The Preparation of 8,11- aminoderivatives of C_s-trishomocubane

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Abstract – The nitrogen containing derivatives of C_S–trishomocubane have been recently shown to possess pharmacological activity. The preparation of 8,11- derivatives of pentacycloundecane complicated because of transannular interaction in C_s-structure. The method of 8,11- C_S–trishomocubane derivatives preparation based on using protecting groups was developed. The structure of newly obtained 8,11- aminoderivatives of C_S–trishomocubane was proved with NMR and GC-MS spectra.

Key words – polycyclic compounds,CS–trishomocubane, aminoderivatives, transannular interaction, antidepressants, protecting groups.

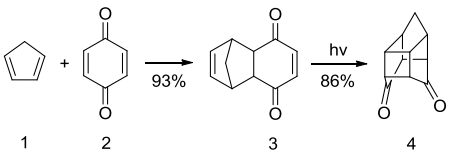
I. Introduction

Polycarbocyclic cage compounds have attracted attention of organic chemists for years, mostly because of their unique properties, e.g. high density, moderate strain energy and great stability, which are the result of their fascinating structural carbocyclic frameworks. In particular, pentacycloundecane derivatives have presented a fairly attractive goal and various synthetic strategies have been developed for their acquirement[1].

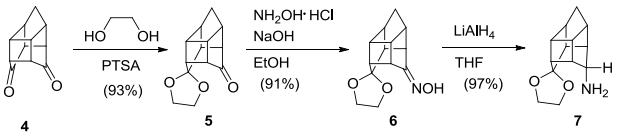
The 8,11- derivatives of pentacyclo [5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (C_S–trishomocubane) have proved to be exceedingly useful as an intermediates in the synthesis of complex substituted polycyclic compounds. They also can be used as ligands to chelate metal ions and for synthesis of crown-ethers [1], [2], [3]. The 8,11-aminoderivatives of pentacycloundecane have been recently shown to possess pharmacological activity that allows them to be used as antiviral agents [4], [5], antidepressants, tranquilizers, and as agents for the treatment of extrapyramidal syndromes [6]. The aim of our work is obtaining of 8,11- derivatives of C_S–trishomocubane, containing amino group. But the obtaining of 8,11-derivatives of C_S–trishomocubane is complicated because of transannular interaction in the polycyclic frame [7].

II. Results and discussions

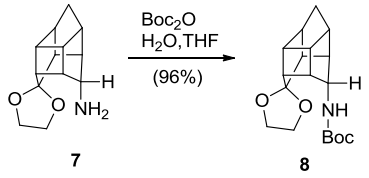
We have proposed the new method that based on using protecting groups into the C_S–trishomocubane cage.



The Diels-Alder reaction of cyclopentadiene (1) and 1,4-benzoquinone (2) gave the well-precedented adduct **3** which underwent [2+2] photocyclization to give pentacyclo[5.4.0.02,6.03,10.05,9]undecane-8,11-dione (Cookson's diketone, 4).



Protection of a single ketone functionality of Cookson's diketone (**4**) as its ethylene acetal gave the ketal **5** [6]. Treatment of **5** with hydroxylamine afforded ketal-oxime **6**. Reduction of oxime **6** with LAH afforded exclusively *endo*-aminoketal **7**. Structure of amine **4** was proved by X-Ray analysis of its *Boc*-derivative **8** (Fig 1).



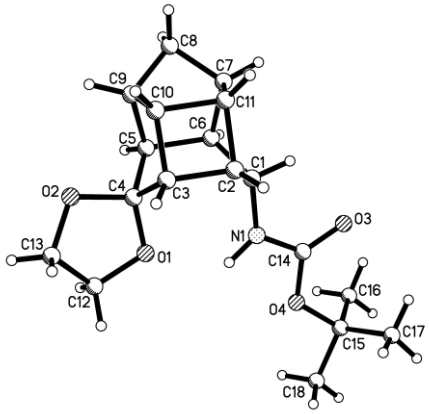
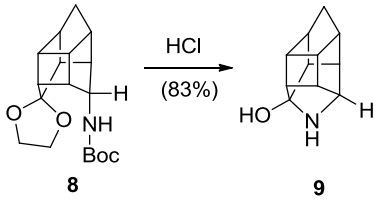
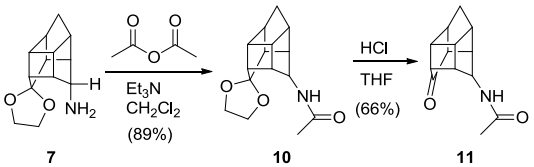


Fig. 1. X-Ray diffraction analis of Boc-derivative of C_S–trishomocubane **8**

It was unable to cleave ketal **8** with saving *Boc*-protection. Treatment of **8** with acid leads to transannular cyclization of aminoketone into aza-compound **9**.



