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Neat carbomethoxypivaloylketene—preparation and chemical reactivity☆

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Abstract—Neat carbomethoxypivaloylketene, the first fairly persistent α-oxoketene stabilized both electronically as well as sterically, is generated by flash vacuum pyrolysis of the corresponding furan-2,3-dione. It adds primary amines to afford pivaloyl-malonic acid amides and undergoes hetero-Diels–Alder reactions to furnish usual and unusual [4+2] adducts. Some stereo- and regiochemical features are verified with aid of 2D NMR experiments and a X-ray structure analysis.

1. Introduction

α-Oxoketenes[2] in general are usually highly reactive molecules, which normally cannot be isolated or observed under ordinary reaction conditions. However, they can be stabilized both sterically and electronically, and ketene carboxylic acid derivatives in particular are known to be remarkably stable.[3–7] On the other hand, the bulky *tert*-butyl group obviously plays an important role in stabilizing ketene moieties dramatically through steric effects. Browsing through the literature of α-oxoketenes of that type, only four compounds were described so far to be obtainable as *neat* compounds: *t*-butyl-pivaloylketene (**A**),[5,8] benzoyl-*t*-butylketene(**B**),[9] dipivaloylketene (**C**)[10] and its dimer, 2-[3,3-dimethyl-2-oxo-1-(oxomethylene)-butyl]-2,6-di-*tert*-butyl-5-pivaloyl-1,3-dioxin-4(2*H*)-one (**D**)[10] (Fig. 1).

The dimeric oxoketene **D** was found to be a suitable starting material to obtain functionalized chiral bridged bis-dioxines[11] which furthermore could serve as novel spacer units in macrocyclic systems.[12] In order to widen the scope of those macrocycles with respect to host–guest chemistry, a change in the substitution pattern of the spacer unit was desirable. One approach to such target molecules should come from a change of the substitution pattern of the α-oxoketene itself. In this respect here we report the generation and chemical behaviour of a further persistent neat α-oxoketene, carbomethoxypivaloylketene (**2**), the first one being stabilized both electronically by an ester moiety as well as sterically by the *t*-butyl group.

2. Results and discussion

Following the already known procedures[13,14] the cyclo-condensation reaction of methyl-4,4-dimethyl-3-oxo-pentanoate and oxalic acid dichloride, catalyzed by dry magnesium dichloride,[15] affords the corresponding

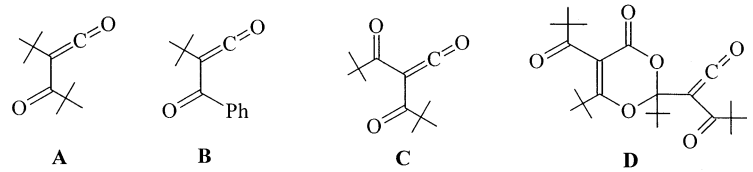

Figure 1. Neat α-oxoketenes stabilized by bulky substituents.

☆ See Ref. 1.

Keywords: flash vacuum pyrolysis; α-oxoketene; hetero-Diels–Alder reactions; 2D NMR spectroscopy; X-ray structure analysis.
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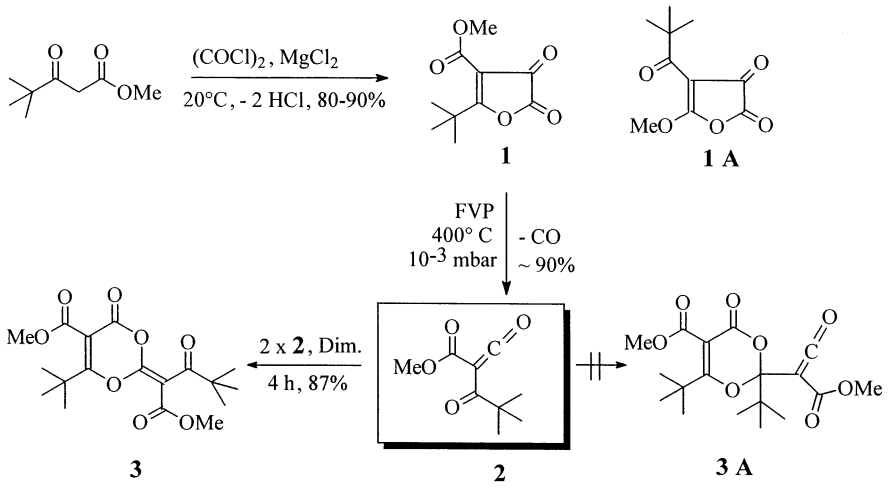


Scheme 1.

5-*t*-butyl-4-methoxycarbonyl-2,3-dihydrofuran-2,3-dione (**1**) in 80–90% yield.

