Scientific paper

Rhodium-Catalyzed Reactions of a Vinyldiazoacetate with *N*-Substituted Semicyclic Enaminones

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Dedicated to Professor Branko Stanovnik on the occasion of his 70th birthday

Abstract

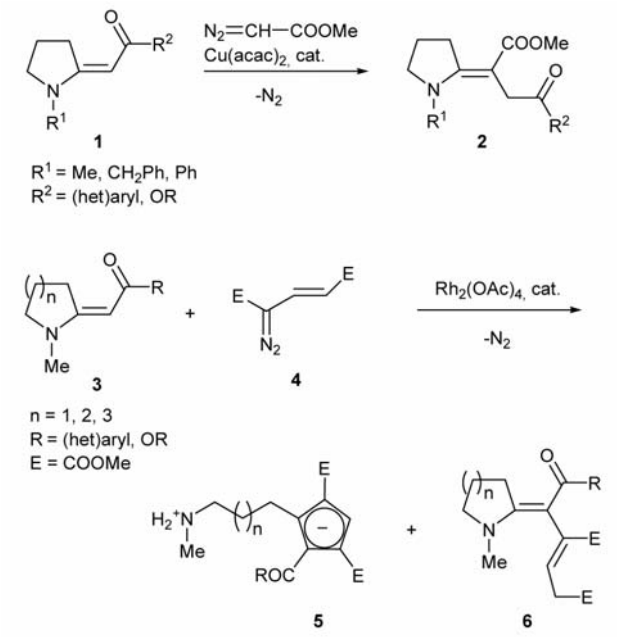
The rhodium-catalyzed reaction of dimethyl 3-diazo-1-propene-1,3-dicarboxylate (**4**) with *N*-substituted five-membered semicyclic enaminones **1** yields (3-ammoniopropyl)cyclopentadienides **7** and/or dienamines **8** which formally represent products of carbenoid insertion into the enaminic β-C–H bond of **1**. The thermal isomerization **8** → **7** is facilitated by electron-donating substitutents at the N atom and at the carbonyl group of the enaminone moiety. Thus, *N*-alkyl substituted dienamines **8** in general undergo the isomerization, while *N*-phenyl substituted analogues do not rearrange. The isomerization behavior of the *N*-methyl-3-(anthracen-9-ylcarbonyl)-substituted dienamine **8c** is complex: isomerization into betaine **7c** is achieved in low yield in the presence of sodium methanolate, while thermal impact in the presence of silica gel generates pentacycle **9** as a result of an intramolecular Diels-Alder reaction at the anthracene moiety. In complete analogy to the transformation **1** → **8**, the rhodium-catalyzed reaction of vinyldiazoacetate **4** with the dimedone-derived 3-morpholinocyclohex-2-en-1-one **11** yields the olefinic C–H insertion product **12**.

Keywords: Cyclopentadienides, diazo compounds, dienamines, enaminones, rhodium carbenoids

1. Introduction

Enaminocarbonyl compounds appear to be versatile substrates for transition-metal promoted carbenoid reactions of diazo compounds, because they offer three centers of enhanced electron density[1] to the electrophilic metal carbene intermediates, namely the N- and β-C atom of the enamine function as well as the carbonyl oxygen atom. Although the multiple reactivity of the N–C=C–C=O unit has found numerous applications in organic synthesis,[2] it appears that the scope of carbenoid reactions with enaminocarbonyl compounds as substrates has not been fully exploited yet. Neverthelesss, the available results confirm that different reaction pathways are possible.

Kascheres and coworkers have studied the copper-catalyzed reactions of diazoketones and diazoacetates with primary and secondary enaminones and have observed products derived from initial insertion of the carbene moiety into the N–H or enaminic β-C–H bond, depending on the structure and the substitution pattern of the enaminone.[3,4] In contrast, we have found that copper-catalyzed alkoxycarbonylcarbene transfer to acyclic tertiary



Scheme 1. Carbenoid reactions of methyl diazoacetate or vinyldiazoacetate **4** with semicyclic enaminocarbonyl compounds.

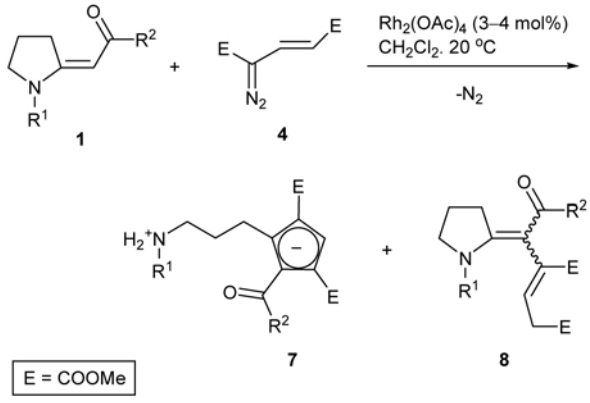
(i.e. *N*,*N*-disubstituted) enaminones and enamino esters yields 2-acyl-3-aminocyclopropane-1-carboxylates, which easily undergo ring-opening.[5] With semicyclic enaminones **1** (Scheme 1), enamino esters **2** are obtained, which appear to be products of carbene insertion into the enaminic double bond.[6] It is likely, however, that these products are also formed via initial cyclopropanation of the enamine double bond followed by spontaneous ring-opening. Notably, the copper-catalyzed reaction of dimethyl diazomalonate with acyclic tertiary enaminones provides dihydrofurans and C-2 substituted enaminones, both in modest yields.[7] In this case, the metal-carbene intermediate does not cyclopropanate the enamine double bond but rather attacks the carbonyl oxygen (carbonyl ylide formation) and the nucleophilic β-C atom of the enamine moiety.

Carbenoid reactions of vinyldiazoacetates have been investigated extensively by H. M. L. Davies and coworkers.[8,9] Metal carbenes derived from these particular diazo compounds are considered to have a donor-acceptor substitution at the carbenic carbon atom, in contrast to the purely acceptor-substituted alkoxycarbonyl and bis(alkoxycarbonyl)carbenoids.[8] This electronic difference often gives rise to changes in reactivity, chemo- and stereoselectivity. We have reported earlier[10] that the rhodium-catalyzed dediazoniation of vinyldiazoacetate **4** in the presence of *N*-methyl-substituted five-, six-, and seven-membered semicyclic enaminones **3** yields (ω-ammonioalkyl)cyclopentadienides **5** (Scheme 1) in fair to excellent yields (R = Ph, 4-substituted phenyl, 2-thienyl, 2-furyl). Only in a few cases (e.g. n = 1, R = OMe, O*t*-Bu), semicyclic dienamines **6** were obtained as competing products, but they could be isomerized thermally into betaines **5**.

In this paper, we present new results on the carbenoid reaction of vinyldiazoacetate **4** with five-membered semicyclic enaminones having substitution patterns different from those of **3**. These results show the scope of the reaction for the preparation of betaines of type **5** and dienamines of type **6**.

2. Results and Discussion

A slight excess of vinyldiazoacetate **4** was treated with a catalytic amount of dirhodium tetraacetate in the presence of a five-membered semicyclic enaminone **1**. Dediazoniation of **4** proceeded smoothly at room temperature, and depending on the substitution pattern of **1**, either a (3-ammoniopropyl)cyclopentadienide **7**, or a semicyclic 1-dienamine **8**, or both products were formed (Scheme 2 and Table 1). $Rh_2(OAc)_4$ was the catalyst of choice: both $Rh_2(CF_3COO)_4$ (ether, r.t.) and copper(I) triflate (CH_2Cl_2, reflux) provided significantly lower product yields, while $Cu(acac)_2$ was totally uneffective.



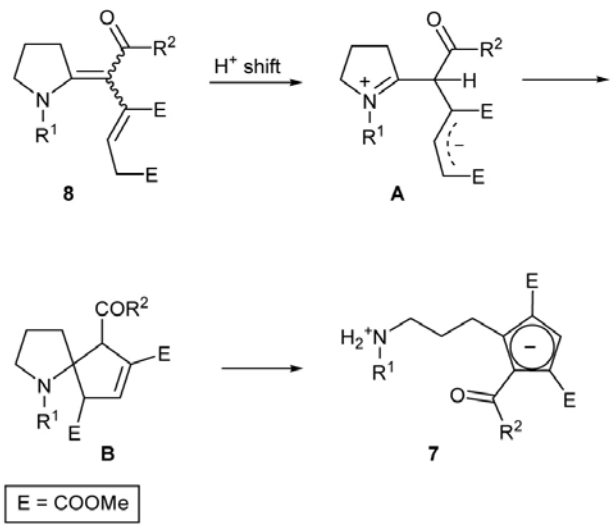
Scheme 2. Carbenoid reactions of vinyldiazoacetate **4** with enaminones **1**. For substituents and yields, see Table 1.

