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Intramolecular photo-cyclization and consecutive rearrangement reactions of diazo-functionalized olefin-esters

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ABSTRACT

A study on intramolecular photo-cyclization reactions with diazo-functionalized olefin-esters is presented. On irradiation of diphenyl diazo methane esters of cinnamic acids, not only the expected addition to the C=C double bond is observed, yielding cyclopropanes, but also the addition to the carboxylic C=O double bond is postulated as an intermediate. These formed intermediates undergo a rearrangement to cyclobutanones which further rearrange photo-assisted to oxetanes.

Both were isolated and characterized. The reaction progress, the impact of the irradiation wavelength and solvent as well as the influence of the electron density of the olefin on the product distribution is described. Also, the detailed reaction mechanism for the photo-reaction cascade is discussed.

1. Introduction

In many important natural products and biologically active substances cyclopropane is a key building block [1]. Also, cyclopropanes are of great importance for organic synthesis in general [2]. However, the formation of cyclopropanes is often performed via cyclopropanation of olefins with less substituted diazo compounds, rendering the method ineffective for total synthesis. This problem has been overcome by the utilization of intramolecular cyclopropanation reactions [3].

To broaden the reaction repertoire of intramolecular cyclopropanation we studied the photo-reactivity of a series of diphenyl diazomethane olefin esters **1-R** (Scheme 1). We anticipated the addition of an in situ generated carbene to the olefinic double bond with the formation of highly substituted cyclopropanes with annellated six-membered lactones **2-R** (left hand side; Scheme 1). Interestingly, the reaction did not proceed cleanly to the desired product but also yielded in cyclobutanones **3-R** which subsequently rearranged to oxetanes **4-R** (right hand side; Scheme 1). To the best of our knowledge, this kind of side reaction has not been observed before. We therefore decided to study this finding in more detail and to examine the product distribution in dependence on the olefin electron density. Thus, we irradiated donor- and acceptor-substituted diphenyl diazomethane olefin esters.

2. Materials and methods

2.1. General procedures

All manipulations and experiments were performed under argon using standard Schlenck techniques and in a glove box filled with argon unless otherwise stated. Pentane and dichloromethane were dried and degassed using a two-column drying system (MBraun) [4], diethyl ether and toluene were distilled from sodium. All solvents were stored under an argon atmosphere. Deuterated solvents were used as received from Deutero GmbH. Cinnamic acid, 4-toluenesulfonhydrazide, 4-toluenesulfonic acid monohydrate and sodium hydride were purchased from Merck, 4-methoxy-cinnamic acid, 4-methyl-cinnamic acid and 4-nitro-cinnamic acid from Sigma–Aldrich and used without further purification. The acid chlorides were synthesized according to literature procedures [5]. Silica with a particle size of 40–63 μm and technical grade solvents were used for flash-chromatography. Column diameter and filling height were chosen according to Still et al. [6] ^{1}H NMR and ^{13}C NMR measurements were performed on a Bruker Avance III 400. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) chemical shifts are given relative to the solvent signal for $CDCl_3$ (7.26 and 77.2) [7], ESI-MS was conducted on a Finnigan LCQ in acetonitrile. Micro analytical analysis was performed in the micro analytical lab of the Technische Universität München. FT-IR was carried out on a

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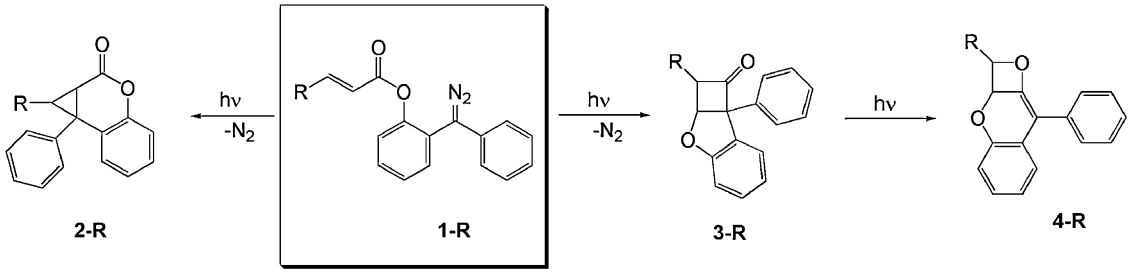


Scheme 1. Products of the photocyclization of diazo-compound **1-R**. R≡Me (Me), *p*-C_6H_4OMe (Ph^{OMe}), *p*-C_6H_4Me (Ph^{Me}), Ph (Ph), *p*-$C_6H_4NO_2$ (Ph^{NO2}).

Jasco FT/IR-460 Plus spectrometer. UV/vis spectra were recorded on a Jasco V-550 spectrophotometer using quartz cuvettes. X-ray single crystal parameters were obtained the following: The single crystals were stored under perfluorinated oil, transferred into a Lindemann capillary, fixed and sealed. Preliminary examination and data collection were carried out on an area detecting system (APEX II, k-CCD) at the window of a rotating anode (Bruker AXS, FR591) and graphite monochromated MoK_a radiation (l = 0.71073 Å). Raw data were corrected for Lorentz, polarization, and, arising from scaling procedure, for latent decay and absorption effects. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas all hydrogen atoms were refined with isotropic displacement parameters. Full-matrix least-square refinements were carried out by minimizing $P(F_0^2 - F_c^2)^2$ with SHELXL-97 weighting scheme [8]. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for non-hydrogen atoms were taken from International Tables for Crystallography [9].

2.2. General procedures for the synthesis of 2-benzophenyl esters

Ester-I: 2.49 mmol alcohol was added to 1 equiv. (2.49 mmol, 59.7 mg) of NaH in 5 ml thf at 0 °C and warmed to ambient temperature. After 15 min 1 equiv. (2.49 mmol) of the appropriate acid chloride was added and stirring continued over night. The reaction was quenched with 15 ml water and extracted three times with Et_2O. The combined organic layers were washed twice with saturated $NaHCO_3$ solution and once with brine, dried over Na_2SO_4, filtered and the solvent removed under reduced pressure to give the anticipated ester.

Ester-II: 16.5 mmol alcohol was dissolved in 5 ml pyridine, 26.4 mmol (1.6 equiv.) of acid chloride were added and the reaction mixture was heated to 100 °C for 2 h. The reaction mixture was poured into a mixture of 200 g of ice and 350 ml of 0.5 m hydrochloric acid and extracted three times with Et_2O. The combined organic layers were washed twice with saturated $NaHCO_3$ solution and once with brine, dried over Na_2SO_4, filtered and the solvent removed under reduced pressure to give the product.

2-benzophenyl crotonate (0-Me) ^{1}H NMR ($CDCl_3$): δ = 1.79 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3), 5.72 (d, $^3J_{HH}$ = 14.7 Hz, 1H, CHCHCO), 6.84 (dq, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 14.7 Hz, 1H, CH_3CHCH), 7.21–7.26 (m, 1H, H_{Ar}), 7.28–7.35 (m, 1H, H_{Ar}), 7.38–7.46 (m, 2H, H_{Ar}), 7.48–7.59 (m, 3H, H_{Ar}), 7.73–7.81 (m, 2H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 18.3 (CH_3), 121.5 (C_{Ar}H), 123.4 (CHCHCO), 125.7 (C_{Ar}H), 128.5 (C_{Ar}H), 130.0 (C_{Ar}H), 130.5 (C_{Ar}H), 132.1 (C_{Ar}), 132.3 (C_{Ar}H), 133.1 (C_{Ar}H), 137.8 (C_{Ar}), 147.4 (CH_3CHCH), 148.9 (C_{Ar}O), 164.3 (CHCOO), 195.1 ($C_{Ar}COC_{Ar}$). ESI-MS: m/z (%): 267.2 (17) [$C_{17}H_{14}O_3H^+$], 289.2 (100) [$C_{17}H_{14}O_3Na^+$], 306.5 (80) [$C_{17}H_{14}O_3H_2ONa^+$], 419.1 (47) [$(C_{17}H_{14}O_3)_3HK^{2+}$], 503.1 (28) [$C_{17}H_{14}O_3(CH_3CN)C_{13}H_9O^{2+}$], 543.5 (17) [$C_{17}H_{14}O_3(CH_3CN)H_2ONaC_{13}H_9O^{2+}$]. elemental analysis for $C_{17}H_{14}O_3$ (266.29 g/mol): calcd.: C 76.68, H 5.30 found: C 76.40, H 5.10.

2-benzophenyl 4-methoxycinnamate (0-Ph^{OMe}): light yellow solid, yield: 83%, route: Ester-I, extraction with an Et_2O/CH_2Cl_2 mixture (1:1). Single crystals suitable for X-ray analysis were obtained by slow evaporation of a saturated ethanol solution. ^{1}H NMR ($CDCl_3$): δ = 3.81 (s, 3H, OCH_3), 6.15 (d, $^3J_{HH}$ = 15.9 Hz, 1H, CHCHCO), 6.87 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H_{Ar}), 7.23–7.63 (m, 10H, H_{Ar}, C_{Ar}CHCH), 7.80 (d, $^3J_{HH}$ = 7.1 Hz, 2H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 55.5 (OCH_3), 113.9 (CHCHCO), 114.4 (C_{ar}H), 123.3 (C_{Ar}H), 125.6 (C_{Ar}), 126.8 (C_{Ar}H), 128.4 (C_{Ar}H), 129.9 (C_{Ar}H), 130.1 (C_{Ar}H), 130.4 (C_{Ar}H), 132.0 (C_{Ar}), 132.2 (C_{Ar}H), 133.1 (C_{Ar}H), 137.7 (C_{Ar}), 146.5 (C_{Ar}CHCH), 148.9 (C_{Ar}O), 161.8 ($C_{Ar}OCH_3$), 165.1 (CHCOO), 195.1 ($C_{ar}COC_{Ar}$). ESI-MS: m/z (%): 161.2 (99) [$C_{10}H_9O_2^+$], 381.2 (100) [$C_{23}H_{18}O_4Na^+$], 421.6 (79) [$C_{23}H_{17}O_4H_2ONa_2^+$], 739.0 (41) [$(C_{23}H_{18}O_4)_2Na^+$], 754.8 (6) [$(C_{23}H_{18}O_4)_2K^+$], 869.0 (7) [$(C_{23}H_{18}O_4)_2$(HCOOH)(HCOO)NaK$^+$]. elemental analysis for $C_{23}H_{18}O_4$ (358.39 g/mol): calcd.: C 77.08, H 5.06 found: C 76.92, H 5.08.

