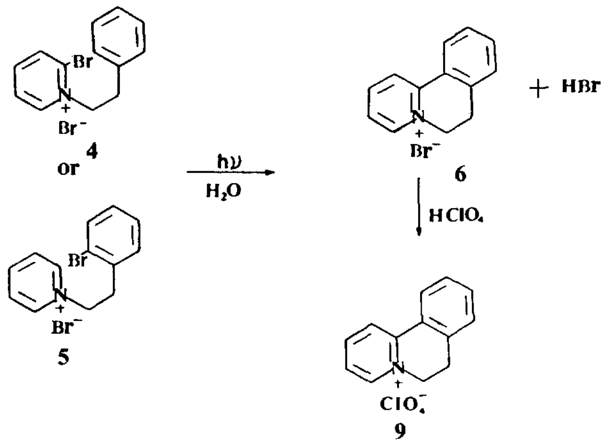
Intramolecular photocyclization reactions of *N*-(arylmethyl)-2-halopyridinium and *N*-[(2-haloaryl)methyl]pyridinium salts have been shown by Fozard *et al.*,[1a] Portlock *et al.*,[1b] and our group[1c] to lead conveniently to 5-membered heterocyclic ring compounds, pyrido[2,1-*a*]isoindolium salts (**3** see Scheme 1). Our interest in the photocyclization of N-(arylmethyl)-2-halopyridinium salts has led us to extend to concept to the preparation of phenanthridine derivatives.

When an aqueous solution of N-(phenylethyl)-2-bromopyridinium bromide[2] (**4**, 1 g, H_2O 600 mL, quartz cell) was irradiated with a high pressure Hg lamp (Hanovia) for 13 hrs, a brown solution was obtained. The reaction was followed by the increasing absorption peak at 312 nm. The developing absorption peak at 312 nm is much the same as **1** or **2**. After stripping off the water, 10 mL of methanol was added to the residue. When 30 mL of acetone were added to the methanol mixture, the flocculent precipitate was filtered out. Although the flocculent material was not identified, it was suspected to be the polymerized side product. The flocculent precipitate was filtered out again by the adding 300 mL of ethylacetate to the mixture.[3] After drying the solvent, adding 5 mL of ethanol and dropping 5 drops of perchloric acid, white crystal **9** was developed, yield 30%, mp. 142-143°C (see Scheme 2).

Observation of two triplet peaks at δ 3.31 (t, J=6 Hz, 2H) and 4.8 (t, J=6 Hz, 2H) in ^{1}H-NMR spectra taken in DMSO-d_6 (300 MHz) indicates two methylene protons of the pyridinium salt **9**. The splitting patterns and coupling constants at δ 8.23 (d, J=9 Hz, 1H), 7.58 (t, J=9 Hz, 1H), 8.60 (t, J=9 Hz, 1H) and 8.66 (d, J=9 Hz, 1H) indicate 7-, 8-, 9- and 10-protons of phenyl group, respectively. A doublet peak at the lowest field, δ9.01 (d, J=6 Hz, 1H) and triplet peak at δ 8.00 (t, J=6 Hz, 1H) are assigned for 4 and 5-protons of the pyridinium ring. A triplet peak at δ 7.65 (t, J=6 Hz, 1H) and a doublet peak at δ 7.52 (d, J=6 Hz, 1H) are assigned for 2 and 1-protons of the pyridinium ring (see Figure 1).[4]



Scheme 1.



Scheme 2.