Because of higher stability of acetamide group in acidic condition we obtained acetamidoketal **10**. Further cleavage of ketal group in mild acidic conditions afforded to ketone **11**.



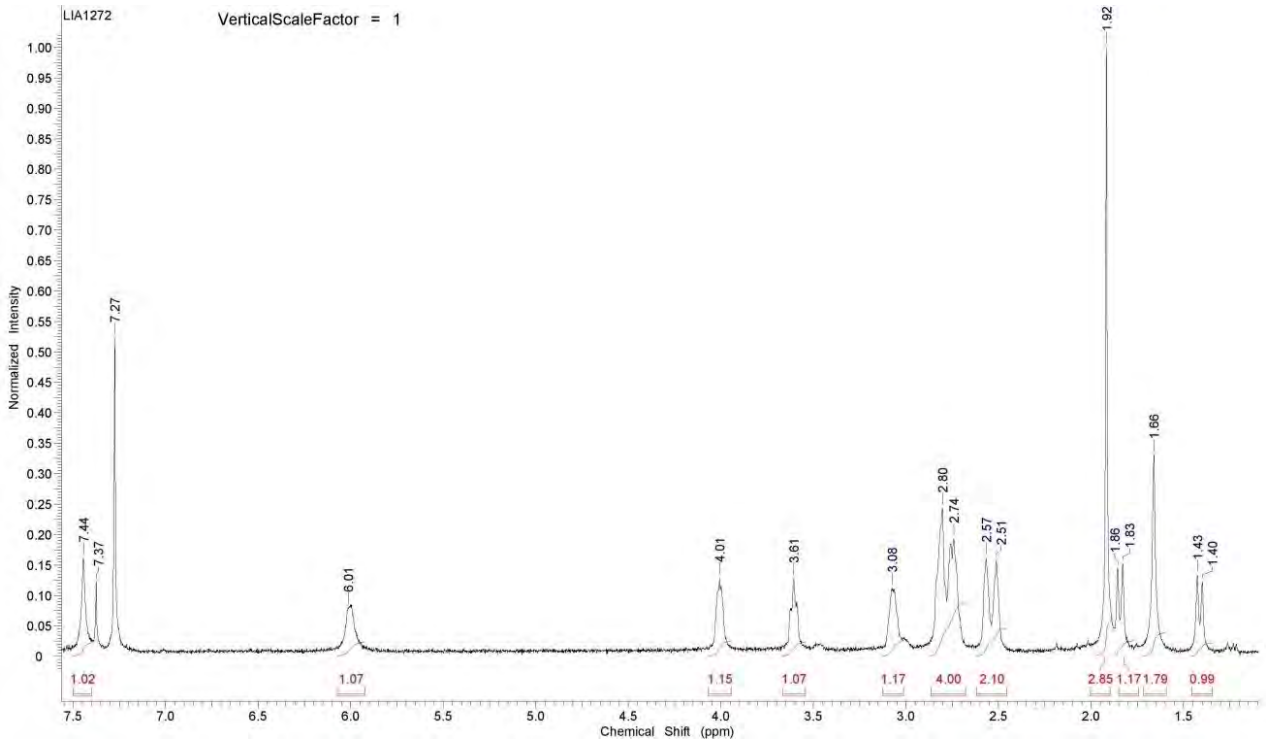
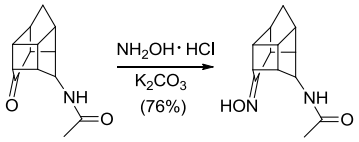


Fig. 2. NMR spectrum of oxime **12**.

Treatment of the last one with hydroxylamine afforded acetamidooxime **12**, that structure was proved with NMR and GC-MS spectrums.

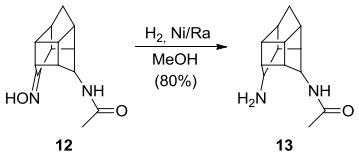


11 **12**

Occurrence of characteristical oxime (7.44, 7.37 ppm) and amide (6.01) peaks in NMR spectrum as well as molecular ion peak (m/z = 232) in MS-spectrum of **12** proves that acetamidooxime was formed.

The fact of oxime obtaining proves that no transannular cyclization take place.

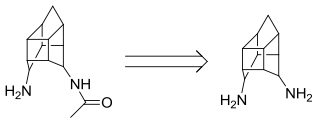
Reduction of oxime **12** with H_2 on Ni/Ra afforded acetoamine **13**.



12 **13**

Conclusion

In the present work, we have developed new method of obtaining of nonsymmetrical 8,11-aminoderivatives of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane. Synthesized monoprotected C_S –diamine can be used for obtaining of corresponding diamine.



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