Structural elucidation of the bright yellow coloured **1** was rather difficult since it is highly sensitive to moisture and easily hydrolyzes to recover the corresponding β-ketoester in variable amounts depending on the specific conditions applied (e.g. dryness of solvents, time needed for measurements). However, from the FTIR spectrum of **1** the carbonyl absorption bands of the furan-2,3-dione moiety are detected at 1840, 1795, 1730 cm^{-1} which agrees very well with those of various similar systems.[13–15] Final confirmation comes from the ^{13}C NMR spectrum: The ring-carbons are found at δ 152.2 [154.8] (s, C-2), 176.0 [179.8] (s, C-3), 111.8 [121.6] (s, C.4) and 193.0 [191.5] ppm (m, C-5), the ester carbonyl at C-4 appears at δ 161.4 ppm. Comparison to the very closely related 4-pivaloyl-5-*t*-butyl-furan-2,3-dione [values in brackets][13] and other 4,5-disubstituted furan-2,3-diones[16–18] indicates a good agreement of chemical shifts and also rules out the regioisomeric form **1A** since the pivaloyl carbon at C-4 should be found at approximately 205–208 ppm, respectively.[13]

Preparative flash vacuum pyrolysis (FVP) of **1** (400°C, 10^{-3}mbar) generates the new α-oxoketene derivative **2**, which is collected on the cold-finger (liquid nitrogen) in up to 90% yield depending on the quality (=purity) of the precursor **1** (see above). Ketene **2** is a colourless liquid at rt, it slowly dimerizes via a rather unusual [4+2] cycloaddition reaction across the ketene carbonyl moiety to give the dioxinone derivative **3** (Scheme 1).[2b] Structural approval for **2** first of all comes from the highly characteristic and strong ketene absorption band in the IR spectrum at 2140 cm^{-1} (dipivaloylketene: 2131 cm^{-1})[10], the two carbonyl absorptions appear at 1750 (ester) and 1720 cm^{-1}(pivaloyl). Singlets at δ 1.25 (*t*-Bu) and 3.87 ppm (OMe) are observed in the ^1H NMR spectrum while the signals of the characteristic carbons are easily assigned by comparison with those of the close related dipivaloylketene[10] [numbers in brackets]: central ketene carbon δ 189.0 (s) [194.0, s], sp^2-carbon 70.9 (s) [52.0, s], pivaloyl carbon: 199.9 (m) [198.9, m], ester-carbonyl 164.4 ppm. The intensities of the ^{13}C NMR signals of **2** are time-dependent since due to its dimerization reaction the increase of the signals coming from the dimer **3** is synchronously accompanied by a decrease of those of the oxoketene molecules. The dimerization process is finished after ca. 4 h at rt.

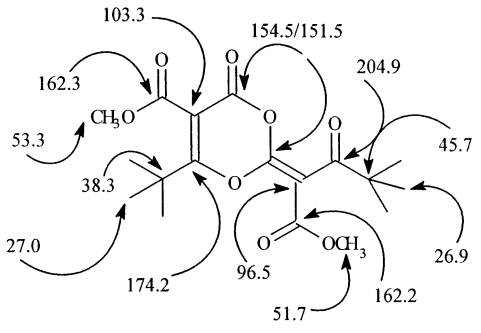
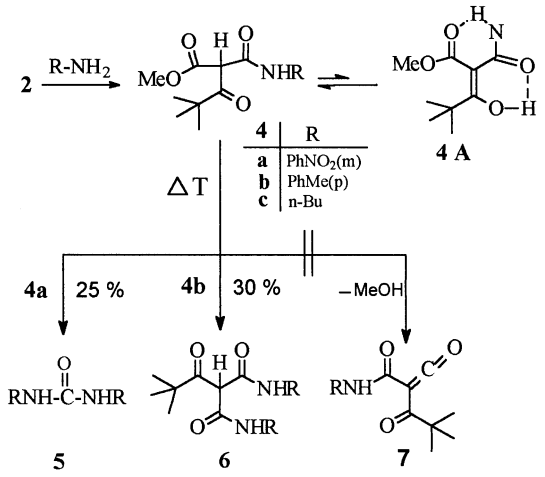


Figure 2. Assignment of 2D-HMBC based ^{13}C NMR data of **3** (ppm).

Structural confirmation of the dioxinone derivative **3** is mainly based on extensive ^{13}C measurements: The correct assignment of all carbons except C-2 and C-4 but including the two methyl ester groups was done with aid of a two-dimensional HMBC[19] experiment (see Fig. 2), while the exact *E*-configuration at the exocyclic C=C-bond was solved with a 2D-NOESY[20] spectrum (mixing time 700 ms). It showed a strong NOE-effect between the *t*-butyl group at C-6 and the OCH_3– of the ester attached to the exocyclic sp^2-carbon, but no interaction between the *t*-butyl groups at C-6 and the pivaloyl moiety at the exocyclic sp^2-carbon (Fig. 2). The remarkable stereoselectivity found is also confirmed by the observation of one single set of both proton and carbon resonances in NMR-spectra up to 500 MHz. Furthermore, from 3D models one can easily see a strong steric interaction of the bulky *t*-butyl groups in case of the *Z*-configurated molecule thus making this stereoisomeric form highly unfavourable.

