(Alkenyl)(amino)carbene Complexes: Potential Starting Materials for the Synthesis of Cyclopropylacetic Acid Derivatives

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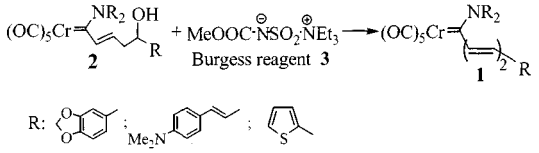
Keywords: Fischer-type carbene complexes / Cyclopropylacetic acid derivatives / Burgess reagent

The (δ-hydroxyalkenyl)(pyrrolidino)carbene complexes, prepared by means of aldol additions of the (propenyl)(pyrrolidino)carbene complex to *p*-nitrobenzaldehyde and 4-pyridinecarbaldehyde, have been treated with methyl *N*-(triethylammoniosulfonyl)carbamate inner salt (Burgess reagent) to afford the corresponding adducts in almost quantitative yields. Treatment of these adducts with NaOH in methanol gave the corresponding conjugated polyunsaturated (amino)carbene complexes in fair yields. Alternatively, heating the adducts to 55–60 °C led to the isolation of cyclopropylacetic acid derivatives as the main reaction products, in yields of 20–40% depending on the polarity of the solvent. The adduct of the aldol addition product of the (propenyl)(pyrrolidino)carbene complex and *p*-$O_2NC_6H_4$–CH=CH–CHO with the Burgess reagent could not be isolated, but directly afforded the cyclopropane derivative as well as the polyunsaturated (amino)-carbene complex. We present herein a brief discussion of the key steps of the mechanism of this cyclopropane ring formation.

Introduction

Fischer-type carbene complexes[1−5] have become increasingly important in the field of synthetic organic chemistry because their particular thermal and photochemical metal-centred reactivities facilitate the preparation of a wide range of valuable organic and organometallic compounds.[6−11] Furthermore, it has recently been shown that the pentacarbonyl(carbene)metal unit is a powerful accepting group in the preparation of "push-pull" molecules, which are interesting structures with potential applications as nonlinear optical (NLO) materials.[12−15] For example, moderate to high second-order nonlinearities have been observed in conjugated polyunsaturated (amino)carbene complexes **1** (with electron-donating aromatic and heteroaromatic substituents R′),[16] which were synthesized in satisfactory yields by means of the dehydration of (amino)(δ-hydroxyalkenyl)carbene complexes **2** using 3 equiv. of methyl *N*-(triethylammoniosulfonyl)carbamate inner salt **3** (the commercially available Burgess reagent)[17] (Scheme 1).



Scheme 1. Synthetic pathway for conjugated polyunsaturated (amino)carbene complexes **1**

Another peculiarity of Fischer-type carbene complexes is their low-energy metal-to-ligand charge transfer (MLCT) transition, where the metal centre donates electrons to the carbene ligand. As a result, the pentacarbonyl(carbene)metal unit can be considered as an amphoteric group, i.e. it behaves as an electron-accepting group in the ground state and as a donating group in the excited state. This dual behaviour of pentacarbonyl(carbene)metal units not only satisfies the prerequisites for good second-order nonlinearity, but also extends the possibility of observing such behaviour to unsaturated Fischer carbene complexes bearing electron-accepting groups at the end of the unsaturated chain. This possibility prompted us to synthesize (amino)carbene complexes of type **1** where R′ was an electron-accepting group such as *p*-nitrophenyl or a pyridine nucleus.

Results and Discussion

According to our previously developed methodology,[16] the propenyl(pyrrolidine)carbene complex **4** was treated with *p*-nitrobenzaldehyde (**5a**), 4-pyridinecarbaldehyde (**5b**), and *p*-nitrocinnamaldehyde (**5c**) to afford the corresponding (amino)(δ-hydroxyalkenyl)carbene complexes **6a−c** in yields of 86%, 99%, and 74%, respectively.

When **4** was treated with **5a**, we invariably observed the formation of some *p*-nitrobenzyl alcohol, which stemmed from reduction of the aldehyde by LDA.[18] The best yields of **6a** were obtained using a 1.5-fold excess of LDA and a

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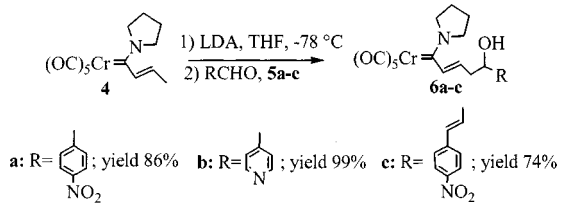
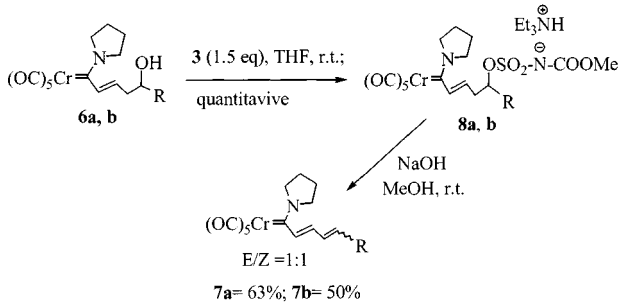
twofold excess of **5a** at a temperature of −40 °C (see Exp. Sect.) (Scheme 2).



Scheme 2. Synthesis of (amino)(δ-hydroxyalkenyl)carbene complexes **6a−c**

In an initial experiment, complex **6a** was treated with 3 equiv. of the Burgess reagent **3** in THF at room temperature. Unexpectedly, the polyunsaturated complex **7a** was recovered in only 6% yield, while the main reaction product, isolated in 55% yield, was the adduct **8a**. Using just 1.5 equiv. of **3**, complex **8a** was obtained in almost quantitative yield. Similarly, **6b** was quantitatively transformed into **8b** using 1.5 equiv. of **3**.

