

## Originalarbeiten • Full Papers

Alkoxy-carbonyl-carbene Transfer to Acyclic Tertiary Enaminones <sup>1)</sup>

G. Maas and A. Müller

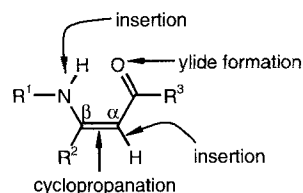
Ulm, Abteilung Organische Chemie I der Universität

Received January 12th, 1998

**Abstract.** Copper-catalyzed alkoxy-carbonyl-carbene transfer from methyl or *tert*-butyl diazoacetate to acyclic enaminoesters **6a,b** and enamino-carboxanilide **13** yields vicinal push-pull-substituted cyclopropanes **7a,b**, **8**, and **14**. In contact with dry silica gel, the latter compounds undergo facile ring-opening leading to enaminoesters **9**, **10**, and **15**. Treatment with aqueous

acid transforms **9** and **10** into 2-acylsuccinates **11** and **12**, and **15** into pyrrolinone **16**. Methoxy-carbonyl-carbene transfer to enamino-ketones **1a–c** does not yield isolable cyclopropanes, but after hydrolytic work-up  $\alpha$ -acyl- $\gamma$ -ketoesters **2a–c** are obtained.

Enaminones represent easily accessible and valuable building blocks in organic synthesis [1]. A major aspect of their reactivity is the presence of three sites for attack by electrophiles (N, C $_{\alpha}$ , and O). Therefore, they are expected also to be good substrates for reactions with electrophilic carbenes and carbenoids. It should be remembered that carbene transfer to appropriate substrates is a highly versatile tool for the construction of carbon frameworks with increased functional and structural complexity [2, 3]. Due to the presence of various reactive sites in an enaminone, the chemoselectivity of a carbene reac-



**Scheme 1** Possible reactions of a carbene with an enaminone

tion becomes an important issue – an aspect that constitutes a recurrent theme especially in the research on transition-metal-catalyzed carbene transfer reactions over the last two decades [4].

Four major transformations can be expected for the reaction between an enaminone and a carbene, namely (Scheme 1) cyclopropanation, insertion into the N-H or

C $_{\alpha}$ -H bond, and carbonyl ylide formation. Hereby, the N-H insertion may be the result of the initial formation of a nitrogen ylide followed by 1,2-shift of a proton. Similarly, electrophilic attack of the carbene unit at C $_{\alpha}$  would create a dipolar intermediate which could isomerize to the formal C,H insertion product by (1,2) proton shift; furthermore, 1,3-cyclization of this intermediate represents one of the possible mechanisms for cyclopropane formation. Cyclopropanation is likely to occur in the reaction of enaminoesters (amino group = morpholino, pyrrolidino, piperidino) with methylene or dichlorocarbene; however, the push-pull-substituted cyclopropanes readily undergo ring-opening, and products derived from the resulting dipolar intermediates are isolated [5]. Stable cyclopropanes were obtained from the copper-catalyzed decomposition of ethyl diazoacetate in the presence of substituted uracils [6] and related compounds [7], all of which can be considered as cyclic *N*-acyl-enaminones.

Kascheres and coworkers [8] have studied the copper-catalyzed decomposition of diazocarbonyl compounds in the presence of primary and secondary enaminones. The result seems to depend mainly on the configuration of the enaminone and on the acylcarbene to be transferred. Thus, acyclic primary (Scheme 1, R<sup>1</sup>NH = NH<sub>2</sub>) and secondary enaminones, both of which occur in the *Z-s-cis* configuration with the possibility of an intramolecular N-H...O bond, react with ketocarbenes R<sup>1</sup>CO-C-R<sup>2</sup> (R<sup>1</sup>/R<sup>2</sup>: Ph/Ph, Me/Ph, Ph/

<sup>1)</sup> Presented in part at the third conference on iminium salts, Stimpfach-Rechenberg (Germany), September 17–19, 1997

Me) by an initial C $\alpha$ -H insertion (followed by cyclocondensation leading to pyrroles), in contrast to the N-H insertion observed with related cyclic enaminones (*E*-*s-trans* configuration) [8]. Copper-catalyzed reactions of ethyl diazoacetate with acyclic primary and secondary enaminones provide pyrroles of unexpected substituent pattern in low yield; the first step seems to be again C $\alpha$ -H insertion of the carbene unit [9]. In contrast to the ketocarbene reactions mentioned above, cyclic enaminones as well as an acyclic (*E*)-enaminone, undergo C $\alpha$ -H rather than N-H insertion [9].

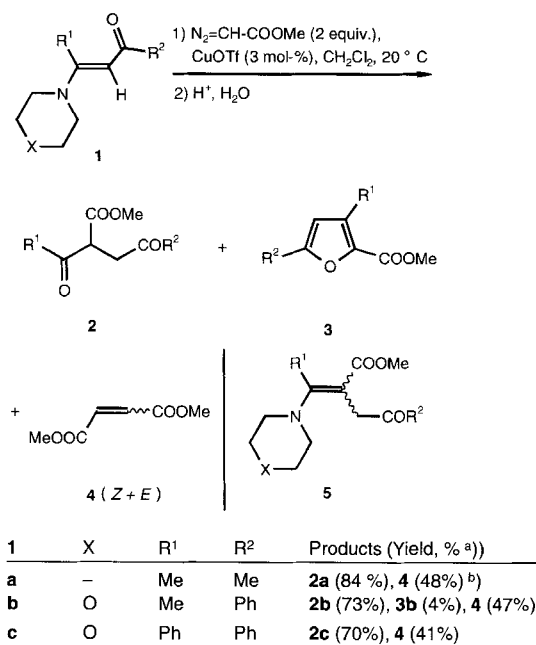
The product corresponding to C $\alpha$ -H insertion of the carbene moiety has also been obtained when 2-diazo-1,1,1-trifluoro-3-nitropropane was combined with 3-morpholino-cyclohex-2-en-1-one [10]; the reaction conditions (20 °C, no catalyst) suggest, however, that this reaction does not include a carbene intermediate.

The reports cited above illustrate the array of possible reaction patterns for carbene transfer to enaminones of different type and structure. In this communication, we want to report our observations on the copper-catalyzed decomposition of diazoacetates in the presence of tertiary acyclic enaminoketones, enaminoesters, and an enamino-carboxamide.

## Results

The catalytic decomposition of methyl diazoacetate (MDA) in the presence of enaminoketones **1a–c** was investigated first (Scheme 2). Initial experiments served to optimize the efficiency of carbene transfer to the enaminones, since it was found that the use of equimolar quantities of **1a** and MDA (which was added slowly over a period of 24 h) furnished diketone **2** in only 41% yield and left about 30% of **1a** unreacted. The yield of **2a** could be doubled when two equivalents of MDA were added to the solution containing **1a** and catalyst over a period of one day. Copper(I) triflate (CuOTf) proved to be the most efficient catalyst for the carbene transfer reaction and allowed to work at room temperature. Less suited than CuOTf were copper(II) acetylacetonate (Cu(acac)<sub>2</sub>), which required to work in boiling ethyl acetate (60% of **2a**, 51% of the carbene dimers **4**) and [Ru<sub>2</sub>(CO)<sub>4</sub>( $\mu$ -OAc)<sub>2</sub>]<sub>n</sub> [11] (23% of **2a**, 48% of **4**). Interestingly, rhodium(II) perfluorobutyrate (Rh<sub>2</sub>(C<sub>3</sub>F<sub>7</sub>COO)<sub>4</sub>), a highly electrophilic catalyst which readily decomposes diazoacetates in non-polar solvents [3a, 12, 13], was totally unsuited for our purpose (CH<sub>2</sub>Cl<sub>2</sub>, reflux, 42 h: 87% of unreacted **1a**, <10% of **2a**, mainly **4**). In this case, the polar enaminone is likely to deactivate the catalyst by coordination.