This type of cyclodimerization of α-oxoketenes is rather uncommon, since usually the [4+2] cycloaddition occurs across the C=C bond of one of the ketene molecules acting as dienophile and leading to α-pyrone derivatives, irrespective of whether the oxoketene is generated as reactive



Scheme 2.

intermediate only or employed as neat compound.[2b] Here it is interesting to note that the formation of dimer **3** is in contrast to the behaviour of the related dipivaloylketene (**C**) which under identical reaction conditions affords dimer **D**, still having a α-oxoketene moiety and thereby serving as starting component for the synthesis of such rare heterocyclic systems as bridged bisdioxines[11] and, subsequently, tetraoxaadamantanes.[21] However, neither acid nor basic catalysis could direct the dimerization of **2** towards formation of the desired target molecule **3A**.

In order to further explore the chemical behaviour of the new oxoketene **2** reactions with N-nucleophiles as well as cycloaddition reactions were investigated.

2.1. Addition of *N*-nucleophiles

Addition of nucleophiles to ketenes[11] as well as α-oxoketenes[2b] is a familiar process and in general leads to carboxylic acid derivatives depending on the nature of the nucleophile applied, e.g. with amines formation of the corresponding amides should be expected. Three types of primary amines have been selected as examples and reacted with **2**: 3-nitroaniline and 4-methoxyaniline as aromatic amines, in order to study the influence of electron-donating versus electron-withdrawing groups, and *n*-butylamine as a representative of alkyl amines. In all cases, as expected, the pivaloyl-malonic ester amide derivatives **4** have been obtained in moderate to excellent yields (Scheme 2).

Remarkably, **4** does not show any tendency to enolize in $CDCl_3$ solution (**4A**) although enols should be stabilized by intramolecular hydrogen bridges. So, through the ^1H NMR spectra (**4a**: δ 5.20, **4b**: 5.38, **4c**: 5.02 ppm) as well as the ^{13}C NMR spectrum of **4b** (δ 64.4 ppm, ^1J=130 Hz), as an example, the presence of a CH-moiety is unambiguously established. Similar observations have been made with close related dipivaloyl acetic acid derivatives.[11,22]

Since the generation of α-oxoketenes by thermolysis of β-ketoesters has been demonstrated in numerous trapping reactions[23–25] compounds **4** were expected upon heating to produce oxoketenes of type **7** as reactive intermediates which in case of R=aryl should possibly afford quinolone derivatives via electrocyclization reactions.[26–28] However, from thermolysis of **4a** bis(3-nitrophenyl)urea **5**[29] was obtained in low yield, while the pivaloyl-malonic *p*-tolylamide **6** was the outcome when **4b** was treated either in boiling xylene or in the solid state at 170°C. Obviously elimination of the corresponding amine is favoured over the extrusion of methanol and its subsequent nucleophilic attack at the amide (**4a**) or the ester moiety (**4b**) were key-steps during those degradation processes. Both the amines could be monitored when the progress of the reaction was controlled by TLC. In case of **4c** no distinct reaction product could be isolated out of the complex reaction mixture.

2.2. Cycloaddition reactions

Neat methoxycarbonyl-pivaloylketene **2** undergoes hetero-Diels–Alder reactions with several mainly electron rich dienophiles as well as heterocumulenes under mild reaction conditions (rt, polar solvent) to afford the expected [4+2] cycloadducts **8**–**14** in moderate yields (~30–80%), compared to compounds of the same type obtained in excellent yields (~80–95%) from cycloaddition reactions of the closely related dipivaloylketene **C**.[18] This probably is due to the presence of the methoxycarbonyl group in **2** and its subsequent cycloadducts, which enhances their solubility, decreases the melting points and makes purification and crystallization more difficult. Isolation of compounds **8**, **10** and **11** is only possible with aid of dry-column flash chromatography (see Section 4).

The significant signal at δ 6.58 ppm (CH)[18] in the ^1H NMR spectrum and two carbonyl absorptions at 1740 and 1665 cm^{-1}, respectively, in the IR confirm the oxazinone skeleton of **8**. The vicinal olefinic protons in the cycloadduct **10** appear at δ 6.36 and 7.72 ppm (^3J=8 Hz).[18] Formation of **10** obviously runs via elimination of ethanol of the unstable intermediate **9**. Attempts to isolate and characterize the primary adduct **9** with aid of ^1H NMR spectroscopy gave mixtures of **9** and **10** only, evidenced by the presence of a OCH_2CH_3 substituent besides the CH=CH moiety, while CH_2 and OCHO-signals could not clearly be identified. Oxoketene **2** also vigorously reacts with ethoxyacetylene to furnish pyrone **11**, the vinylic proton of which is observed at δ 5.50 ppm, which again agrees well with chemical shifts found from several related compounds.[18,30] The oxazinone systems **12** and **14** were obtained from applying diisopropylcarbodiimide or diphenylketene-*N*-(4-methylphenyl)-imine,[31] respectively, as examples for heterocumulenes as dienophiles. In order to exclude the presence of a pyrimidinedione scaffold **13** resulting from a possible *Dimroth*-rearrangement[32,33] of the primary formed adduct **12**, an X-ray structure analysis revealed unambiguously the presence of an oxazine ring system including an imino-lactone moiety for **12**.

