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SYNTHESIS OF AZONIA DERIVATIVE OF HEXAHELICENE

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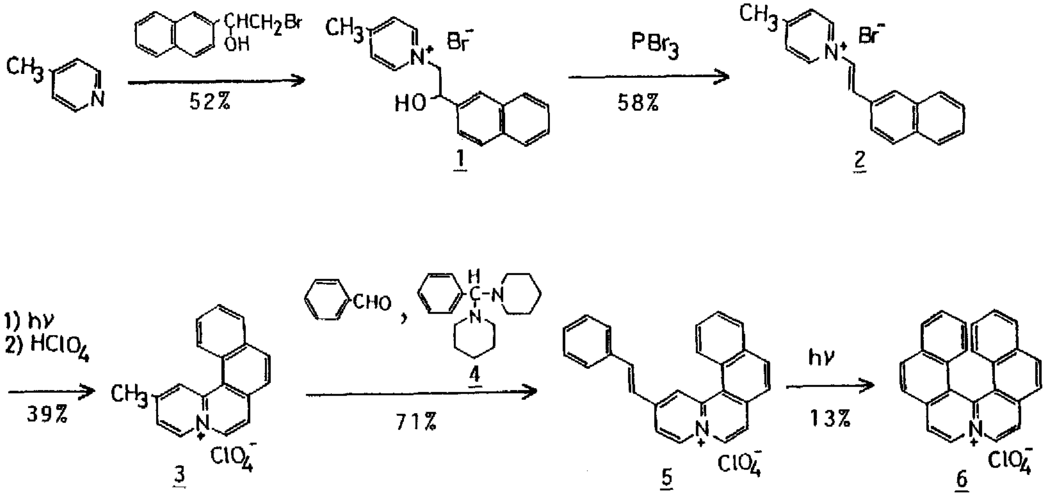
Abstract: The azonia derivative of hexahelicene, 4a-azoniaphenanthro[3,4-c]phenanthrene perchlorate, has been synthesized by photo-cyclization of 2-styrylnaphtho[1,2-a]quinolizinium perchlorate.

Since it was first described in 1956, the helicenes have attracted considerable interest and many helicenes and heterohelicenes containing pyridine, thiophene, or furan rings have been synthesized.[1] To date, however, no heterohelicenes containing quinolizinium ring have been reported. We now report the first example of azonia derivative of hexahelicene.

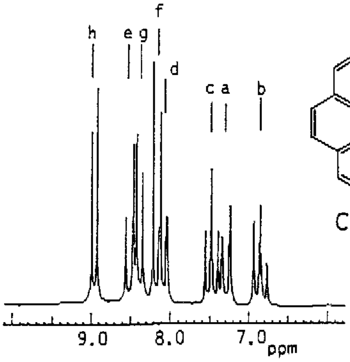
We reported previously that 2-methylbenzo[a]quinolizinium salt, whose methyl group located para position to azonia nitrogen, easily reacted with benzaldehyde derivatives to afford 2-styryl derivatives.[2] Therefore the key precursor, the styryl derivative (5), was prepared as shown in Scheme 1 using the aldol type condensation.

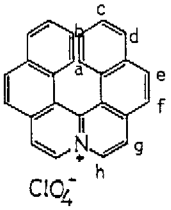


Scheme 1.

The 4-methylpyridinium salt (1)[3] was dehydrated with PBr_3 to yield the olefin (2)[3], which was photocyclized to afford 2-methylnaphtho[1,2-a]-quinolizinium perchlorate (3)[3] in 39% yield. The reaction of (3) with benzaldehyde in the presence of piperidine, however, gave many products including small amount of the styryl derivative (5). The trans-styryl derivative (5)[3] was successfully prepared by using the adduct (4)[4] instead of piperidine. The compound (5) was photocyclized in methanol in the presence of iodine by the irradiation with a Pyrex-filtered light($\lambda > 320$ nm) to afford azonia derivative of hexahelicene (6), 4a-azoniaphenanthro[3,4-c]phenanthrene perchlorate, in 13% yield. The spectral and analytical data confirmed the proposed structure. In particular, the higher field shift of the protons of (6) was observed(Fig.1), compared with polycondensed azonia aromatic compounds (benzo[a]quinolizinium, naphtho[1,2-a]-quinolizinium, and 2a-azoniadibenzo[c,g]phenanthrene salts), whose protons appeared between 7.8 and 9.5ppm[5].

Further work towards the synthesis of higher members in this series of azoniahelicenes are in progress.





6

MS(FAB): 330$(M-ClO_4)^+$

EA: C, 69.49; H, 3.81; N, 3.26.

$C_{25}H_{16}NClO_4$ requires C, 69.85; H, 3.75; N, 3.26%.

$\lambda_{max}^{MeOH}(\varepsilon)$: 435nm(10600), 413(7400) 362sh, 328(21600).

Fig. 1. ^1H NMR(90MHz, CD_3CN) of 6.

References

1) R. H. Martin, Angew. Chem., Int. Ed. Engl., 13, 649 (1974) and references therein.

2) S. Arai, M. Yamazaki, K. Nagakura, M. Ishikawa, and M. Hida, J. Chem. Soc. Chem. Commun., 1983, 1037.

3) Satisfactory spectroscopic and analytical data were obtained for all new compounds.

4) The adduct(4) has been proposed to be an active intermediate on the Knoevenagel condensation of active methylene compound with benzaldehyde in the presence of piperidine. G. Jones, Org. Reactions, 15, 204(1967).

5) S. Arai, T. Takeuchi, M. Ishikawa, T. Takeuchi, M. Yamazaki, and M. Hida, J. Chem. Soc. Perkin Trans. 1, 1987, 481.

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