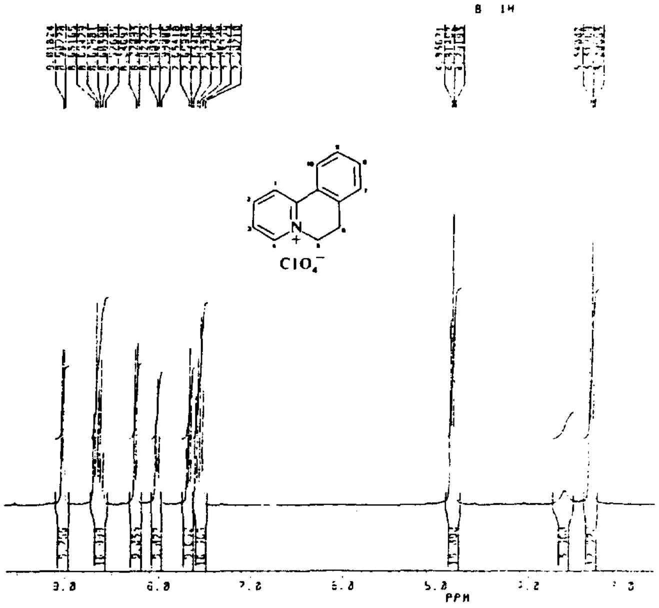
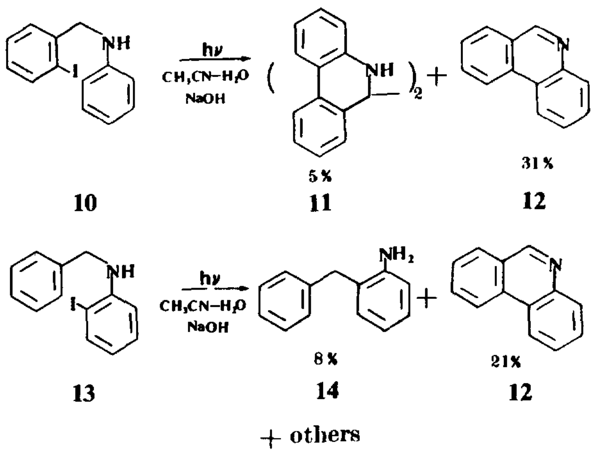


Figure 1. ^{1}H-NMR spectrum of pyrido[2,1-a]-3H, 4H-isoquinolinium perchlorate in DMSO-d_6.

Although the intramolecular photocyclized product seems to be the only product in the reaction with monochromatic light, the isolated yield of the preparative reaction with broad light spectrum was moderately low. The optimum conditions for the preparation were not studied further. However, the reaction is simple and useful for 6-membered *N*-heterocyclic ring formation. The same product **9**, could also be prepared by the photocyclization of *N*-[(2-bromophenyl)ethyl]-pyrininium bromide **5**,[5] *N*-(phenylethyl)-2-chloropyridinium chloride **8**[6] or *N*-(phenylethyl)-2-chloropyridinium bromide **7** under the above photochemical reaction condition of **4** (see Scheme 2).

When an aqueous acetonitrile soution of *N*-(2-iodobenzyl) aniline (**10**, 1 g, 0.003 mole, 500 mL, acetonitrile/water=9/1) in the presence of a base such as sodium hydroxide (0.16 g) was irradiated with a high pressure Hg lamp for 20 hrs,



Scheme 3.

a brown solution was obtained. After stripping off the solvent, 100 mL of ethylether was added to dissolve the reaction residue. After being washed with water, the etheral solution was concentrated and developed with benzene/diethyl ether (19/1) solvent on TLC. The products (R_f=0.2), phenanthridine (**12**, 178 mg, 31% yield, mp. 105-106℃, lit mp. 106-107 ℃)[6] and 5,5′,6,6′-tetrahydro-6,6′-biphenanthridyl (R_f=0.8, **11**, 30 mg, 5%, mp. 176-183℃, lit. 175-185℃)[7] was obtained. The photochemical reaction of N-benzyl-2-iodoaniline (**13**) gave phenanthridine (**12**) (128 mg, 22%) and 2-benzylaniline (**14**) (96 mg, 16%) under the above photochemical reaction condition of **10**. The latter probably came from secondary Photo-Fries type reaction of photoreduction product *N*-benzylaniline. We are studying the mechanistic pathway of the photocyclization reactions.