The crystal structure analysis of **12** confirmed the compound as the *Z*-isomer with respect to the exocyclic C=N bond. The *E*-isomer would be hindered by the isopropyl group at N-3 (Fig. 3). The isopropylimino group is almost co-planar to the oxazine ring, the methoxycarbonyl plane is inclined at an angle of 85.9(1)° to the plane of the oxazine ring [max. deviation from least-squares plane 0.029 (6) Å].

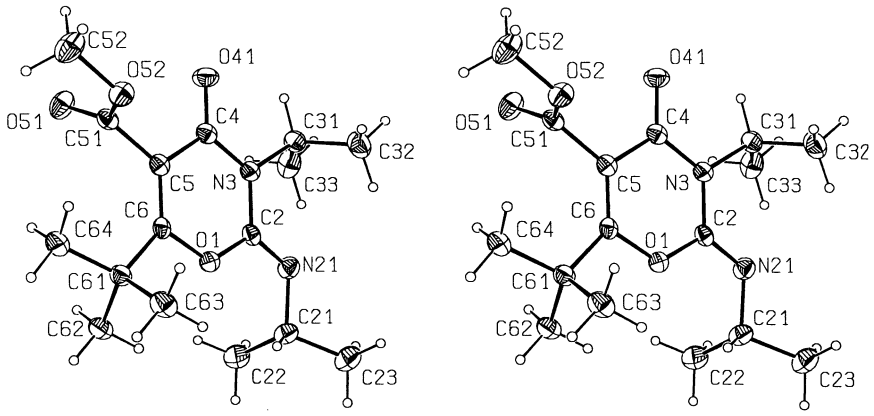
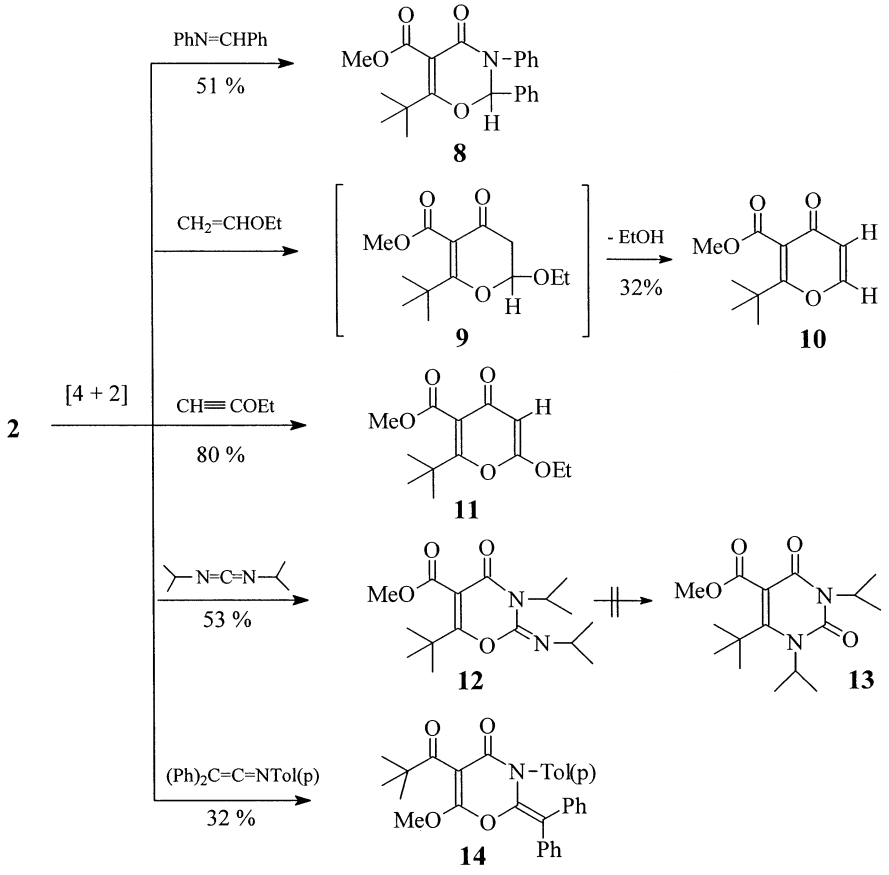


Figure 3. Stereoscopic ORTEP[37] plot of **12** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level.