Treatment of the adducts **8a** and **8b** with methanolic NaOH at room temperature gave the corresponding polyunsaturated carbenes **7a**,**b** in yields of 63% and 50%, respectively, as 1:1 (*E*)/(*Z*) isomeric mixtures about the newly formed double bond (Scheme 3).



Scheme 3. Synthesis of polyunsaturated (amino)carbenes **7a**,**b**

All our attempts to separate the (*E*)/(*Z*) isomeric mixtures into pure components were unsuccessful. However, as better nonlinearities are obtained with all double bonds in the polyenic spacer in the *trans* configuration, it was important to obtain the pure *trans* isomers in order to allow adequate evaluation of their nonlinear optical properties.

In his original report, on the basis of solvent and isotope effects,[17] Burgess demonstrated that the dehydration of alcohols using reagent **3** involves: (i) the formation of adduct **9**, (ii) C−OSO_2 bond breaking in adduct **9** with formation of the intimate ion pair **11**, and finally (iii) *syn* elimination of the triethylammonium salt **10** of *N*-(methoxycarbonyl)-sulfamic acid. The overall process usually yields the corresponding alkene with a high degree of (*E*) regioselectivity (Figure 1).

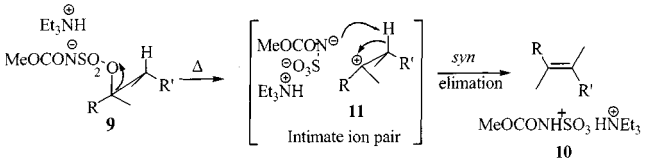
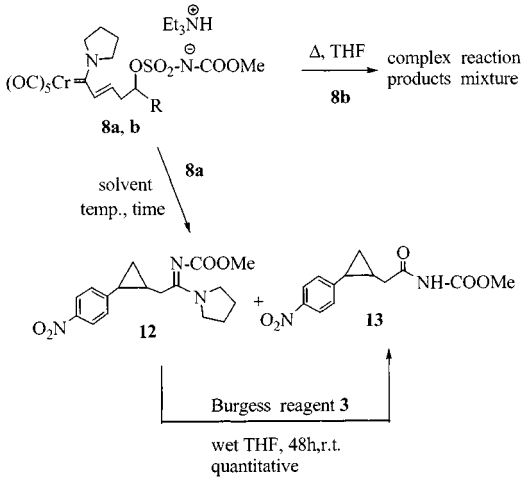


Figure 1. Mechanism of dehydration using the Burgess reagent

In an attempt to obtain pure (*E*) isomers of complexes **7a** and **7b**, the adducts **8a**,**b** were heated in refluxing THF. Under these conditions, the adduct **8b** unexpectedly evolved into a complex mixture of unidentified reaction products, while (besides a trace amount of **7a**) **8a** gave the cyclopropylacetic acid derivative **12** as the main reaction product in 20% yield (Scheme 4, Table 1, Entry 2).



Scheme 4. Thermal evolution of the adduct **8a**

Table 1. Summary of the obtained results

Entry	Solvent	*T* [°C]	*t* [h]	Yield of 12 (%)
1	DMF	55−60	2	decomposition
2	THF	67	3	20
3	toluene	55−60	15	30
4	$Cl(CH_2)_2Cl$	55−60	24	43[a]
5	toluene	55−60	15	27[b]
6	none	55−60	168	decomposition

[a] Overall yield in cyclopropane derivatives **12** and **13**. − [b] Experiment performed in the presence of 2 equiv. of *t*BuOCONH$_2$.

The formation of moderate yields of a cyclopropane derivative was the surprising result of an interesting skeletal rearrangement of the starting adduct **8a**. Given that the biological properties of cyclopropylacetic acid derivatives make them important organic compounds,[19−24] we decided to investigate this reaction in more detail.

We started by focusing on the experimental parameters, such as the reaction temperature, the nature of the solvent, and the possible presence of additives. None of the experiments showed any appreciable reaction at temperatures below 55−60 °C, but at such temperatures the reaction times

and fate of **8a** were found to be strongly influenced by the polarity of the solvent. In DMF (a more polar solvent than THF), **8a** was completely consumed within 2 h at 55−60 °C, but underwent extensive decomposition leading to an intractable product mixture (Table 1, Entry 1). In less polar solvents such as toluene, in which **8a** is only partially soluble, its complete consumption required 15 h at the same temperature, which led to a considerable improvement in the yield of **12** (Table 1, Entry 3). An additional experiment was carried out by heating **8a** to 55−60 °C in the absence of a solvent. After 7 d, adduct **8a** had been completely consumed, but generated only a complex and intractable mixture of products similar to that produced by the reaction performed in DMF (Table 1, Entry 6).[25] These results clearly show that both the solubility of **8a** in the reaction medium and the polarity of the latter are crucial factors in the conversion of **8a** to **12**.

A suitable solvent for the transformation of **8a** to **12** should therefore simultaneously satisfy three prerequisites: (i) a boiling point of 60 °C or higher, (ii) a polarity comparable to or lower than that of THF; and (iii) the capacity to dissolve **8a** completely. Adduct **8a** is highly soluble in halogenated solvents; 1,2-dichloroethane is one of the most common and also satisfies all three of the aforementioned criteria.[26] The experiment performed using this solvent required 24 h at 55−60 °C to reach completion and, as expected, led to high yields of the cyclopropylacetic acid derivative, which was recovered as a mixture of derivatives **12** and **13** in 43% overall yield (Scheme 4; Table 1, Entry 4).