Table 1. Carbenoid reactions of vinyldiazoacetate **4** with enaminones **1**; products and isolated yields.

1, 7, 8	R^1	R^2	Yield of betaine 7 [%]	Yield of dienamine 8 [%]	Conversion 8 → 7
a	Me	1-adamantyl	52	0	
b	Me	2'-nitrobiphenylyl [C_6H_4-4-(C_6H_4-2-NO_2)]	37[a]	n.i.	6 h in boiling ethyl acetate/MeOH (5:1)
c	Me	anthracen-9-yl	0	28[b]	see text
d	*i*-Pr	2-thienyl	52	0	
e	$CH_2CH{=}CH_2$	2-thienyl	79[a]	[c]	5–6 h at 20 °C
f	CH_2Ph	C_6H_4-4-Cl	13	53[b]	200 °C/10 min[d]
g	CH_2Ph	C_6H_4-4-OMe	15	63[b]	200 °C/10 min[d]
h	CH_2Ph	2-furyl	0	65[b]	200 °C/10 min[d]
i	Ph	C_6H_4-4-Cl	0	74	not achieved
j	Ph	2-thienyl	0	73	not achieved

[a] Yield obtained after complete isomerization **8** → **7**; n.i. = not isolated.
[b] Mixture of two diastereomers.
[c] Due to gradual isomerization **8** → **7** at r.t., a reliable yield of **8** cannot be given.
[d] Isomerization **8** → **7** is accompanied by unspecific decomposition of **8**.

The NMR data (^{1}H: Exp. Part; ^{13}C: Table 2) of betaines **7** are in good agreement with those reported earlier[10] including the data of a related betaine the structure of which has been confirmed by X-ray diffraction analysis.[11] According to the NMR spectra, dienamines **8e–h** were obtained as a mixture of two diastereomers, while **8c,i,j** were isomerically pure. C,H correlation spectra allowed a satisfactory spectral assignment in most cases. Based on the analysis of the chemical shift differences, we conclude that the pairs of diastereoisomers differ by the configuration at the enaminic double bond, but we made no efforts to assign the *Z* and *E* configuration. For the second double bond in the molecule (α,β-unsaturated ester), we assume the *Z* configuration for general steric reasons. Furthermore, the observation of diastereotopic allylic CH_2 protons for all dienamines, as well as diastereotopic allylic or benzylic NCH_2 protons in the case of **8e–h**, indicates axial chirality due to the non-planarity of the diene moiety and restricted rotation around the =C–C= single bond.



Scheme 3. Proposed pathway for the isomerization **8** → **7**.

Table 2. ^{13}C NMR data (125.77 MHz, $CDCl_3$, δ values) for betaines **7**.

Compound	NCH_2	NCH_2-CH_2	NCH_2-CH_2CH_2	CH_{cp}	Other C_{cp}	OCH_3	*C*OOMe	Further Signals
8a	47.8	25.4	24.4	121.6	110.7, 111.5, 125.6, 126.1	50.1, 50.5	167.56, 167.77	28.3, 32.9 (C-1_{ad}), 36.6, 38.9, 50.3 (NMe), 221.2 (C=O)
8b	48.0	27.0	23.2	121.5	111.4, 115.0, 124.1, 126.9	49.0, 49.5	165.6, 166.1	32.3 (NMe), 123.8, 128.7, 129.0, 131.7, 132.9, 134.1, 138.5, 142.9, 148.8, 193.7 (C=O)
8c[a]	50.2	27.9	25.0	126.6	115.4, 119.6, 140.2, 140.6	49.5, 51.0	169.4, 169.8	33.2 (NMe), 126.1, 126.9, 127.7, 128.7, 129.3, 130.5, 132.6, 195.0
8d	43.3	24.9	23.1	124.8	113.6, 117.0, 123.9, 131.3	50.4, 50.6	167.4, 167.7	18.8 (CH*Me*$_2$), 49.0 (*C*HMe$_2$), 127.6, 133.5, 135.6, 148.2, 186.7 (C=O)
8e	45.9	24.8	23.2	125.1	114.0, 117.1, 123.8, 127.7	50.3, 50.7	167.3, 167.8	49.0 (NCH_2 allyl), 123.75 (=CH_2), 131.5, 133.9, 135.9, 158.2, 186.9 (C=O)
8f	47.1	25.1	23.5	130.5	113.9, 116.9, 123.7, 125.0	50.3, 50.4	167.1, 167.3	51.2 (N*C*H$_2$Ph), 127.8, 128.0, 128.7, 129.2, 131.0, 140.7, 194.4 (C=O)
8g	47.0	24.8	23.4	124.3	113.4, 116.6, 123.6, 131.9	50.2, 50.4, 50.8	167.23, 167.29	55.3 (N*C*H$_2$Ph), 113.02, 113.06, 128.6, 129.6, 130.6, 134.9, 135.6, 162.3 (C_{ar}OMe), 195.0 (C=O)
8h	47.1	24.6	23.6	125.2	114.9, 117.2, 122.4, 136.9	50.3, 50.7	166.3, 167.4	51.0 (N*C*H$_2$Ph), 112.5, 119.3, 129.1, 129.4, 129.6, 130.4, 145.3, 155.2, 181.5 (C=O)

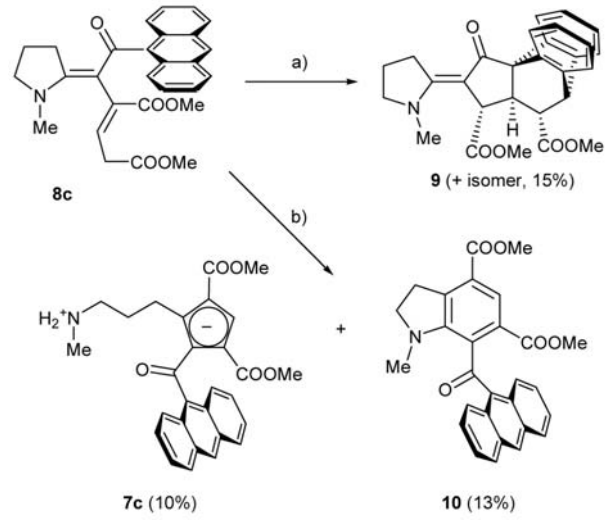
[a] In methanol-d_4.

Most of the dienamines **8** can be rearranged thermally to form the isomeric betaines **7** (Table 1), as was already reported for two *N*-methyl substituted analogues.[10] The rate of isomerization obviously depends both on the *N*-substituent and on the substituent R^2 of the acyl moiety. The data suggest that the isomerization is facilitated by electron-donating substituents which enhance the electron density at the C=C bond of the enaminone moiety (e.g., *N*-alkyl substituents and the adamantyl group at C=O). This interpretation is in line with our mechanistic proposal[10] according to which the rearrangement starts with a proton transfer from the allylic position (=CH–C*H*$_2$–COOMe) to the electron-rich β-position of the enamine double bond, followed by a 1,5-cyclization of the formed betaine **A** and ring-chain transformation of spiro compound **B** (Scheme 3). The latter step requires a proton transfer from the cyclopentene ring to the pyrrolidine nitrogen atom and is surely facilitated by an electron-donating substituent R^1. In agreement with these arguments, the two *N*-phenyl substituted dienamines **8i** and **8j** were found to be thermally stable even at 200 °C. On the other hand, the influence of aromatic substituents in the acyl moiety is not clear.

A particular behavior was found for anthracene-substituted dienamine **8c** (Scheme 4) which could not be rearranged thermally into betaine **7c**. A thermogravimetric analysis revealed that decomposition of **8c** started around

200 °C. However, when **8c** was heated in toluene in the presence of activated silica for 14 h, two products were formed in low yield. While one of the products remains unknown, the second one was identified as polycycle **9** (two isomers) by an X-ray diffraction analysis (Fig. 1). This compound likely arises from an allylic double bond shift in **8c**, followed by an intramolecular Diels-Alder reaction at the anthracene system.[12,13]

We checked next the possibility of a base-assisted isomerization of dienamine **8c**. Treatment with 0.1 equiv of NaOMe resulted only in a sluggish reaction which after some days gave a mixture of several unidentified products



Scheme 4. Conditions: a) toluene, 180 °C, 14 h, silica gel. b) NaOMe (1 equiv), MeOH, 15 h, r.t.

