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DIASTEREOTOPIC *gem*-DIMETHOXY GROUPS WITH A RING-PUCKERED MEISENHEIMER-TYPE σ-ADDUCT

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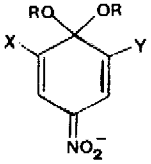
Equivalence of the gem-dialkoxy groups of σ-adducts is a firm notion in chemistry since the time of Meisenheimer.[1] However, this situation, when it is recognized that it simply relies on the planarity (or mean planarity) of the ring for all systems reported so far, such as with cyclohexadiene (1)[2] or cycloheptatriene (2)[3] systems, is open to question.

We report, therefore, the first σ-adduct where ring puckering induces nonequivalence of the gem-dialkoxy groups. Thus, during our efforts towards the total synthesis of zoanthoxanthins,[4] the idea was to induce ring puckering in a type-2 adduct by inhibiting negative charge dispersal on the seven-membered ring[3] through benzene annelation.

The idea, though unprofitable with 2-methoxy-4,5-benzotropone, where reluctanc~~y~~e towards o-quinoid forms resulted in resistance to potassium methoxide addition, worked well with 2-methoxy-3-nitro-4,5-benzotropone.[5] In fact, on the mixing of a ca. 2.5 M solution of 2-methoxy-3-nitro-4,5-benzotropone (3) in dried DMSO with the five-fold excess of a concentrated methanolic solution of potassium methoxide, orange crystals of 4, m.p. 189° from DMSO, precipitated. The structure of 4, which is the first σ-adduct isolated from troponoids,[6] is supported by elemental analysis, by the observation that on acidification of a DMSO solution of 4, 3 is immediately reformed in quantitative yield, and, finally, by the ^1H nmr



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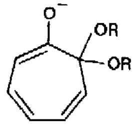

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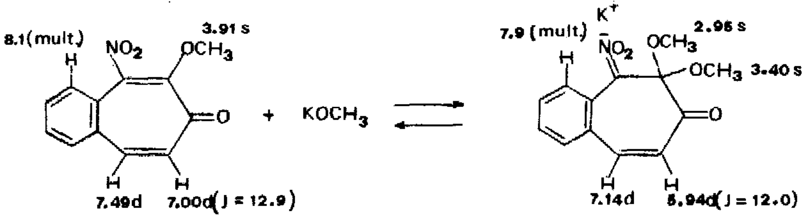
spectrum (Scheme) which clearly shows the diastereotopism of the gem-dimethoxy groups.



3 4

Scheme ^{1}H nmr data at ordinary probe temperature, ca. 27°, (δ in ppm with respect to internal TMS; J in cps) for solutions of the pure compounds in $(CD_3)_2SO$

The nonequivalence of the dimethoxy groups of 4 gradually disappears with the raising of the temperature until at 63° the two methoxyl signals coalesce into a sharp singlet at δ3.18 which integrates for six protons, no other detectable change occurring in the spectrum. The phenomenon is reversed on the cooling of the solution. Line shape analysis before and after the coalescence temperature gave 12 kcal mol^{-1} activation energy which refers to conformational inversion of the puckered seven-membered ring of 4 and not to methoxyl exchange of 4 via either S$_N$1 or S$_N$2 processes.[7] In fact, in the presence of excess $KOCD_3$ no detectable methoxyl exchange of 4 occurred even above the coalescence temperature.

We recognize that ring strain, induced by annelation, may also contribute to the energy barrier measured with 4. This, together with induction of ring puckering in cyclohexadiene systems (1), is under investigation.

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