The *N*-acylcarbamate ester function[27−31] present in the new cyclopropylacetic acid derivative **13** arose from hydrolysis of the *N*-(methoxycarbonyl)amidine function of **12** during workup of the reaction mixture and subsequent purification by column chromatography. The identity of **13** was confirmed by treating **12** with wet SiO_2 or 1 equiv. of the Burgess reagent in wet THF. In the latter case, a quantitative conversion into **13** was observed after 48 h at room temperature.

Since a methyl carbamate unit was present in the structure of **12**, an experiment was performed in which **8a** was heated in toluene in the presence of 2 equiv. of *tert*-butyl carbamate (H_2NCOO*t*Bu) as an external reagent, in order to ascertain whether exchange of the carbamate moiety could occur. The presence of the additive did not affect either the reaction time or the yield of **12** (Table 1, Entry 5), and there was no incorporation of H_2NCOO*t*Bu into the structure of the final product. This result excludes any participation of free $MeOCONH_2$ in the mechanism of cyclopropane ring formation.

All of the results obtained from the aforementioned experiments are collected in Table 1. The formation of cyclopropane **12** and/or **13** was completely stereoselective, since only the *trans* diastereoisomer was obtained. Each ^1H resonance signal of the cyclopropylacetic acid moiety was assigned by means of selective spin-decoupling experiments. The relative spatial disposition of the substituents on the cyclopropane ring was ascertained by means of a NOESY experiment performed on **13**, for which the cyclopropane proton resonances were not superimposed by those of the pyrrolidine moiety. The cross-peak analysis clearly showed a significant NOE between the methylene protons of the CH_2CON group and two protons of the cyclopropane moiety (H_2 and H_3 in Figure 2), which is only possible for a *trans* configuration of the cyclopropane ring (Figure 2).

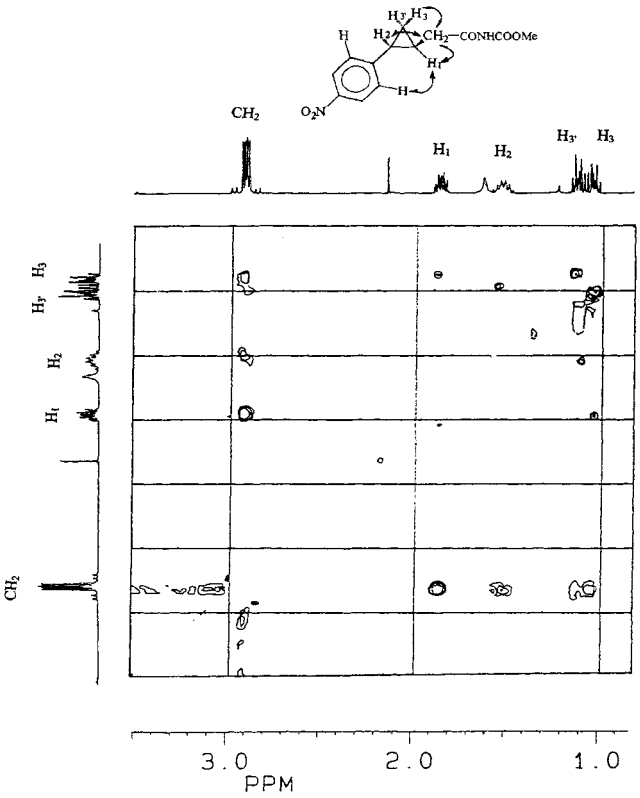
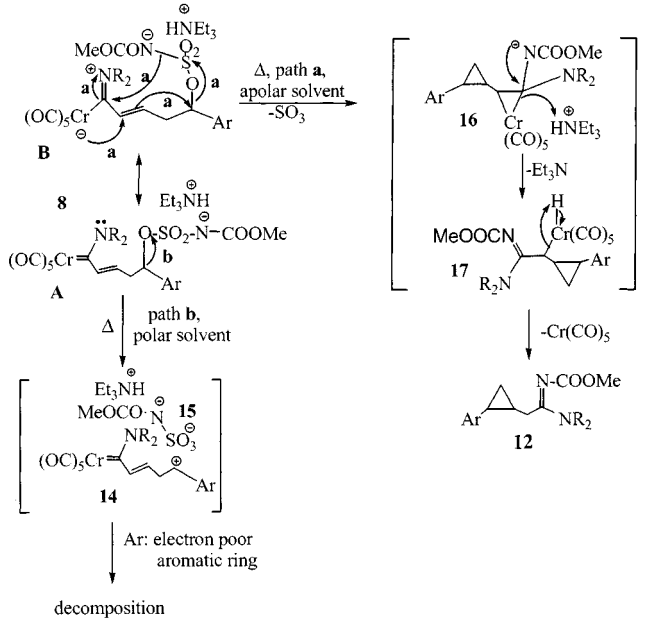


Figure 2. NOESY experiment on **13**

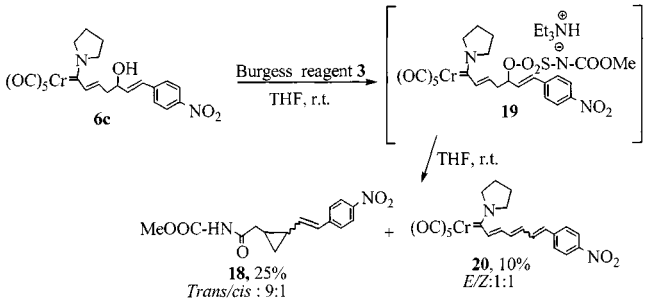
As indicated in Figure 1, the dehydration of alcohols using the Burgess reagent **3** occurs by formation of the intimate ion pair **11**, the formation of which should be favoured by the fact that electron-donating substituents bound to the carbinolic carbon atom stabilize the positive charge. This was realized using complexes **2**, where R′ is an electron-rich aromatic or heteroaromatic nucleus, treatment of which with the Burgess reagent **3** led directly to the polyunsaturated carbene complexes **1** at room temperature, without any formation of the corresponding adducts **8** (Scheme 1). In the case of aldols **6a**,**b**, the strong electron-withdrawing effect of the NO_2 group or pyridine ring should hinder any incipient development of a positive charge on the carbinolic carbon atom that would lead to C−O bond fission, thus making the Burgess adducts **8a**,**b** sufficiently stable to allow their isolation. At this point, the thermal evolution of **8** is greatly influenced by the polarity of the reaction solvent. Apart from the case of adduct **8b**, where the presence of the pyridine nucleus seems to be the most important factor underlying the thermal decomposition, strongly polar solvents (Scheme 5, path b) such as DMF are able to: (i) ionize the C−OSO_2R bond forming an intimate ion pair **14:15**, and (ii) dissociate the intimate ion pair producing the naked