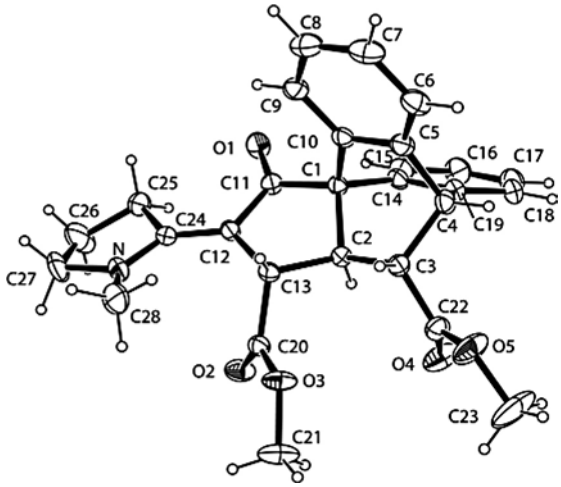


Figure 1. Molecular structure of **9** in the solid state (ORTEP diagram). Thermal displacement ellipsoids are shown at the 20% level. Selected bond lengths (Å): N–C24 1.323(4); C12–C24 1.374(3); C11–C12 1.440(3); C11–O1 1.240(2). Selected torsion angles (°): C13–C12–C24–N 12.3(4); O1–C11–C12–C24 –1.2(4); C12–C13–C20–O2 21.6(3); C2–C3–C22–O4 24.7(4).

including oligomers. The reaction with 1 equiv of NaOMe generated a complex mixture of products from which the expected betaine **7c** and 2,3-dihydroindole **10** could be isolated in low yields. The constitution of **10** was firmly established by X-ray diffraction analysis (Fig. 2). The mode of formation of **10**, which includes the loss of four hydrogen atoms, is not yet clear.

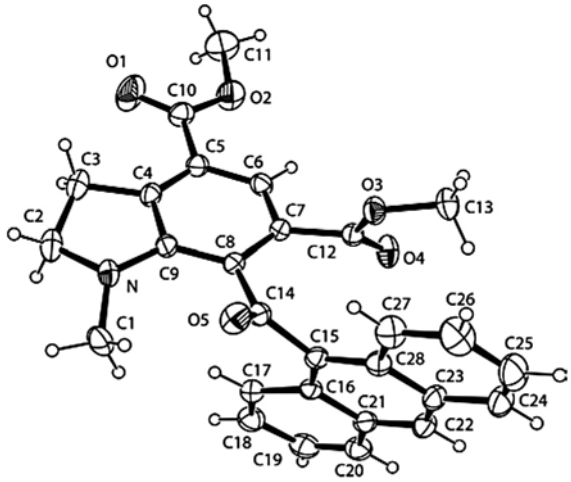
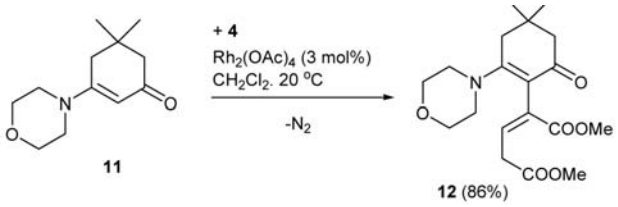


Figure 2. Molecular structure of **10** in the solid state (ORTEP diagram). Thermal displacement ellipsoids are shown at the 30% level. Selected bond lengths (Å): N–C9 1.375(2); C4–C5 1.371(3); C5–C6 1.408(2); C6–C7 1.372(2); C7–C8 1.421(2); C8–C9 1.414(2); C8–C9 1.414(2).

Dienamines **8** can be considered as the formal insertion products of a vinylcarbene moiety into the enaminic β-C–H bond of semicyclic enaminones **1**. The formation of **8** is likely to occur by an initial electrophilic attack of the metal carbenoid derived from vinyldiazoacetate **4** at the electron-rich β-position of the enamine double bond followed by a proton shift. We have performed a few experiments to explore the scope of this reactivity pattern. Thus, it was found that the rhodium-catalyzed reaction of vinyldiazoacetate **4** with the dimedone-derived morpholinocyclohexenone **11**, which is not of the same structural type as the semicyclic enaminones **1**, occurs in a completely analogous manner and provides the formal carbene insertion product **12** in high yield (Scheme 5). Like dienamines **8**, compound **12** has axial chirality due to restricted rotation about the single bond connecting the vinylcarbene moiety with the cyclohexenone ring, causing the CH_2 protons of the cyclohexenone ring and in the allylic side chain to be diastereotopic. Compound **12** was found to be thermally stable up to 150 °C, with unspecific decomposition taking place at higher temperatures. It is interesting to note that an analogous C–H insertion at enaminone **11** occurs with the carbene generated thermally from 1,1,1-trifluoro-2-diazo-3-nitropropane.[14]



Scheme 5. Carbenoid C–H insertion reaction of vinyldiazoacetate **4** with enaminone **11**.

3. Conclusions

In this study, we have collected new results on the competitive formation of betaines **7** and dienamines **8** from the carbenoid reaction of semicyclic five-membered enaminones **1** and vinyldiazoacetate **4**. Substituents which enhance the basicity of the ring nitrogen atom (e.g. R^1 = *i*Pr vs. Me, Me vs. CH_2Ph) facilitate the direct formation of betaines during the reaction, as well as the thermal isomerization **8** → **7**. On the other hand, a phenyl substituent prevents the formation of a betaine. An effect of substituent R^2 in the acyl moiety of the enaminone **1** (or dienamine **8**) is also obvious, but a general explanation cannot be given.

Another aspect of our results comes from a comparison with carbenoid reactions between enaminones and dimethyl diazomalonate.[7] With both types of diazo compounds, vinyldiazoacetates **4** and diazomalonates, carbenoid insertion into the enaminic β-C–H bond is the "normal" pathway, no matter whether enaminones such as **1** and **11** or acyclic tertiary enaminones are used as substrates. However, while the copper-catalyzed reaction of the last mentioned enaminones and dimethyl diazomalonate also yields a product derived from carbenoid attack at the carbonyl oxygen of the enaminone, we did not observe comparable products in our experiments with vinyldiazoacetate **4**, although it is a vinylogous relative of the diazomalonates.

4. Experimental Section

4. 1. General Information

NMR spectra: Bruker AMX 500 (^{1}H: 500.14 MHz; ^{13}C: 125.77 MHz) and Bruker AC 200 (^{1}H: 200.13 MHz; ^{13}C: 50.32 MHz) spectrometers. Unless stated otherwise, all spectra were recorded with the former instrument in $CDCl_3$ solutions. TMS was used as the internal standard; δ values are reported in ppm (m_c = centered multiplet). When necessary, ^{13}C signal assignments were derived from C,H COSY, HSQC and gradient-selected HMBC spectra. IR spectra: Perkin-Elmer IR spectrophotometer 883; wavenumbers [cm^{-1}] are given. Elemental analyses: Perkin Elmer EA 240. Mass spectra: Varian MAT 711 (FD spectra) and SSQ 7000 (EI spectra). Column chromatography was performed under hydrostatic pressure (silica gel Si 60, Macherey-Nagel, 0.063–0.2 mm) and under medium-pressure conditions (Merck Lobar columns, Lichroprep Si 60, particle size 40–63 μm, two columns (240 × 10 mm and 310 × 25 mm) connected; gradient pump Merck-Hitachi L6200).

4. 2. Materials

Solvents were dried according to standard methods and stored under an argon atmosphere. All reactions were carried out in rigorously dried glassware under an argon atmosphere.