References and Notes

1. (a) A. Fozard and C. K. Bradsher, *J. Org. Chem.*, **32**, 2966 (1967); (b) D. E. Portlock, M. J. Kane, J. A. Bristol, and R. E. Lyle, *J. Org. Chem.*, **38**, 2351 (1973); (c) Y.-T. Park, C.-H. Joo, C.-D. Choi and K.-S. Park, *J. Heterocyclic Chem.*, **28**, 1083 (1991).
2. The pyridinium salt **4** was prepared by reaction of 2-phenylethyl bromide with 2-bromopyridine, yield 14%, mp. 150 ℃; UV (water): λ_{max} 278 (3.87); IR (potassium bromide): ν Aromatic CH 3040; ν Aliphatic CH 2945; ν Aromatic CC 1610 cm^{-1}; ^{1}H-NMR (D_2O): δ 3.8 (t, J=7 Hz, 2H), 5.5 (t, J=7.0 Hz, 2H), 7.3-7.6 (m, 5H), 8.2 (t, J=6 Hz, 1H), 8.6 (t, J=6 Hz, 1H), 8.9 (m, 2H).
   Anal. Calcd. for $C_{13}H_{13}NBr_2$: C, 45.51; H, 3.82; N, 4.08. Found: C, 45.32; H, 3.61; N, 4.20.
3. We could not obtain the pyridinium bromide salt **6** as a pure product However, we could get clean crystal of the pyridinium perchlorate **9**.
4. The pyridinium salt, **9** was identified with IR, UV and elemental analysis; UV (water): λ_{max} (4.14), IR (potassium bromide) ν Aromatic CH 3060, ν alipatic CH 2900 and aromatic CC 1650 cm^{-1}.
   Anal. Calcd. for $C_{13}H_{12}NClO_4$: C, 55.43; H, 4.29; N, 4.97. Found: C, 55.45; H, 4.32; N, 4.83.
5. N-[(2-Bromophenyl)ethyl]pyridinium bromide (**5**) was prepared by reaction of 2′-(2-bromophenyl)ethyl bromide with pyridne (yield 50%). 2′-(2-bromophenyl)ehtyl bromide was prepared by addition of hydrogen bromide to 2-bromostyrene in the presnece of benzoylperoxide (57% yield). The pyridinium salt **5** was obtained as a white crystal, yield 50%, mp. 187-188℃, UV (H_2O): λ_{max} 259.2 (ε 3.64), IR (potassium bromide): ν aromatic CH 3025, ν alipatic CH 2940, ν aromatic C=C 1670 cm^{-1}: ^{1}H-NMR (D_2O): δ 3.9 (t, J=6 Hz, 2H), 5.3 (t, J=6 Hz, 2H), 7.4-7.9 (m, 4H), 8.3-8.9 (m, 5H).
   Anal. Cald. for $C_{13}H_{13}NBr_2$: C, 45.51; H, 3.82; N, 4.08. Found C. 45.29; H, 3.90; N, 4.06.
6. CRC, "Handbook of Chemistry and Physics" 70ed , P.C-404.
7. K. Mizuno, C. Pac, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **46**, 3316 (1973). The dimer **11** was identified based on mp., IR and NMR data. IR (chloroform): ν N-H stretching 3260 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 4.70 (s, 2H, CH), 6.7-9.2 (m, 16H, Aromatic).

Catalytic Hydroacylation of Aldehyde with α,ω-dienes by Rh(I) and Isomerization of the Terminal olefin to the Internal olefin

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C-H bond activation by transition metals is one of current interests in organometallic chemistry[1]. Especially aldehydic C-H bond cleavage and its application to organic synthesis of ketones through hydroacylation have been studied[2]. One of the major limitation for this process is decarbonylation[3]. To solve this problem, aldimines were applied for the synthesis of ketimines, the precursor of ketones, through C-H bond cleavage of the aldimines with C=N bond instead of C=O bond, using picoline system which can be used for good cyclometallation tool and can be easily removed by hydrolysis after the reaction[4]. Another good cyclometallation tool is a 8-quinolinyl system which does not show any decarbonylation, since they form the stable 5-membered ring metallacyclic complexes[5]. As a model study for hydrometallation through C-H bond activation, it has been applied to many different reactions such as C-C bond cleavage of the strained ring molecule[6], synthesis of β,γ-unsaturated ketones[7], and to the elucidation of olefin isomerization mechanism[8]. In this paper we report the catalytic hydroacylation of aldehyde and isomerization of olefin by Rh(I) with α,ω-dienes.

Results and Discussion

Compound **1**, 8-quinolinecarboxaldehyde, reacted with 1,5-hexadiene in toluene under Wilkinson's complex (**2**) as catalyst. After heating for 6 h at 130℃, the reaction mixtures