carbocation **14**, the high reactivity of which should account for the complex mixture of the compounds obtained in DMF or in the absence of solvent. In line with the experimental results (path a), the ionizing and dissociating processes are inhibited in solvents of low polarity, and so the evolution of adduct **8a** (which can be visualized more clearly starting from the resonance structure **B** obtained from resonance structure **A** by delocalizing the nitrogen lone pair over the carbonylmetal portion) may involve a pericyclic reaction (a homo-retroene-type reaction implying an eight-membered transition state), in which the MeOOC−N unit is directly transferred to the carbenic carbon atom with the simultaneous elimination of SO_3 and the formation of intermediate **16**. This pericyclic process, which is probably also assisted by the occupied d-orbitals of chromium(0), could account for the observed highly *trans* stereoselectivity. Starting from **16**, protonation of the chromium atom to give intermediate **17**, followed by reductive elimination of $Cr(CO)_5$, leads to **12** (Scheme 5).



Scheme 5. Proposed mechanism for the formation of cyclopropylacetic acid derivative **12**

The reaction was then extended to the aldol addition product **6c**. A first experiment performed at room temperature in THF using 3 equiv. of the Burgess reagent did not lead to the recovery of the expected adduct **19**, but rather to the corresponding cyclopropane derivative **18** in 25% yield as a 9:1 *trans*/*cis* mixture, along with 10% of a 1:1 (*E*)/(*Z*) mixture of the polyunsaturated complex **20**. Replacing THF with toluene did not lead to any appreciable improvement in the yield of cyclopropane derivative **18**. With the aim of isolating adduct **19**, experiments were also performed in THF at lower temperatures, but no reaction was observed between **6c** and the Burgess reagent **3** in the temperature range −40 °C to 0 °C (Scheme 6).



Scheme 6. Reaction of the complex **6c** with the Burgess reagent

Conclusion

We have reported herein a new aspect of the reactivity of Fischer-type carbene complexes. Thus, we have shown that (amino)(ω-hydroxyalkenyl)carbene complexes can be transformed into polyunsaturated (amino)carbene complexes or cyclopropylacetic acid derivatives depending on the electronic nature of the substituents bound to the carbinolic carbon atom and the experimental conditions. The equivalence of the pentacarbonyl(amino)carbene moiety to a carboxylic acid masked as an *N*-(methoxycarbonyl)amidine function is a further peculiar feature of the evolution of adduct **8a** into a cyclopropylacetic acid derivative, and it is noteworthy that this function has not hitherto been mentioned in the literature. We have also highlighted the possibility that the $Cr(CO)_5$ moiety may be involved in the stabilization of a positive charge at a position α to the carbenic centre. To the best of our knowledge, this behaviour has never been reported before. Furthermore, cyclopropylacetic acid derivatives are interesting substrates exhibiting biological properties. However, their synthesis is not always straightforward and hence their preparation starting from (amino)(ω-hydroxyalkenyl)carbene complexes may represent a useful alternative to the few other known methodologies, despite the moderate yield. Finally, the problems encountered in purifying the all-*trans* polyunsaturated (amino)carbenes **7a**,**b** and **19** have so far hampered any meaningful evaluation of their nonlinear properties.

Experimental Section

General: Complex **4** was prepared according to published procedures.[32] The aldehydes **5a**−**c** were purchased from Aldrich Chemical Co.; **5a**,**c** were used as received, whereas **5b** was distilled immediately prior to use. The Burgess reagent was purchased from Fluka or could be readily prepared according to the procedure described in the literature.[17] The reagent *n*BuLi (1.6 M hexane solution) was purchased from Merck and titrated just before use. THF was dried by refluxing in the presence of Na/benzophenone ketyl. MeOH was dried by refluxing in the presence of CaH_2. All manipulations were performed under an inert gas. − Flash and dry (anhydrous) chromatography were performed using Merck silica gel 60, 230−400 mesh. − Melting points were measured using a Büchi 510 melting point apparatus and are uncorrected. − IR spectra were recorded using a Perkin−Elmer 1725X FT-IR spectrophotometer. − NMR spectra were obtained with a Bruker AC300 spectrometer. − The

mass spectra (EI, FAB) were collected using a VG Analytical 7070 EQ instrument.

