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Stereoselectivity in the Paternò-Büchi Reaction of 2,2-Diisopropyl-1,3-dioxol with Methyl Trimethylpyruvate[1]

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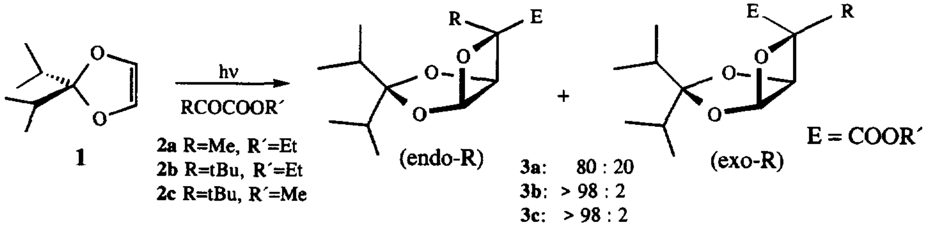
ABSTRACT : Photocycloaddition of 2,2-diisopropyl-1,3-dioxol (**1**) with methyl trimethylpyruvate (**2c**) leads to the bicyclic oxetane **3c** in high (> 98%) diastereoisomeric excess. X-ray analysis of **3c** revealed the *endo*-tert.-butyl configuration. Semiempirical calculations (AM1) indicate that kinetic product control exists which can be rationalized with spin-orbit coupling elements.

The stereochemistry of the Paternò-Büchi reaction[2] of triplet-excited carbonyl compounds with electron-rich alkenes has been studied in detail in the last years and a persuasive relationship between stereocontrol and spin-orbit coupling elements has been postulated.[3] Thus, the configuration-determining steps are coupled with geometrical restrictions from the spin inversion process.[4] As a result aromatic aldehydes photochemically add to cycloalkenes with high *endo* preference.[3b] An additional factor in these cases could be charge transfer interactions between the aromatic residues at the carbonyl component and the spin-bearing carbon atom of the cycloalkene. To exclude this possibility we looked for a non-aromatic triplet carbonyl species which undergoes photocycloaddition with the predicted[3a] stereoselectivity. Recently, Mattay and Buchkremer published the reaction of substituted pyruvates with the 1,3-dioxol **1**.[5] They reported a 80:20 ratio in favor of the *endo* methyl diastereoisomer **3a** in case of ethyl pyruvate addition to **1**. The ethyl trimethylpyruvate **2b** gave only one diastereoisomer, the configuration of which could not be determined. We synthesized the corresponding oxetane **3c** from the methyl ester **2c**.



X-ray structure analysis of compound **3c** revealed the *endo* tert. butyl configuration.[6] In the crystal the oxetane ring is puckered with a χ-angle of 15.9°. The corresponding value from a AM1-RHF[7] calculation is 9.9°. The difference in the heat of formation (ΔH_f) between the *exo*- and the *endo*-tert.-butyl diastereoisomer from AM1 is + 2.6 kcal/Mol, thus indicating that the *exo*-diastereomer (not detected in the photocycloaddition) is by far the thermodynamically more stable photoproduct. For comparison, the $\Delta\Delta H_f$-values [ΔH_f(endo)-ΔH_f(exo)] for the photoadducts of benzaldehyde with 2,3-dihydrofuran (which served as model compound in our first study on the stereochemistry of Paternò-Büchi reactions[3d]) and 2,2-diisopropyl-1,3-dioxol[8] were determined to 2.2 and 1.8 kcal/Mol, respectively. These results show that the observed stereoselectivity corresponds to contrathermodynamic control in all cases independent of the nature of the steric more demanding substituent at the oxetane bridge. Thus, the hypothesis of SOC-controled spin inversion as essential factor for the stereochemistry of the photocycloaddition reaction is supported by these results.[10]

ACKNOWLEDGEMENT

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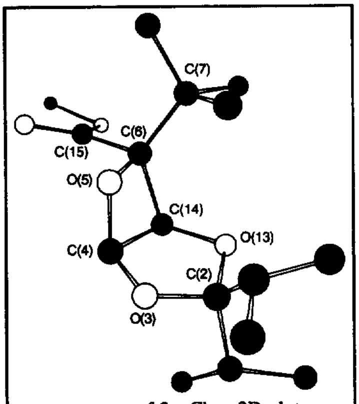

x-ray structure of 3c: Chem3D plot

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