Vinyldiazoacetate **4**[10] and enaminocarbonyl compounds **1e**[15] and **1f-j**[6] were prepared by literature methods. The synthesis of **1a** by Eschenmoser's sulfide contraction method[16] is described below. Enaminones **1b-d** were synthesized from lactam acetals by analogy to a literature method.[17]

(*E*)-1-(1-Adamantyl)-2-(1-methyltetrahydro-1*H*-2-pyrrolylidene)-1-ethanone (1a). A solution of 1-methylpyrrolidine-2-thione (1.07 g, 9.27 mmol) in anh. THF (7 mL) was gradually added to a solution of 1-adamantyl bromomethyl ketone[18] (2.39 g, 9.27 mmol) in anh. THF (7 mL). A voluminous white solid started to form after a few minutes. More THF (7 mL) was added, the mixture was stirred overnight, and the solvent was replaced by acetonitrile (60 mL). To the stirred white suspension was added triphenylphosphane (2.20 g, 8.39 mmol) and triethylamine (1.25 mL, 9.97 mmol). A yellow solution was formed within 30 min which was stirred for another 30 min. During partial evaporation of the solvent, the major part of the formed by-products (Ph_3P=S and $NEt_3 \times HBr$) precipitated in solid form and was filtered off. The mother liquor was evaporated to dryness, and the residue was separated by column chromatography (silica gel, 50 g, ether as eluent). The product was obtained as the second fraction and recrystallized from diethyl ether. Yield: 0.523 g (22%), large clear crystals. Mp 103 °C. ^{1}H NMR: δ 1.71 (m_c, 6H, 3 × CH_2-adamantyl), 1.85 (d, *J* 10.0 Hz, 6H, 3 × CH_2-ad.), 1.94 (m_c, 2H, NCH_2CH_2), 2.02 (m_c, 3H, 2 × CH-ad.), 2.87 (s, 3H, NMe), 3.22 (t, *J* 7.5 Hz, 2H, =CCH_2), 3.37 (t, *J* 7.0 Hz, 2H, NCH_2), 5.18 (s, 1H, =CH). ^{13}C NMR: δ 20.9 (NCH_2CH_2), 28.6 (3 × $CH_{adamantyl}$), 33.2 (C-1 ad.), 33.4 (NMe), 36.9 (3 × CH_2 ad.), 39.7 (C-2,8,9 ad.), 44.3 (=CCH_2), 54.2 (NCH_2), 84.2 (NC=*C*H), 166.6 (N*C*=), 202.2 (C=O). IR (KBr): ν 1634, 1548, 1483, 1447, 1415, 1207, 1163, 1097 (all s) cm^{-1}. Anal. Calcd for $C_{17}H_{25}NO$ (259.39): C 78.72, H 9.71, N 5.40. Found C 78.55, H 9.68, N 5.39.

(*E*)-2-(1-Isopropyltetrahydro-1*H*-2-pyrrolylidene)-1-(2-thienyl)-1-ethanone (1d). Yellow crystals, mp 120 °C. ^{1}H NMR: δ 1.21 (d, 6H, $CHMe_2$), 1.92 (quin, 2H, NCH_2CH_2), 3.34 (t, 4H, NCH_2, =CCH_2), 4.01 (sept, 1H, $CHMe_2$), 5.63 (s, 1H, =CHCO), 7.01 (dd, 1H, *J* 5.0 and

3.7 Hz, 4-H_{thie}), 7.35 (dd, 1H, *J* 5.0 and 1.0 Hz), 7.52 (dd, 1H, *J* 3.7 and 1.0 Hz). ^{13}C NMR: δ 19.1 (CH*Me*$_2$), 20.3 (NCH$_2$*C*H$_2$), 34.1 (=C*C*H$_2$), 45.9 (NCH$_2$), 46.1 (N*C*HMe$_2$), 85.6 (=*C*HCO), 126.9, 127.2, 129.0, 149.4, 166.3 (N*C*=), 179.8 (C=O). Anal. Calcd for $C_{13}H_{17}NOS$ (235.35): C 66.34, H 7.28, N 5.95. Found C 66.06, H 7.12, N 5.98.

Catalytic Decomposition of Dimethyl (*E*)-3-Diazo-1-propene-1,3-dicarboxylate (4) in the Presence of Enaminones 1; General Procedure. A solution of **4** (1.2 equiv relative to the enaminone) in dichloromethane (5 mL) was added during 10–24 h with an infusion pump to a stirred solution of enaminone **1** (1.5–3.5 mmol) and $Rh_2(OAc)_4$ (3–4 mol %). Stirring was continued until evolution of nitrogen had ceased or until the IR absorption of the diazo group had disappeared (normally 1–2 h). In some cases, most of the betaine **7** crystallized from the mixture and was collected by filtration. An additional small portion of product was then obtained by column chromatography of the mother liquor (silica gel, elution with ethyl acetate). If the product did not crystallize from the reaction mixture, the solvent was removed at 20 °C/0.01 mbar, and the residue was fractionated by column chromatography over silica gel. Elution with ethyl acetate furnished the following fractions: a) a small amount of unidentified products; b) a mixture of dienamine **8** (if formed) and catalyst which was separated by a second column chromatography (Merck Lobar columns, silica gel, elution with ethyl acetate). Further elution with methanol yielded betaine **7**, which was purified further by chromatography (Merck Lobar columns, silica gel, elution with ethyl acetate).

Reaction with Enaminone 1a; 3-[2-(1-Adamantyl)carbonyl-3,5-di(methoxycarbonyl)cyclopentadienide] propyl(methyl)ammonium (7a): 478 mg (1.84 mmol) of **1a**, 407 mg (2.21 mmol) of **4**, 29 mg (0.067 mmol) of $Rh_2(OAc)_4$. Time for addition of **4**: 100 h. Betaine **7a** was isolated by column chromatography and recrystallized from ethyl acetate (395 mg, 52%). Slightly beige powder, mp 161 °C dec. ^{1}H NMR: δ 1.64–1.80 (m, 6H, $CH_{2\ adamantyl}$), 1.84 (m_c, 6H, 3 × CH_2 ad.), 1.95 (m_c, 3H, 3 × CH ad.), 2.04 (m_c, 2H, NCH$_2$C*H*$_2$), 2.35–2.55 (m, 2H, CH$_2$C=C), 2.53 (s, 3H, NMe), 2.95 (m_c, 2H, NCH$_2$), 3.61 (s, 3H, OMe), 3.65 (s, 3H, OMe), 7.08 (s, 1H, =CH_{cp}), 8.26 (br s, 2H, N^+H_2). ^{13}C NMR: Table 2. IR (KBr). ν 3431 (m), 3100–2400 (broad bands), 1739 (m), 1678 (s), 1624 (vs), 1469 (vs), 1246 (vs), 1211 (s), 1192 (s), 1165 (vs), 1137 (s), 1083 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{33}NO_5$ (415.53): C 69.37, H 8.00, N 3.37. Found C 68.36, H 7.84, N 3.10.

Reaction with Enaminone 1b: The product mixture was subjected to column chromatography (cc) over silica gel. On elution with ethyl acetate, betaine **7b** and dienamine **8b** were obtained in the same fraction. This fraction was submitted to cc again, this time using ethyl acetate/MeOH (5:1). This procedure gave pure **7b** and a mixed fraction containing **7b** and **8b**. Complete isomerization of **8b** to **7b** was achieved by keeping the latter fraction at reflux for 6 h. The betaine precipitated as a yellow powder on concentrating the cold ethyl acetate solution (37% yield). Mp 177 °C dec. ^{1}H NMR (DMSO-d_6): δ 1.94 (m_c, 2H, NCH$_2$C*H*$_2$), 2.55 (s, 3H, NMe), 2.80–2.90 (m, 4H, NCH$_2$ and N(CH$_2$)$_2$C*H*$_2$), 3.03 (s, 3H, OMe), 3.60 (s, 3H, OMe), 6.91 (s, 1H, CH_{cp}), 7.30–7.45 and 7.85–7.98 (2 × m, 8H_{aryl}), 8.41 (br s, 2H, N^+H_2). ^{13}C NMR: Table 2. IR (KBr). ν 3440 (m), 3060–2300 (broad bands), 2503 (m), 1738 (w), 1644 (s), 1524 (s), 1491 (s), 1446 (s), 1244 (vs) cm^{-1}. Anal. Calcd for $C_{26}H_{26}N_2O_7$ (478.50): C 65.26, H 5.48, N 5.85. Found C 64.49, H 5.42, N 5.35.