2-benzophenyl 4-methylcinnamate (0-Ph^{Me}): yellow crystals, yield: 86%, route: Ester-I. ^{1}H NMR ($CDCl_3$): δ = 2.36 (s, 3H, CH_3), 6.24 (d, $^3J_{HH}$ = 16.0 Hz, 1H, CHCHCO), 7.16 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H_{Ar}), 7.27–7.62 (m, 10H, H_{Ar}, C_{Ar}CHCH), 7.80 (d, $^3J_{HH}$ = 7.2 Hz, 2H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 21.6 (CH_3), 115.4 (CHCHCO), 123.4 (C_{Ar}H), 125.7 (C_{Ar}), 128.4 (C_{Ar}H), 128.5 (C_{Ar}H), 129.7 (C_{Ar}H), 129.9 (C_{Ar}H), 130.5 (C_{Ar}H), 131.4 (C_{Ar}H), 132.0 (C_{Ar}), 132.3 (C_{Ar}H), 133.1 (C_{Ar}H), 137.7 (C_{Ar}), 141.3 ($C_{ar}CH_3$), 146.9 (C_{Ar}CHCH), 148.9 (C_{Ar}O), 165.0 (CHCOO), 195.1 ($C_{ar}COC_{Ar}$). ESI-MS: m/z (%): 145.2 (85) [$C_{10}H_9O^+$], 365.2 (98) [$C_{23}H_{18}O_3Na^+$], 405.7 (100) [$C_{23}H_{17}O_3H_2ONa_2^+$], 475.8 (39) [$C_{23}H_{18}O_3$(HCOOH)(HCOO)NaK$^+$], 717.0 (41) [$(C_{23}H_{18}O_3)_2Na^+$], 837.1 (10) [$(C_{23}H_{18}O_3)_2$(HCOOH)(HCOO)NaK$^+$]. elemental analysis for $C_{23}H_{18}O_3$ (342.39 g/mol): calcd.: C 80.68, H 5.30 found: C 79.56, H 5.54.

2-benzophenyl cinnamate (0-Ph): off-white solid, yield: >99%, route: Ester-II. ^{1}H NMR ($CDCl_3$): δ = 6.29 (d, $^3J_{HH}$ = 16.0 Hz, 1H, CHCHCO), 7.30–7.43 (m, 9H, H_{Ar}), 7.50–7.60 (m, 4H, H_{Ar}, C_{Ar}CHCH), 7.81 (d, $^3J_{HH}$ = 7.3 Hz, 2H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 116.6 (CHCHCO), 123.4 (C_{Ar}H), 125.8 (C_{Ar}H), 128.4 (C_{Ar}H), 128.5 (C_{Ar}H), 129.0 (C_{Ar}H), 130.0 (C_{Ar}H), 130.5 (C_{Ar}H), 130.8 (C_{Ar}H), 132.0 (C_{Ar}), 132.3 (C_{Ar}H), 133.2 (C_{Ar}H), 134.2 (C_{Ar}), 137.8 (C_{Ar}), 146.9 (C_{Ar}CHCH), 148.9 (C_{Ar}O), 164.9 (CHCOO), 195.0 ($C_{ar}COC_{Ar}$). ESI-MS: m/z (%): 351.2 (100) [$C_{22}H_{16}O_3Na^+$], 391.8 (50) [$C_{22}H_{16}O_3(CH_3CN)Na^+$], 475.9 (77) [$C_{22}H_{16}O_3(CH_3CN)_3Na^+$], 565.1 (57) [$C_{22}H_{16}O_3(CH_3CN)C_{14}H_9O_2^+$], 605.6 (85) [$C_{22}H_{16}O_3(CH_3CN)C_{14}H_9O_2K^+$], 678.9 (19) [$(C_{22}H_{16}O_3)_2Na^+$]. elemental analysis for $C_{22}H_{16}O_3$ (328.36 g/mol): calcd.: C 80.47, H 4.91 found: C 80.20, H 4.86.

2-benzophenyl 4-nitrocinnamate (0-Ph^{NO2}): white solid, yield: 85%, route: Ester-I. ^{1}H NMR ($CDCl_3$): δ = 6.45 (d, $^3J_{HH}$ = 16.0 Hz, 1H, CHCHCO), 7.31 (d, $^3J_{HH}$ = 8.1 Hz, 1H, H_{Ar}), 7.38 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H_{Ar}), 7.43 (t, $^3J_{HH}$ = 7.6 Hz, 2H, H_{Ar}), 7.48–7.66 (m, 6H, H_{Ar}, C_{Ar}CHCH), 7.80 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H_{Ar}), 8.22 (d, $^3J_{HH}$ = 16.0 Hz, 2H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 120.9

(CHCHCO), 123.2 (C_{Ar}H), 124.6 (C_{Ar}H), 126.0 (C_{Ar}H), 128.5 (C_{Ar}H), 129.0 (C_{Ar}H), 130.0 (C_{Ar}H), 130.7 (C_{Ar}H), 131.7 (C_{Ar}), 132.5 (C_{Ar}H), 133.2 (C_{Ar}H), 137.6 (C_{Ar}), 140.1 (C_{Ar}), 143.6 (C_{Ar}CHCH), 148.7 (C_{Ar}O), 148.8 (C_{Ar}N), 164.0 (CHCOO), 194.8 ($C_{ar}COC_{Ar}$). ESI-MS: *m/z* (%): 176.1 (64) [$C_9H_6NO_3^+$], 768.8 (45) [$(C_{22}H_{15}NO_5)_2Na^+$]. elemental analysis for $C_{22}H_{15}NO_5$ (373.36 g/mol): calcd.: C 70.77, H 4.05, N 3.75 found: C 70.61, H 4.12, N 3.64.

2.3. General procedure for the synthesis of hydrazones

4.19 mmol carbonyl compound was dissolved in toluene, 780 mg (4.19 mmol) of tosylhydrazine and one crystal of *para*-toluene sulfonic acid monohydrate added and refluxed over night. The solvent was removed under reduced pressure and the residue stirred in pentane and filtered off to give the product.

2-(phenyl(2-tosylhydrazono)methyl)phenyl crotonate (0^{TH}-Me): white solid, yield: 67%, single crystals suitable for X-ray analysis were obtained by slow evaporation of a saturated ethanol solution. ^{1}H NMR ($CDCl_3$): δ = 1.70 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CHC*H*$_3$), 2.42 (s, 3H, C_{Ar}C*H*$_3$), 5.40 (d, $^3J_{HH}$ = 14.3 Hz, 1H, CHC*H*CO), 6.52 (dq, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 15.4 Hz, 1H, CH$_3$C*H*CH), 7.15–7.46 (m, 10H, H_{Ar}), 7.50–7.60 (m, 1H, H_{Ar}), 7.73 (s, 1H, N*H*), 7.90 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 18.3 (CH*C*H$_3$), 21.8 (C_{Ar}CH$_3$), 120.7 (C_{ar}H), 123.7 (CH*C*HCO), 125.8 (C_{Ar}), 127.3 (C_{Ar}H), 127.4 (C_{Ar}H), 128.4 (C_{Ar}H), 128.7 (C_{Ar}H), 129.5 (C_{Ar}H), 130.0 (C_{Ar}H), 130.2 (C_{Ar}H), 131.7 (C_{Ar}H), 135.8 (C_{Ar}), 136.1 (C_{Ar}), 143.7 (C_{Ar}), 148.0 (CH$_3$*C*HCH), 148.3 (C_{Ar}O), 151.2 ($C_{Ar}CNC_{Ar}$), 164.9 (*C*HCOO). ESI-MS: *m/z* (%): 367 (21) [$C_{20}H_{19}N_2O_3S^+$], 435.1 (22) [$C_{24}H_{22}N_2O_4SH^+$], 457.2 (100) [$C_{24}H_{22}N_2O_4SNa^+$]. elemental analysis for $C_{24}H_{22}N_2O_4S$ (434.51 g/mol): calcd.: C 66.34, H 5.10, N 6.45, S 7.38 found: C 65.83, H 5.10, N 6.44, S 7.34.

2-(phenyl(2-tosylhydrazono)methyl)phenyl 4-methoxycinnamate (0^{TH}-Ph^{OMe}): creamy solid, yield: 86%. ^{1}H NMR ($CDCl_3$): δ = 2.21 (s, 3H, C*H*$_3$), 3.85 (s, 3H, OC*H*$_3$), 5.87 (d, $^3J_{HH}$ = 15.9 Hz, 1H, CHC*H*CO), 6.89 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H_{Ar}), 7.19–7.4 (m, 9H, H_{Ar}), 7.40–7.44 (m, 3H, H_{Ar}, C_{Ar}C*H*CH), 7.53–7.59 (m, 2H, H_{Ar}), 7.83 (s, 1H, N*H*), 7.90 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 21.6 (*C*H$_3$), 55.6 (O*C*H$_3$), 113.1 (CH*C*HCO), 114.5 (C_{Ar}H), 123.7 (C_{Ar}H), 125.8 (C_{Ar}), 126.7 (C_{Ar}), 127.3 (C_{Ar}H), 128.0 (C_{Ar}H), 128.0 (C_{Ar}H), 128.4 (C_{Ar}H), 128.5 (C_{Ar}H), 129.4 (C_{Ar}H), 130.0 (C_{Ar}H), 130.2 (C_{Ar}H), 131.7 (C_{Ar}H), 135.7 (C_{Ar}), 136.2 (C_{Ar}), 143.7 (C_{Ar}), 147.1 (C_{Ar}CHCH), 148.4 (C_{Ar}O), 151.1 ($C_{Ar}CNC_{Ar}$), 162.1 (C_{Ar}OCH$_3$), 165.8 (CH*C*OO). ESI-MS: *m/z* (%): 161.2 (14) [$C_{10}H_9O_2^+$], 367.2 (9) [$C_{20}H_{18}N_2O_3SH^+$], 527.0 (2) [$C_{30}H_{26}N_2O_5SH^+$], 549.3 (100) [$C_{30}H_{26}N_2O_5SNa^+$], 565.1 (2) [$C_{30}H_{26}N_2O_5SK^+$], 1075.0 (15) [$(C_{30}H_{26}N_2O_5S)_2Na^+$], 1091.1 (7) [$(C_{30}H_{26}N_2O_5S)_2K^+$]. elemental analysis for $C_{30}H_{26}N_2O_5S$ (526.60 g/mol): calcd.: C 68.42, H 4.98, N 5.32, S 6.09 found: C 67.27, H 5.06, N 5.18, S 6.24.

