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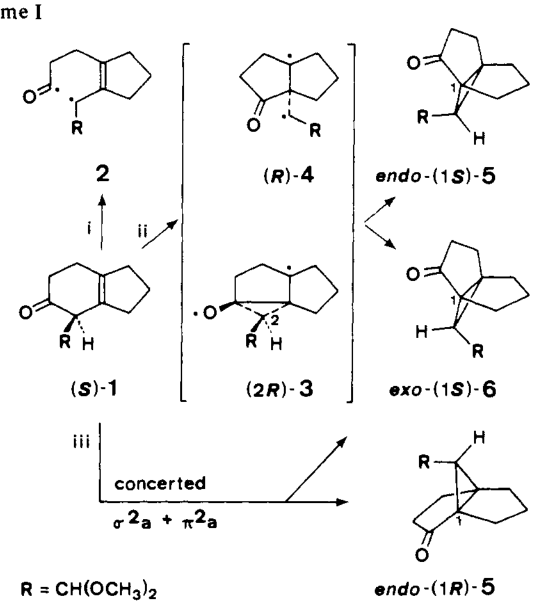
Photochemistry of a Cyclohex-3-enone. Evidence for a Stepwise Pathway in an Oxadi-π-methane Rearrangement

Sir:

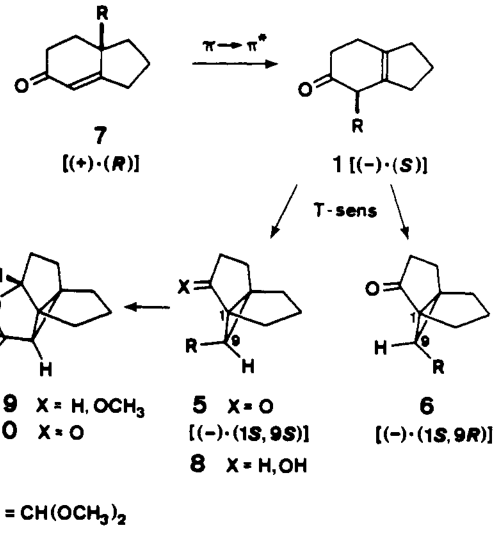
Triplet excited β,γ-unsaturated ketones undergo an oxadi-π-methane (ODPM) rearrangement involving a formal 1,2 ($\alpha \rightarrow \beta$) acyl shift and three-ring formation through $\alpha \rightarrow \gamma$ bonding.[1] One of the early examples was reported for $\Delta^{1,9}$-2-octalone.[2] We describe now a study with the related cyclohexenone (−)-**1** designed to differentiate between the three currently debated principal mechanisms for the ODPM rearrangement which can be applied to the formation of products *endo*-**5** and *exo*-**6**. These mechanisms are summarized in Scheme I:[3] (i) α-Cleavage to the achiral diradical **2** which recombines to *racemic* endo and exo products; (ii) an alternative stepwise mechanism proceeding via intermediates of type **3** and/or **4** furnishing endo and exo products of *identical* C-1 configuration; (iii) a photochemically allowed concerted ${}_{\sigma}2_a + {}_{\pi}2_a$ cycloaddition leading to endo and exo products with *opposite C*-1 configuration.[4] The products **5** and **6** formed by the concerted mechanism iii would retain the enantiomeric purity of the starting ketone. In a reaction course of type ii a partial loss of the initial enantiomeric purity may, but need not, result for **5** and **6** depending on the extent to which certain of the steps involved are subject to stereoselective control.[5]

Irradiation of ketone *rac*-**7** with 254-nm light in methanol led to a specifically $\pi \rightarrow \pi^*$ induced 1,3-allylic shift of the dimethoxymethyl substituent[6] and formation of **1**.[7,8] Triplet sensitization of **1**, using acetone solution and 254 nm, furnished a ca. 2:1 ratio of the cyclopropyl ketones **5** and **6** (20% yield at full conversion and after chromatographic separation). Separate photolyses of **5** and **6** under the conditions of their formation resulted in the decomposition of both compounds to as yet unknown products while the two isomers did not interconvert and their ratio remained constant. The endo configuration of the dimethoxymethyl group in **5** was established by reduction with $NaBH_4$ and oxalic acid-catalyzed cyclization of the resulting hydroxyacetal **8** in methanol to **9**. Jones oxidation of **9** gave lactone **10**, ir 1775 cm^{-1} (in CCl_4). The overall yield for **5** → **10** was 44%. Application of the same reaction sequence to **6** failed to give an analogous cyclization.