Under the optimized reaction conditions (CuOTf as catalyst, two equivalents of MDA added slowly), NMR spectra of the crude product mixtures obtained from



a) Yield of **2** and **3** based on **1**, yield of **4** *E/Z* mixture based on diazo compound. b) Yields obtained with Cu(acac)<sub>2</sub> as catalyst (ethyl acetate, 80 °C): **2a**, 60%; **4**, 51%.

## Scheme 2

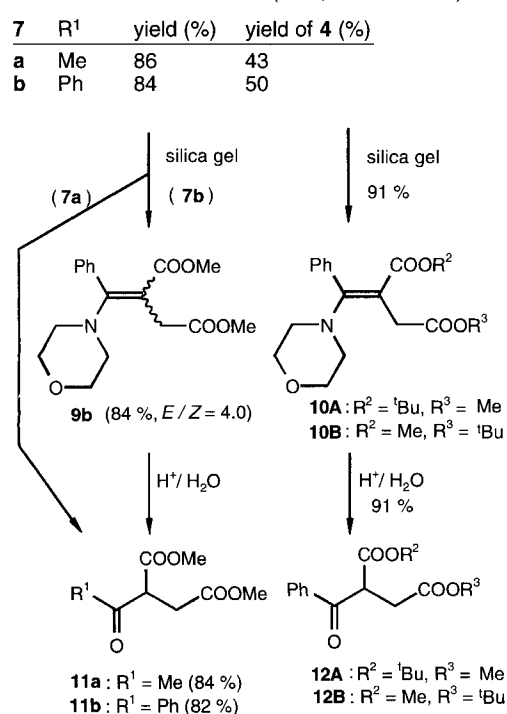
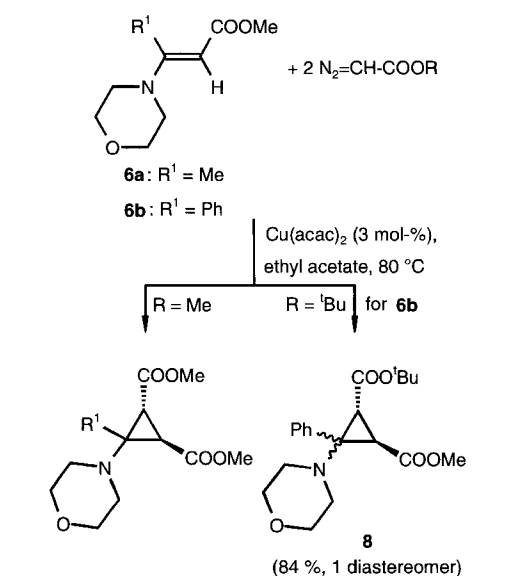
**1a–c** suggested, besides the signals of the formal carbene dimers **4** and of diketones **2**, the presence of enaminoesters **5** (<sup>1</sup>H NMR:  $\delta$ (CH<sub>2</sub>) = 2.8–2.9 ppm). Related compounds were isolated from carbene transfer to semicyclic enaminoesters [14]. Diketones **2** result obviously from partial hydrolysis of **5**, and since a separation by distillation or chromatography was not possible, the product mixture was hydrolyzed deliberately to furnish ultimately 1,4-diketones **2a–c** in good yields. In line with the proposed constitution, an ABX spin system is present in the <sup>1</sup>H NMR spectra of these products (for the CHCH<sub>2</sub> group in the alternative structure **21** (Scheme 5), a simple A<sub>2</sub>B system would result when R<sup>1</sup> = R<sup>2</sup>).

In the case of **1b**, furan **3b** was obtained additionally in low yield. For the mechanistic discussion (see below), it is important to state that the constitution of **3b** was derived from NMR experiments (C,H correlation and gradient-selected HMBC spectra, see Experimental) and that the <sup>1</sup>H NMR chemical shifts exhibit significant differences with respect to the known isomer, methyl (2-methyl-5-phenylfuran) carboxylate [15].

We reasoned that enaminoesters **5**, detected in the product mixtures of Scheme 2, had resulted from a ring-opening reaction of initially formed (2-aminocyclopropyl)ketones. In fact, when methyl or *tert*-butyl diazoacetate were decomposed under the catalytic action of copper(II) acetylacetonate in the presence of enaminoesters **6a,b**, 1-morpholinocyclopropane-2,3-dicarbo-

xylates **7a**, **b** and **8** were formed in high yield, even without a high-solution technique, and could be isolated from the reaction mixture by crystallization. In each case, only one diastereomer was observed by NMR. While the rather low value of the coupling constant between the ring protons ( $^3J = 6.0\text{--}6.3\text{ Hz}$ ) indicated a *trans*-relationship for the carboxylate groups in all cases, the relative stereochemistry at the disubstituted ring atom in **8** could not be established.

All three cyclopropanes are very moisture-sensitive (especially so **7a**) and were stored, therefore, in an atmosphere of dry argon. When their solutions in dry ethyl

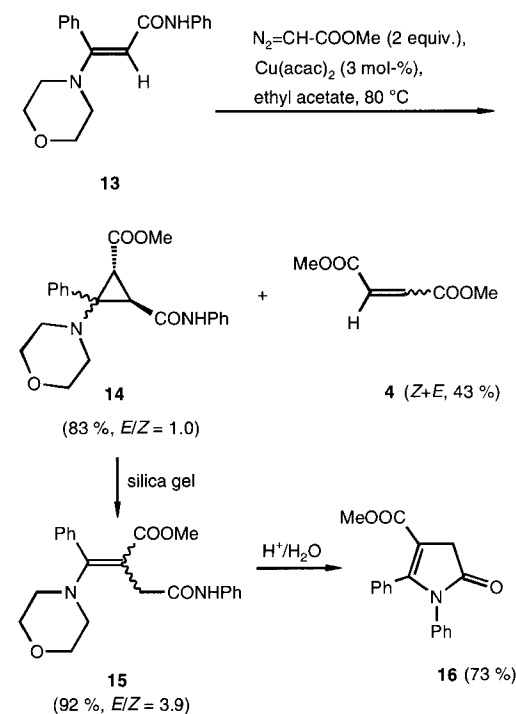


Scheme 3

acetate were passed over a short column with dry silica gel, quantitative ring-opening occurred, and the new enaminoesters **9b** (*E/Z* mixture) and **10A/B** (3.6:1 mixture of the two positional isomers) could be isolated. While an NMR experiment suggested that *E*-**9b** was the major component of the diastereomeric mixture (ROESY, cross-peak for CH<sub>2</sub>-allyl/NCH<sub>2</sub>), the very similar <sup>1</sup>H and <sup>13</sup>C chemical shifts did not allow to differentiate between **10A** and **10B**.

Under the given conditions, **9a** could not be found; instead, 2-acetyl-succinate **11a** was obtained. Acid-catalyzed hydrolysis of **9b** and **10A/B** produced the 2-acyl-succinates **11b** and **12A/B** as well. The formation of a mixture of structural isomers **12A/B** indicates that the precursor mixture **10A/B** consists also of two structural isomers and not of the *Z,E* diastereomers of one enaminoester. Considering the fact that the C1–C2 and the C1–C3 bond of cyclopropane **8** should be more or less equally susceptible to the ring-opening reaction, the formation of two structural isomers (**10A/B**) is to be expected anyway.

Copper-catalyzed carbene transfer from MDA to enaminoester **13** led to similar results as in the cases of enaminoesters (Scheme 4). Again, cyclopropanation took place in high yield, and the moisture-sensitive cyclopropane **14** was isomerized smoothly to enaminoester **15** (mixture of diastereomers with very similar <sup>1</sup>H chemical shifts, no stereochemical assignment) under the action of silica gel. Treatment of **15**



Scheme 4

with aqueous acid did not produce a 4-oxocarboxanilide but rather the cyclocondensation product **16**.