2-(phenyl(2-tosylhydrazono)methyl)phenyl 4-methylcinnamate (0^{TH}-Ph^{Me}): creamy solid, yield: 67%. ^{1}H NMR ($CDCl_3$): δ = 2.41 (s, 3H, C*H*$_3$), 2.46 (s, 3H, C*H*$_3$), 6.43 (d, $^3J_{HH}$ = 16.0 Hz, 1H, CHC*H*CO), 6.63–6.76 (m, 1H, H_{Ar}), 7.02 (d, $^3J_{HH}$ = 8.1 Hz, 1H, H_{Ar}), 7.09–7.16 (m, 1H, H_{Ar}), 7.19–7.34 (m, 6H, H_{Ar}, N*H*), 7.38 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H_{Ar}), 7.48 (d, $^3J_{HH}$ = 8.0 Hz, 3H, H_{Ar}), 7.57–7.60 (m, 2H, H_{Ar}), 7.80 (d, $^3J_{HH}$ = 7.2 Hz, 1H, C_{Ar}C*H*CH), 7.84 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 21.5 (*C*H$_3$), 21.6 (*C*H$_3$), 115.9 (CH*C*HCO), 117.6 (C_{Ar}H), 118.7 (C_{Ar}), 118.8 (C_{Ar}H), 127.1 (C_{Ar}H), 127.8 (C_{Ar}H), 127.9 (C_{Ar}H), 128.4 (C_{Ar}H), 129.3 (C_{Ar}H), 129.7 (C_{Ar}H), 129.7 (C_{Ar}H), 130.0 (C_{Ar}H), 130.1 (C_{Ar}H), 130.6 (C_{Ar}H), 130.7 (C_{Ar}H), 131.3 (C_{Ar}), 131.8 (C_{Ar}H), 134.7 (C_{Ar}H), 141.4 ($C_{ar}CNC_{Ar}$), 147.5 (C_{Ar}CHCH), 158.8 (C_{Ar}O), 172.2 (CH*C*OO). ESI-MS: *m/z* (%): 145.2 (9) [$C_{10}H_9O^+$], 367.3 (24) [$C_{20}H_{18}N_2O_3SH^+$], 511.1 (2) [$C_{30}H_{26}N_2O_4SH^+$], 533.3 (100) [$C_{30}H_{26}N_2O_4SNa^+$], 549.2 (3) [$C_{30}H_{26}N_2O_4SK^+$], 1043.0 (12) [$(C_{30}H_{26}N_2O_4S)_2Na^+$], 1059.1 (4) [$(C_{30}H_{26}N_2O_4S)_2K^+$].

2-(phenyl(2-tosylhydrazono)methyl)phenyl cinnamate (0^{TH}-Ph): off-white solid, yield: 53%. ^{1}H NMR ($CDCl_3$): δ = 2.16 (s, 3H, C*H*$_3$), 5.98 (d, $^3J_{HH}$ = 16.0 Hz, 1H, CHC*H*CO), 7.17–7.47 (m, 16H, H_{Ar}, C_{Ar}C*H*CH), 7.54–7.61 (m, 1H, H_{Ar}), 7.78 (s, 1H, N*H*), 7.89 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 21.6 (*C*H$_3$), 115.7 (CH*C*HCO), 123.7 (C_{Ar}H), 125.8 (C_{Ar}), 127.3 (C_{Ar}H), 127.5 (C_{Ar}H), 128.5 (C_{Ar}H), 128.6 (C_{Ar}H), 129.1 (C_{Ar}H), 129.5 (C_{Ar}H), 130.1 (C_{Ar}H), 130.3 (C_{Ar}H), 131.1 (C_{Ar}H), 131.8 (C_{Ar}H), 133.9 (C_{Ar}), 135.6 (C_{Ar}), 136.1 (C_{Ar}), 143.9 (C_{Ar}), 147.4 (C_{Ar}CHCH), 148.3 (C_{Ar}O), 151.1 ($C_{ar}CNC_{Ar}$), 165.5 (CH*C*OO). ESI-MS: *m/z* (%): 367.1 (16) [$C_{20}H_{18}N_2O_3SH^+$], 497.1 (21) [$C_{29}H_{24}N_2O_4SH^+$], 519.2 (100) [$C_{29}H_{24}N_2O_4SNa^+$], 535.2 (7) [$C_{29}H_{24}N_2O_4SK^+$], 764.2 (10) [$(C_{29}H_{24}N_2O_4S)_3HK^{2+}$], 1014.9 (19) [$(C_{29}H_{24}N_2O_4S)_2Na^+$], 1031.0 (17) [$(C_{29}H_{24}N_2O_4S)_2K^+$]. elemental analysis for $C_{29}H_{24}N_2O_4S$ (496.58 g/mol): calcd.: C 70.14, H 4.87, N 5.64, S 6.46 found: C 69.94, H 4.89, N 5.68, S 6.46.

2-(phenyl(2-tosylhydrazono)methyl)phenyl 4-nitrocinnamate (0^{TH}-Ph^{NO2}): creamy solid, yield: 61%. ^{1}H NMR ($CDCl_3$): δ = 2.27 (s, 3H, C*H*$_3$), 6.20 (d, $^3J_{HH}$ = 16.1 Hz, 1H, CHC*H*CO), 7.21–7.49 (m, 11H, H_{Ar}, C_{Ar}C*H*CH), 7.53 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H_{Ar}), 7.60 (t, $^3J_{HH}$ = 7.8 Hz, 1H, H_{Ar}), 7.73 (s, 1H, N*H*), 7.91 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H_{Ar}), 8.24 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 21.7 (*C*H$_3$), 120.2 (CH*C*HCO), 123.6 (C_{ar}H), 124.3 (C_{Ar}H), 125.2 (C_{Ar}), 127.3 (C_{Ar}H), 127.7 (C_{Ar}H), 128.5 (C_{Ar}H), 128.5 (C_{Ar}H), 129.0 (C_{Ar}H), 129.5 (C_{Ar}H), 130.1 (C_{Ar}H), 130.3 (C_{Ar}H), 131.9 (C_{Ar}H), 135.6 (C_{Ar}), 136.0 (C_{Ar}), 139.9 (C_{Ar}), 143.9 (C_{Ar}), 144.2 (C_{Ar}CHCH), 148.0 (C_{Ar}O), 148.9 (C_{Ar}N), 150.6 ($C_{Ar}CNC_{Ar}$), 164.3 (CH*C*OO). ESI-MS: *m/z* (%): 542.2 (56) [$C_{29}H_{23}N_3O_6SH^+$], 564.2 (100) [$C_{29}H_{23}N_3O_6SNa^+$], 1105.0 (47) [$(C_{29}H_{23}N_3O_6S)_2Na^+$], 1121.1 (41) [$(C_{29}H_{23}N_3O_6S)_2K^+$]. elemental analysis for $C_{29}H_{23}N_3O_6S$ (541.57 g/mol): calcd.: C 64.31, H 4.28, N 7.76, S 5.92 found: C 63.97, H 4.33, N 7.64, S 5.73.

2.4. General procedure for the synthesis of diazo compounds

1.42 mmol tosyl hydrazone was added to 34.1 mg (1.42 mmol) NaH in 10 ml thf at 0 °C, warmed to ambient temperature and stirred over night. The solvent was removed in vacuo, the residue taken up in 15 ml toluene and heated to 75 °C for 45 min. Again the solvent was removed in vacuo afterwards, the residue extracted with pentane and filtrated until the filtrate was colorless. The diazo compounds were isolated by removal of the solvent in vacuo.

2-(diazo(phenyl)methyl)phenyl crotonate (1-Me): red oil, yield: 43%. ^{1}H NMR ($CDCl_3$): δ = 1.87 (d, ^3J**HH** = 6.9 Hz, 3H, *C*H$_3$), **5.89** (dd, $^3J_{HH}$ = 1.7 Hz, $^3J_{HH}$ = 15.5 Hz, 1H, CHC*H*CO), 7.00 (dq, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 15.5 Hz, 1H, CH$_3$C*H*CH), 7.07–7.13 (m, 2H, H_{Ar}), 7.20–7.36 (m, 6H, H_{Ar}), 7.42–7.46 (m, 1H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 18.4 (*C*H$_3$), 121.5 (C_{Ar}H), 122.3 ($C_{Ar}CNC_{Ar}$), 123.8 (C_{Ar}H), 123.9 (CH*C*HCO), 124.9 (C_{Ar}H), 126.5 (C_{Ar}H), 128.5 (C_{Ar}H), 129.1 (C_{Ar}H), 130.0 (C_{Ar}H), 130.3 (C_{Ar}), 130.5 (C_{Ar}), 147.5 (CH$_3$*C*HCH), 148.5 (C_{Ar}O), 164.3 (CH*C*OO). FT-IR (KBr plates, cm^{-1}): 3089 (w), 3060 (m), 3030 (w), 2925 (m), 2851 (m), 2046 (s, N_2), 1970 (w), 1737 (s, CO), 1654 (s), 1597 (m), 1500 (w), 1494 (s), 1440 (s), 1381 (w), 1299 (s), 1254 (m), 1194 (m), 1149 (m), 1090 (m), 1030 (w), 976 (s), 910 (w), 828 (w), 816 (m), 814 (w), 753 (m), 693 (m), 647 (m), 579 (m), 523 (w), 477 (m). UV/vis (pentane, nm): 208 (s, Ar), 286 (s, N_2).

