α -Methylene- β -Lactones as Novel Allene Equivalents: Regioselective [4+2] Cycloaddition and Stereoselective Decarboxylation for the Introduction of *exo*-Alkylidene Functionalities

Waldemar Adam* and Ludwig Hasemann

Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-8700 Würzburg, Germany

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Abstract: β -Lactone-capped allene dienophiles afforded with cyclopentadiene spiro- β -lactone as [4+2] cycloadducts, which on thermal decarboxylation gave regio- and stereoselectively E-5-alkylidene 2-norbornenes.

Allenes constitute an extensively investigated class of compounds¹, which can serve as useful dieno- and dipolarophiles for cycloaddition². Unfortunately, simple alkyl-substituted allenes are rather sluggish in their reactivity and display poor regio- and stereoselectivity. For this reason, a number of allene equivalents have been developed³, which permit transformations not directly possible with allenes. For example, 2,3-diphenylsulfonyl-1-propene^{3b} reacts with nitrones to afford cycloadducts, which after elimination of benzene-sulfinic acid lead to 5-methyleneisoxazolines as E/Z isomers. We herein report a novel allene equivalent, namely



the α -methylene- β -lactone 1, which not only is conveniently accessible⁴, but which is sufficiently reactive towards 1,3-dienes and undergoes regio- and stereoselective cycloaddition (Scheme 1).

 α -Methylene- β -lactones 1 can be prepared through photooxygenation of acrylic acid derivatives⁵, through direct cyclization of α -methylene- β -hydroxy carboxylic acids⁶, or by rhodium-catalyzed, hydrosilylative cyclocarboxylation of propargyl alcohols⁷. As dienophiles, they cycloadd with cyclopentadiene to the corresponding diastereomeric spiro- β -lactones 2 in good yields (50-70 %)^{4b}. The use of Ti(OiPr)₄ as Lewis acid catalyst lowers the reaction time significantly, so that β -lactone 2b was obtained already in 9h at 20 °C instead of 20h.

The spectral data (¹H and ¹³C NMR, IR and MS) are in support of the suggested structures. Thus, the characteristic bridgehead protons 1-H and 4-H appear in the ¹H NMR for *exo-* and *endo-2a* respectively at 2.99 and 3.45 ppm and at 2.99 and 3.18 ppm, while for *exo-* and *endo-2b* they are located respectively at 2.98 and 3.21 ppm and at 3.01 and 3.13 ppm. The ¹³C NMR signals for the bridgehead carbon atoms of *exo, endo-2a* are to be found as doublets respectively at 42.1 and 49.4 ppm and at 42.6 and 52.1 ppm; for *exo, endo-2b* these are observed respectively at 42.1 and 50.1 ppm and at 42.7 and 52.0 ppm. The newly generated methylene group at C-3 appears as triplet at 31.8-33.0 ppm. Characteristic for the spiro- β -lactone structure is the singlet at

61.6-63.0 ppm for C-2 and the carbonyl band of these [4+2] cycloadducts at ca. 1820 cm⁻¹. NOE experiments established convincingly the assigned stereochemistry (Fig.1). For example, for the *exo-2* isomer irradiation of the bridgehead 1-H proton caused an enhancement (2.2 %) of 8-H and *vice versa* (2.1 %), while irradiation of the olefinic 6-H proton gave an enhancement (1.8 %) of the 8-H and *vice versa* (2.5 %). For the *endo-2* isomer, besides the 1-H/8-H interactions (6.2 %/3.6 %), irradiation of 8-H enhanced the *anti* 7'-H proton to the extent of 1.1 %.

Figure 1: NOE results for exo- and endo-2 of the cycloaddition of α -methylene- β -lactone 1 with cyclopentadiene by diastereofacial exo and endo attack.



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This cycloaddition exhibits a high diastereofacial selectivity in that the *exo* and *endo* attacks take place from the side of the α -methylene- β -lactone 1 opposite of the β -alkyl substituent (Fig.1). Thus, of the four possible diastereomers, only the two cycloadducts *exo*, *endo*-2 were observed in a ratio of 75:25. Preliminary results show that other diene partners, e.g. 1,3-cyclohexadiene, give analogous results.⁸

On pyrolysis of the spiro- β -lactones 2a,b at 40 °C and 0.1 torr, the E-5-alkylidene-2-norbornenes 3a,b (Scheme 1) were obtained stereochemically pure in high yields (ca. 80 %). The characterization and assignment of the stereochemistry of the known 3a was achieved through comparison with the published spectral data⁹ and that of the unknown 3b by ¹H and ¹³C NMR, IR and MS as well as NOE experiments. In the ¹H NMR of 3b the 8-H proton is located at 5.11 ppm and in the ¹³C NMR the olefinic carbons of the exomethylenic group are to be found at 126.6 and 138.7 ppm. The C=C stretching vibration is observed at 1625 cm⁻¹. NOE experiments established the *E* configuration of the exomethylene group. On irradiation of the 8-H signal an enhancement (3.4%) of the 4-H proton was detected and *vice versa* (4.7%); irradiation of the 9-H signal gave an enhancement (1.7%) of *endo* 6-H and *vice versa* (2.2%). Consequently, decarboxylation of the spiro- β -lactones 2, produced the *E* configurated 5-alkylidene-2-norbornenes 3, which are cycloadducts of cyclopentadiene and the corresponding allenes, in high yield and under rigorous stereocontrol. The novel α -methylene- β -lactone dienophiles 1 represent, therefore, masked allenes (Scheme 1), with which complex olefins of defined regio-and stereochemistry can be prepared, in the present case *E*-5-alkylidene-2-norbornenes 3. This constitutes a useful alternative to the classical Wittig olefination reaction; in fact, for the present substrates the latter works poorly.¹⁰

In Scheme 1 the unprecedented synthetic methodology is presented in overview. Thus, the sequence may be formally viewed as an "decarboxylative" cycloaddition of acrylic acid derivatives to 1,3-dienes in a regio- and stereoselective manner. As key molecule in this sequence serves the α -methylene- β -lactone 1, which functions as allene equivalent. This versatile building block should be valuable for preparative purposes and of general interest, since besides the here reported [4+2] cycloaddition, it can be used for 1,3-dipolar cycloadditions, radical and nucleophilic Michael additions, and electrophilic additions under preservation of the β -lactone ring.⁴ Subsequent decarboxylation of the resulting β -lactones provides a convenient entry into regio- and stereochemically defined functionalized olefins.¹¹ Acknowledgements: We thank the DFG (SFB 347 "Selektive Reaktionen Metall-aktivierter Moleküle") and the Fonds der Chemischen Industrie for generous financial support.

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