General Procedure for the Preparation of Complexes 6b,c: The aldehydes **5b**,**c** (1.2 equiv.) were added at −78 °C under an inert gas to a tetrahydrofuran solution of the conjugated base of complex **4** [generated by treating 1 mmol of **4** with 1.3 mmol of freshly prepared LDA (from distilled diisopropylamine and *n*BuLi) at −78 °C for 20 min]. The mixture was allowed to react at −78 °C and the progress of the reaction was monitored by TLC (eluent CH_2Cl_2/light petroleum ether, 1:1). It was seen to be practically complete after 1 h, and then the mixture was quenched by the addition of saturated ammonium chloride solution (10 mL) and extracted with CH_2Cl_2 (2 × 50 mL). The combined organic phases were dried with Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by means of dry chromatography eluting with light petroleum ether/CH_2Cl_2 (2:8) furnished 0.41 g of **6b** (99%); eluting with light petroleum ether/diethyl ether (3:7) furnished 0.36 g of **6c** (74%). − **6b:** Pale-yellow solid; m.p. 118 °C (dec.) (from diisopropyl ether/hexane at −78 °C). − IR (Nujol): $\tilde{\nu}$ = 3232 [ν(OH)], 2051 [ν(CO) *trans*], 1969−1886 cm^{-1} [broad, ν(CO) *cis*]. − ^1H NMR (300 MHz, $CDCl_3$): δ = 2.09 [m, 2 H, (*E*)-NCH_2CH_2], 2.16 [m, 2 H, (*Z*)-CH_2CH_2N], 2.29 (m, 1 H, OH), 2.62 (m, 2 H, −CH=CHCH_2), 3.49 [m, 2 H, (*E*)-NCH_2CH_2], 4.13 [m, 2 H, (*Z*)-CH_2CH_2N], 4.87 (m, 1 H, C*H*OH), 5.24 (dt, 1 H, J_{trans} = 16.2 Hz, J_{vic} = 7.2 Hz, −CH=C*H*−CH_2), 6.54 (br. d, 1 H, J_{trans} = 16.2 Hz, C*H*=CH−CH_2), 7.31 (d, 2 H, J_{ortho} = 4.8 Hz, pyridine), 8.58 (d, 2 H, J_{ortho} = 4.8 Hz, pyridine). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.9 [(*E*)-C−N−*C*], 25.2 [(*Z*)-*C*−N−C], 42.0 (−CH=CH−*C*H_2), 55.0 [(*E*)-N−*C*−C], 62.8 [(*Z*)-C−*C*−N], 71.8 (CHOH), 119.8 (Cr=C−CH=*C*H−CH_2), 120.9 (CH, pyridine), 143.3 (CH, pyridine), 149.3 (Cr=C−*C*H=CH−CH_2), 153.5 (C_q, pyridine), 217.8 (CO_{cis}), 232.3 (CO_{trans}), 263.8 (Cr=*C*−C). − $C_{19}H_{18}CrN_2O_6$ (422.35): calcd. C 54.03, H 4.30, N 6.63; found C 54.42, H 4.46, N 6.73. − **6c:** Orange-bronze solid; m.p. 42 °C (dec.) (from diisopropyl ether/hexane at −78 °C). − IR (neat): $\tilde{\nu}$ = 3391 [ν(OH)], 2051 [ν(CO) *trans*], 1968−1901 [broad, ν(CO) *cis*], 1596 [ν(C=C)], 1515 [$\nu(NO_2)_{asym.}$], 1343 cm^{-1} [$\nu(NO_2)_{sym.}$]. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.91 (d, 1 H, *J* = 4.3 Hz, OH), 2.00 [m, 2 H, (*E*)-NCH_2CH_2], 2.13 [m, 2 H, (*Z*)-CH_2CH_2N], 2.50 (m, 2 H, −CH=CH−CH_2), 3.62 [m, 2 H, (*E*)-NCH_2CH_2], 4.12 [m, 2 H, (*Z*)-CH_2CH_2N], 4.50 (m, 1 H, C*H*OH), 5.28 (m, 1 H, −CH=C*H*−CH_2), 6.44 [dd, 1 H, J_{trans} = 15.9 Hz, J_{vic} = 5.7 Hz, CH(OH)−C*H*=CH−Ar], 6.56 (br. d, 1 H, J_{trans} = 16.2 Hz, Cr=C−C*H*=CH−CH_2), 6.72 [d, 1 H, J_{trans} = 15.9 Hz, CH(OH)−CH=C*H*−Ar], 7.50 (d, 2 H, J_{ortho} = 8.7 Hz, arom.), 8.12 (d, 2 H, J_{ortho} = 8.75 Hz, arom.). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.1 [(*E*)-N−C−*C*], 25.3 [(*Z*)-*C*−C−N], 40.6 (−CH=CH−*C*H_2), 55.3 [(*E*)-N−*C*−C], 59.2 [(*Z*)-C−*C*−N], 71.7 (CH−OH), 120.1 (Cr=C−CH=*C*H−CH_2), 124.0 (CH, arom.), 127.0 [CH(OH)−*C*H=CH−Ar], 128.1 (CH, arom.), 136.3 [CH(OH)−CH=*C*H−Ar], 143.1 (C_q, arom.), 143.9 (Cr=C−*C*H=CH−CH_2), 147.0 (C_q, arom.), 218.0 (CO_{cis}), 223.3 (CO_{trans}), 264.5 (Cr=*C*−C). − MS (FAB^+); *m*/*z*: 492 [M^+, low intensity], 436 [M^+ − 2 CO], 406 [M^+ − 3 CO], 378 [M^+ − 4 CO], 350 [M^+ − 5 CO]. − $C_{22}H_{20}CrN_2O_8$ (492.41): calcd. C 53.61, H 4.06, N 5.68; found C 53.28, H 4.16, N 5.58.