Notably, cyclopropane **14** was obtained as a mixture of two diastereomers. NMR data suggest them to be the two C-3 epimers, since the rather small coupling between the vicinal cyclopropyl protons ( $^3J=6.2$  and  $6.6$  Hz, respectively) indicates a *trans*-relationship between the carboxyl groups in both isomers. Although an epimerization of the cyclopropane under the reaction conditions cannot be excluded totally, it seems more likely that the cyclopropanation of **13**, supplied as the pure *E*-isomer, was not stereospecific and has included an intermediate where the stereochemical information of the C=C bond was lost (see Discussion section).

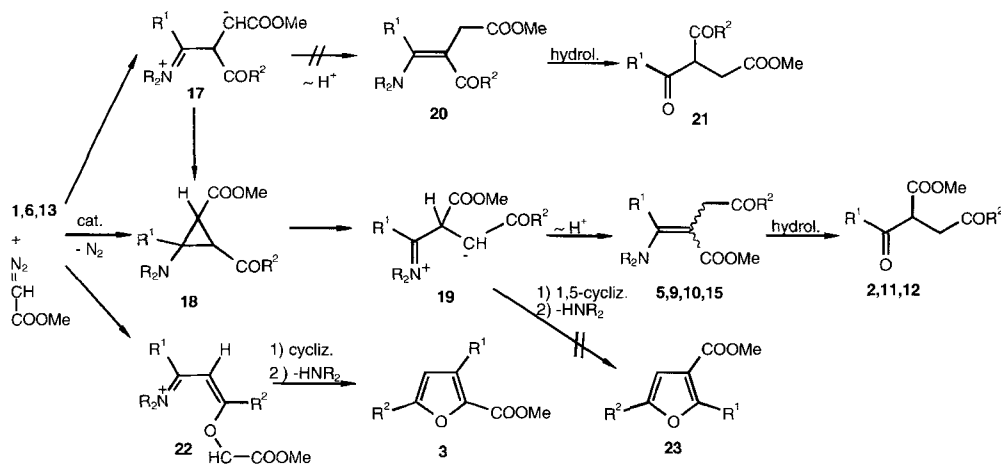
## Discussion

We have shown in this report that copper-catalyzed transfer of alkoxy-carbonyl-carbenes to acyclic tertiary enaminoesters and an enaminocarboxanilide leads to 1-aminocyclopropane-2,3-dicarboxylic acid derivatives **7**, **8**, and **14** in high yield. It comes as no surprise that these vicinal donor-acceptor-substituted cyclopropanes undergo facile, acid-catalyzed ring-opening to give enaminoesters **9**, **10**, and **15** when exposed to dry silica gel. This behaviour is typical not only for 1-amino-2-acceptor-substituted cyclopropanes [16, 17], but also for their 1-oxy-2-acceptor-substituted relatives [18, 19], and is responsible for their usefulness in organic synthesis. Since the enaminoesters resulting from cyclopropane ring-opening can be easily hydrolyzed, a convenient access to tricarbonyl compounds such as **11** and **12** is provided. In the reaction of enaminoketones **1**, the expected donor-acceptor-substituted cyclopropanes could not be isolated, but it is reasonable to assume that the diketesters **2** isolated after hydrolytic work-up were formed *via* the same reaction sequence as in the case of the enaminoesters. Since enaminones **1** are derived from

1,3-diketones, the synthesis of 1,4-diketones **2** by our method constitutes an easy and efficient homologation method, in which an alkoxy-carbonyl carbene unit is inserted in the carbon chain of a 1,3-diketone. Of course, the homologation strategy also applies for enaminoesters **6a,b** and enaminocarboxamide **13**, except for the fact that these compounds are prepared mainly from propiolic acid derivatives rather than from  $\beta$ -ketoesters. Enaminoesters and methylene ( $\text{CH}_2$ ), in part also dichlorocarbene, react analogously [5].

From a mechanistic point of view (Scheme 5), it is interesting to note that copper-catalyzed carbene transfer to secondary rather than tertiary enaminones typically results in a formal insertion of the carbene into the  $\text{C}_\alpha\text{-H}$  bond of the enaminone (see Introduction), while tertiary enaminones are cyclopropanated. It is not far-fetched to propose that both reaction pathways begin with an electrophilic attack of a metal-carbene complex at the sufficiently electron-rich enaminic  $\beta$ -position, and that the dipolar intermediate **17** so formed can react further either by (1,2) proton shift ( $\rightarrow$  formal C,H insertion product **20**) or by 1,3-cyclization ( $\rightarrow$  cyclopropane **18**) [20]. In fact, the observed non-stereospecific cyclopropanation of enaminocarboxanilide **13** would be in line with the intermediacy of betaine **17**. On the other hand, the isomerization **17** $\rightarrow$ **20** does not seem to occur in our cases, since products of type **21** were not found after hydrolytic work-up.

Formation of furan **3b** is attributed to a 1,5-cyclization of carbonyl ylide intermediate **22**. Reaction of carbenes or carbenoids with a carbonyl function to form a carbonyl ylide is not unusual [21, 22], and in view of the enhanced negative charge density on the oxygen atom of an enaminoketone function, we were surprised that this reaction mode was at best a minor one in the case of **1a-c**. Similar 1,5-cyclization reactions have been reported for carbonyl ylides derived from  $\alpha$ -alkoxymethylene ketones [23] or from  $\alpha,\beta$ -unsaturated ketones [24] and acylcarbenes. 1,5-Cyclization of beta-



Scheme 5

ine **19**, the proposed intermediate in the acid-catalyzed ring-opening reaction of cyclopropane **18**, followed by elimination of  $\text{HNR}_2$  would give furan **23** rather than **3**. Obviously, the cyclization **19**→**23** does not take place, in line with earlier observations where the ester-carbonyl oxygen atom was found not to be nucleophilic enough for this reaction [25].

Support of this work by the Fonds der Chemischen Industrie is gratefully acknowledged.

## Experimental

The NMR spectra were taken on Bruker AMX 500 ( $^1\text{H}$ : 500.14 MHz;  $^{13}\text{C}$ : 125.77 MHz) and Bruker AC 200 ( $^1\text{H}$ : 200.13 MHz;  $^{13}\text{C}$ : 50.32 MHz) instruments;  $\text{CDCl}_3$  was used as solvent. As the internal reference,  $\text{Me}_4\text{Si}$  was used for the proton spectra, and the solvent signal for the  $^{13}\text{C}$  NMR spectra [ $\delta(\text{CDCl}_3) = 77.0$  ppm]. IR spectra were recorded on a Perkin-Elmer IR 883 spectrometer. Mass spectra were obtained on a Varian MAT 711 instrument. Microanalyses were carried out with Perkin-Elmer EA 240 and EA 2400 instruments. Column chromatography was performed under hydrostatic conditions (silica gel Si60, Macherey-Nagel, 0.063–0.2 mm) and under medium-pressure conditions (Merck LiChroprep columns, Si60, particle size 40–63  $\mu\text{m}$ ; two columns (240  $\times$  10 mm and 310  $\times$  25 mm) connected; gradient pump Merck-Hitachi L6200).

All reactions except for the hydrolyses were carried out in baked-out glassware and under an argon atmosphere. Slow addition of the diazoacetates was performed by means of a syringe pump (Bioblock Scientific, model A-99) at a flow rate of about 0.25 ml/h.

The following compounds were prepared by literature procedures: Copper(I) triflate benzene complex [ $\text{Cu}(\text{O}_3\text{SCF}_3) \cdot 0.5 \text{C}_6\text{H}_6$ ] [26], **1a** [27], **1b** [28], **1c** [29], **6a** [5], **6b** [30], **13** [31], methyl diazoacetate [32], *tert*-butyl diazoacetate [33].