Reaction with Enaminone 1c: After a total reaction time of 3 days, the solvent was evaporated, and the residue was stirred with ethyl acetate, yielding crude dienamine **8c** as a solid. Recrystallization from hot ethyl acetate furnished yellow-beige crystals, mp 66 °C, in 28% yield. ^{1}H NMR: δ 2.00–2.06 (m, 2H, NCH$_2$C*H*$_2$), 2.82 (s, 3H, NMe), 2.98 and 3.02 (AB part of ABX spin system, 2H, =CHC*H*$_2$), 3.22 (t, 2H, =CCH$_2$), 3.52 (m_c, 2H, NCH$_2$), 3.72 (s, 3H, OMe), 3.91 (s, 3H, OMe), 7.12 (X part of ABX system, 1H, =CH), 7.30–7.45 and 7.85–7.98 (2 × m, 8$H_{anthryl}$), 8.39 (s, 1H, 10-$H_{anthryl}$). ^{13}C NMR: δ 21.2 (C-4$_{pyrr}$), 35.2 (=CH*C*H$_2$), 37.7 (NMe), 51.9 (C-3$_{pyrr}$), 52.0 (OMe), 52.1 (OMe), 56.7 (NCH$_2$), 105.5 (=*C*COOMe), 124.8 (NC=*C*), 125.0 (C-10$_{anthryl}$), 125.2, 127.0, 128.3, 132.2 (=*C*HCH$_2$), 133.0, 135.2, 167.2 (N*C*=C), 168.2 and 170.9 (COOMe), 193.3 (C=O). IR (KBr). ν 1740 (s), 1714 (s), 1536 (vs), 1238 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{27}NO_5$ (457.52): C 73.51, H 5.95, N 3.06. Found C 73.36, H 6.02, N 3.00.

Reaction with Enaminone 1d: The reaction was carried out with **4** (469 mg, 2.55 mmol), **1d** (500 mg, 2.12 mmol) and $Rh_2(OAc)_4$ (34 mg, 0.077 mmol, 3 mol %) according to the general procedure and gave only betaine **7d** (430 mg, 52% yield). Viscous yellow oil. ^{1}H NMR: δ 1.22 (d, *J* 6.5 Hz, 6H, CH*Me*$_2$), 2.17 (m_c, 2H, CH$_2$), 2.86 (m_c, 2H, CH$_2$), 3.17 (m_c, 2H, NCH$_2$), 3.24 (sept, *J* 6.5 Hz, 1H, C*H*Me$_2$), 3.40 (s, 3H, OCH$_3$), 3.72 (s, 3H, OCH$_3$), 7.00 (dd, *J* 5 and 4 Hz, 1H, 4-$H_{thienyl}$), 7.29 (s, 1H, =CH_{cp}), 7.41 (dd, *J* 4 and 1 Hz, 1H, $H_{thienyl}$), 7.48 (dd, *J* 5 and 1Hz, 1H, $H_{thienyl}$), 8.82 (br s, N^+H_2). ^{13}C NMR: Table 2. IR (neat): ν 3450–2300 (br, N^+H_2), 1721 (sh), 1645 (br, vs, C=O), 1484 (s), 1435 (vs), 1413 (vs), 1266 (vs), 1233 (vs) cm^{-1}. Anal. Calcd for $C_{20}H_{25}NO_5S$ (391.49): C 61.36, H 6.44, N 3.58. Found: C 61.5, H 6.4, N 3.3.

Reaction with Enaminone 1e: The reaction was carried out with **4** (443 mg, 2.41 mmol), **1e** (500 mg, 2.01 mmol) and $Rh_2(OAc)_4$ (43 mg, 0.096 mmol, 4 mol %) and furnished betaine **7e** and dienamine **8e** in a combined yield of

741 mg (79%). Neat dienamine **8e** rearranges to form **7e** within a few hours at r.t.

Data for betaine **7e**: Viscous yellow oil. ^{1}H NMR: δ 2.12 (m_c, 2H, NCH_2CH_2), 2.86 (m_c, 2H, CH_2–Cp), 3.02 (m_c, 2H, NCH_2), 3.39 (m_c, 2H, NCH_2 allyl), 3.40 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 5.32–5.35 (m, 2H, CH=CH_2), 5.73 (m_c, 1H, CH=CH_2), 7.00 (dd, *J* 4.9 and 3.9 Hz, 1H, 4-$H_{thienyl}$), 7.31 (s, 1H, CH_{cp}), 7.41 (dd, ^3J 3.9 Hz, $|^4J|$ 1.1 Hz, 1H, 3-$H_{thienyl}$), 7.50 (dd, ^3J 5.0 Hz, $|^4J|$ 1.1 Hz, 1H, 5-$H_{thienyl}$), 9.09 (br s, 2H, N^+H_2). ^{13}C NMR: Table 2. IR (film): ν 3200–2200 (br, NH_2^+), 1732 (s), 1643 (vs), 1483 (s), 1442 (s), 1410 (s), 1266 (vs), 1236 (vs), 1195 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{23}NO_5S$ (389.47): C 61.68, H 5.95, N 3.60. Found: C 61.6, H 6.1, N 3.5.

Data for dienamine **8e**: Viscous yellow oil, 2:1 mixture of diastereomers. In the following, data for the minor isomer are given in brackets. ^{1}H NMR: δ 1.86–2.06 (m, 2H, 4-$H_{2\ pyrrolidine}$, both isomers), 2.55 [3.23] (m_c, 3-$H_{2\ pyrr}$), 3.05–3.45 (several m, CH_2COOMe, NCH_2 ring, both isomers), 3.62–3.71 (4 × s, OMe, both isomers), 3.78–3.83 [4.05–4.16] (m, 2H, NCH_2CH=), 5.10–5.25 (m, 2H, CH=CH_2, both isomers), 5.62 [5.82] (m_c, 1H, CH=CH_2), 6.92 (br dd, *J* 4.3 Hz, 1H, 5-$H_{thienyl}$), 7.13 [7.02] (X part of ABX system, 1H, NCH_2CH=), 7.30–7.38 (m, 2H, 3- and 4-$H_{thienyl}$, both isomers). ^{13}C NMR: δ 21.8 [20.3] (C-4_{pyrr}), 35.2 [33.7] (CH_2CO), 36.4 [45.7] (CH_2), 51.9 (OCH_3), 52.1 (OCH_3), 53.6 [52.5] (NCH_2CH), 53.9 [56.0] (C-5_{pyrr}), 98.6 [96.5] (NC=*C*), 118.9 [118.3] (=CH_2), 126.8 (C-$4_{thienyl}$), 129.7 (C-$3_{thienyl}$), 129.9 (C-$5_{thienyl}$), 131.5 (CH), 134.4, 136.6 [137.4], 147.2 (C-$2_{thienyl}$), 165.0 (NC=), 167.4 [167.6] (C=O), 170.6 [168.2] (C=O), 184.1 [180.0] (C=O). IR (film): ν 1736 (s), 1715 (s), 1667 (s), 1592 (s), 1511 (s), 1474 (m), 1436 (s), 1415 (s), 1353 (m), 1265 (vs) cm^{-1}. Anal. Calcd for $C_{20}H_{23}NO_5S$ (389.47): C 61.68, H 5.95, N 3.60. Found: C 61.0, H 6.3, N 3.3.

Reaction with Enaminone 1f: The reaction was carried out with **4** (410 mg, 2.22 mmol), **1f** (500 mg, 1.86 mmol) and $Rh_2(OAc)_4$ (29 mg, 0.07 mmol, 3 mol %) and furnished betaine **7f** (97 mg, 13% yield) and dienamine **8f** (397 mg, 53% yield). Heating of **8f** in a Kugelrohr apparatus at 200 °C for 10 min resulted in partial decomposition and formation of betaine **7f**, which could be isolated after chromatography in 26% yield.

Data for betaine **7f**: Yellow oil. ^{1}H NMR: δ 2.17 (m_c, 2H, NCH_2CH_2), 2.93 (m_c, 4H, $NCH_2CH_2CH_2$), 3.21 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 3.93 (s, 2H, NCH_2Ph), 7.26–7.33 (m, 8H, CH and H_{aryl}), 7.62 (dd, 2H, H_{aryl}), 9.27 (br s, 2H, N^+H_2). ^{13}C NMR: Table 2. IR (film): ν 3400–2200 (br, N^+H_2), 1738 (sh), 1643 (vs), 1590 (s), 1544 (m), 1484 (s), 1443 (s), 1409 (s), 1350 (m), 1233 (vs), 1199 (s), 1170 (s) cm^{-1}. MS (FD, 8 kV): *m/z* (%) 468 (90) [MH^+], 467 (100) [M^+, ^{35}Cl], 435 (27) [$M^+ - CH_3OH$], 403 (10) [$M^+ - 2\ CH_3OH$]. Anal. Calcd for $C_{26}H_{26}ClNO_5$ (467.95): C 66.74, H 5.60, N 2.99. Found: C 66.9, H 5.7, N 3.1.