2-(diazo(phenyl)methyl)phenyl 4-methoxycinnamate (1-Ph^{OMe}): red oil, yield: 49%. ^{1}H NMR ($CDCl_3$): δ = 3.85 (s, 3H, OC*H*$_3$), 6.32 (d, $^3J_{HH}$ = 16.0 Hz, 1H, CHC*H*CO), 6.91(d, $^3J_{HH}$ = 8.7 Hz, 2H, H_{Ar}), 7.06–7.14 (m, 3H, H_{Ar}), 7.24–7.39 (m, 6H, H_{Ar}), 7.41–7.49 (m, 2H, H_{Ar}), 7.63 (d, $^3J_{HH}$ = 16.0 Hz, 1H, C_{Ar}C*H*CH). ^{13}C NMR ($CDCl_3$): δ = 55.6 (O*C*H$_3$), 114.1 (CH*C*HCO), 114.5 (C_{Ar}H), 122.2 (C_{Ar}), 123.8 (C_{Ar}H), 123.9 (C_{Ar}H), 124.9 (C_{Ar}H), 126.5 (C_{Ar}H), 127.0 (C_{Ar}), 128.4 (C_{Ar}), 128.5 (C_{Ar}H), 129.1 (C_{Ar}H), 129.9 (C_{Ar}H), 130.2 (C_{Ar}H), 146.6 (C_{Ar}CHCH), 148.6 (C_{Ar}O), 161.9 (C_{Ar}OCH$_3$), 165.2 (CH*C*OO). FT-IR (KBr plates, cm^{-1}): 3066 (m), 3036 (m), 2954 (m), 2931 (m), 2842

(m), 2046 (s, N_2), 1726 (s, CO), 1636 (m), 1602 (s), 1568 (w), 1512 (m), 1486 (m), 1442 (m), 1419 (w), 1307 (m), 1255 (m), 1195 (m), 1173 (w), 1128 (s), 1030 (m), 982 (m), 919 (w), 852 (w), 828 (m), 777 (m), 694 (m), 665 (w), 636 (w), 568 (w), 553 (m), 509 (m). UV/vis (pentane, nm): 208 (s, Ar), 227 (s, Ar), 293 (s, N_2).

2-(diazo(phenyl)methyl)phenyl 4-methylcinnamate (1-Ph^{Me}): red oil, yield: 25%. ^{1}H NMR ($CDCl_3$): δ = 2.38 (s, 3H, CH_3), 6.40 (d, $^3J_{HH}$ = 16.0 Hz, 1H, CHC*H*CO), 7.07–7.13 (m, 3H, H_{Ar}), 7.20 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H_{Ar}), 7.27–7.42 (m, 7H, H_{Ar}), 7.47 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H_{Ar}), 7.64 (d, $^3J_{HH}$ = 16.0 Hz, 1H, C_{Ar}C*H*CH). ^{13}C NMR ($CDCl_3$): δ = 21.7 (*C*H$_3$), 155.6 (CHCHCO), 122.3 (*C*Ar), 123.8 (C_{Ar}H), 123.9 (C_{Ar}H), 124.9 (C_{Ar}H), 126.5 (C_{Ar}H), 128.5 (C_{Ar}H), 129.1 (C_{Ar}H), 129.8 (C_{Ar}H), 130.0 (C_{Ar}H), 130.5 (C_{Ar}), 131.6 (C_{Ar}), 141.4 (C_{Ar}), 147.0 (C_{Ar}CHCH), 148.6 (C_{Ar}O), 165.0 (CHCOO). FT-IR (KBr plates, cm^{-1}): 3029 (w), 2925 (s), 2850 (m), 2043 (s, N_2), 1730 (s, CO), 1687 (w), 1628 (m), 1599 (m), 1496 (m), 1449 (m), 1411 (w), 1374 (w), 1314 (w), 1269 (w), 1240 (s), 1195 (s), 1180 (s), 1142 (w), 1098 (w), 1031 (w), 987 (m), 946 (m), 919 (m), 866 (w), 815 (m), 753 (m), 697 (m), 628 (w), 499 (m), 473 (w). UV/vis (pentane, nm): 208 (m, Ar), 222 (m, Ar), 286 (s, N_2).

2-(diazo(phenyl)methyl)phenyl cinnamate (1-Ph): red oil, yield: 34%. ^{1}H NMR ($CDCl_3$): δ = 6.44 (d, $^3J_{HH}$ = 16.0 Hz, 1H, CHC*H*CO), 7.04–7.17 (m, 2H, H_{Ar}), 7.25–7.42 (m, 5H, H_{Ar}), 7.44–7.52 (m, 2H, H_{Ar}), 7.66 (d, $^3J_{HH}$ = 16.0 Hz, 1H, C_{Ar}C*H*CH). ^{13}C NMR ($CDCl_3$): δ = 116.8 (CHCHCO), 122.3 (C_{Ar}CNC$_{Ar}$), 123.8 (C_{Ar}H), 123.9 (C_{Ar}H), 125.0 (C_{Ar}H), 126.7 (C_{Ar}H), 128.5 (C_{Ar}H), 128.6 (C_{Ar}H), 128.9 (C_{Ar}), 129.1 (C_{Ar}H), 129.2 (C_{Ar}H), 130.0 (C_{Ar}H), 130.5 (C_{Ar}), 130.9 (C_{Ar}H), 134.3 (C_{Ar}), 147.0 (C_{Ar}CHCH), 148.5 (C_{Ar}O), 164.9 (CHCOO). FT-IR (KBr plates, cm^{-1}): (m), 3029 (m), (w), 2925 (m), 2856 (w), 2045 (vs, N_2), 1957 (w), 1732 (vs, CO), 1666 (w), 1634 (s), 1597 (m), 1577 (w), 1496 (s), 1449 (s), 1308 (s), 1235 (s), 1193 (s), 1133 (s), 1100 (w), 1029 (w), 979 (s), 949 (w), 945 (w), 916 (w), 860 (m), 751 (s), 693 (s), 619 (m), 577 (w), 561 (w), 473 (m). UV/vis (pentane, nm): 208 (s, Ar), 282 (s, N_2).

2-(diazo(phenyl)methyl)phenyl 4-nitrocinnamate (1-Ph^{NO2}): orange solid, yield: 39%, extraction with Et_2O instead of pentane. ^{1}H NMR ($CDCl_3$): δ = 6.54 (d, $^3J_{HH}$ = 16.0 Hz, 1H, CHCHCO), 7.05–7.13 (m, 3H, H_{Ar}, C_{Ar}C*H*CH), 7.27–7.40 (m, 6H, H_{Ar}), 7.48 (d, $^3J_{HH}$ = 7.5 Hz, 1H, H_{Ar}), 7.60–7.69 (m, 2H, H_{Ar}), 8.25 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 121.0 (*C*HCOO), 122.1 (C_{Ar}), 123.7 (C_{Ar}H), 123.9 (C_{Ar}H), 124.3 (C_{Ar}H), 125.1 (C_{Ar}H), 126.9 (C_{Ar}H), 128.5 (C_{Ar}CNC$_{Ar}$), 128.6 (C_{Ar}H), 129.0 (C_{Ar}H), 129.1 (C_{Ar}H), 130.1 (C_{Ar}H), 130.3 (C_{Ar}), 140.2 (C_{Ar}), 143.7 (C_{Ar}CHCH), 148.2 (C_{Ar}O), 148.8 (C_{Ar}N), 163.8 (CHCOO). FT-IR (KBr plates, cm^{-1}): 3091 (m), 2942 (m), 2852 (m), 2046 (s, N_2), 1734 (s, CO), 1643 (w), 1598 (m), 1520 (s), 1486 (m), 1449 (w), 1404 (w), 1345 (s), 1237 (w), 1199 (m), 1140 (m), 976 (w), 844 (w), 755 (m), 699 (m), 662 (w), 579 (w). UV/vis (pentane, nm): 208 (s, Ar), 291 (s, N_2).

2.5. Irradiation

General irradiation conditions:

Irradiations were performed in a Rayonet RPR-100 reactor (Southern New England Ultra Violet Company, Connecticut, USA) using RPR-4190 Å and RPR-3000 Å fluorescent lamps [10].

General preparative irradiation procedure:

50 mg diazo compound was dissolved in 20 ml dry, degased toluene and distributed evenly into four Duran irradiation tubes under argon and the reaction mixture was irradiated at the given wavelength (300 nm: RPR-3000 Å; 419 nm: RPR-4190 Å) for 2 h. After removal of the solvent under reduced pressure the products were separated by flash chromatography (SiO_2; 9:1 pentane/Et_2O).

General analytical irradiation procedure:

10 mg diazo compound was dissolved in 4 ml of the desired dry, degased solvent in a Duran irradiation tube under argon and the reaction mixture was irradiated at the given wavelength (300 nm: RPR-3000 Å; 419 nm: RPR-4190 Å) for the stated time. After removal of the solvent under reduced pressure the crude product mixture was dissolved in $CDCl_3$ and the NMR measurement was performed.

Concentrations:

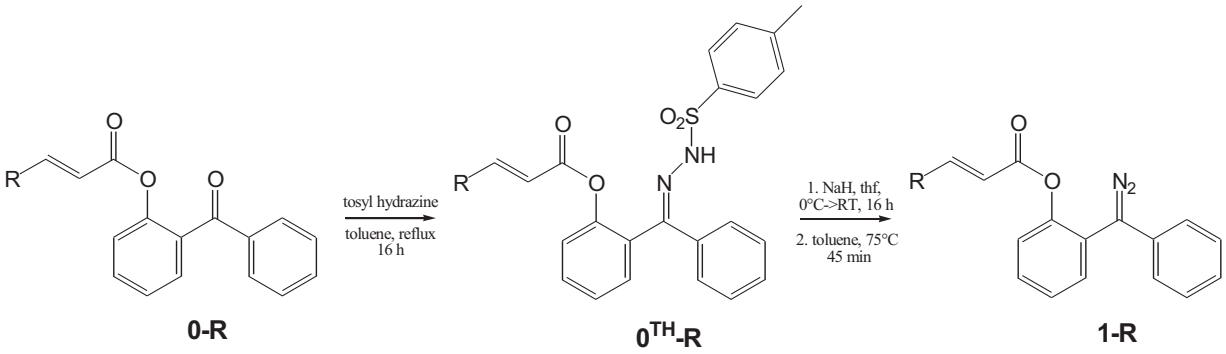
1-*p*-anisyl: 0.0067 mol/l;
1-*p*-tolyl: 0.0071 mol/l;
1-phenyl: 0.0073 mol/l;
1-*p*-nitrophenyl: 0.0065 mol/l;
1-Me: 0.0090 mol/l.