A somewhat unusual result was found from the reaction of **2** and diphenylketene-*p*-tolylimine: the constitution of the reaction product **14** indicated, that the addition occured across the C=N-bond of the ketenimine, confirmed by the absence of any signal for a $(Ph)_2C$ (sp^3) carbon in the ^{13}C NMR spectrum. This way of addition of keteneimines on to α-oxoketenes is in good agreement with some rare examples given in the literature.[13,34] More interestingly, instead of the pivaloyl-carbonyl as usual, the less active ester carbonyl group is involved in that cycloaddition process. Structural evidence for **14** in particular came from long range (2,3 and 4-bonds) ^1H–^{13}C scalar couplings as observed in an HMBC experiment.[19] Thereby, correlations from the proton signal of the *t*-butyl group to the carbon signal at 201.5 ppm as well as from the methoxy group and the ^{13}C resonance at 172.7 ppm were observed. Furthermore, a strong NOE between the methoxy group and one of the phenyls of the diphenylmethylidene moiety supports the formation of the oxazinone scaffold having a substitution pattern as outlined in Scheme 3. There are very few examples for such a mode of cycloaddition to the carbonyl group of an acid derivative[35,36] and there is no case where the reacting ketene offers a 'true' keto-carbonyl as an alternative. The reason for this unexpected behaviour could be found in the strong steric hinderance of the bulky *t*-butyl group in the *s*-*Z*-conformation required and the diphenylmethylidene unit of the



Scheme 3.

ketenimine during the approach of the reactants thus forming the transition state of the reaction, while if the ester carbonyl participates in the oxa-1,3-diene system the steric interaction is minimized. This can easily be seen from suitable *Dreiding*-molecular models.

3. Conclusion

Neat methoxycarbonyl-pivaloylketene **2**, the first stable α-oxoketene stabilized both electronically as well as sterically, is obtained in excellent yield from FVP of the corresponding furan-2,3-dione **1**. It slowly dimerizes to furnish the uncommon dioxinone derivative **3** solely present in its *Z*-configuration. Addition of primary amines to **2** afford the corresponding pivaloyl-malonic acid derivatives **4** which in solution obviously avoid any enolization. Oxoketene **2** also serves as 1,3-oxadiene in hetero-Diels–Alder reactions with various dienophiles to give the expected adducts **8**–**13** as well as the unexpected regioisomer **14**. Structural confirmation as well as regio- and stereochemical peculiarities of all reaction products are established with aid of intense NMR spectroscopic measurements and an X-ray analysis of **12**.

4. Experimental

4.1. General

All chemicals used in the syntheses were purchased from Aldrich Chemical Co. and Fluka Chemie AG and used without further purification. Solvents were dried according to standard protocols. Melting points were determined on a Tottoli Apparatus and are uncorrected. Microanalyses were performed on a C, H, N Automat Carlo Erba 1106. IR spectra (KBr-pellets) were recorded with a Perkin–Elmer 298, the FTIR spetrum of **1** was performed with a UNICAM Galaxy series 7000 instrument.

1D-^{1}H and ^{13}C NMR spectra were recorded on a 200 MHz Varian LX 200 and a 360 MHz Bruker AMX 360 spectrometer whereas HMBC and 2D NOESY spectra were acquired on a Bruker Avance 500 MHz spectrometer. The mixing time was set to 700 ms in all NOESY experiments.

4.1.1. 5-*t*-Butyl-4-methoxycarbonyl-2,3-dihydrofuran-2,3-dione (1). To a solution of 1.26 g of methyl 4,4-dimethyl-3-oxopentanoate in 15 ml of dry diethylether and catalytic amounts of $MgCl_2$, 1.05 g of oxalylchloride, dissolved in 10 ml of dry ether, were added under nitrogen. The flask was fitted with a $CaCl_2$-tube and allowed to stand at rt under vigorous stirring for about 2 h. During the reaction, the colour of the solution turned yellow. Then the reaction mixture is first evaporated at rt, then at 55°C to completely remove the remaining amounts of oxalylchloride. The product **1** starts to crystallize from the dark yellow oil after cooling to rt, it can be used for flash-vacuum-pyrolysis without further purification. For analytical purposes traces of remaining oxalyl chloride as well as hydrochloric acid were removed at the vacuum line (10^{-3} mbar) and after triturating with dry ether the compound is obtained as bright yellow crystals (80–90%), mp 80°C; FTIR (neat): 1840 (O–C═O), 1815, 1795, 1715 cm^{-1} (C═O); ^{13}C NMR ($CDCl_3$): 25.5–27.5 (C(CH_3)$_3$), 37.0 (H_3C–O), 52.2 (*C*(CH$_3$)$_3$), 111.8 (CO–*C*═C), 152.2 (*C*═O), 161.4 (Ester–C═O), 176.0 (*C*═O), 193.0 (O–*C*═C); Anal. calcd for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70; Found: C, 56.96; H, 6.01.

4.1.2. 2,2-Methoxycarbonyl-pivaloylketene (2). 1.45 g of **1** were put into a sublimation tube (85°C) and pyrolysed with aid of a FVP equipment (preparative mode) under high vacuum (4×10^{-2} mbar) at 400°C for about 3 h. The product **2** is condensed on to a cold finger and after warming to rt, 0.98 g (78%) of **2** are obtained as slightly yellow, oily liquid. IR (KBr): 2970 (CH), 2140 (C═C═O), 1750, 1710 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$): 1.25 (s, *t-But*), 3.78 (s, *Me*O); ^{13}C NMR ($CDCl_3$): 27.7–28.7 (C(*C*H$_3$)$_3$), 47.8 (*C*(CH$_3$)$_3$), 54.0 (MeO), 70.9 (*C*═C═O), 164.4 (Ester–*C*═O), 189.0 (C═*C*═O), 199.9 (C═O).

