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Synthesis of Benzo[c]quinolizinium Salts by Photocyclization

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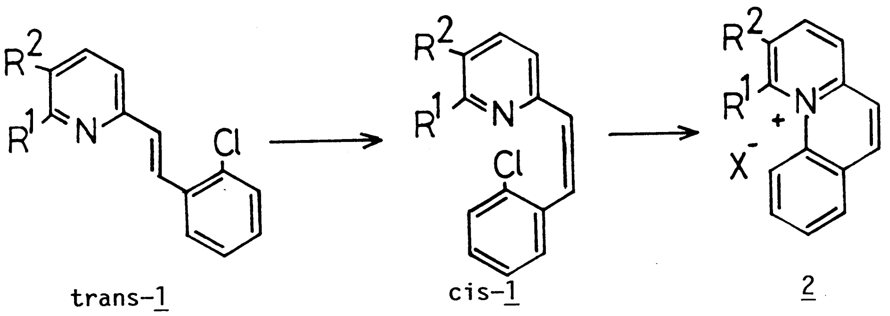
The photocyclization of 2-[2-(2-chlorophenyl)vinyl]-6-methylpyridine and 2-[2-(2-chlorophenyl)vinyl]quinoline in acetonitrile afforded new compounds 1-methylbenzo[c]-quinolizinium salt and dibenzo[c,f]quinolizinium salt in 56% and 41% yields, respectively.

We reported recently that the photocyclization of N-styrylpyridinium salts is a convenient method for the preparation of polycyclic azonia aromatic compounds incorporating a benzo[a]quinolizinium ring, in which 8a position of phenanthrene ring is replaced by a quaternary nitrogen.$^{1)}$ Their structural isomers, benzo[c]quinolizinium salts, in which 4a position of phenanthrene ring is replaced by a quaternary nitrogen, have been synthesized by an intramolecular thermal cyclization$^{2)}$ (Scheme 1). The thermal cyclization of cis-**1b** and **1c**, however, was unsuccessuful because of steric hindrance.$^{2)}$ These results have prevented the synthesis of polycyclic azonia aromatic compounds incorporating benzo[c]quinolizinium ring. In order to circumvent this difficulty photocyclization was examined and is herein reported.



trans-1 cis-1 2

1 and 2	R^1	R^2
a	H	H
b	CH_3	H
c	$-(CH=CH)_2-$	

The benzene solution of trans-2-[2-(2-chlorophenyl)vinyl]pyridines **1a-c** was irradiated with a 300 W high-pressure Hg lamp through a Pyrex filter ($\lambda > 280$ nm) to give cis-trans mixtures. The cis-derivative(**1a**) in the mixture underwent intramolecular quaternization at 170 °C to afford **2a** in 47% yield. The cyclization of cis-**1b** and **1c**, however, failed and trans-**1b** and **1c** were recovered, respectively. The compound **2a** was also obtained by the irradiation on the acetonitrile solution of trans-**1a** (6×10^{-5} mol · dm^{-3}). The yield, however, reached a maximum (34%) after 9 min and then decreased. This suggested the photo-decomposition of the product **2a** under irradiation. The yield was found to remain unchanged at a maximum value (54%) by the irradiation with the selected wavelength ($290 < \lambda < 340$ nm and $\lambda > 400$ nm) using aqueous potassium chromate solution filter. The compound **1a** was also photocyclized under these conditions by using ethanol, sulfolane, and formamide as solvent in 8, 36, and 9% yields, respectively.

The photocyclization was successfully applied to the synthesis of 1-methylbenzo[c]quinolizinium salt **2b** and dibenzo[c,f]quinolizinium salt **2c**. The acetonitrile solution of trans-**1b** was irradiated through an aqueous potassium chromate solution filter to afford the desired **2b**3) in 56% yield in spite of the steric hindrance in cis-**1b**. The salt **2c**4) was obtained in 41% yield by the photocyclization of **1c** in acetonitrile with the irradiation through an aqueous nickel sulfate solution filter ($280 < \lambda < 360$ nm and $\lambda > 430$ nm).

The synthesis of fused polycyclic azonia aromatic compounds incorporating a benzo[c]quinolizinium ring by the photocyclization is now in progress.

References

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3) **2b** (X=ClO_4): pale yellow needles from ethanol, mp 115-116 °C ; UV (CH_3CN) 256 (log ε 4.46), 360 (3.97), and 376 nm (4.07); ^1H NMR (DMSO-d_6) δ = 3.32 (3H, m, CH_3) and 7.9-8.9 (9H, m, ArH). Found: C, 57.02; H, 4.36; N, 4.65%. Calcd for $C_{14}H_{12}NClO_4$: C, 57.24; H, 4.13; N, 4.77%.

4) **2f** (X=ClO_4): yellow crystals from ethanol, mp 255-257 °C ; UV (CH_3CN) 268 (log ε 4.49), 277 (sh), 366 (sh), 384 (4.11), and 405 nm (4.26); ^1H NMR(DMSO-d_6) δ = 8.0-9.1(m, ArH). Found: C, 61.68; H, 3.66; N, 4.12%. Calcd for $C_{17}H_{12}NClO_4$: C, 61.92; H, 3.67; N, 4.25%.

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