1,2-Dihydrocyclobuta[*b*]quinoline

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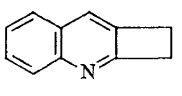
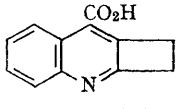
WE describe the preparation and characterization of 1,2-dihydrocyclobuta[*b*]quinoline (I), the first heterocyclic analogue of naphthocyclobutene. The first synthesis of this compound was reported by Wilk, Schwab, and Rochlitz,[1] who obtained (I) (6%) from a sealed-tube reaction of anthranil with cyclobutanone in the presence of mercuric sulphate.

We report the preparation of the same compound in good yield *via* a Friedlander synthesis. Treatment of an ethanolic solution of cyclobutanone and *o*-aminobenzaldehyde with concentrated potassium hydroxide for 3 days at room temperature afforded (I) (55%) (m.p. 96·5—97·4°; picrate, m.p. 236—237° decomp.). The product was also obtained in 25% yield from the same reactants under the conditions of acid catalysis recently reported[2] for this type of condensation. Dihydrocyclobuta[*b*]-quinoline was characterized by its mass spectrum (molecular ion at *m/e* 155; peaks at $M-15$ and $M-28$ *inter alia*) and its proton magnetic resonance spectrum (A_2B_2 pattern with multiplets centred at τ 6·47 and 6·87, assigned to the protons of the methylene groups bonded to the α- and β-carbons, respectively).



(I)



(II)

The most arresting feature of this structure is the effect that the fused, four-membered ring exerts on the basicity of the molecule. For a series of compounds the half-neutralization potentials (HNP) in acetic anhydride at 25° were determined by titration with perchloric acid in acetic acid.[3] The

results are given in the Table. It is clear that (I) is at least ten times less basic than comparable compounds that do not contain a fused, strained ring. This constitutes the first observtaion of the influence of such a ring system on an adjacent hetero-atom. That the fused cyclobutene ring also causes abnormal effects in an electronically excited state is evident from the fluorescence data reported by Wilk and co-workers.[1]

An alternative route to this new ring system was secured by a Pfitzinger reaction, which gave 8-carboxy-1,2-dihydrocyclobuta[*b*]quinoline (II) in 20% yield. Thus, condensation of isatin with cyclobutanone for 1 hr. in refluxing ethanolic potassium hydroxide gave (II) (m.p. 281—282°).† The product, however, did not undergo decarboxylation under a variety of conditions known to effect smoothly the same reaction for the analogous compound containing a fused cyclopentene ring.

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TABLE

Basicities of substituted quinolines

Compound	HNP	pK_a*
2,3-Dimethylquinoline	285 mv	5·99
Quinaldine	305	5·70
1,2-Dihydrocyclopenta[*b*]quinoline	322	5·45
Quinoline	349	5·06
1,2-Dihydrocyclobuta[*b*]quinoline	384	4·55

* Values are based on the known pK_a's of quinoline and quinaldine in water and the assumption that the HNP in Ac_2O and pK_a in water are linearly related (ref. 3).

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† Satisfactory analyses were obtained for all new compounds.

[1] M. Wilk, H. Schwab, and J. Rochlitz, *Annalen*, 1966, **698**, 149.
[2] E. A. Fehnel, *J. Org. Chem.*, 1966, **31**, 2899.
[3] C. A. Streuli, *Analyt. Chem.*, 1958, **30**, 997.