4.1.3. 6-*t*-Butyl-5-methoxycarbonyl-2-[3,3-dimethyl-1-methoxycarbonyl-2-oxobutylidene]-1,3-dioxin-4-one (3). 0.98 g of neat α-oxoketene **2** is kept at rt for ca. 4 h. During that time the colour of the oily liquid changes from light yellow to orange. Triturating the liquid with cold hexane precipitated 0.72 g (74%) of the dimer **3** as a colourless solid. Recrystallization from hexane affords **3** in small, colourless needles, mp: 104°C; IR (KBr): 2980, 1785, 1735, 1720, 1695, 1635 cm^{-1} (C═O); ^{1}H NMR($CDCl_3$): 1.23, 1.33 (s, *t-But*), 3.73, 3.85 (s, *Me*O); ^{13}C NMR ($CDCl_3$): 27.0–27.2 (C(*C*H$_3$)$_3$), 38.2, 45.9 (*C*(CH$_3$)$_3$), 52.0, 53.4 (H_3C–O), 96.7 (s), 103.4 (s), 151.7 (s, C═C), 154.7 (s), 162.4, 162.5 (m, Ester), 174.4 (m, O–*C*═C), 205.0 (m, C═O) (see also Fig. 2). Anal. calcd for $C_{18}H_{24}O_8$: C, 58.69; H, 6.56; Found: C, 58.75; H, 6.81.

4.2. Synthesis of malonic acid derivatives 4a–c. Common procedure

Appropriate amounts of **2** and the corresponding amine were dissolved in minimum amounts of dry ether (**4c**: no solvent) and allowed to react for 2–12 h with stirring at rt. The colourless precipitate (**4c**: yellow paste) formed was triturated with cold ether (**4c**: *n*-hexane) and dried.

4.2.1. 4,4-Dimethyl-2-methoxycarbonyl-1-*m*-nitrophenyl-aminopentan-1,3-dione (4a). 0.91 g of **2** and 0.68 g of 3-nitroaniline afford 1.22 g (77%) of **4a** (reaction time 4 h), mp: 122°C; ^{1}H NMR ($CDCl_3$): 1.25 (s, *t-But*), 3.83 (s, *Me*O), 5.20 (s, *H*–C), 7.50, 7.87, 8.50 (m, *Aromat*), 9.30 (s, *H*–N); Anal. calcd for $C_{15}H_{18}N_2O_6$: C, 55.90; H, 5.63; N, 8.69; Found: C, 55.58; H, 5.53; N, 8.92.

4.2.2. 4,4-Dimethyl-2-methoxycarbonyl-1-*p*-tolylamino-pentan-1,3-dione (4b). 0.94 g of **2** and 0.54 g of 4-toluidine yield 1.38 g (94%) of **4b** (reaction time 2 h), mp: 135°C; IR (KBr): 3320 (H–N), 2965 (CH), 1755, 1715, 1660 (C═O), 1605 cm^{-1} (Aromat); ^{1}H NMR (DMSO-d$_6$): 1.15 (s, *t-But*), 2.31 (d, H_3C–Ph), 3.72 (H_3C–O), 5.38 (*H*–C), 7.19, 7.44 (m, *Aromat*), 10.28 (s, *H*–N); ^{13}C NMR (DMSO-d$_6$): 208.0 (m, pivaloyl–C═O), 169.9 (m, ester–C═O), 164.6 (d, amide–C═O), 139.3 (t, *ipso*-C), 136.8 (m, *ipso*-C), 132.5, 122.5 (d, ^{1}J=162 Hz, Aromat-C), 64.4 (d, ^{1}J=130 Hz, CH), 56.5 (q, ^{1}J=145.7 Hz, OCH$_3$), 48.1 (s, *C*(CH$_3$)$_3$), 28.7 (q,

^1J=137.2 Hz, C(CH_3)$_3$), 23.8 (q, ^1J=125 Hz, CH_3). Anal. calcd for $C_{16}H_{21}NO_4$: C, 65.96; H, 7.26; N, 4.80; Found: C, 65.97; H, 7.25; N, 4.72.

4.2.3. 1-*n*-Butylamino-4,4-dimethyl-2-methoxycarbonyl-pentan-1,3-dione (4c). 0.44 g of **2** and 0.2 g of *n*-butylamine (under N_2-atmosphere) yielded 0.13 g (21%, from *n*-hexane) of **4c**, mp: 88°C; IR (KBr): 3270 (H–N), 2980, 1755, 1715, 1645 cm^{-1} (C=O); ^{1}H NMR(CDCl$_3$): 0.93 (t, CH_2–CH_3), 1.25 (s, *t-But*), 1.35 (q, CH_2–CH_3), 1.50 (q, CH_2–CH_2), 3.25 (q, CH_2–N), 3.73 (*s, Me*O), 5.02 (s, *H*–C), 6.98 (s, *H*–N).