Scheme I



Scheme II



Compound (−)-**1**, CD $\Delta\epsilon_{max}^{297}$ +3.3,[9] of 54% enantiomeric purity[10] was obtained as follows: Fractional crystallization of the hydrazide prepared from (−)-*N*-aminomenthyl carbamate[11] and the carboethoxy precursor of **7** gave partially resolved (+)-**7**, $\Delta\epsilon_{max}^{340}$ +3.3.[9] Photorearrangement of this compound into (−)-**1** occurred without loss of enantiomeric purity.[12]

The two ODPM rearrangement products, which were isolated after a ca. 90% conversion of (−)-**1** in the acetone-sensitized photolysis, were optically active and the enantiomeric purities were 42% for recovered **1** and 48% each for **5** and **6**. The CD exhibited identical negative Cotton effects, $\Delta\epsilon_{max}^{296}$ −1.3,[9] for both the endo and exo isomer, (−)-(1*S*,9*S*)-**5** and (−)-(1*S*,9*R*)-**6**, respectively.[12]

The partial racemization in the order (−)-**1** > (−)-**5** = (−)-**6** during the photolysis must be due mostly to a process competing with the ODPM rearrangement, probably to reversible α-cleavage (**1** $\rightleftarrows$ **2**). Similar acetone-sensitized epimerizations have been observed previously.[18,19] The essentially full retention of enantiomeric purity during the rearrangement and the formation of endo and exo products with identical C-1 configuration *eliminate the*, a priori least favorable,[20] *α-cleavage* (path i) *entirely*[22] *and the allowed concerted cycloaddition* (path iii) *at least as the major reaction course.* There remains a stepwise mechanism of type ii which alone, irrespective of the detailed pathway, can account for the formation of the major product **5** (and equally well also for **6**), barring its unlikely generation in a single $_{\sigma}2_s + {}_{\pi}2_a$ step which is forbidden in the terms of orbital symmetry control.[4,24]

The high stereoselectivity of this reaction deserves some speculative comment although a definitive interpretation must await precise knowledge of the intermediate(s) involved. Solvent dependent uv and NMR spectral changes[25] indicate that the ground-state conformational equilibrium of **1** in a polar medium favors the half-chair or boat forms with the dimethoxymethyl substituent in the (pseudo)equatorial position. The rearrangement to (1S)-**5** and -**6** requires the same conformation of triplet **1**. It would in fact be acceptable to assume that ground and excited states adopt similar conformational preferences in similarly polar solvents.

A stepwise reaction course corresponding to ii, as established now as the most likely mechanism[24] for (the major part of) the ODPM rearrangement of **1**, need not be general to similar transformations of any other β,γ-unsaturated ketone. Nevertheless, it is compatible with all other examples which have been studied in some detail.[23,26] Only two[19,23e] of those cases, which conform to the mechanistic expectations of an allowed $_{\sigma}2 + {}_{\pi}2$ cycloaddition, require as an additional condition that a single intermediate corresponding to **3** be formed and converted directly to product with inversion at the β-carbon.

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(9) The CD data were measured in hexane at 22° and the $\Delta\epsilon$ values given are corrected for 100% enantiomeric purity.[10]

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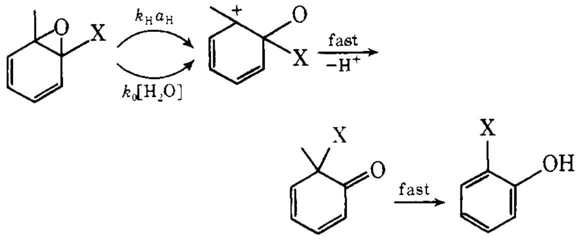
Modes of Acid Catalysis in the Aromatization of Arene Oxides

Sir:

The aromatization of arene oxides has previously been shown to occur by H_3O^+ (k_H) and spontaneous or water (k_0) catalysis (eq 1).[1] Both mechanisms involve rate determining carbocation formation when the migrating group (X) is H.[2] We report herein results which establish that the ring opening reaction is subject to general acid catalysis



(1)