Preparation of Complex 6a: The aldehyde **5a** (2 equiv.) was added at −40 °C under an inert gas to a tetrahydrofuran solution of the conjugated base of complex **4** [generated by treating 1 mmol of **4** with 1.5 mmol of freshly prepared LDA (from distilled diisopropylamine and *n*BuLi) at −78 °C for 20 min]. The mixture was allowed to react at −40 °C and the progress of the reaction was monitored by TLC (eluent CH_2Cl_2/light petroleum ether, 1:1). It was seen to be practically complete after 4 h, and then the mixture was quenched by the addition of saturated ammonium chloride solution (10 mL) and extracted with CH_2Cl_2 (2 × 50 mL). The combined organic phases were dried with Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by means of dry chromatography (eluent: light petroleum ether/CH_2Cl_2, 2:8), which furnished 0.40 g of **6a** (86%), along with 0.033 g (22%) of *p*-nitrobenzyl alcohol and 0.031 g (10%) of the unchanged starting complex **4**. − **6a:** Orange solid, m.p. 90 °C (dec.) (from diisopropyl ether/hexane at −78 °C). − IR (Nujol): $\tilde{\nu}$ = 3447 [ν(OH)], 2047 [ν(CO) *trans*], 1964−1892 [broad, ν(CO) *cis*], 1519 [$\nu(NO_2)_{asym.}$], 1348 cm^{-1} [$\nu(NO_2)_{sym.}$]. − ^1H NMR (300 MHz, $CDCl_3$): δ = 2.01 [m, 2 H, (*E*)-NCH_2CH_2], 2.10 [m, 2 H, (*Z*)-CH_2CH_2N], 2.35 (d, 1 H, J_{vic} = 3.8 Hz, OH), 2.61 (m, 2 H, −CH=CH−CH_2), 3.50 [m, 2 H, (*E*)-NCH_2CH_2], 4.10 [m, 2 H, (*Z*)-CH_2CH_2N], 4.94 (m, 1 H, C*H*OH), 5.28 (dt, 1 H, J_{trans} = 16.2 Hz, J_{vic} = 7.2 Hz, −CH=C*H*−CH_2), 6.56 (br. d, 1 H, J_{trans} = 16.2 Hz), 7.55 (d, 2 H, J_{ortho} = 8.6 Hz, arom.), 8.59 (d, 2 H, J_{ortho} = 8.6 Hz, arom.). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.0 [(*E*)-N−C−*C*], 25.2 [(*Z*)-*C*−C−N], 45.5 (−CH=CH−*C*H_2), 55.2 [(*E*)-N−*C*−C], 59.1 [(*Z*)-C−*C*−N], 72.6 (CH−OH), 119.5 (Cr=C−CH=*C*H−CH_2), 123.6 (CH, arom.), 126.5 (CH, arom.), 144.1 (Cr=C−*C*H=CH−CH_2), 147.2 (C_q, arom.), 151.1 (C_q, arom.), 217.9 (CO_{cis}), 223.2 (CO_{trans}), 263.7 (Cr=*C*−C). − $C_{20}H_{18}CrN_2O_8$ (466.37): calcd. C 51.50, H 3.89, N 6.00; found C 51.55, H 3.84, N 5.91.

General Procedure for the Preparation of Complexes 8a,b: A solution of the Burgess reagent (1.5 equiv.) in THF (7 mL) was added dropwise over a period of 5 min at room temperature under an inert gas to a solution of the respective aldol complex **6a**,**b** (1 mmol) in THF (5 mL). The mixture was allowed to react at the same temperature, and the progress of the reaction was monitored by TLC (eluent CH_2Cl_2/light petroleum ether, 8:2). The reaction was seen to be complete after 1 h or 30 min, respectively, and each mixture was then quenched by the addition of water (5 mL). Most of the organic solvent was removed under reduced pressure. The crude oil was taken up in dichloromethane (50 mL) and the resulting solution was washed with water (2 × 10 mL). The organic phase was dried with Na_2SO_4, filtered through a Celite pad, and the solvent was removed under reduced pressure. The crude adducts **8a**,**b** were collected in almost quantitative yields. Since these adducts slowly decomposed on standing, they were only characterized by ^1H NMR and IR and then used without purification. All attempts to obtain analytically pure samples of these complexes were unsuccessful. − **8a:** Orange oil. − IR (neat): $\tilde{\nu}$ = 2051 [ν(CO) *trans*], 1969−1914 [broad, ν(CO) *cis*], 1722 [ν(C=O) ester], 1521 [$\nu(NO_2)_{asym.}$], 1347 [$\nu(NO_2)_{sym.}$], 1293 and 1159 cm^{-1} [$\nu(SO_2)$]. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27 [t, 9 H, J_{vic} = 7.1 Hz, $N(CH_2CH_3)_3$], 1.96 [m, 2 H, (*E*)-NCH_2CH_2], 2.07 [m, 2 H, (*Z*)-CH_2CH_2N], 2.77 (m, 2 H, −CH=CH−CH_2), 3.11 [q, 6 H, J_{vic} = 7.1 Hz, $N(CH_2CH_3)_3$], 3.47 (s, 3 H, OCH_3), 3.53 [m, 2 H, (*E*)-NCH_2CH_2], 4.05 [m, 2 H, (*Z*)-CH_2CH_2N], 5.10 (dt, 1 H, J_{trans} = 16.2 Hz, J_{vic} = 7.0 Hz, −CH=C*H*−CH_2), 5.68 (t, 1 H, J_{vic} = 6.1 Hz, Cr=C−CH=CH−CH_2−C*H*−OSO_2), 6.48 (br. d, 1 H, J_{trans} = 16.2 Hz, −C*H*=CH−CH_2), 7.57 (d, 2 H, J_{ortho} = 8.5 Hz, arom.), 8.17 (d, 2 H, J_{ortho} = 8.5 Hz, arom.). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.1 [$N(CH_2CH_3)_3$], 24.8 [(*E*)-N−C−*C*], 25.1 [(*Z*)-*C*−C−N], 40.3 [$N(CH_2CH_3)_3$], 45.5 (−CH=CH−*C*H_2), 51.9 (OCH_3), 55.4 [(*E*)-N−*C*−C], 59.0 [(*Z*)-C−*C*−N], 79.2 (CH−OSO_2), 117.5 (Cr=C−CH=*C*H−CH_2), 123.2 (CH, arom.), 127.1 (CH, arom.), 143.9 (Cr=C−*C*H=CH−CH_2), 147.2 (C_q,