### Methyl Diazoacetate and Enaminoketones **1a–c**

#### *Methyl 2-acetyl-4-oxopentanoate (2a)*; Typical Procedure

Enaminoketone **1a** (260 mg, 1.70 mmol) was dissolved in dichloromethane (10 ml) and copper(I) triflate ( $\text{CuO}_3\text{SCF}_3 \times 0.5 \text{C}_6\text{H}_6$ , 25.1 mg, 3 mol-%) was added. To this solution, methyl diazoacetate (341 mg, 3.40 mmol) dissolved in  $\text{CH}_2\text{Cl}_2$  (5 ml) was added during 24 h with a syringe pump. The solvent was evaporated, and the residue was separated by column chromatography (silica gel, 40 g, ethyl acetate as eluant). The first fraction contained dimethyl maleate and dimethyl fumarate (*Z*- and *E*-**4**); yield: 118 mg (48%, based on diazo-ester). The second fraction contained **2a** and **5**. The solvent was replaced by  $\text{CH}_2\text{Cl}_2$  (40 ml), and this solution was extracted with aqueous HCl (10%, 2  $\times$  40 ml), saturated aqueous  $\text{NaHCO}_3$  (2  $\times$  50 ml), and water (40 ml) and was dried ( $\text{MgSO}_4$ ). Product **2a** was purified by column chromatography (Merck Lobar column, ether-petroleum ether (7:3)) and obtained as an oil; yield: 254 mg (84%, based on enaminone). Alternative work-up: If only product **2a** needs to be isolated,

the first column chromatography can be skipped. In this case, the product mixture is hydrolyzed as described above, and the product is purified by Lobar column chromatography. – IR (KBr):  $\nu/\text{cm}^{-1} = 1739$  (CO), 1715 (CO), 1266. –  $^1\text{H}$  NMR (400.1 MHz):  $\delta/\text{ppm} = 2.19$  (s, 3H,  $\text{CH}_3$ ), 2.35 (s, 3H,  $\text{CH}_3$ ), 2.95/3.15/4.03 (ABX system,  $\text{CH}_2\text{CH}$ ), 3.74 (s, 3H,  $\text{OCH}_3$ ). –  $^{13}\text{C}$  NMR (100.6 MHz):  $\delta/\text{ppm} = 29.57$ , 29.97 (2 $\text{CH}_3$ ), 41.51 ( $\text{CH}_2$ ), 52.01 ( $\text{OCH}_3$ ), 53.47 (CH), 169.19, 201.99, 205.43 (all C=O).

$\text{C}_8\text{H}_{12}\text{O}_4$  Calcd.: C 55.81 H 6.91  
(172.14) Found: C 54.5 H 6.9.

#### *Methyl 2-acetyl-4-oxo-4-phenylbutanoate (2b)* and *Methyl 3-methyl-5-phenylfuran-2-carboxylate (3b)*

The reaction was carried out according to the procedure described for **2a**, with **1b** (500 mg, 2.17 mmol), methyl diazoacetate (433 mg, 4.32 mmol), and copper(I) triflate (32.6 mg, 0.13 mmol). The crude product mixture was subjected to Lobar column chromatography (ether – petroleum ether (7:3)) to furnish first *Z,E*-**4** (146 mg, 47%), then **3b** (18 mg, 4%). The third fraction was hydrolyzed as described above, and evaporation of the organic solvent followed by bulb-to-bulb distillation at 150  $^\circ\text{C}$ /0.009 mbar gave **2b** as a colorless liquid; yield: 370 mg (73%).

**2b**: IR (film):  $\nu/\text{cm}^{-1} = 1742$  (CO), 1720 (CO), 1685 (CO), 1263. –  $^1\text{H}$  NMR (200.13 MHz):  $\delta/\text{ppm} = 2.44$  (s, 3H,  $\text{CH}_3$ ), 3.55/3.75/4.24 (ABX system,  $^3J_{\text{A,X}} = 5.7$ ,  $^3J_{\text{B,X}} = 8.1$ ,  $^2J_{\text{A,B}} = 18.5$  Hz,  $\text{CH}_2\text{CH}$ ), 3.77 (s, 3H,  $\text{OCH}_3$ ), 7.40–7.60 and 7.90–8.10 (m, 5H,  $\text{C}_6\text{H}_5$ ). –  $^{13}\text{C}$  NMR (50.32 MHz):  $\delta/\text{ppm} = 30.25$  ( $\text{CH}_3$ ), 37.43 ( $\text{CH}_2$ ), 52.70 (CH), 53.62 ( $\text{OCH}_3$ ), 128.11, 128.73, 133.49, 135.99 (*i*- $\text{C}_{\text{Ph}}$ ), 169.39 (COOR), 197.03 (C=O), 202.21 (C=O).

$\text{C}_{13}\text{H}_{14}\text{O}_4$  Calcd.: C 66.67 H 6.02  
(234.21) Found: C 66.31 H 6.11.

**3b**: Colorless solid, *m.p.* 51  $^\circ\text{C}$ . – IR (KBr):  $\nu/\text{cm}^{-1} = 1722$  (CO), 1650 (CO), 1484, 1451, 1438, 1400, 1299, 1231, 1199, 1166, 1119, 1104, 1078. –  $^1\text{H}$  NMR (500.14 MHz):  $\delta/\text{ppm} = 2.39$  (s, 3H,  $\text{CH}_3$ ), 3.91 (s, 3H,  $\text{OCH}_3$ ), 6.59 (s, 1H, 4-H), 7.33 (tt, 1H, *p*- $\text{H}_{\text{Ph}}$ ), 7.39 (m<sub>c</sub>, 2H, *m*- $\text{H}_{\text{Ph}}$ ), 7.71 (m<sub>c</sub>, 2H, *o*- $\text{H}_{\text{Ph}}$ ). –  $^{13}\text{C}$  NMR (125.77 MHz):  $\delta/\text{ppm} = 11.69$  ( $\text{CH}_3$ ), 51.35 ( $\text{OCH}_3$ ), 110.14 (C-4), 124.79, 128.75, 129.56, 133.11 (*i*- $\text{C}_{\text{Ph}}$ ), 139.39 (C-3), 155.72 (C-5), 156.15 (C-1), 160.01 (C=O). – Gradient-selected HMBC cross-peaks: C-2 with 4-H, 4- $\text{CH}_3$ ; C-3 with 4-H, 4- $\text{CH}_3$ ; 4-C with 4- $\text{CH}_3$ ; 5-C with *o*- $\text{H}_{\text{Ph}}$ , 4-CH. – MS (EI, 70 eV):  $m/z$  (%) = 216 (100) [ $\text{M}^+$ ], 185 (58), 158 (33).

$\text{C}_{13}\text{H}_{12}\text{O}_3$  Calcd.: C 72.22 H 5.59  
(216.21) Found: C 72.21 H 5.31.

#### *Methyl 2-benzoyl-4-oxo-4-phenylbutanoate (2c)*

The reaction was carried out according to the procedure described for **2a**, with **1c** (500 mg, 1.70 mmol), methyl diazoacetate (341 mg, 3.40 mmol), and copper(I) triflate (25.1 mg, 0.10 mmol). Work-up yielded *Z*- and *E*-**4** (112 mg, 41%) and **2c** (352 mg, 70%).

**2c**: Colorless solid, *m.p.* 88  $^\circ\text{C}$  (ether). – IR (KBr):  $\nu/\text{cm}^{-1} = 1739$  (CO), 1681 (CO), 1597, 1449, 1275, 1219, 1161, 1075, 1044. –  $^1\text{H}$  NMR (500.14 MHz):  $\delta/\text{ppm} = 3.71$  (s, 3H,  $\text{OCH}_3$ ), 3.74/3.82/5.14 (ABX system,  $^3J_{\text{A,X}} = 6.0$ ,  $^3J_{\text{B,X}} = 7.6$ ,  $^2J_{\text{A,B}} = 18.2$  Hz,  $\text{CH}_2\text{CH}$ ), 7.47–7.61 (m, 6  $\text{H}_{\text{Ph}}$ ), 7.99–8.1 (m, 4  $\text{H}_{\text{Ph}}$ ).