Data for dienamine **8f**: Yellow oil, 1.3:1 mixture of diastereomers. In the following, the data for the second isomer are given in brackets (in some cases, assignments may be interchanged). ^{1}H NMR: δ 1.97–2.04 (m, 2H, 4-$H_{2\ pyrrolidine}$), 3.14 [2.56] (m_c, 2H, 3-$H_{2\ pyrr}$), 2.86 [2.92] (AB part of ABX system, $|J_{AB}|$ 20.4 Hz, $J_{AX} = J_{BX}$ = 7.2 Hz, 2H, CH_2CO), 3.35 [3.73] (m_c, 2H, 5-$H_{2\ pyrr}$), 4.42 [4.64] (AB system, $|^2J|$ 16.0 [16.7] Hz, 2H, NCH_2Ph), 3.54, 3.59 [3.65, 3.66] (4 × s, 3H, COOMe), 6.87 [6.79] (X part of ABX system, $^3J_{AX} = {}^3J_{BX}$ = 7.2 Hz, 1H, =$CHCH_2$), 7.06–7.39 (m_c, 9H, H_{Ar}). ^{13}C NMR: δ 22.4 [21.8] (C-4_{pyrr}), 35.5, 36.7 [35.1, 35.7] (CH_2), 51.2, 52.0, 52.2 (4 × COO*Me*), 52.1 [54.4] (NCH_2Ph), 54.2 [57.0] (C-5_{pyrr}), 99.0 [97.0] (NC=*C*), 127.2, 127.6, 127.7, 127.8, 128.3, 128.7, 128.5, 129.1, 129.4 (all C_{Ar}), 134.4, 135.6, 135.9, 136.3 [137.0] (=*C*HCH_2) 141.3 [140.6] (C-Cl), 156.5 (N*C*=C), 167.2, 167.4, 167.9, 170.4 (all *C*OOMe), 193.2 [188.1] (C=O). IR (film): ν 1737 (s), 1712 (s), 1668 (m), 1612 (s), 1589 (s), 1566 (m), 1518 (s), 1434 (s), 1265 (vs), 1199 (m), 1171 (m), 1088 (m) cm^{-1}. MS (FD, 8 kV): *m/z* (%) 467 (100) [M^+, ^{35}Cl]. Anal. Calcd for $C_{26}H_{26}ClNO_5$ (467.95): C 66.74, H 5.60, N 2.99. Found: C 66.7, H 5.6, N 3.4.

Reaction with Enaminone 1g: The reaction was carried out with **4** (359 mg, 1.95 mmol), **1g** (500 mg, 1.62 mmol) and $Rh_2(OAc)_4$ (34 mg, 0.08 mmol, 4 mol %) and furnished betaine **7g** (113 mg, 15% yield) and dienamine **8g** (473 mg, 63% yield). Heating of **8g** in a Kugelrohr apparatus at 200 °C for 10 min resulted in both unspecific decomposition and formation of betaine **7g** which could be isolated after chromatography in 27% yield.

Data for betaine **7g**: Yellow oil. ^{1}H NMR: δ 2.15 (m_c, 2H, NCH_2CH_2), 2.85 (m_c, 2H, NCH_2CH_2), 2.95 (m_c, 2H, CH_2–Cp), 3.23 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.83 (NCH_2Ph), 3.89 (s, 3H, OCH_3), 6.84–7.68 (m, 9H, H_{aryl}), 7.31 (s, 1H, CH_{cp}), 9.39 (br s, 2H, N^+H_2). ^{13}C NMR: Table 2. MS (FD, 8 kV): *m/z* = 463 (100) [M^+], 431 (29) [$M^+ - CH_3OH$], 399 (8) ($M^+ - 2\ CH_3OH$). Anal. Calcd for $C_{27}H_{29}NO_6$ (463.53): C 69.96, H 6.30, N 3.02. Found: C 69.7, H 6.4, N 3.0.

Data for dienamine **8g**: Yellow oil, 1.2:1 mixture of diastereomers. ^{1}H NMR, signal assignments to one or the other isomer are not made: δ 1.94 [1.94] (m_c, 2H, NCH_2CH_2), 2.55 (m_c, 1H, NCH), 2.80–3.10 (several m, 4 H), 3.32 (m_c, 1H), 3.54, 3.60, 3.66, 3.67, 3.77, 3.79 (all s, 3H, OMe of both isomers), 4.39 [4.58] [m_c, AB part of ABX system, $|^2J|$ 18.0 Hz, 2H, NCH_2Ph), 6.69–7.47 (m, 10H, H_{aryl} and CH_2CH=). ^{13}C NMR, signals assignments to one or the other isomer are not made: δ 20.4 and 22.0 (C-4_{pyrr}); 35.0, 35.2, 35.4 and 36.5 (C-3_{pyrr} and CH_2COOMe); 50.2, 51.8, 55.1 (3 × OCH_3); 54.2 (NCH_2 $_{ring}$), 53.9 and 56.9 (NCH_2Ph), 97.5 and 99.8 (NC=*C*); 127.1, 127.3, 127.5, 128.4, 128.6, 128.8, 129.0, 129.89, 129.92, 134.6, 134.8, 135.2, 135.6, 135.8; 136.3 [136.5] (=*C*HCH_2); 161.0 (C_{aryl}OMe), 164.5 [166.0] (N*C*=C),

189.3 [194.1] (C=O). IR (film): ν 1643 (br, s), 1603 (s), 1484 (s), 1442 (s), 1265 (vs), 1169 (s) cm^{-1}. Anal. Calcd for $C_{27}H_{29}NO_6$ (463.53): C 69.96, H 6.30, N 3.02. Found: C 69.9, H 6.3, N 3.4.

Reaction with Enaminone 1h: The reaction was carried out with **4** (413 mg, 2.25 mmol), **1h** (500 mg, 1.87 mmol) and $Rh_2(OAc)_4$ (40 mg, 0.09 mmol, 4 mol %) and furnished dienamine **8h** (512 mg, 65% yield). Heating of **8h** in a Kugelrohr apparatus at 200 °C for 10 min resulted in both unspecific decomposition and formation of betaine **7h**, which could be isolated after chromatography in 28% yield.

Data for betaine **7h**: Yellow oil. ^{1}H NMR: δ 2.20 (m_c, 2H, NCH_2CH_2), 2.80–3.00 (m, 4H, $NCH_2CH_2CH_2$), 3.50 (s, 3H, OMe), 3.67 (s, 3H, OMe), 3.79 (pseudo-t, 2H, NCH_2Ph), 6.49 (dd, *J* 3.5 and 1.5 Hz, 1H, H_{furyl}), 6.86 (d, *J* 3.5 Hz, 1H, H_{furyl}), 7.50 (dd, *J* 1.5 and 0.5 Hz, 1H, H_{furyl}). ^{13}C NMR: Table 2. IR (film): ν 3400–2300 (br, N^+H_2), 1738 (sh), 1668 (s), 1573 (s), 1530 (s), 1473 (s), 1442 (s), 1411 (s), 1392 (s), 1265 (s), 1235 (s), 1146 (s), 1105 (m) cm^{-1}. MS (FD, 8 kV): *m/z* (%) 423 (100) [M^+], 391(7) [$M^+ - CH_3OH$)]. Anal. Calcd for $C_{24}H_{25}NO_6$ (423.46): C 68.07, H 5.95, N 3.31. Found: C 68.1, H 6.2, N 3.4.

Data for dienamine **8h**: Yelllow oil, 2:1 mixture of diastereomers. In the following, data for the minor isomer are given in brackets. ^{1}H NMR: δ 1.90–2.04 (m, 2H, NCH_2CH_2, both isomers), 2.98 [2.55] ("t", 2H, CH_2CH=), 3.26 [3.26] (m_c, 2H, 3-$H_{2\ pyrr}$), 3.54 and 3.59 [3.66, 3.70] (s, 3H, OCH_3), č3.6 (m_c, NCH_2, both isomers), 4.40 [4.60] (AB system, $|^2J|$ 16.0 [15.7] Hz, 2H, NCH_2Ph), 6.33 [6.30] (br s, 1H, 4-H_{furyl}), 6.81 [6.65] (br s, 1H, 3-H_{furyl}), 7.06 (d, 2H, H_{aryl}), 7.18–7.31 (m, 3H, H_{aryl}), 7.25 [7.01] (br s, 1H, =$CHCH_2$), 7.36 [7.35] (br s, 1H, 5-H_{furyl}). ^{13}C NMR: δ 21.8 [20.3] (C-4_{pyrr}), 36.2 [34.9] (C-3_{pyrr}), 35.0 [35.6] (CH_2CO), 52.1, 52.3 (2 × OCH_3, both isomers), 54.3 (C-5_{pyrr}), 54.5 (NCH_2Ph), 97.9 (NC=*C*), 111.0 (C-4_{furyl}), 114.8 (C-3_{furyl}), 127.2, 127.5, 128.4, 128.7, 133.7 (all C_{aryl}) 136.0 (=$CHCH_2$), 137.0 (=$CCOOCH_3$), 143.8 (C-5_{furyl}), 154.6 (C-2_{furyl}), 156.3 (N*C*=C) 167.7, 170.9, 179.9 (3 × C=O). IR (film): ν 1737 (s), 1713 (s), 1609 (s), 1518 (s), 1469 (s), 1436 (s), 1265 (vs) cm^{-1}. MS (EI, 70eV): *m/z* 423 (31) [M^+], 392 (4) [$M^+ - CH_3OH$], 364 (4), 350 (100) [$M^+ - CH_2COOCH_3$], 328 (31) [$M^+ - CH_2COOCH_3 - CH_3OH$]. Anal. Calcd for $C_{24}H_{25}NO_6$ (423.46): C 68.07, H 5.95, N 3.31. Found: C 68.0, H 6.4, N 3.1.