arom.), 147.9 (C_q, arom.), 158.8 (CO, ester), 217.6 (CO_{cis}), 223.4 (CO_{trans}), 262.3 (Cr=*C*−C). − **8b:** Bright-orange oil. − IR (neat): $\tilde{\nu}$ = 2051 [ν(CO) *trans*], 1959−1896 [broad, ν(CO) *cis*], 1720 [ν(CO) ester], 1260 and 1161 cm^{-1} [ν(SO_2)]. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.25 [m, 9 H, N(CH_2CH_3)$_3$], 1.95 [m, 2 H, (*E*)-NCH_2CH_2], 2.10 [m, 2 H, (*Z*)-CH_2CH_2N], 2.72 (m, 2 H, −CH=CH−CH_2), 3.11 [m, 6 H, N(CH_2CH_3)$_3$], 3.48 [m, 5 H, (*E*)-NCH_2CH_2 + OCH_3], 4.05 [m, 2 H, (*Z*)-CH_2CH_2N], 5.20 (m, 1 H, −CH=C*H*−CH_2), 5.68 (t, 1 H, J_{vic} = 5.9 Hz, Cr=C−CH=CH−CH_2−C*H*−OSO_2), 6.50 (br. d, 1 H, J_{trans} = 15.9 Hz, Cr=C−C*H*=CH−CH_2), 7.31 (d, 2 H, J_{ortho} = 5.0 Hz, pyridine), 8.58 (d, 2 H, J_{ortho} = 5.0 Hz, pyridine).

General Procedure for the Preparation of Complexes 7a,b: A solution of NaOH (12 equiv.) in dry MeOH (10 mL) was added dropwise over a period 5 min at room temperature under an inert gas to a solution of the respective adduct **8a**,**b** (0.5 mmol) in dry MeOH (20 mL). The mixture was allowed to react at the same temperature, and the progress of the reaction was monitored by TLC (eluent AcOEt/MeOH, 9:1). It was seen to be complete after 22 h. The solvent was then removed under reduced pressure, the crude oil was taken up in water, and the resulting residue was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic phases were dried with Na_2SO_4 and the solvent was removed under reduced pressure. The crude reaction mixture was purified by dry chromatography (**7a**: eluent CH_2Cl_2, **7b**: eluent CH_2Cl_2/AcOEt, 9:1) to furnish 0.22 g of **7a** (63%) and 0.20 g of **7b** (50%). − **7a:** (*E*)/(*Z*) mixture; bright-orange oil. − IR (neat): $\tilde{\nu}$ = 2050 [ν(CO) *trans*], 1970−1903 [broad, ν(CO) *cis*], 1592 cm^{-1} [ν(C=C)]. − ^1H NMR (300 MHz, $CDCl_3$): δ = 2.02−2.22 [m, 4 H, (*Z*)-CH_2CH_2N, (*E*)-NCH_2CH_2], 3.68 [m, 2 H, (*E*)-NCH_2CH_2], 4.18 [m, 2 H, (*Z*)-CH_2CH_2N], 5.93, 6.61, 6.85 (m, 4 H, −C*H*=C*H*−C*H*=C*H* *cis* + *trans*), 7.52 (d, 2 H, J_{ortho} = 8.8 Hz, arom.), 8.20 (d, 2 H, J_{ortho} = 8.8 Hz, arom.). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.1 [(*E*)-N−C−*C*], 25.5 [(*Z*)-*C*−C−N], 55.7 [(*E*)-N−*C*−C], 58.9 [(*Z*)-C−*C*−N], 118.3, 122.8, 123.7, 124.1, 126.8, 126.9, 128.2, 129.1, 129.5, 143.8, 145.4 (−C*H*=C*H*−C*H*=C*H* *cis* and *trans* + CH arom.), 143.0 (C_q, arom.), 143.4 (C_q, arom.) 147.4 (C_q, arom.), 147.5 (C_q, arom.), 217.6 (CO_{cis}), 223.3 (CO_{trans}), 263.8 (Cr=*C*−C). − $C_{20}H_{16}CrN_2O_7$ (448.35): calcd. C 53.57, H 3.60, N 6.25; found C 53.92, H 3.78, N 6.08. − MS (FAB$^+$); *m*/*z*: 448 [M^+, low intensity], 392 [M^+ − 2 CO], 364 [M^+ − 3 CO], 336 [M^+ − 4 CO], 308 [M^+ − 5 CO]. **7b:** (*E*)/(*Z*) mixture; red oil. − IR (neat): $\tilde{\nu}$ = 2051 [ν(CO) *trans*], 1981−1866 [br., ν(CO) *cis*], 1598 cm^{-1} [ν(C=C)]. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.94−2.20 [m, 4 H, (*Z*)-CH_2CH_2N, (*E*)-NCH_2CH_2], 3.62 [m, 2 H, (*E*)-NCH_2CH_2], 4.15 [m, 2 H, (*Z*)-CH_2CH_2N], 6.15, 6.40, 6.80 (m, 4 H, −C*H*=C*H*−C*H*=C*H* *cis* + *trans*), 7.19 (d, 2 H, J_{ortho} = 5.4 Hz, pyridine), 8.57 (d, 2 H, J_{ortho} = 5.4 Hz, pyridine). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.9 [(*E*)-N−C−*C*], 25.2 [(*Z*)-*C*−C−N], 55.6 [(*E*)-N−*C*−C], 59.0 [(*Z*)-C−*C*−N], 110.0, 114.3, 120.5, 122.6, 123.2, 123.4, 128.5, 130.98, 131.11, 132.1, 132.3, 143.5, 145.1, 149.7, 150.0 (−C*H*=C*H*−C*H*=C*H*- *cis* and *trans* + CH pyridine), 143.9 (C_q pyridine), 144.3 (C_q pyridine), 217.4 (CO_{cis}), 223.2 (CO_{trans}), 263.2 (Cr=*C*−C). − $C_{19}H_{16}CrN_2O_5$ (404.35): calcd. C 56.43, H 4.00, N 6.93; found C 56.81, H 4.12, N 6.63. − MS (FAB$^+$); *m*/*z*: 404 [M^+, low intensity], 348 [M^+ − 2 CO], 320 [M^+ − 3 CO], 292 [M^+ − 4 CO], 264 [M^+ − 5 CO].