4.2.4. *N*,*N*′-Bis(3-nitrophenyl)-urea (5).[29] 0.4 g of **4a** were heated for 2 h at 170°C in a round-bottomed flask, fitted with a $CaCl_2$-tube. After cooling down to rt the residue was triturated with ether and the mixture was stirred at rt for 1 h. The precipitate is filtered by suction and recrystallized from methanol yielding 90 mg (25%) of the urea **5**[30] as a light brown powder, mp 245°C (Ref. 30: 248°C); IR (KBr): 3365 (H–N), 1685 (C=O), 1600 cm^{-1} (Aromat); ^{1}H NMR (DMSO-d$_6$): 7.60, 7.82, 8.60 (m, *Aromat*), 9.40 (s, *H*–N); Anal. calcd for $C_{13}H_{10}N_4O_5$: C, 51.66; H, 3.31; N, 18.53; Found: C, 51.59; H, 3.23; N, 18.44.

4.2.5. 1,1-Bis (*p*-toluidylcarbonyl)-3,3-dimethyl-butan-2-one (6). (a) 0.35 g of **4b** were refluxed in 20 ml xylene for 3 h. Then the solution was evaporated until the product started to precipitate. The reaction mixture was cooled over night in the refrigerator and then filtered by suction. The crude product is washed with cold hexane, yielding 0.10 g (23%) of **6** as a brownish powder, identified by comparison with the product obtained under (b). (b) 0.5 g of **4b** were heated for 2 h at 170°C in a round-bottomed flask, fitted with a $CaCl_2$-tube. After cooling down to rt the residue was triturated with ether and the mixture was stirred at rt for 1 h. The precipitate is then filtered by suction and recrystallized from methanol to give 0.20 g (32%) of **6** as small bright beige platelets, mp: 199°C; IR (KBr): 3285 (H–N), 2980 (CH), 1715, 1660, 1615 cm^{-1} (C=O); ^{1}H NMR (DMSO-d$_6$): 1.23 (s, *t-Bu*), 2.30 (t, H_3C–Ph), 5.27 (s, *H*–C), 7.15, 7.40 (m, *Aromat*), 9.22 (s, *H*–N); Anal. calcd for $C_{22}H_{26}N_2O_3$: C, 72.11; H, 7.15; N, 7.64; Found: C, 72.03; H, 7.19; N, 7.60.

4.2.6. 6-*t*-Butyl-2,3-diphenyl-5-methoxycarbonyl-oxazin-4-one (8). 0.2 g of **2** were added to a solution of 0.2 g of *N*-benzylidenaniline in acetonitrile under N_2-atmosphere and stirred at rt over night. The solvent is evaporated and the remaining yellow oil was purified by dry flash chromatography (DCFC), using hexane/ethylacetate 3:1 as an eluent. The obtained light yellow oil was triturated with cold hexane and the precipitated solid was filtered by suction. Recrystallization from *n*-hexane yielded 0.2 g (51%) of **8** as fine, colourless crystals, mp: 102°C; IR (KBr): 2960, 1740 (Ester), 1665 (C=O), 1615 cm^{-1} (Aromat); ^{1}H NMR(CDCl$_3$): 1.10 (s, *t-Bu*), 3.82 (s, *Me*O), 6.58 (s, *H*–C), 7.20, 7.45 (m, *Aromat*); Anal. calcd for $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83; Found: C, 72.17; H, 6.44; N, 3.84.

4.2.7. 2-*t*-Butyl-3-methoxycarbonyl-pyran-4-one (10). 1.00 g of **2** were admixed with 0.4 g of ethylvinylether under N_2-atmosphere and stirred overnight. The obtained orange oil was dried on the vacuum line and afterwards purified by DCFC, using hexane/ethylacetate 3:2 as an eluent. This yielded 0.36 g (32%) **10** as a yellow oil. IR (Film): 2960, 1740 (ester carbonyl), 1650, 1620 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$): 1.33 (s, *t*-Bu), 3.88 (s, *Me*O), 6.36, 7.73 (dd, *J*=8 Hz); Anal. calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71; Found: C, 62.96; H, 6.76. Signals related to **9** (see Section 2): ^{1}H NMR (CDCl$_3$): 1.20 (s, *t-But*), 1.42 (m, *Et*O), 3.75 (s, *Me*O), 3.90 (q, *Et*O), 6.37 (d, cycl. CH_2), 7.72 (m, O–C*H*–O).

4.2.8. 2-*t*-Butyl-6-ethoxy-3-methoxycarbonyl-pyran-4-one (11). 0.44 g of **2** were added to 0.33 g of ethoxyacetylene (50% solution in hexane) under N_2 atmosphere. The strong exothermic reaction was stirred at rt for 1 h, then the reaction mixture was flushed again with nitrogen and stored over night at −15°C. The dark coloured mixture was purified by DCFC, using hexane/ethylacatate 2:1 as a solvent. The obtained orange oil was dried by lyophilization on the vacuum line, during that procedure it started to solidify, yielding 0.49 g (80%) of **11** as colourless needles, mp: 48°C; IR (KBr): 2960, 1730, 1645, 1620 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$): 1.32 (s, *t*-Bu), 1.44 (t, *Et*O), 3.87 (s, MeO), 4.15 (q, EtO), 5.50 (s, H–C=C); Anal. calcd for $C_{13}H_{18}O_5$: C, 61.40; H, 7.13; Found: C, 61.53; H, 7.25.