1-(4-Methoxyphenyl)-7b-phenyl-1,1a-dihydrocyclopropa[c]chromen-2(7bH)-one (2-Ph^{OMe}): white solid, R_f = 0.35. ^{1}H NMR ($CDCl_3$): δ = 2.80 (d, $^3J_{HH}$ = 4.8 Hz, 1H, CHC*H*CO), 3.04 (d, $^3J_{HH}$ = 4.8 Hz, 1H, C_{Ar}C*H*CH), 3.73 (s, 3H, OCH_3), 6.82–7.22 (m, 9H, H_{Ar}), 7.29–7.55 (m, 6H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 31.9 (*C*HCOO), 38.3 (C_{Ar}CHCH), 41.8 (C_{Ar}C), 55.4 (OCH_3), 113.8 (C_{Ar}H), 114.6 (C_{Ar}), 117.8 (C_{Ar}H), 124.4 (C_{Ar}H), 126.2 (C_{Ar}), 127.6 (C_{Ar}H), 128.2 (C_{Ar}H), 128.7 (C_{Ar}H), 128.9 (C_{Ar}H), 130.0 (C_{Ar}), 132.1 (C_{Ar}H), 135.0 (C_{Ar}H), 149.5 (C_{Ar}O), 158.8 (C_{Ar}O), 166.1 (CHCOO). ESI-MS: *m*/*z* (%): 313.3 (100) [$C_{21}H_{17}O_2H^+$], 343.3 (27) [$C_{23}H_{18}O_3H^+$]. FT-IR (KBr plates, cm^{-1}): 2953 (m), 2924 (m), 2834 (w), 1749 (s, CO), 1606 (m), 1515 (s), 1455 (m), 1249 (s), 1032 (m), 829 (w), 757 (m), 702 (m).

1,7b-Diphenyl-1,1a-dihydrocyclopropa[c]chromen-2(7bH)-one (2-Ph): white solid, R_f = 0.60. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a saturated $CHCl_3$ solution. ^{1}H NMR ($CDCl_3$): δ = 2.85 (d, $^3J_{HH}$ = 5.4 Hz, 1H, CHC*H*CO), 3.14 (d, $^3J_{HH}$ = 5.4 Hz, 1H, C_{Ar}C*H*CH), 6.70–6.80 (m, 2H, H_{Ar}), 2.80–2.91 (m, 2H, H_{Ar}), 7.07–7.19 (m, 6H, H_{Ar}), 7.20–7.30 (m, 4H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 31.8 (CHCOO), 38.7 (C_{Ar}CHCH), 42.1 (C_{Ar}C), 117.8 (C_{Ar}H), 124.4 (C_{Ar}H), 125.6 (C_{Ar}), 127.2 (C_{Ar}H), 127.7 (C_{Ar}H), 127.9 (C_{Ar}H), 128.2 (C_{Ar}H), 128.3 (C_{Ar}H), 128.3 (C_{Ar}H), 128.7 (C_{Ar}H), 132.0 (C_{Ar}H), 134.4 (C_{Ar}H), 134.9 (C_{Ar}H), 149.5 (C_{Ar}H), 166.0 (CHCOO). ESI-MS: *m*/*z* (%): 283.3 (100) [$C_{21}H_{14}OH^+$], 313.2 (38) [$C_{22}H_{16}O_2H^+$], 378.3 (28) [$C_{24}H_{19}NO_2Na^+$]. FT-IR (KBr plates, cm^{-1}): 3061 (m), 2923 (m), 1757 (vs, CO), 1604 (w), 1486 (m), 1453 (m), 1211 (s), 1112 (w), 957 (w), 750 (s), 699 (s), 571 (w).

1-(4-Nitrophenyl)-7b-phenyl-1,1a-dihydrocyclopropa[c]chromen-2(7bH)-one (2-Ph^{NO2}): yellow solid, R_f = 0.24, eluent (9:2 pentane/Et_2O). ^{1}H NMR ($CDCl_3$): δ = 2.92 (d, $^3J_{HH}$ = 5.2 Hz, 1H, CHC*H*CO), 3.21 (d, $^3J_{HH}$ = 5.2 Hz, 1H, C_{Ar}C*H*CH), 6.87 (d, $^3J_{HH}$ = 8.5 Hz, 2H, H_{Ar}), 6.97–7.21 (m, 5H, H_{Ar}), 7.27–7.54 (m, 4H, H_{Ar}), 7.99 (d, $^3J_{HH}$ = 8.5 Hz, 2H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 29.9 (*C*HCOO), 38.0 (C_{Ar}CHCH), 43.1 (C_{Ar}C), 118.0 (C_{Ar}H), 123.4 (C_{Ar}H), 124.7 (C_{Ar}H), 127.7 (C_{Ar}H), 128.5 (C_{Ar}H), 128.8 (C_{Ar}H), 128.9 (C_{Ar}H), 129.1 (C_{Ar}H), 129.2 (C_{Ar}), 131.8 (C_{Ar}H), 133.8 (C_{Ar}), 142.5 (C_{Ar}), 147.0 (C_{Ar}N), 149.4 (C_{Ar}O), 165.0 (CHCOO). ESI-MS: *m*/*z* (%): 282.3 (100) [$C_{21}H_{13}OH^+$], 328.2 (29) [$C_{21}H_{13}NO_3H^+$], 358.2 (10) [$C_{22}H_{15}NO_4H^+$]. FT-IR (KBr plates, cm^{-1}): 2925 (s), 1760 (s, CO), 1602 (m), 1520 (s), 1455 (w), 1345 (s), 1213 (m), 1110 (w), 853 (w), 760 (s), 703 (s).

2-(4-Methoxyphenyl)-7b-phenyl-2,2a-dihydrobenzo[d]cyclobuta[b]furan-1(7bH)-one (3-Ph^{OMe}): white solid, R_f = 0.65. ^{1}H NMR ($CDCl_3$): δ = 3.78 (s, 3H, OCH_3), 4.76 (d, $^3J_{HH}$ = 3.7 Hz, 1H, C*H*CHO), 5.43 (d, $^3J_{HH}$ = 3.7 Hz, 1H, CHC*H*O), 6.87 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_{Ar}), 6.96 (t, $^3J_{HH}$ = 7.4 Hz, 1H, H_{Ar}), 7.04 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H_{Ar}), 7.15–7.23 (m, 3H, H_{Ar}), 7.26–7.31 (m, 2H, H_{Ar}), 7.32–7.43 (m, 4H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 55.5 (OCH_3), 69.7 (*C*HCHO), 80.4 (CHCCO), 85.5 (CHCHO), 111.8 (C_{Ar}H), 114.6 (C_{Ar}H), 122.4 (C_{Ar}H), 126.0 (C_{Ar}H), 126.1 (C_{Ar}), 126.3 (C_{Ar}H), 127.6 (C_{Ar}), 128.0 (C_{Ar}H), 128.6 (C_{Ar}H), 129.1 (C_{Ar}H), 130.4 (C_{Ar}H), 137.3 (C_{Ar}), 159.2 (C_{Ar}O), 159.6 (C_{Ar}O), 203.0 (CCOCH). ESI-MS: *m*/*z* (%): 313.3 (100) [$C_{21}H_{17}O_2H^+$]. FT-IR (KBr plates, cm^{-1}): 2957 (w), 2927 (m),



0-R **0^{TH}-R** **1-R**

R	Yield [%]
Me	67
Ph^{OMe}	86
Ph^{Me}	67
Ph	53
Ph^{NO2}	61

R	Yield [%]
Me	43
Ph^{OMe}	49
Ph^{Me}	25
Ph	34
Ph^{NO2}	39

Scheme 2.

2830 (w), 1779 (s, CO), 1607 (s), 1513 (s), 1461 (m), 1251 (s), 1179 (w), 1068 (m), 1031 (m), 831 (w), 753 (m), 699 (w).

2,7b-Diphenyl-2,2a-dihydrobenzo[d]cyclobuta[b]furan-1(7bH)-one (3-Ph): white solid, R_f = 0.86. ^{1}H NMR ($CDCl_3$): δ = 4.69 (d, $^3J_{HH}$ = 3.3 Hz, 1H, *CH*CHO), 5.35 (d, $^3J_{HH}$ = 3.3 Hz, 1H, CHCHO), 6.83 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H_{Ar}), 6.90 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H_{Ar}), 7.06–7.29 (m, 12H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 70.2 (*C*HCHO), 80.5 (*C*CO), 85.1 (CHCHO), 111.8 (C_{Ar}H), 122.4 (C_{Ar}H), 126.0 (C_{Ar}H), 126.3 (C_{Ar}H), 127.5 (C_{Ar}H), 127.6 (C_{Ar}), 127.8 (C_{Ar}H), 128.0 (C_{Ar}H), 129.1 (C_{Ar}H), 129.2 (C_{Ar}H), 130.4 (C_{Ar}H), 134.0 (C_{Ar}), 137.2 (C_{Ar}), 159.6 (C_{Ar}O), 202.5 (*C*COCH). ESI-MS: *m*/*z* (%): 283.4 (100) [$C_{21}H_{14}OH^+$]. FT-IR (KBr plates, cm^{-1}): 3064 (w), 2929 (w), 1780 (s, CO), 1604 (m), 1495 (w), 1472 (w), 1461 (w), 1223 (m), 1063 (w), 752 (s), 697 (s).

2,8-Diphenyl-2,2a-dihydrooxeto[3,2-*b*]chromene (4-Ph): white solid, irradiation time: 4 h. ^{1}H NMR ($CDCl_3$): δ = 5.73 (s, 1H, *CH*O), 5.85 (s, 1H, *CH*C_{Ar}), 6.71–6.84 (m, 2H, H_{Ar}), 6.89–7.03 (m, 3H, H_{Ar}), 7.21–7.34 (m, 6H, H_{Ar}), 7.37–7.47 (m, 3H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 77.1 (*C*HO), 109.6 (*C*HC$_{Ar}$), 116.7 (CH*C*O), 121.2 (C_{Ar}H), 123.4 (C_{Ar}H), 126.0 (C_{Ar}H), 127.4 (C_{Ar}H), 128.1 (C_{Ar}H), 128.5 (C_{Ar}H), 128.8 (C_{Ar}H), 128.9 (C_{Ar}H), 129.4 (C_{Ar}), 129.7 (C_{Ar}H), 131.1 (C_{Ar}H), 136.9 (C_{Ar}), 138.2 (C_{Ar}), 140.7 (C_{Ar}CC_{Ar}), 153.9 (C_{Ar}O). ESI-MS: *m*/*z* (%): 283.3 (100) [$C_{21}H_{14}OH^+$]. FT-IR (KBr plates, cm^{-1}): 3080 (m), 3050 (m), 2931 (m), 1736 (m), 1602 (m), 1479 (s), 1449 (s), 1263 (m), 1196 (s), 1061 (m), 750 (s), 698 (s).