–  $^{13}\text{C}$  NMR (125.77 MHz):  $\delta/\text{ppm}$  = 38.30 ( $\text{CH}_2$ ), 48.53 (CH), 52.77 ( $\text{OCH}_3$ ), 128.21, 128.87, 128.89, 128.96, 133.52, 133.63, 136.02, 136.07, 169.76 ( $\text{COOR}$ ), 194.67 ( $\text{C}=\text{O}$ ), 196.80 ( $\text{C}=\text{O}$ ).

$\text{C}_{18}\text{H}_{16}\text{O}_4$  Calcd.: C 72.97 H 5.44  
(296.28) Found: C 73.22 H 5.29.

### Enaminoester 6a and Methyl Diazoacetate

*Dimethyl (1 $\alpha$ ,2 $\beta$ )-3-methyl-3-morpholinocyclopropane-1,2-dicarboxylate (7a)*

A solution of methyl diazoacetate (540 mg, 5.4 mmol) in ethyl acetate (10 ml) was added during 1 h to a solution of enaminoester **6a** (500 mg, 2.7 mmol) and copper(II) acetylacetonate (42.3 mg, 0.16 mmol, 3 mol-%) in refluxing ethyl acetate. The solvent was then replaced by ether (10 ml), and after filtration to remove most of the catalyst, cyclopropane **7a** was obtained in pure form by three crystallizations at  $-20^\circ\text{C}$ ; yield 597 mg (86%, based on **6a**). The carbene dimers *Z*- and *E*-**4** were isolated and separated by Lobar column chromatography (ether–petroleum ether (3:7)) of the combined filtrates; yield 169 mg (43% based on diazoester).

**7a**: Colorless solid, *m.p.*  $76^\circ\text{C}$  (dec.). – IR (KBr):  $\nu/\text{cm}^{-1}$  = 1743 (CO), 1728 (CO), 1441, 1343, 1313, 1301, 1263, 1227, 1213, 1162, 1113. –  $^1\text{H}$  NMR (500.14 MHz):  $\delta/\text{ppm}$  = 1.29 (s, 3H,  $\text{CH}_3$ ), 2.31 and 2.49 (AB system,  $^3J = 6.3$  Hz, 1-H, 2-H), 2.55 (ddd,  $^2J = 9.1$  Hz, 2H,  $\text{NCH}_2$ ), 2.57 (ddd,  $^2J = 9.1$  Hz, 2H,  $\text{NCH}_2$ ), 3.56 (ddd,  $^2J = 8.8$  Hz, 2H,  $\text{OCH}_2$ ), 3.63 (broadened ddd, 2H,  $\text{OCH}_2$ ), 3.68 (s, 3H,  $\text{OCH}_3$ ), 3.70 (s, 3H,  $\text{OCH}_3$ ). –  $^{13}\text{C}$  NMR (125.77 MHz):  $\delta/\text{ppm}$  = 9.42 ( $\text{CH}_3$ ), 33.61 and 33.73 (C-1, C-2), 49.15 ( $\text{NCH}_2$ ), 51.89 ( $\text{OCH}_3$ ), 51.99 ( $\text{OCH}_3$ ), 54.00 (C-3), 67.13 ( $\text{OCH}_2$ ), 168.37 ( $\text{C}=\text{O}$ ), 170.10 ( $\text{C}=\text{O}$ ). – MS (EI, 70 eV):  $m/z$  (%) = 257 (18) [ $\text{M}^+$ ], 226 (14), 198 (100) [ $\text{M}^+ - \text{COOCH}_3$ ].

$\text{C}_{12}\text{H}_{19}\text{NO}_5$  Calcd.: C 56.03 H 7.45 N 5.45  
(257.24) Found: C 55.36 H 6.98 N 5.2.

*Dimethyl 2-acetylbutanedioate (11a)*

A solution of cyclopropane **7a** (597 mg, 2.3 mmol) in dichloromethane (50 ml) was placed in a separating funnel and treated successively with aqueous HCl (10 %,  $2 \times 50$  ml), saturated aqueous  $\text{NaHCO}_3$  ( $2 \times 50$  ml), and water. After drying with  $\text{MgSO}_4$ , the organic layer was concentrated, and the residue was distilled bulb-to-bulb at  $150^\circ\text{C}/0.005$  mbar; yield of **11a**: 367 mg (84%). – IR (film):  $\nu/\text{cm}^{-1}$  = 1738 (CO), 1437, 1361, 1267. –  $^1\text{H}$  NMR (500.14 MHz):  $\delta/\text{ppm}$  = 2.35 (s, 3H,  $\text{CH}_3$ ), 2.84/2.98/4.00 (ABX system,  $^3J_{\text{A,X}} = 6.0$ ,  $^3J_{\text{B,X}} = 8.0$ ,  $^2J_{\text{A,B}} = 17.6$  Hz,  $\text{CH}_2\text{CH}$ ), 3.68 (s, 3H,  $\text{OCH}_3$ ), 3.76 (s, 3H,  $\text{OCH}_3$ ). –  $^{13}\text{C}$  NMR (125.77 MHz):  $\delta/\text{ppm}$  = 29.63 ( $\text{CH}_3$ ), 31.89 ( $\text{CH}_2$ ), 51.55 ( $\text{OCH}_3$ ), 51.91 ( $\text{OCH}_3$ ), 54.20 (CH), 168.65 (COOR), 171.54 (COOR), 201.31 (COCH<sub>3</sub>).

$\text{C}_8\text{H}_{12}\text{O}_5$  Calcd.: C 51.06 H 6.43  
(188.15) Found: C 51.23 H 6.45.

### Enaminoester 6b and Methyl Diazoacetate

*Dimethyl (1 $\alpha$ ,2 $\beta$ )-3-morpholino-3-phenylcyclopropane-1,2-dicarboxylate (7b)*

The reaction was carried out as described above for **7a**, with enaminoester **6b** (500 mg, 2.02 mmol), methyl diazoacetate (405 mg, 4.04 mmol), and 31.7 mg (0.12 mmol)  $\text{Cu}(\text{acac})_2$ ;

yield of **7b**: 542 mg (84%); yield of *Z,E*-**4**: 146 mg (50%).

**7b**: Very moisture-sensitive yellowish crystals, *m.p.*  $118^\circ\text{C}$ . – IR (KBr):  $\nu/\text{cm}^{-1}$  = 1700 (CO), 1664 (CO), 1560, 1148, 1097. –  $^1\text{H}$  NMR (500.14 MHz):  $\delta/\text{ppm}$  = 2.45–2.54 (m, 4H,  $\text{N}(\text{CH}_2)_2$ ), 2.85 and 2.89 (AB system,  $^3J = 6.0$  Hz, 1-H, 2-H), 3.47 (s, 3H,  $\text{OCH}_3$ ), 3.47–3.60 (m, 4H,  $\text{O}(\text{CH}_2)_2$ ), 3.76 (s, 3H,  $\text{OCH}_3$ ), 7.17–7.35 (m, 5H,  $\text{C}_6\text{H}_5$ ). –  $^{13}\text{C}$  NMR (125.77 MHz):  $\delta/\text{ppm}$  = 33.58 and 35.40 (C-1, C-2), 49.92 ( $\text{N}(\text{CH}_2)_2$ ), 51.90 ( $\text{OCH}_3$ ), 52.05 ( $\text{OCH}_3$ ), 60.94 (C-3), 67.06 ( $\text{O}(\text{CH}_2)_2$ ), 128.02, 128.21, 129.73, 131.89 (*i*-C), 168.19 ( $\text{C}=\text{O}$ ), 169.06 ( $\text{C}=\text{O}$ ).

$\text{C}_{17}\text{H}_{21}\text{NO}_5$  Calcd.: C 63.95 H 6.63 N 4.39  
(319.30) Found: C 62.83 H 6.59 N 4.36.