4.2.9. 6-*t*-Butyl-3-isopropyl-2-isopropylimino-5-methoxycarbonyl-oxazin-4-one (12). 0.35 g of **2** were added to a solution of 0.30 g of diisopropylcarbodiimide in a small amount of acetonitrile. The flask was fitted with a $CaCl_2$-tube and the mixture was stirred over night. The solvent was evaporated at 50°C affording a highly viscose orange oil which crystallized partly at rt. The crude mixture was dissolved in a minimum amount of dry ether and allowed to vaporize slowly to give large, colourless crystals, washed with small amounts of ice-cold pentane and sucked off strongly yielding 0.31 mg (53%) of **12**, mp: 67°C; IR (KBr): 2965, 1740, 1700, 1660, 1635 cm^{-1}; ^{1}H NMR (CDCl$_3$): 1.20 (s, *t-Bu*), 1.25 (d, CH_3–CH), 1.42 (d, CH_3CH–N=), 3.83 (s, MeO), 4.10, 4.43 (m, H*C*–N); ^{13}C NMR (CDCl$_3$): 18.6, 24.1 (CH_3–CH), 27.5 (C(CH_3)$_3$), 37.5 ($C(CH_3)_3$), 46.0, 47.1 (CH_3–*C*H), 52.8 (CH_3O), 107.5 (*C*=C), 138.4 (*C*=N), 159.9 (C=*C*–O), 165.2 (O–*C*=O), 167.9 (*C*=O); Anal. calcd for $C_{16}H_{26}N_2O_4$: C, 61.92; H, 8.44; N, 9.10; Found: C, 61.87; H, 8.57; N, 9.02.

4.2.10. 6,6-Diphenyl-2-methoxy-3-pivaloyl-5-*p*-tolylimino-pyran-4-on (14). 0.34 g of **2** were added to a solution of 0.52 g of *N*-4-tolyl-diphenylketenimine in dry diethylether and the mixture was stirred over night. The obtained precipitate was filtered off by suction, washed with cold pentane and dried, yielding 0.25 g (29%) of **14** as a white powder, mp: 143°C; IR (KBr): 2960, 1705, 1670, 1640 (C=O), 1610 cm^{-1} (Aromat); ^{1}H NMR (CDCl$_3$): 1.28 (s, *t-But*), 2.15 (s, CH_3–Ph), 3.65 (s, *Me*O), 6.85, 7.05, 7.30 (m, *Aromat*); ^{13}C NMR (CDCl$_3$): 26.0–27.6 (C(CH_3)$_3$), 54.1 ($C(CH_3)_3$), 55.8 (*C*(Ph)$_2$), 57.4 (CH_3O), 59.1 (CH_3-Ph), 92.4 (s, *C*=C), 117.0 (*C*=N), 125.5–142.0 (m, *Aromat*), 161.3 (s, *C*=O), 162.8 (q, C=*C*–O), 206.9 (s, *t*-But-*C*=O); Anal. calcd for $C_{30}H_{29}NO_4$: C, 77.07; H, 6.48; N, 2.97; Found: C, 76.81; H, 6.25; N, 2.99.

4.3. Crystal structure analysis of 12

All the measurements were performed on a STOE-4-circle diffractometer using graphite-monochromatized MoK_α radiation at 95 K: $C_{16}H_{26}N_2O_4$, M_r 310.39, triclinic, space group *P*-1, a=9.159 (6) Å, b=10.672 (6) Å, c=10.963 (7) Å, α=96.68 (5)°, β=112.54 (5)°, γ=109.95 (5)°, V=891.8 (10) Å^3, Z=2, d_{calc}=1.156 g cm^{-3}, μ=0.083 mm^{-1}. A total of 3665 reflections were collected ($2\Theta_{max}$=50°), from which 3130 were unique (R_{int}=0.0955), with 2516 having $I>2\sigma(I)$. The structure was solved by direct methods (SHELXS-97)[38] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[39] The non-hydrogen atoms were refined with anisotropic displacement parameters. The tertiary H-atoms were refined with isotropic displacement parameters and idealized geometries with C–H distances of 1.00 Å, the other H-atoms were refined with common isotropic displacement parameters for the H-atoms of the same methyl group and idealized geometries with C–H distances of 0.98 Å. For 209 parameters final *R* indices of R=0.0589 and wR^2=0.1640 (GOF=1.031) were obtained. The largest peak in a difference Fourier map was 0.272e Å^{-3}. The final atomic parameters, as well as bond lengths and angles are deposited at the Cambridge Crystallographic Data Centre (CCDC 160448).

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