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LETTERS

A Stable Cyclopentenyl Trication Derivative

Ronald Breslow* and Christian Werner
Department of Chemistry, Columbia University
New York, New York 10027

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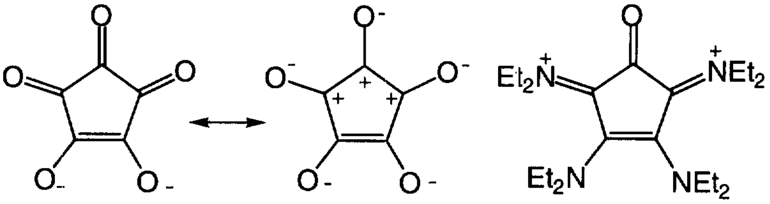
Abstract:. A cyclopentenyl trication stabilized by five propylamino substituents was prepared, as well as a related cyclopentadienone derivative.

Keywords: aromaticity, cyclic cations, polyamino derivatives

The cyclopentadienyl anion, with six pi electrons, is a well known aromatic system. However, using a simple theoretical treatment we pointed out some years ago[1] that the cyclopentenyl trication, with two pi electrons, would also be aromatic in the sense that it is more stabilized by conjugation than is a linear analog. In general, all cyclic conjugated systems that have 4n + 2 pi electrons are more stabilized than are their linear analogs, until the number of pi electrons is twice the number of carbons in the ring, although the cyclic advantage is maximal for systems with numbers of pi electrons closest to the number of carbons.[1] Thus the six pi electron cyclopentadienyl anion is more stabilized by aromaticity than is the two pi electron cyclopentenyl trication. Even so, with suitable electron donor substituents cyclopentenyl trication derivatives can be stable isolable species. For example, the croconate dianion 1 can be considered a cyclopentenyl trication carrying five oxyanion substituents. The dication 2 that we prepared previously[2] is also a stabilized derivative of the trication.



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We now wish to report the preparation of a cyclopentenyl trication 7 stabilized by five amino substituents. Treatment of croconic acid dimethyl ether 3 with an

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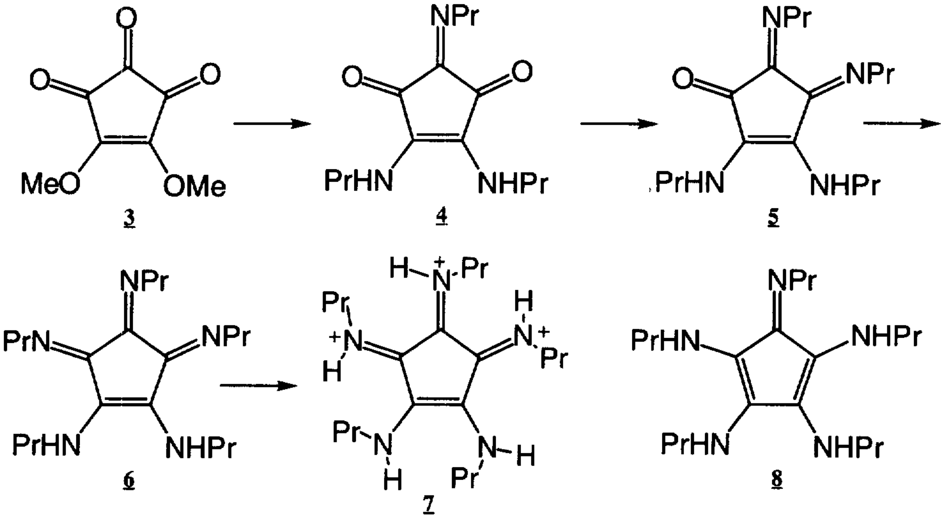
excess of propylamine afforded compound 4, in 80-95% yield (^{1}HNMR). The fourth and fifth nitrogens were added with 10-20 equiv. $TiCl_4$ and excess propylamine to yield 5 in 70-85% yield (^{1}H and ^{13}C NMR), along with 1-3% of 6 (^{1}H and ^{13}C NMR, MS). Compounds 5 and 6 were isolated by chromatography on silica with THF/triethylamine/hexane.

Treatment of 6 with three equivalents of HBF_4 in $CHCl_3$ afforded trication 7, as the BF_4^- salt which oiled out of the $CHCl_3$ solution. ^{1}H NMR (300 MHz, CD_3CN): δ 1.25 (CH_3, t, J = 7 Hz), 1.90 (CH_2, m), 3.80 (CH_2, q, coupled to CH_2 and NH, J = 7 Hz), 8.80 (NH, broad), all with the correct relative peak areas. ^{13}C NMR (300 MHz, CD_3CN): δ 10.0 (CH_3), 22.5 (CH_2), 53 (CH_2, broad), 147 (C_5 ring, broad). The carbons and hydrogens attached to nitrogen are broadened. The 5 equivalent downfield shifted propyl groups in the proton NMR indicate at least C_5 symmetry.



The analog of 7 carrying methyl groups instead of propyl groups was also prepared as a solid BF_4^- salt using methylamine in the above procedure. Furthermore, the related compound 8 was prepared in solution by reaction of excess propylamine with hexachlorocyclopentadiene, but its sensitivity has so far prevented its isolation in pure form. The monoprotonation of 8, or the two-electron reduction of 7 or the methyl analog, should lead to a stabilized symmetrical cyclopentadienyl cation derivative. Such studies will be reported elsewhere.

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References and Notes

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