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LITHIATION OF THE CYCLOALKENO [b] QUINOLINES BY PHENYLLITHIUM[1a,2]

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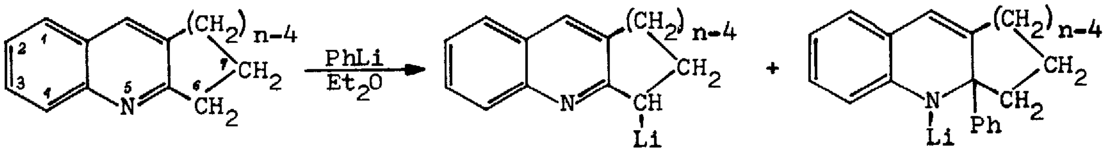
The lithiation of 2-phenylcyclohepteno- and cycloocteno[b]pyridines by phenyllithium in ether[4] gave, in addition to metalation of α-methylene groups, ortho metalated phenyls as kinetic products. These latter rearranges to form the α-methinelithium compounds[1b].

We have now compared the lithiation[5] of the cycloalkeno [b] quinolines 1 with that of quinaldine 2 as an aliphatic reference to determine whether the reaction course depends on the size of cycloalkene ring.

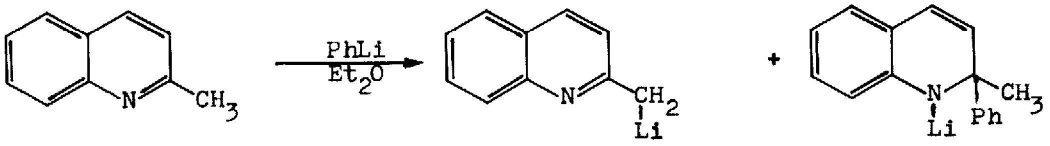
Compounds 1a and 1b are known[6] to give α-lithiated products 3a and 3b. Quinaldine 2 with phenyllithium has been reported to give the α-metalated species 5 with[7] or without[8] addition product 6.



1
a, n=5; b, n=6;
c, n=7; d, n=8

3
Yields: a, 97%; b, 96%;
c, 61%; d, 33%

4
Yields: a, <1%; b, <1%;
c, 31%; d, 48%



2

5
Yield: 95%

6
Yield: <1%

We found that in the reaction of the compounds 1a, 1b and 2 α-lithiated species 3a, 3b and 5 were accompanied by trace amounts of the addition products 4a, 4b and 6. In the case of the compounds 1c and 1d the significant difference of the reaction course was observed. By the competitive process, besides the α-lithiated compounds 3c and 3d, in a large percentage the addition products 4c and 4d were formed.

Although the observed results cannot be univocally explained, it is possible to assume that the competitive process is caused by weaker acidity of the appropriate C-H bonds of compounds 1 in which $n>6$. In the cases of α-picolyl- and quinaldyllithium, it has been reported that α-anionic carbon atoms are nearly sp^2 hybridized[9]. A plausibly weaker acidity of the compounds 1c and 1d which form mesomerically stabilized α-lithiated species 3c and 3d is probably due to „steric inhibition of resonance". This latter is effected by transannular H···H nonbonded interaction between hydrogens of the carbons 7-10 and 7-11 respectively, which hinder coplanarity of the methine groups and quinoline nuclei. The molecular models of the compounds 1, in which tetrahedral carbon atom 6 was replaced by trigonal one, support this point of view.

Similar results, as for compounds 1, were obtained in the lithiation of the cycloalkeno[b]pyridines[10].

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References and Notes

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3. Taken in part from T. J. Michalski Msc. Thesis, University of Łódź, 1975.
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