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## Abstract of the dissertation of Marko Soltau

german title:

### Synthese und Photochemie von 4-substituierten 2*H*-1-Benzo(thio)pyran-2-onen

This thesis deals with the investigation of the photochemical behaviour of four different 4-alkynyl-substituted (*thio*)coumarins **1a-c** & **3** and four different 4-methyl-substituted (*thio*)coumarins **4a/b**, **5** & **6**.

Compounds **1a-c** were synthesized by means of a palladium<sup>0</sup>-catalyzed SONOGASHIRA-reaction from 2-oxo-2*H*-benzo-(*thio*)-pyran-4-yl-4-methylbenzenesulfonate (**7a**) & (**7b**), which in turn were obtained from previously synthesized 4-hydroxythiocoumarin (**9a**), and from commercially available 4-hydroxycoumarin (**9b**), respectively.

The synthesis of **3** by coupling of 4-bromocoumarin (**22b**) with the trifluoroalkynylborate **23** was unsuccessful due to nonacceptable yields, and must still be improved.

The 4-methyl-substituted coumarins **4b** and **5** were synthesized via a PECHMANN-reaction. The appropriate phenols **29b** and **31** were converted to the coumarins with ethylacetoacetate (**30**) in the presence of an excess of AlCl<sub>3</sub>. The 4-methyl-substituted thiocoumarins **4a** and **6** were obtained via a two-stage synthesis starting from the appropriate thiophenols **29a** and **36**, which were treated with the diketene-acetone-adduct **33b** followed by cyclisation with AlCl<sub>3</sub>.

The photochemical investigations aimed at photocycloadditions to 2,3-dimethylbut-2-ene. Compounds **1a-c** were also irradiated in the presence of enines **20** and **21**, respectively.

Dimerization reactions in solution led to a main product, isolated in acceptable yields, for **4a/b**, **5** & **6** in each case, while **1a-c** in solution do not dimerize.

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The irradiation of **1a-c** in presence of **2** afforded the tetracycles **48a-c** as main products. As by-products **45a/b** and **46b/c** were formed, however no **45c** or **46a**. A product relation of 3.3 (**48a**): 1 (**45a**), 6.6 (**48b**): 2 (**46b**): 1 (**45b**) and 2.8 (**48c**): 1 (**46c**) resulted. The compounds **45a/b** are [2+2]-photocycloadducts, from which **45a** could be isolated, while **45b** was not to be separated from **46b**. The compounds **46b/c** result from a H-atom-transfer as competition reaction to **45b/c**. Compound **46c** was isolated successfully.

The main products **48a-c** are formed via a multi-step process. In a first step a carbene is formed in a [2+3]-photocycloaddition, followed by a further cyclisation step leading to intermediate **47a-c**. Stabilization of **47a-c** occurs under recovery of the aromatic system by a 1,5- respectively 1,9-H-shift to **48a-c**. Isolation of **48b/c** was not possible. In the case of **48a** an isomerisation to **49a** was observed. A sequential transformation to **50a** occurs via a deprotonation/protonation sequence from **48a** and **49a**. The structure of **50a** was proven by determination of the x-ray crystal structure.

The photochemical conversions of **1b/c** with **20** or **1a/b** with **21** led to products **51b**, **51c**, **52a** and **52b**, respectively. Isolation was successful for **51b** and **51c**. With **52a** and **52b** too many by-products were found, whereas the [2+2]-photocycloadducts could only be detected in traces.

The conversion of the 4-methyl-substituted compounds **4a/b**, **5** and **6** in presence of **2** led to the [2+2]-photocycloadducts **55a/b**, **56** and **57**.

Irradiation of **4a/b**, **5** and **6** in the absence of added alkenes led to cyclodimers **58a/b**, **59** and **60**. An exact structural determination of **60** was achieved with the help of x-ray analysis.