Reaction with Enaminone 1i: The reaction was carried out with **4** (186 mg, 1.0 mmol), **1i** (250 mg, 0.83 mmol) and $Rh_2(OAc)_4$ (13.3 mg, 3 mol %) and furnished dimethyl 5-(4-chlorophenyl)-5-oxo-4-(1-phenyltetrahydro-*1H*-pyrrol-2-ylidene)pent-2(*Z*)-ene-1,3-dicarboxylate (**8j**) as a colorless oil (278 mg, 74% yield). The NMR spectra showed the presence of a single diastereoisomer. ^{1}H NMR: δ 2.12 (m_c, 2H, NCH_2CH_2), 2.91 (AB part of ABX system, $|^2J_{AB}|$ 18.0 Hz, $^3J_{AX} = {}^3J_{BX}$ = 6.9 Hz, 2H, $CHCH_2C$=O), 3.22 (m_c, 2H, =CCH_2), 3.46 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.79 (m_c, 1H, NCH), 3.87 (m_c, 1H, NCH), 6.31 (t, X part of ABX system, 1H, =$CHCH_2$), 6.88–7.18 (m, 5H, C_6H_5), 7.22 and 7.43 (AA'BB', 4H, C_6H_4Cl). ^{13}C NMR: δ 22.0 (C-4_{pyrr}), 35.6 (=CCH_2 und CH_2C=O), 51.7 (OCH_3), 52.0 (OCH_3), 56.8 (NCH_2), 102.1 (NC=*C*), 124.6, 126.2, 127.9, 129.2, 129.5 (all C_{aryl}), 136.1 (CCl), 155.6 (*i*-C_{aryl}), 163.7, 166.3 ($COOCH_3$), 170.3 ($COOCH_3$), 193.9 (C=O). IR (film): ν 1719 (s), 1599 (s), 1589 (s), 1492 (s), 1435 (s), 1263 (vs), 1090 (vs), 1044 (s), 1013 (s), 909 (vs) cm^{-1}. MS (FD, 8 kV): *m/z* 453 (100%) [M^+]. Anal. Calcd for $C_{25}H_{24}ClNO_5$ (453.92): C 66.15, H 5.33, N 3.09. Found: C 66.5, H 5.4, N 3.4.

Reaction with Enaminone 1j: The reaction was carried out with **4** (410 mg, 2.22 mmol), **1j** (500 mg, 1.86 mmol) and $Rh_2(OAc)_4$ (29 mg, 0.07 mmol, 3 mol %) and furnished dimethyl 5-(2-thienyl)-5-oxo-4-(1-phenyltetrahydro-*1H*-pyrrol-2-ylidene)pent-2-ene-1,3-dicarboxylate (**8i**) as a yellow oil (577 mg, 73% yield). The NMR spectra showed the presence of a single diastereoisomer. ^{1}H NMR: δ 2.08–2.17 (m, 2H, NCH_2CH_2), 2.98/3.02 (AB part of ABX system, $^3J_{AX} = {}^3J_{BX}$ = 7.7 Hz, $|^2J_{AB}|$ 18.2 Hz, 2H, CH_2CO), 3.34 (m_c, 2H, C=CCH_2), 3.66 (s, 3H, OCH_3), 3.72 and 3.92 (m_c, 2H, NCH_2), 3.84 (s, 3H, OCH_3), 6.48 (X part of ABX system, 1H, =$CHCH_2$), 6.90 (dd, *J* 5.9 and 3.8 Hz, 1H, 4-$H_{thienyl}$), 7.00 (d, *J* 8.2 Hz, 2H), 7.09 (t, *J* 7.4 Hz, 1H), 7.19 (t, *J* 8 Hz, 2H), 7.34 (dd, *J* = 3.8 and 1.1 Hz, 1H, 3-$H_{thienyl}$), 7.36 (dd, *J* =5.5 and 1.1 Hz, 1H, 5-$H_{thienyl}$). ^{13}C NMR: δ 22.1 (C-4_{pyrr}), 35.3 (CH_2CO), 35.4 (*C*-3_{pyrr}), 51.7 (OCH_3), 51.9 (OCH_3) 56.8 (NCH_2), 102.0 (NC=*C*), 124.2, 126.1, 126.7 (C-$4_{thienyl}$), 128.9, 130.4 (C-$3_{thienyl}$), 130.5 (C-$5_{thienyl}$), 133.6, 135.6, 142.7, 147.0 (C-$2_{thienyl}$), 163.4 (N*C*=C), 166.5, 170.5, 185.1 (3 × C=O). IR (film): ν 1737 (s), 1718 (s), 1658 (m), 1601 (s), 1510 (s), 1491 (s), 1475 (m), 1453 (m), 1435 (m), 1413 (m), 1353 (m), 1319 (m), 1275 (m), 1200 (m), 1169 (m), 1077 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) 425 (21) [M^+], 394 (3) [$M^+ - OCH_3$], 366 (3) [$M^+ - COOCH_3$], 352 (100) [$M^+ - CH_2COOCH_3$), 111(19) [COC_4H_3S]. Anal. Calcd for $C_{23}H_{23}NO_5S$ (425.50): C 64.92, H 5.45, N 3.29. Found: C 65.0, H 5.7, N 3.4.

Synthesis of Polycycle 9: Dienamine **8c** (99 mg, 0.22 mmol), activated silica gel (ca. 10 mg), and anhydrous toluene (3 mL) were placed in a thick-walled Schlenk tube, and the mixture was heated at 180 °C for 14 h. After cooling, the solvent was evaporated and the residue was submitted to column chromatography over silica gel. Elution with ethyl acetate gave two distinct fractions. The first one furnished an orange-red solid (3 mg) which was discarded. The section (green) fraction was concentrated and kept at –20 °C for 3 days. Compound **9** was obtained as a colorless solid (15 mg, 15% yield), mp 211 °C. ^{1}H NMR

data indicate the presence of two isomers, but only the data of the major isomer are given here: δ 2.04 and 2.11 (2 × m_c, 2H, NCH_2CH_2), 2.60 (dd, *J* 10.3 and 6.1 Hz, 1H), 2.78 (s 3H, NCH_3), 2.87 (d, *J* 5.9 Hz, 1H), 3.18 (d, *J* 10.5 Hz, 1H), 3.34 (m_c, $J_1 = J_2$ = 8.5 Hz, 2H, CH_2C=), 3.47 (t, *J* 10.0 Hz, 2H, NCH_2), 3.57 (s, 3H, OMe), 3.61 (s, 3H, OMe), 4.70 (s, 1H), 7.02–7.96 ($8H_{arom}$). ^{13}C NMR: δ 20.8 (C-4_{pyrr}), 33.7 (C-3_{pyrr}), 35.1 (NMe), 41.0, 48.0, 49.1, 50.0, 51.8 and 51.9 (COO*Me*), 58.5, 98.7, 121.7–126.3 (8 signals), 138.4, 139.1, 140.2, 143.5, 165.2 (C-2_{pyrr}), 195.7 (C=O). IR (KBr). ν 1742 (s), 1649 (m), 1553 (s) cm^{-1}.