*Dimethyl 2-[(Z)- and (E)-1-morpholino-1-phenyl-methyl-ene]-butanedioate (9b)*

A solution of cyclopropane **7b** (540 mg, 1.7 mmol) in ethyl acetate was passed over a Lobar column or over normal silica gel (0.063–0.2 mm) which had been dehydrated at  $100^\circ\text{C}/20$  mbar for 24 h. Pure **9b** was obtained by crystallization from ether as pale-yellow crystals; yield 505 mg (93%), mixture of two diastereomers (*E/Z* = 4.0 according to  $^1\text{H}$  NMR), *m.p.*  $99^\circ\text{C}$ . – IR (KBr):  $\nu/\text{cm}^{-1}$  = 1729 (CO), 1693 (CO), 1581, 1561, 1446, 1431, 1408, 1282, 1271, 1253, 1184, 1165, 1120, 1107. – NMR data: Separate signals of the minor isomer in brackets.  $^1\text{H}$ -NMR (500.14 MHz) of *E*-**9b**:  $\delta/\text{ppm}$  = 2.99 (s, 2H,  $\text{CH}_2$ ), 3.10 (t, 4H,  $\text{N}(\text{CH}_2)_2$ ), 3.61 [3.56] (s, 3H,  $\text{OCH}_3$ ), 3.70 (t, 4H,  $\text{O}(\text{CH}_2)_2$ ), 3.73 [3.76] (s, 3H,  $\text{OCH}_3$ ), 7.18–7.23 and 7.32–7.43 (m, 5H,  $\text{C}_6\text{H}_5$ ). –  $^{13}\text{C}$  NMR (125.77 MHz) of *E*-**9b**:  $\delta/\text{ppm}$  = 37.09 [33.59] ( $\text{CH}_2$ ), 51.06 ( $\text{OCH}_3$ ), 51.41 [49.92] ( $\text{N}(\text{CH}_2)_2$ ), 51.58 ( $\text{OCH}_3$ ), 67.48 [67.06] ( $\text{O}(\text{CH}_2)_2$ ), 96.49 ( $\text{N}=\text{C}=\text{C}$ ), 128.75 [128.03], 129.74 [129.37], 137.28, 156.1 (*i*- $\text{C}_{\text{Ph}}$ ), 162.25 ( $\text{N}=\text{C}=\text{C}$ ), 167.52 ( $\text{C}=\text{O}$ ), 173.60 ( $\text{C}=\text{O}$ ). – MS (FD, 8 kV):  $m/z$  (%) = 319 (100) [ $\text{M}^+$ ].

$\text{C}_{17}\text{H}_{21}\text{NO}_5$  Calcd.: C 63.95 H 6.63 N 4.39  
(319.31) Found: C 64.06 H 6.77 N 4.26.

*Dimethyl 2-benzoylbutanedioate (11b)*

Synthesis from **9b** as described above for **7a**→**11a**; colorless liquid; yield 82%. – IR (film):  $\nu/\text{cm}^{-1}$  = 1739 (CO), 1686 (CO), 1438, 1412, 1260, 1162, 1099, 1021. –  $^1\text{H}$  NMR (200.13 MHz):  $\delta/\text{ppm}$  = 3.04/3.10/4.88 (ABX system,  $^3J_{\text{A,X}} = 6.9$ ,  $^3J_{\text{B,X}} = 7.5$ ,  $^2J_{\text{A,B}} = 18.6$  Hz,  $\text{CH}_2\text{CH}$ ), 3.67 (s, 3H,  $\text{OCH}_3$ ), 3.68 (s, 3H,  $\text{OCH}_3$ ), 4.8 (t,  $^3J = 7.2$  Hz, 1H, CH), 7.44–7.60 (m, 3H<sub>Ph</sub>), 8.0–8.04 (m, 2H<sub>Ph</sub>). –  $^{13}\text{C}$  NMR (50.32 MHz):  $\delta/\text{ppm}$  = 33.06 ( $\text{CH}_2$ ), 49.26 (CH), 52.10 ( $\text{OCH}_3$ ), 52.83 ( $\text{OCH}_3$ ), 128.76, 128.89, 133.73, 135.79 (*i*- $\text{C}_{\text{Ph}}$ ), 169.16 (COOR), 171.69 (COOR), 194.0 ( $\text{C}=\text{O}$ ).

$\text{C}_{13}\text{H}_{14}\text{O}_5$  Calcd.: C 62.40 H 5.64  
(250.20) Found: C 62.0 H 5.5.

### Enaminoester 6b and tert-Butyl Diazoacetate

*Tert-butyl 2-methoxycarbonyl-3-morpholino-3-phenylcyclopropane-1-carboxylate (8)*

Synthesis as described above for **7a**, from **6b** (500 mg, 2.02 mmol), *tert*-butyl diazoacetate (575 mg, 4.04 mmol), and  $\text{Cu}(\text{acac})_2$  (31.7 mg, 0.12 mmol); moisture-sensitive colorless solid; yield 592 mg (84%); *m.p.*  $135^\circ\text{C}$ . – IR (KBr):  $\nu/\text{cm}^{-1}$  = 1730 (CO), 1710 (CO), 1449, 1367, 1334, 1310, 1294, 1264, 1235, 1223, 1164, 1113, 1069. –  $^1\text{H}$  NMR (500.14 MHz):

$\delta/\text{ppm}$  = 1.51 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 2.42 (broad m, 2H, NCH<sub>2</sub>), 2.58 (m<sub>c</sub>, 2H, NCH<sub>2</sub>), 2.59/2.80 (AB system, <sup>3</sup>J = 6.4 Hz, 1-H, 2-H), 3.49 (s, 3H, OCH<sub>3</sub>), 3.58 (m<sub>c</sub>, 4H, O(CH<sub>2</sub>)<sub>2</sub>), 7.15–7.17 (m, 2H<sub>ph</sub>), 7.27–7.34 (m, 3H<sub>ph</sub>). – <sup>13</sup>C NMR (125.77 MHz):  $\delta/\text{ppm}$  = 28.11 (C(CH<sub>3</sub>)<sub>3</sub>), 33.48 and 36.70 (C-1, C-2), 49.96 (N(CH<sub>2</sub>)<sub>2</sub>), 51.85 (OCH<sub>3</sub>), 61.11 (C-3), 66.95 (O(CH<sub>2</sub>)<sub>2</sub>), 81.14 (OC(CH<sub>3</sub>)<sub>3</sub>), 127.96, 128.12, 129.86, 132.18 (*i*-C), 166.66 (C=O), 169.40 (C=O).

C<sub>20</sub>H<sub>27</sub>NO<sub>5</sub> Calcd.: C 66.47 H 7.53 N 3.88  
(361.39) Found: C 65.93 H 7.26 N 4.03.

*C*<sup>1</sup>-*tert*-Butyl *C*<sup>4</sup>-methyl 2-(and 3-)[1-morpholino-1-phenyl-methylene]butanedioate (**10A/B**)

Synthesis from cyclopropane **8** as described above for **7b**→**9b**. The yellow oil obtained was a mixture of **10A/B** (3.6:1 by <sup>1</sup>H NMR); yield 91%. – IR (film):  $\nu/\text{cm}^{-1}$  = 1740 (C=O), 1684 (C=O), 1567, 1445, 1416, 1366, 1315, 1279, 1252, 1166, 1118, 1105. – NMR data: Signals of the minor isomer are given in brackets, no assignment to either **10A** or **10B** was made. <sup>1</sup>H NMR (500.14 MHz):  $\delta/\text{ppm}$  = 1.44 [1.00] (s, 9H, *t*Bu), 2.96 [2.89] (s, 2H, CH<sub>2</sub>), 3.05 [3.05] (t, 4H, N(CH<sub>2</sub>)<sub>2</sub>), 3.63 [3.56] (s, 3H, OCH<sub>3</sub>), 3.66 [3.60] (t, 4H, O(CH<sub>2</sub>)<sub>2</sub>), 7.31–7.43 (m, 5H, C<sub>6</sub>H<sub>5</sub>). – <sup>13</sup>C NMR (125.77 MHz):  $\delta/\text{ppm}$  = 28.21 [27.39] (C(CH<sub>3</sub>)<sub>3</sub>), 37.55 [35.87] (CH<sub>2</sub>), 50.84, 51.04, 51.36, 51.68 (OCH<sub>3</sub> and N(CH<sub>2</sub>)<sub>2</sub> of both isomers), 67.41 (O(CH<sub>2</sub>)<sub>2</sub>), 78.82 [79.04] (C(CH<sub>3</sub>)<sub>3</sub>), 99.34 (N–C=C), 127.96, 128.52, 128.81, 128.59, 129.96, 137.55 [138.79] (*i*-C<sub>ph</sub>), 160.51 (N–C=C), 166.38 (C=O), 173.60 (C=O).