(Z)-6-((E)-2-oxo-1-phenylpent-3-enylidene)cyclohexa-2,4-dienone (6): white solid, R_f = 0.2. ^{1}H NMR ($CDCl_3$): δ = 1.87 (d, $^3J_{HH}$ = 7.2 Hz, 3H, C*H*$_3$), 6.53 (d, $^3J_{HH}$ = 15.2 Hz, 1H, CHC*H*CO), 6.77 (dq, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 15.2 Hz, 1H, CH_3C*H*CH), 7.27–7.61 (m, 7H, H_{Ar}), 7.75 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ = 18.7 (CH_3), 128.5 (C_{Ar}H), 128.9 (C_{Ar}H), 129.0 (C_{Ar}H), 129.9 (C_{Ar}H), 130.0 (C_{Ar}H), 130.1 (C_{Ar}H), 131.0 (C_{Ar}H), 133.1 (CHCHCO), 137.4 (C_{Ar}), 139.5 (C_{Ar}), 140.6 (C_{Ar}), 146.7 (CH_3*C*HCH), 192.9 (*C*O), 197.4 (*C*O). ESI-MS: *m*/*z* (%): 209.2 (50) [$C_{14}H_9O_2^+$], 233.2 (53) [$C_{17}H_{13}O^+$], 251.1 (100) [$C_{17}H_{14}O_2H^+$]. FT-IR (KBr plates, cm^{-1}): 3070 (w), 3040 (w), 2980 (w), 2936 (w), 1667 (s, CO), 1621 (m), 1448 (m), 1284 (s), 1147 (w), 969 (w), 931 (m), 760 (m), 704 (m), 637 (w).

3. Results and discussion

3.1. Synthesis of diphenyl diazomethane olefin esters (*1-R*)

We chose the synthesis route shown in Scheme 2 to synthesize our starting material **1-R**.

The synthesis of benzophenyl-2-esters **0-R** from the alcohol and the adequate acid chloride, following standard literature procedures [11], gave the anticipated esters in good to excellent yields.

The ester **0-R** was then reacted with tosyl hydrazine. In contrast to the common procedures [13,14] no alcohols could be used as solvent in this reaction because of ester cleavage. A procedure by Jones et al. [15] using CH_2Cl_2 as solvent resulted in no conversion. Therefore, a synthesis by Guldi et al. [16] was modified and the ester and tosyl hydrazine were refluxed in toluene over night in the presence of catalytic amounts of toluene sulfonic acid to result in the desired tosyl hydrazones in good yields.

The synthesis of the diazo compounds was achieved, via the Bamford–Stevens reaction [17], by deprotonation of the hydrazone with sodium hydride over night and subsequent thermal rearrangement by a modified procedure of Tomioka et al. [18]. Due to the low volatility of the diazo esters these could not be separated by distillation and therefore heating had to be performed in toluene, not neat, and extraction with pentane or diethyl ether depending on the solubility of the ester had to be performed. The hydrazide salt is isolable and can be stored under an argon atmosphere, but direct conversion of the deprotonation residue after removal of the solvent in vacuo proved successful without loss of yields.

The received diazo esters are stable in air. They can be handled in air at ambient temperature and stored at −35 °C in air without any decomposition even after months. However at ambient temperature they decompose slowly in substance and within days in solution. In the FT-IR spectra two prominent bands are observed, the one around 1730 cm^{-1} being assigned to the C=O stretching frequency of the carboxyl C=O double bond and the one at around 2045 cm^{-1} to the typical N≡N stretching vibration [19].

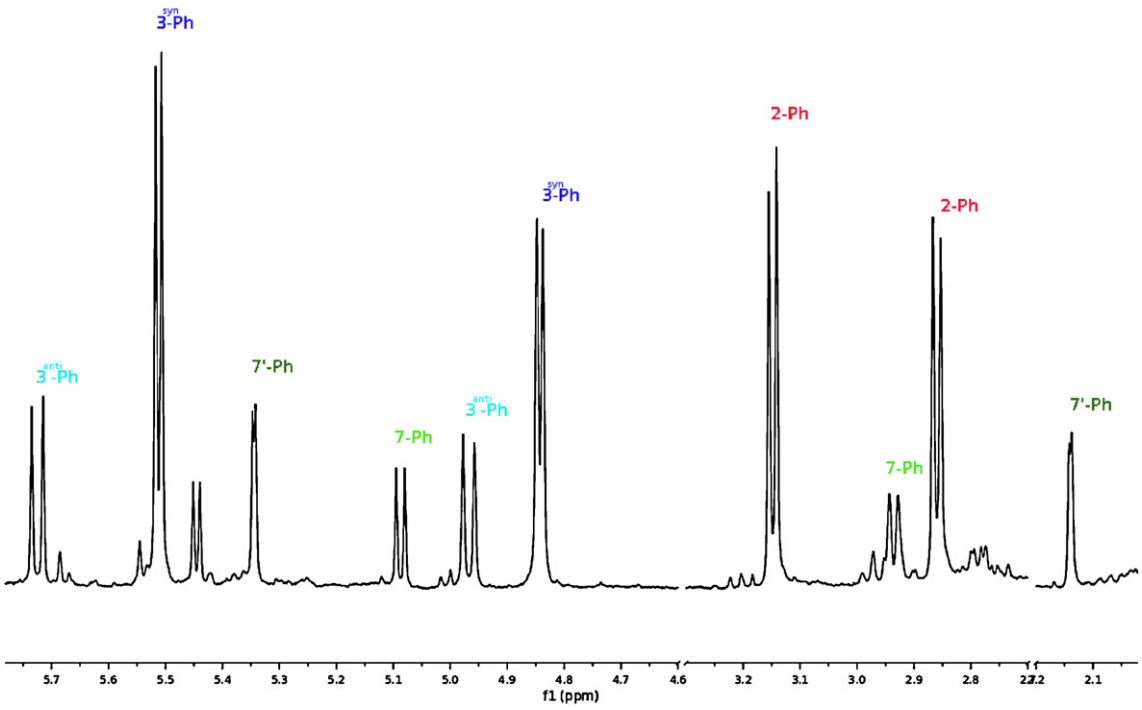


Fig. 1. ^{1}H NMR spectrum excerpt of a sample of **1-Ph** irradiated at 300 nm for 1 h (products **7-Ph** and **7′-Ph** are explained below in the text).

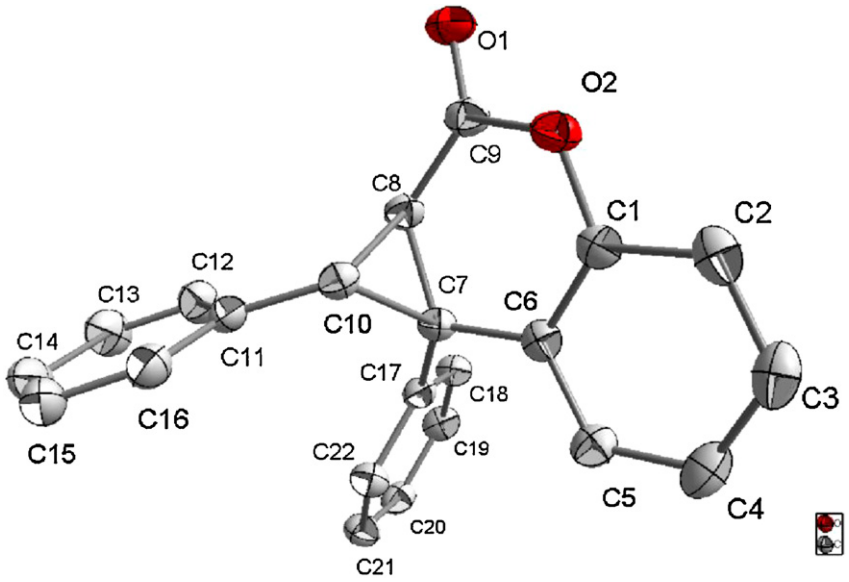


Fig. 2. ORTEP [12] representation of cyclopropane **2-Ph**. Thermal ellipsoids are given at 50% probability level. Hydrogen atoms are omitted for clarity.

All substances where isolated as red solids or oils showing absorption bands in the aromatic region of the UV/vis range as well as at around 290 nm. The latter absorption band is caused by the diazo group (Table 1).

Table 1
Selected UV/vis bands of diazo esters.

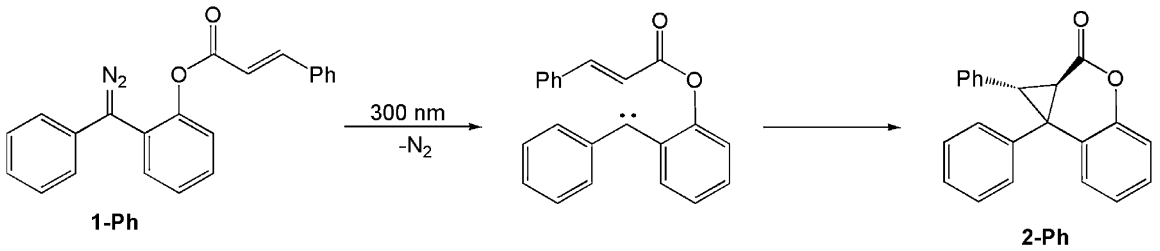
	N_2 (nm)
1-Me	286
1-Ph^{OMe}	293
1-Ph^{Me}	286
1-Ph	282
1-Ph^{NO2}	291

3.2. Irradiation experiments with *1-Ph*

On irradiation of **1-Ph** at 300 nm, which was chosen due to its proximity to the absorption frequency of the diazo group, for 1 h, several different products were obtained, whereof three are shown in the detail of the ^{1}H NMR spectrum in Fig. 1 (**3-Ph** and **7-Ph** with two diastereomers).