Synthesis of Betaine 7c and Dimethyl 7-(9-anthrylcarbonyl)-2,3-dihydro-1-methyl-1*H*-indole-4,6-dicarboxylate (10): A solution of $NaOCH_3$ in methanol, prepared from sodium (4.2 mg, 0.18 mmol) and anhydrous methanol (5 mL), was added to an ice-cooled solution of dienamine **8c** (84 mg, 0.18 mmol) in anh. methanol (15 mL). The mixture was allowed to react for 15 h, giving rise to at least six products as indicated by TLC. After neutralization of the orange-colored solution with aqueous NH_4Cl, dihydroindole **10** separated as an orange solid within 10 min (11 mg, 13% yield). The mother liquor was chromatographed over silica gel. Elution with ethyl acetate furnished betaine **7c** as the slowest moving fraction: 8 mg (10% yield) of an ochre powder, mp 207 °C dec.

Data for **7c**: ^{1}H NMR (CD_3OD): δ 2.05 (br, 2H, Cp–CH_2), 2.34 (br, 2H, NCH_2CH_2), 2.61 (s, 3H, NMe), 2.88 (br, 2H, NCH_2), 3.37 (s, 3H, OMe), 3.79 (s, 3H, OMe), 7.14 (s, 1H, CH_{cp}), 7.35–7.46 (m, 4H), 7.93 (d, *J* 8.6 Hz, 2H), 8.00 (d, *J* 8.4 Hz, 2H), 8.45 (s, 1H). ^{13}C NMR: Table 2. IR (KBr). ν 3447 (br. m), 1738 (w), 1686 (s), 1656 (s) 1535 (s), 1490 (s), 1443 (s), 1232 (vs) cm^{-1}. Anal. Calcd for $C_{28}H_{27}NO_5$ (457.52): C 73.51, H 5.95, N 3.06. Found C 72.89, H 5.93, N 3.14.

Data for **10**: ^{1}H NMR: δ 2.65 (s, 3H, COOMe), 2.78 (s, 3H, NMe), 3.51 (NCH_2CH_2), 3.80 (t, 2H, NCH_2), 3.88 (s, 3H, COOMe), 7.26 (s, 1H), 7.45 (m_c, 4H), 8.01 (d, *J* 5.5 Hz, 2H), 8.30 (d, *J* 6.0 Hz, 2H), 8.59 (s, 1H). ^{13}C NMR: δ 28.8 (C-3), 39.9 (NMe), 51.6/52.0 (COO*Me*), 56.8 (C-2), 118.3 (C-5), 122.8 (C-6), 125.2, 125.3 (C-4), 127.7, 125.8, 126.7, 128.1, 130.6, 131.1, 132.5, 132.7, 140.5 (C-3a), 152.4 (C-7a), 166.1/168.4 (*C*OOMe), 195.1 (C=O). IR (KBr): ν 1726 (vs), 1644 (m), 1567 (m), 1299 (s), 1241 (vs), 1091 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) 453 (100) [M$^+$], 421 (71).

Dimethyl 2-(4,4-dimethyl-2-morpholino-6-oxocyclohexen-1-en-1-yl)-1-propene-1,3-dicarboxylate (12): The reaction was carried out with **4** (527 mg, 2.86 mmol), 5,5-dimethyl-3-morpholinocyclohex-2-en-1-one (**11**) (500 mg, 2.38 mmol), and $Rh_2(OAc)_4$ (38 mg, 3 mol %) according to the general procedure. Crystallization from ether at –10 °C yielded slightly beige crystals, mp 110 °C. Yield: 747 mg (86%). ^{1}H NMR: δ 1.11 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 2.23 and 2.31 (AB system, $|^2J|$ 16.0 Hz, 2H, CH_2C=O, ring), 2.34 and 2.47 (AB system, $|^2J|$ 16.0 Hz, 2H, CH_2, ring), 2.91 and 3.09 (AB part of ABX system, $|^2J_{AB}|$ 18.0 Hz, $^3J_{AX} = {}^3J_{BX}$ = 6.0 Hz, 2H, =CHCH_2CO), 3.21/3.23 (2 × t, *J* 4.8 Hz, 2H, NCH^AH^B), 3.32/3.43 (2 × t, *J* 4.8 Hz, 2H, NCH^AH^B), 3.70 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 4.75 (t, *J* 4.8 Hz, 4H, $O(CH_2)_2$), 6.97 (X part of ABX system, 1H, =C*H*CH_2). ^{13}C NMR: δ 28.2 (CH_3), 28.7 (CH_3), 31.8 (*C*$(CH_3)_2$), 35.4 (*C*H_2COOCH_3), 42.9 (CH_2), 49.2 (N$(CH_2)_2$), 49.9 (*C*H_2C=O, ring), 51.9 (OCH_3), 52.0 (OCH_3), 66.9 ($O(CH_2)_2$), 108.3 (NC=*C*), 133.1 (C=*C*COOCH_3), 134.0 (*C*H=CCOOCH_3), 163.0 (N*C*=C), 167.5, 176.7, 194.9 (3 × C=O). IR (KBr): ν 1733, 1715, 1702, 1628 (C=O) cm^{-1}. Anal. Calcd for $C_{19}H_{27}NO_6$ (365.42): C 62.45, H 7.45, N 3.83. Found: C 62.3, H 7.4, N 4.0.

X-ray Crystal Structure Detemination for 9 and 10. Single crystals were obtained by evaporation of a solution in ethyl acetate in both cases. Data collection was performed at 293(2) K on an image-plate diffractometer (Stoe IPDS) using monochromated Mo-*K*α radiation (λ = 0.71073 Å). Both structures were solved by direct methods and refined (F^2 values) using a full-matrix least-squares method. Hydrogen atom positions were calculated geometrically and treated as riding on their bond neighbors in the refinement procedure. Software for struc-

Table 1. Summary of crystallographic data and structure refinement details for compounds **9** and **10.**

	9	**10**
Formula	$C_{28}H_{27}NO_5$	$C_{28}H_{23}NO_5$
M_r	457.51	453.47
Cryst. size, mm^3	0.46 × 0.38 × 0.26	0.46 × 0.35 × 0.23
Crystal system	orthorhombic	monoclinic
Space group, *Z*	$P\,2_12_12_1$, 4	$P\,2_1/n$, 4
a, Å	9.5743(9)	13.257(3)
b, Å	12.9563(8)	9.051(2)
c, Å	19.8049(13)	19.386(5)
α, deg	90	90
β, deg	90	104.55(3)
γ, deg	90	90
V, Å^3	2456.7(3)	2251.5 (9)
D_{calcd}, g cm^{-3}	1.237	1.338
μ(MoK_α), mm^{-1}	0.085	0.092
F(000), e	968	952
hkl range	±11, ±15, –23→24	±16, ±11, ±23
θ_{min}, θ_{max}, °	2.06, 25.98	2.14, 25.92
Refl. measured	19515	18750
Refl. unique (R_{int})	4740 (0.0545)	4357 (0.0750)
Param. refined	310	310
$R(F)$/w$R(F^2)$ (all reflections)[a]	0.0839 / 0.0926	0.0886 / 0.1186
Goodness of fit (GoF)[b]	0.841	0.644
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.17/–0.16	0.15/–0.16

[a] $R(F) = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$.

[b] GoF = $[\Sigma w(|F_o| - |F|_c)^2 / (N_{obs} - N_{param})]^{1/2}$.

ture solution and refinement: SHELX-97 [19]; molecule plots: ORTEP-3 [20]. Further details are provided in Table 3. CCDC-697829 (**9**) and -697830 (**10**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* .

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Povzetek

Z rodijem katalizirane reakcije dimetil 3-diazo-1-propen-1,3-dikarboksilata (**4**) z N-substituiranim petčlenskimi semicikličnimi enaminoni **7** vodijo do (3-amoniopropil)ciklopentadienov **8** in/ali dienaminov **9**, ki formalno predstavljajo vrinjanje karbenoida v enaminsko C–H vez. Termično izomerizacijo olajšujejo elektrondonorski substituenti na dušiku in na karbonilni skupini enaminona. Na splošno N-alkil substituirani dienamini **9** izomerizirajo, medtem ko izomerizacija ne poteče pri N-fenil substituiranih spojinah **9**. Izomerizacijske lastnosti N-metil-3-(antracen-9-ilkarbonil) substituiranega dienamina **9c** so kompleksne; z natrijevim metoksidom poteče izomerizacija do betaina, medtem ko pod termičnimi pogoji v prisotnosti silikagela nastane pentacikel **10**, kot produkt intramolekularne Diels-Alderjeve reakcije na antracenskem preostanku. Rodij-katalizirana reakcija vinildiazoacetata **4** s 3-molfolinocikloheks-2-en-1-onom **12** pa je analogna s pretvorbo enaminona **7** v dienamin **9**.