C<sub>20</sub>H<sub>27</sub>NO<sub>5</sub> Calcd.: C 66.47 H 7.53 N 3.88  
(361.39) Found: C 65.95 H 7.57 N 3.93.

*C*<sup>1</sup>-*tert*-Butyl *C*<sup>4</sup>-methyl 2-benzoylbutanedioate and .....3-benzoylbutanedioate (**12A/12B**)

The mixture of enaminoesters **10A/B** was hydrolyzed as described for **7a**→**11a**, and a mixture of **12A** and **12B** was obtained as a colorless liquid (2:1 according to <sup>1</sup>H NMR); yield 91%. – IR (film):  $\nu/\text{cm}^{-1}$  = 1731 (CO), 1686 (CO), 1369, 1253, 1153. – NMR data: Signals of the minor isomer are given in brackets, no assignment to either **12A** or **12B** was made. <sup>1</sup>H NMR (500.14 MHz):  $\delta/\text{ppm}$  = 1.44 [1.32] (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 2.95/3.01/4.84 (ABX system, <sup>3</sup>J<sub>A,X</sub> = 6.5, <sup>3</sup>J<sub>B,X</sub> = 8.1, <sup>2</sup>J<sub>A,B</sub> = 17.0 Hz, CH<sub>2</sub>CH), [3.01/3.05/4.78 (ABX system, <sup>3</sup>J<sub>A,X</sub> = 6.5, <sup>3</sup>J<sub>B,X</sub> = 7.7, <sup>2</sup>J<sub>A,B</sub> = 17.0 Hz, CH<sub>2</sub>CH)], 3.67 [3.68] (s, 3H, OCH<sub>3</sub>), 7.47–7.59 (m, 3H<sub>ph</sub>), 8.05 (m<sub>c</sub>, 2H<sub>ph</sub>). – <sup>13</sup>C NMR (125.77 MHz):  $\delta/\text{ppm}$  = 27.91 [27.61] (C(CH<sub>3</sub>)<sub>3</sub>), 34.45 [32.79] (CH<sub>2</sub>), 49.40 [50.77] (CH), 52.62 [51.91] (OCH<sub>3</sub>), 81.31 [82.44] (OC(CH<sub>3</sub>)<sub>3</sub>), 167.61, 169.30, 170.17, 171.86 (COOR of both isomers), 194.12 [194.46] (COPh). – MS (CI, 70 eV):  $m/z$  (%) = 293 (4) [MH<sup>+</sup>], 237 (100).

C<sub>16</sub>H<sub>20</sub>O<sub>5</sub> Calcd.: C 65.75 H 6.89  
(292.28) Found: C 64.42 H 6.94.

**Enaminocarboxanilide 13 and Methyl Diazoacetate**

*Methyl (1 $\alpha$ ,2 $\beta$ ,3 $\alpha$  and 1 $\alpha$ ,2 $\beta$ ,3 $\beta$ )-3-morpholino-3-phenyl-2-(phenylcarbamoyl)cyclopropane-1-carboxylate (**14**)*

Synthesis as described for **7a**, from **13** (500 mg, 1.62 mmol), methyl diazoacetate (325 mg, 3.2 mmol), and Cu(acac)<sub>2</sub> (25.4 mg, 0.01 mmol); yield 511 mg (83 %), 1:1 mixture of

diastereomers; *m.p.* 127 °C. – IR (KBr):  $\nu/\text{cm}^{-1}$  = 3444 (br, NH), 1733 (C=O, ester), 1655 (C=O, amide), 1600, 1551, 1446, 1225, 1176, 1113. – NMR data: Signals of the second diastereomer are given in brackets. <sup>1</sup>H NMR ([D<sub>6</sub>]acetone, 500.14 MHz):  $\delta/\text{ppm}$  = 2.38–2.50 [2.50–2.61] (m, 4H, N(CH<sub>2</sub>)<sub>2</sub>), 2.80 and 2.97 [2.91 and 3.07] (AB system, <sup>3</sup>J = 6.6 [6.2] Hz, 2-H, 3-H), 3.52 [3.75] (s, 3 H, OCH<sub>3</sub>), 3.59 [3.49] (m<sub>c</sub>, 4H, O(CH<sub>2</sub>)<sub>2</sub>), 7.01–7.72 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 9.73 [9.70] (broad s, 1H, NH). – MS (FD, 8 kV):  $m/z$  (%) = 380 (100) [M<sup>+</sup>], 261 (13), 119 (23).

C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub> Calcd.: C 69.46 H 6.36 N 7.36  
(380.41) Found: C 69.10 H 6.13 N 7.03.

*Methyl 2-[(Z)- and (E)-]-3-morpholino-3-phenyl-2-[(phenyl-carbamoyl)methyl]-2-propenoate (**15**)*

Synthesis from cyclopropane **14** by analogy with **7b**→**9b**; moisture-sensitive colorless solid, *E/Z* = 3.9; yield 92%; *m.p.* 127 °C. – IR (KBr):  $\nu/\text{cm}^{-1}$  = 3400–3000 (NH), 1733 (C=O, ester), 1660 (C=O, amide), 1594, 1539, 1112. – NMR data: Signals of minor isomers are given in brackets. <sup>1</sup>H NMR (500.14 MHz):  $\delta/\text{ppm}$  = 2.95 [3.06] (pseudo-t, 4H, N(CH<sub>2</sub>)<sub>2</sub>), 3.14 (s, 2H, CH<sub>2</sub>), 3.61 [3.72] (s, 3H, OCH<sub>3</sub>), 3.75 [3.69] (m<sub>c</sub>, O(CH<sub>2</sub>)<sub>2</sub>), 6.89–7.69 (m, 10H, 2C<sub>6</sub>H<sub>5</sub>), 10.39 [9.92] (broad s, 1H, NH); in a ROESY spectrum, the major isomer (*E*) showed a cross-peak for allyl-CH<sub>2</sub>/ring-OCH<sub>2</sub>. – <sup>13</sup>C NMR (125.77 MHz):  $\delta/\text{ppm}$  = 36.21 [35.78] (CH<sub>2</sub>), 51.05 [50.19] (OCH<sub>3</sub>), 51.94 [52.00] (N(CH<sub>2</sub>)<sub>2</sub>), 67.15 [67.25] (O(CH<sub>2</sub>)<sub>2</sub>), 119.36, 119.42, 123.57, 123.70, 128.02, 128.20, 128.46, 128.69, 128.77, 129.07, 129.21, 129.6, 130.0, 135.47, 136.0, 138.06, 138.56 (C<sub>ph</sub> of both isomers), 156.19 (N–C=C), 165.87 (C=O), 172.91 (C=O). – MS (EI, 70 eV):  $m/z$  (%) = 380 (12) [M<sup>+</sup>], 321 (10), 288 (100) [M<sup>+</sup> – NHPh], 260 (98) [M<sup>+</sup> – CONHPh].

C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub> Calcd.: C 69.46 H 6.36 N 7.36  
(380.40) Found: C 69.01 H 6.29 N 7.11.