Compound **2-Ph** could be isolated and single crystals of it suitable for X-ray diffraction analysis could be gained by slow evaporation of a concentrated chloroform solution. Fig. 2 shows the depiction of a molecule in the solid state.

On this basis **2-Ph** could be unequivocally proven to be the expected irradiation product, resulting from the elimination of N_2



Scheme 3.

on irradiation followed by the attack of the generated carbene on the C=C double bond (Scheme 3).

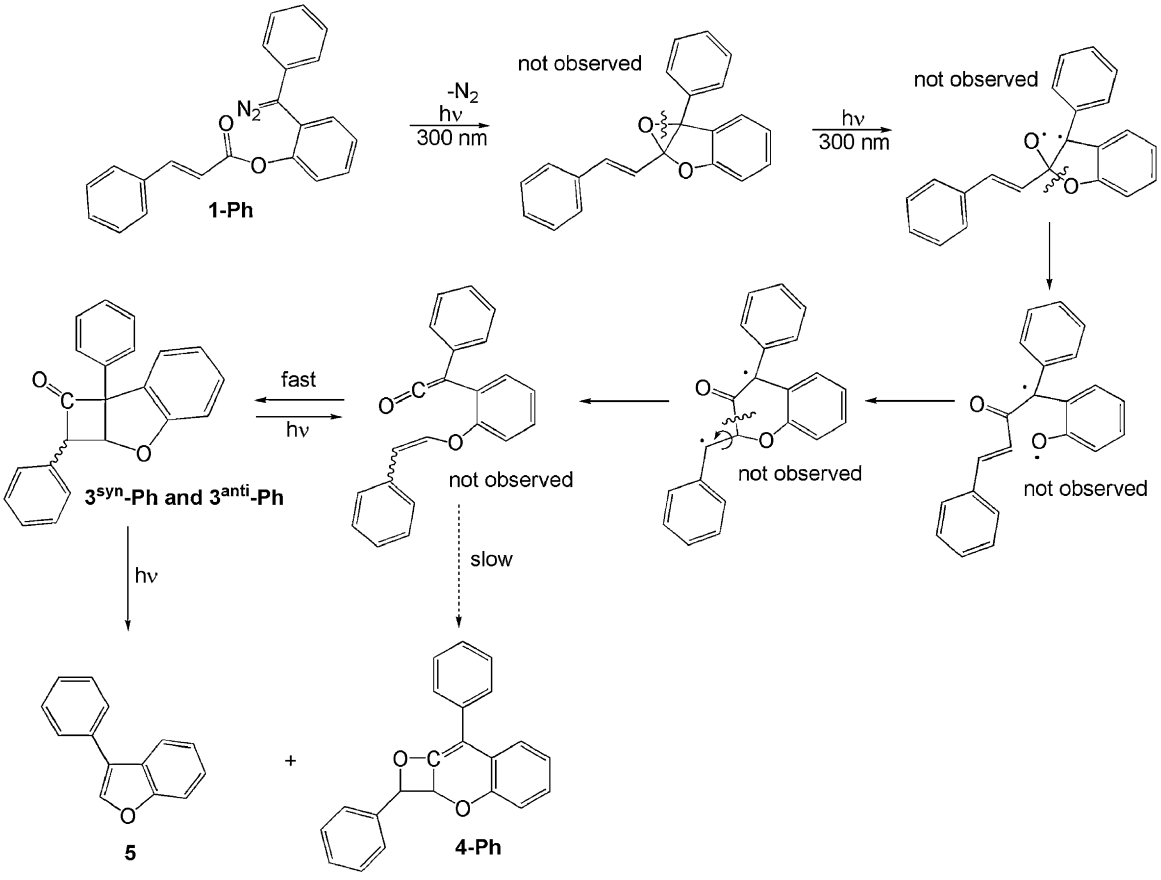
The chemical shifts of 2.9 ppm and 3.1 ppm in the ^{1}H NMR spectra ($^{3}J_{HH}$ = 5 Hz) are typical for ester substituted cyclopropanes as is the shift of 31 ppm, 38 ppm and 42 ppm in ^{13}C NMR spectroscopy [20]. The carbonyl stretching frequency at ca. 1760 cm^{-1} is in the typical range of six membered lactones [21]. All cyclopropanes **2-R** were isolated as colorless solids and show similar spectroscopic properties to **2-Ph**.

A second product (**3^{syn}-Ph** and **3^{anti}-Ph)** present in larger amount in the irradiation mixture (Fig. 1) could be isolated by column chromatography. These signals are assigned to the two possible syn/anti-diastereomers of the cyclobutanone **3-Ph** shown in Scheme 1 on the basis of our NMR and IR spectroscopic as well as ESI-MS results. These cyclobutanones show extreme low field shifts for the two hydrogen atoms tethered to the four-membered ring as expected for phenyl substituted annellated keto ethers. The major diastereomer shows $^{3}J_{HH}$ coupling constants of 3.3 Hz. The $^{3}J_{HH}$ coupling constant for the minor diastereomer is 7.8 Hz. On this basis we conclude that the major diastereoisomer is substituted in a syn-configuration concerning the cyclobutyl hydrogens, while the minor diastereomer is anti-substituted. The structure assignment is further supported by COSY, HMQC and HMBC spectroscopy. The C=O stretching vibration of 1780 cm^{-1} is in the range expected for four-membered cyclic ketones [21].

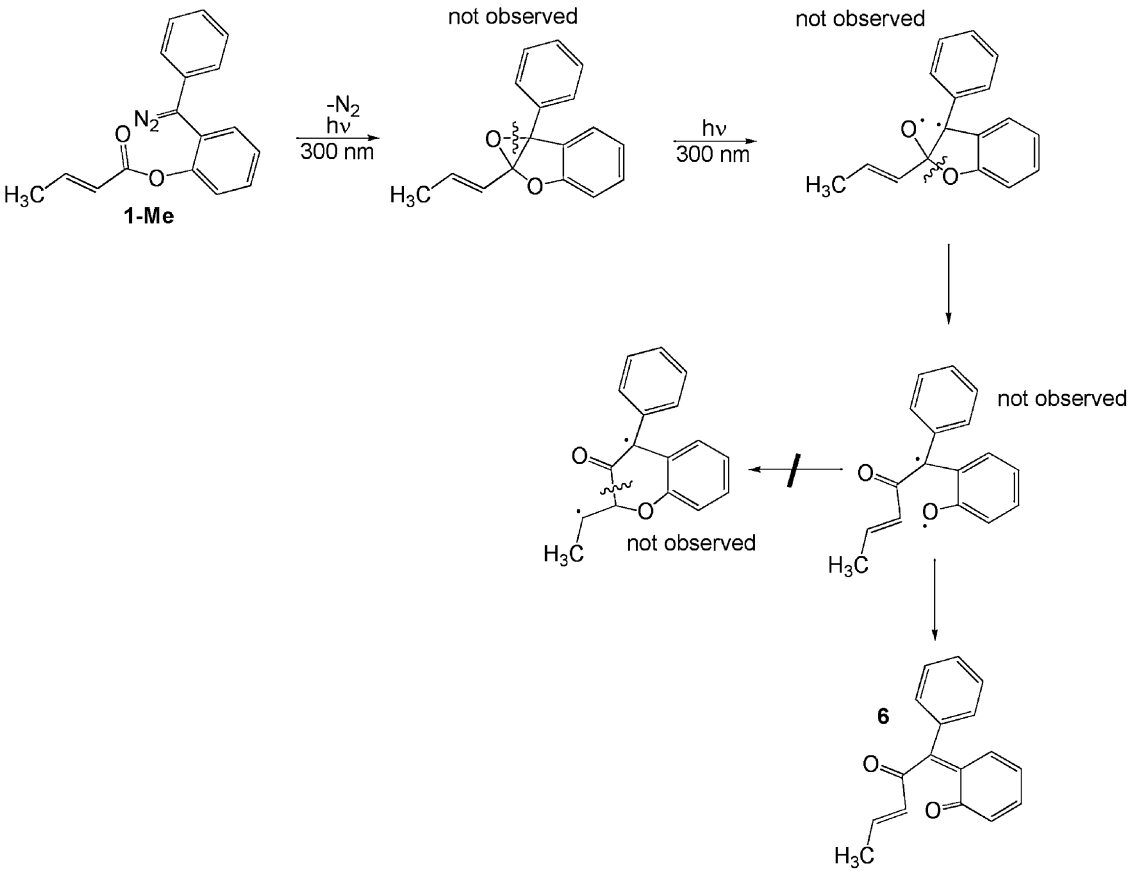
We propose the reaction cascade in Scheme 4 to explain the formation of **3^{syn}-Ph** and **3^{anti}-Ph**.

The generated carbene reacts with the C=O double bond rather than with the C=C double bond. The formed epoxide is radically opened on further irradiation releasing ring strain and yielding in two mesomerically stabilized radicals and a C=O double bond. The phenoxy radical attacks the C=C double bond which again leads to a mesomerically stabilized benzylic radical from which a ketene and a C=C double bond is reformed. This compound undergoes a [2+2] cycloaddition to generate **3^{syn}-Ph** and **3^{anti}-Ph**. Support for the correctness of this sequence is found by the fact that if **1-Me** is irradiated, instead of **3^{syn}-Me** and **3^{anti}-Me** the only product found is compound **6** in Scheme 5.

Compound **6** could be isolated by column chromatography and is assigned on the basis of the ^{1}H and ^{13}C NMR and IR



Scheme 4.



Scheme 5.