*Methyl 2,3-dihydro-1,5-diphenyl-2-oxo-3H-pyrrole-4-carboxylate (**16**)*

A solution of **15** (472 mg, 1.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 ml) was placed in a separation funnel and treated successively with aqueous HCl (10 ml, 2 × 50 ml), saturated aqueous NaHCO<sub>3</sub> (2 × 50 ml), and water. The organic layer was dried (MgSO<sub>4</sub>), concentrated and separated chromatographically (Lobar column, eluant ether–petroleum ether (9:1)); yield: 360 mg (73 %); *m.p.* 166 °C (ether). – IR (KBr):  $\nu/\text{cm}^{-1}$  = 1736 (CO), 1688 (CO), 1435, 1373, 1357, 1228, 1170, 1148, 1110. – <sup>1</sup>H NMR (500.14):  $\delta/\text{ppm}$  = 3.63 (s, 3H, OCH<sub>3</sub>), 3.70 (s, 2H, CH<sub>2</sub>), 6.94–6.96 (m, 2H<sub>ph</sub>), 7.17–7.46 (m, 8H<sub>ph</sub>). – <sup>13</sup>C NMR (125.77 MHz):  $\delta/\text{ppm}$  = 37.55 (C-3), 51.12 (OCH<sub>3</sub>), 105.21 (C-4), 127.61, 127.63, 128.75, 129.29, 129.43, 129.48, 134.20 (all C<sub>ph</sub>), 154.68 (C-5), 163.46 (C=O), 174.86 (C=O). – MS (FD, 8 kV):  $m/z$  (%) = 293 [M<sup>+</sup>].

C<sub>18</sub>H<sub>14</sub>NO<sub>3</sub> Calcd.: C 73.93 H 4.83 N 4.79  
(292.29) Found: C 73.81 H 4.71 N 4.76.

**References**

- [1] a) J. V. Greenhill, Chem. Soc. Rev. **1977**, 6, 277; b) V. G. Granik, Russ. Chem. Rev. (Engl. Transl.) **1984**, 53, 383

- [2] Methoden der organischen Chemie (Houben-Weyl), Vol. E19b (Carbene(oide), Carbene), M. Regitz (ed.), Thieme, Stuttgart 1989
- [3] a) M. P. Doyle, in Comprehensive Organometallic Chemistry II, Vol. 12 (L. S. Hegeudus, ed.), Elsevier, Oxford 1995, Chapters 5.1 and 5.2; b) T. Ye, M. A. McKervey, Chem. Rev. **1994**, 94, c) H. M. L. Davies in Comprehensive Organic Chemistry (B. Trost, ed.), Pergamon, Oxford 1986, Chapter 4.8
- [4] a) M. P. Doyle, Chem. Rev. **1986**, 86, 919; b) G. Maas, Top. Curr. Chem. **1987**, 137, 77; A. Padwa, D. J. Austin, Angew. Chem. **1994**, 106, 1881; Angew. Chem. Int. Ed. Engl. **1994**, 33, 1797
- [5] H. Bieräugel, J. M. Akkerman, J. C. Lapierre Armande, U. K. Pandit, Rec. Trav. Chim. Pays-Bas **1976**, 94, 266
- [6] a) H. P. M. Thiellier, G. J. Koomen, U. K. Pandit, Tetrahedron **1977**, 33, 1493; b) H. P. M. Thiellier, A. M. van den Burg, G. J. Koomen, U. K. Pandit, Heterocycles **1974**, 2, 467
- [7] J. Elguero, C. Ochoa, M. Stud, Heterocycles **1982**, 17, 401
- [8] M. N. Eberlin, C. Kascheres, J. Org. Chem. **1988**, 53, 2084
- [9] R. Augusti, M. N. Eberlin, C. Kascheres, J. Heterocycl. Chem. **1995**, 32, 1335
- [10] A. Y. Aizikovitch, V. Y. Korotaev, L. E. Yaroslavtseva, Russ. J. Org. Chem. (Engl. Transl.) **1994**, 30, 1045
- [11] G. Maas, T. Werle, M. Alt, D. Mayer, Tetrahedron **1993**, 49, 881
- [12] M. P. Doyle, S. N. Mahapatro, A. C. Caughey, M. S. Chinn, M. R. Colman, N. K. Harn, A. E. Redwine, Inorg. Chem. **1987**, 26, 3070
- [13] G. Maas, M. Gimmy, M. Alt, Organometallics **1992**, 11, 3813
- [14] A. Müller, Dissertation, University of Ulm, 1998; A. Müller, A. Maier, R. Neumann, G. Maas, Eur. J. Org. Chem. **1998**, in press
- [15] I. Minami, M. Yuhara, H. Watanabe, J. Tsuji, J. Organomet. Chem. **1987**, 334, 225
- [16] E. Vilsmaier, in The Chemistry of the Cyclopropyl Group, Z. Rappoport (ed.), Wiley, Chichester 1987, chapter 22
- [17] H. Henniges, C. Gussetti, H.-C. Militzer, M. S. Baird, A. de Meijere, Synthesis **1994**, 1471
- [18] E. Wenkert, Acc. Chem. Res. **1980**, 13, 27; E. Wenkert, Heterocycles **1980**, 14, 1703
- [19] H.-U. Reißig, Top. Curr. Chem. **1988**, 144, 73
- [20] See lit. [4b] for mechanisms of acylcarbene reactions with other electron-rich C=C bonds
- [21] A. Padwa, S. F. Hornbuckle, Chem. Rev. **1991**, 91, 263
- [22] M. Alt, G. Maas, Tetrahedron **1994**, 50, 7435; Chem. Ber. **1994**, 127, 1534
- [23] D. L. Storm, T. A. Spencer, Tetrahedron Lett. **1967**, 1865; T. A. Spencer, R. M. Villarica, D. L. Storm, T. D. Weaver, R. J. Friary, J. Posler, P. R. Shafer, J. Am. Chem. Soc. **1967**, 89, 5497; S. T. Murayama, T. A. Spencer, Tetrahedron Lett. **1969**, 4479
- [24] O. Anac, A. Daut, Liebigs Ann. Chem. /Recl. **1997**, 1249
- [25] M. L. Graziano, R. Scarpati, J. Chem. Soc., Perkin Trans. 1 **1985**, 289
- [26] R. G. Salomon, J. K. Kochi, J. Am. Chem. Soc. **1973**, 95, 1889
- [27] N. J. Leonard, J. A. Adamcik, J. Am. Chem. Soc. **1959**, 81, 595
- [28] R. Fusco, G. Bianchetti, D. Pocar, R. Ugo; Gazz. Chim. Ital. **1962**, 92, 1040
- [29] N. H. Cromwell, J. Am. Chem. Soc. **1940**, 62, 2897
- [30] S. M. Sharaf, S. K. El-Sadany, E. A. Hamed, A.-H. A. Youssef, Can. J. Chem. **1991**, 69, 1445
- [31] R. A. Ferri, G. Pitacco, E. Valentin, Tetrahedron **1978**, 34, 2537
- [32] a) N. E. Searle, Org. Synth. Coll. Vol. IV, **1963**, 424; b) H.-U. Reißig, J. Reichelt, T. Kunz, Org. Synth. **1992**, 71, 189
- [33] M. Regitz, J. Hocker, A. Liedhegener, Org. Synth. Coll. Vol. V, **1973**, 179

Address for correspondence:  
 Prof. Dr. Gerhard Maas  
 Abteilung Organische Chemie I  
 Universität Ulm  
 Albert-Einstein-Allee 11  
 D-89069 Ulm  
 Fax: +49-(731)-205-2803  
 E-mail: gerhard.maas@chemie.uni-ulm.de

## IMPERIAL-OEL-IMPORT

D-20095 Hamburg, Bergstraße 11, Fax 33 65 86, Telefon 33 85 33, FS 2-161 561

Pflanzliche und tierische Öle und Fette  
 Tallölprodukte aller Art – Abietinsäure  
 Wollfettprodukte aller Art – Lanolin  
 Caprylsäure – Palmitinsäure  
 Paraffin – Harz – Terpentinöl  
 Stearinpech – Sulfatpech  
 Petroleumsulfonate  
 Furfurol – Pyridin  
 Furfurylalkohol  
 Naphthensäure  
 Lecithin  
 Stearin