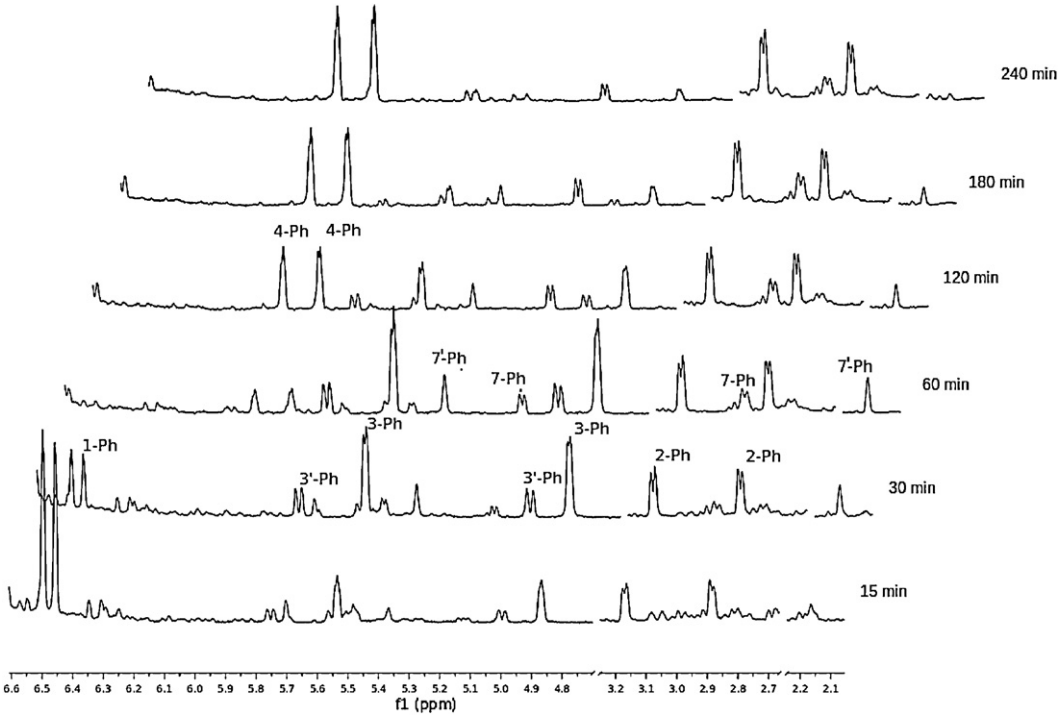
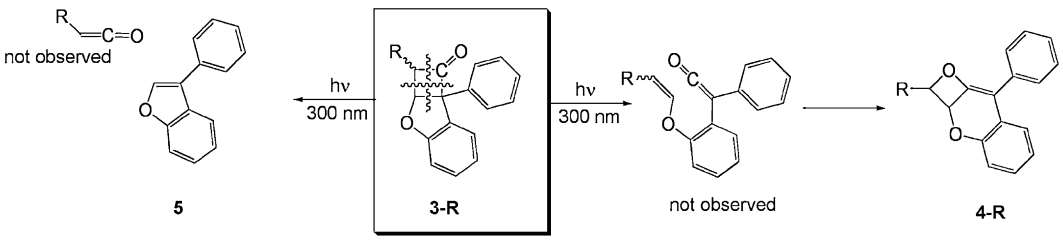


Fig. 3. ^{1}H NMR of the reaction progress on irradiation of **1-Ph**.



Scheme 6.

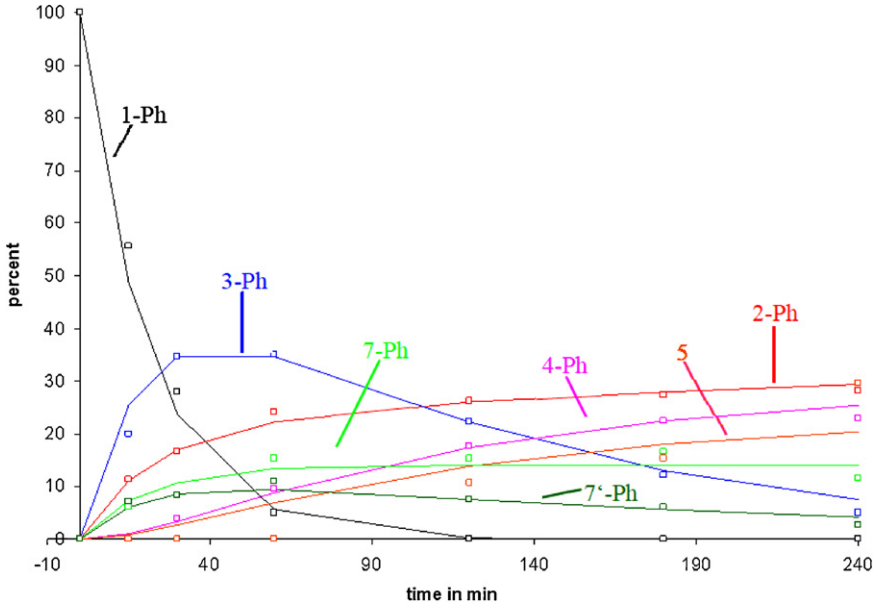


Fig. 4. Time conversion plot for the irradiation of diazo compound **1-Ph** at 300 nm in toluene.

spectroscopic results as well as ESI-MS. In case of a methyl-substituted C=C-double bond a radical attack of the double bond does not generate a mesomerically stabilized benzylic radical and an internal electronic rearrangement is more favorable.

Compounds **7-Ph** and **7′-Ph** (Fig. 1) were present in too small amounts to be isolated and characterized unequivocally.

On further irradiation at 300 nm the signals accounted for the cyclobutanone **3-Ph** is depleted and two new doublets are detected at about 5.7 and 5.9 ppm (Fig. 3). The amount of **2-Ph** slightly increases while that of **7′-Ph** decreases accordingly. **7-Ph** is not effected by longer irradiation times. The newly formed product is the oxetane **4-Ph** which is generated besides 3-phenyl benzofurane **5** (Scheme 6). The structure of **4-Ph** was assigned on the basis of its ^{1}H and ^{13}C NMR, COSY, IR- and ESI-MS spectra.

The formation of **4-Ph** and **5** is explained by a [2+2]-photo-cycloreversion of **3-Ph** (Scheme 6). This is in analogy to the opening of cyclobutanones, generating a ketene and olefins described by Staudinger [22] thermally, by Koda et al. [23] laser induced and was achieved by Majima et al. [24] via photo-sensitizers. The postulated ketenes were not observed, though. The spectroscopic properties of 3-phenyl benzofurane **5** match the ones given in the literature [25].

3.3. Kinetic evaluation of the irradiation reaction cascade

The time conversion plot in Fig. 4 shows that the diazo compound is almost completely converted after 1 h and the formation of oxetane **4-Ph** and benzofurane **5** begins after a reasonable amount of cyclobutanone **3-Ph** has been generated on irradiation at 300 nm. **3-Ph** is, thus, the kinetic product, while **4-Ph** and **5** are the thermodynamically more stable final compounds (Table 2).

3.4. Solvent, wavelength and C=C electron density dependence on the reaction cascade

Irradiation was also conducted in different solvents and at different wavelengths. Since the cyclobutanone ring opening was

Table 2
Composition of the reaction mixture in dependence of time when **1-Ph** is irradiated at 300 nm in toluene.

Time (min)	**1-Ph** (%)	**2-Ph** (%)	**3-Ph** (%)	**4-Ph** (%)	**5** (%)	**7-Ph** (%)	**7′-Ph** (%)
0	100	0	0	0	0	0	0
15	55.6	11.3	20.0	0	0	6.0	7.1
30	28	16.7	34.7	3.9	0	8.4	8.3
60	5	24.1	35.0	9.7	0	15.4	10.9
120	0	26.4	22.2	17.7	10.8	15.3	7.6
180	0	27.3	12.1	22.4	15.4	16.6	6.2
240	0	28.2	4.9	22.9	29.7	11.6	2.7

Table 3
Solvent dependent product distribution after 1 h irradiation in toluene of **1-Ph**.

	λ (nm)	**2-Ph**	**3-Ph**	**4-Ph**	**7-Ph**
Pentane	300	1	1.56	0.3	0.78
Pentane	419	1	4.42	–	–
PhMe	300	1	1.45	0.4	0.92
PhMe	419	1	6.45	–	–
Et_2O	300	1	0.43	0.63	0.46
CH_2Cl_2	419	1	4.42	–	–

Table 4
Regio-selectivity in diazo compounds **1-R** on irradiation at 300 nm in toluene.

R	Hammett-Parameter σ_p	C=O/C=C-attack
$\mathbf{Ph}^{\mathbf{OMe}}$	−0.27	3.43
$\mathbf{Ph}^{\mathbf{Me}}$	−0.17	1.92
Ph	0	1.70
$\mathbf{Ph}^{\mathbf{NO2}}$	0.78	0.44

considered to be photo-induced by excitation via the π-systems of the phenyl rings, non-aromatic solvents were included to enforce this pathway. The performance in toluene and pentane was comparable, though. The content of oxetane **4-Ph** was highest in Et_2O probably because of a stabilization of the ketene by the ether. On changing to longer irradiation wavelengths, the cyclobutanone opening was suppressed completely (Table 3).

Interestingly, no **7-Ph/7′-Ph** was found at 419 nm. The reaction did proceed in CH_2Cl_2 comparable to pentane without any side reactions caused by the halogenated solvent. At both wavelengths toluene favored the cyclobutanone formation relative to **2-Ph** more strongly than non-aromatic solvents.

We also changed the electron density of the C=C double bond by variation of the substituent **R**. In Table 4 is listed the ratio of C=O vs. C=C attack, determined through the amounts of **2-Ph** vs. **3-Ph** + **4-Ph** + **5** after 2 h of irradiation at 300 nm in toluene.

As can be seen from these results the less electron-rich the C=C double bond becomes, the more favored is the attack of the carbene at this position compared to a C=O attack in accordance with the nucleophilic character of the carbene.

4. Conclusions

On irradiation of the diazo olefin esters **1-R** at 300 or 419 nm initially the two main products **2-R** and **3-R** are detected. The formation of those could be explained and supported by additional experiments. In case of **2-R** the in situ generated carbene attacks the olefinic double bond as well as the CH bonds connected to it via CH-insertion. In case of **3-R** it is proposed that the carboxylic double bond reacts additionally. The kinetics of the formation of all products could be quantified at 300 nm irradiation. The more electron deficient the olefin is, the more **2-R** is formed. At 300 nm **3-R** reacts further forming the oxetane **4-R** via cyclo-reversion reaction. The energy provided by light at 419 nm is insufficient to re-open cyclobutanone **3-R**.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2012.12.005.

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