General Procedure for the Thermal Treatment of Adduct 8a: Adduct **8a** (0.36 g, 0.5 mmol), dissolved or suspended in 20 mL of the chosen solvent, was heated at 55−60 °C until it could no longer be detected by TLC (eluent AcOEt; see Table 1 for solvents and reaction times). The black tarry material formed was filtered off, and the solution was concentrated under reduced pressure. Dry column chromatography of the crude reaction mixture (eluent AcOEt) afforded the cyclopropylacetic acid derivative **12** in the yields shown in Table 1. − **12:** Pale-yellow oil. − IR (neat): $\tilde{\nu}$ = 1668 [ν(C=O)], 1597 [ν(C=N)], 1567 [$\nu(NO_2)_{asym.}$], 1343 cm^{-1} [$\nu(NO_2)_{sym.}$]. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.05−1.16 (m, 2 H, CH_2 cyclopropane), 1.34 [m, 1 H, MeOCON=C(N)−CH_2−$CH_{cyclopropane}$], 1.86−2.04 (m, 5 H, N−CH_2−C*H*$_2$ pyrrolidine + Ar−$CH_{cyclopropane}$), 2.93 [dd, 1 H, $J_{gem.}$ = 17.0 Hz, $J_{vic.}$ = 7.0 Hz CH_3OCONH−CO−C*H*(H)-cyclopropane], 3.00 [dd, 1 H, $J_{gem.}$ = 17.0 Hz, $J_{vic.}$ = 6.8 Hz CH_3OCONH−CO−C(H)*H*-cyclopropane], 3.55 (m, 4 H, N−C*H*$_2$−CH_2 pyrrolidine), 3.69 (s, 3 H, CH_3O), 7.12 (d, 2 H, *J* = 8.7 Hz, arom.), 8.09 (d, 2 H, *J* = 8.7 Hz, arom.). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.6 (CH_2 cyclopropane), 22.0 (CH cyclopropane), 23.4 (CH cyclopropane), 24.3 (NCH_2CH_2), 25.4 (NCH_2CH_2), 33.5 [CH_3OCON=C(N)−*C*H_2-cyclopropane], 47.8 (NCH_2CH_2), 48.2 (NCH_2CH_2), 52.5 (CH_3O), 123.3 (CH, arom.), 126.2 (CH, arom.), 142.5 (C_q, arom.), 151.0 (C_q, arom.), 166.1 (C=N), 192.0 (C=O). − $C_{17}H_{21}N_3O_4$ (331.55): calcd. C 61.61, H 6.39, N 12.68; found C 61.98, H 6.65, N 12.31. − MS (EI); *m*/*z*: 330 [M^+ − 1].

Hydrolysis of Cyclopropylacetic Acid Derivative 12: The Burgess reagent **3** (0.5 g) was added to a solution of cyclopropylacetic acid derivative **12** (0.05 g, 0.15 mmol) in a mixture of THF (5 mL) and water (5 mL). The resulting mixture was allowed to react at room temperature for 45 h (whereupon no starting material could be detected by TLC; eluent AcOEt). The organic solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried with Na_2SO_4 and the solvent was removed under reduced pressure to afford 0.041 g of **13** (ca. 100%) as a pale-yellow solid, m.p. 138 °C (from CH_2Cl_2/pentane). − IR (Nujol): $\tilde{\nu}$ = 3218 [ν(NH)], 1759 [ν(C=O)], 1686 [ν(C=O)], 1510 [$\nu(NO_2)_{asym.}$], 1344 cm^{-1} [$\nu(NO_2)_{sym.}$]. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.05−1.19 (m, 2 H, CH_2 cyclopropane), 1.48 (m, 1 H, MeOCONH−CO−$CH_2CH_{cyclopropane}$), 1.90 (dt, 1 H, J_{vic1} = 9.3 Hz, J_{vic2} = 8.6 Hz, Ar$CH_{cyclopropane}$), 2.89 [dd, 1 H, $J_{gem.}$ = 17.0 Hz, $J_{vic.}$ = 7.0 Hz, CH_3OCONH−CO−C(H)*H*-cyclopropane], 2.93 [dd, 1 H, $J_{gem.}$ = 17.0 Hz, $J_{vic.}$ = 6.8 Hz, CH_3OCONH−CO−C*H*(H)-cyclopropane], 3.77 (s, 3 H, CH_3O), 7.17 (d, 2 H, *J* = 8.7 Hz, arom.), 7.50 (br. s, 1 H, NH), 8.13 (d, 2 H, *J* = 8.7 Hz, arom.). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.5 (CH_2 cyclopropane), 19.4 (CH cyclopropane), 22.9 (CH cyclopropane), 40.4 (CH_3OCONH−CO−*C*H_2-cyclopropane), 53.1 (CH_3O), 123.5 (CH, arom.), 126.4 (CH, arom.), 145.9 (C_q, arom.), 150.9 (C_q, arom.), 152.3 (C=O), 173.4 (C=O). − $C_{13}H_{14}N_2O_5$ (278.27): calcd. C 56.11, H 5.07, N 10.07; found C 55.88, H 5.09, N 10.14.

Reaction of Complex 6c with Burgess Reagent: A solution of the Burgess reagent (3 equiv.) in THF (7 mL) was added dropwise over a period of 5 min at room temperature under an inert gas to a solution of the aldol complex **6c** (1 mmol) in THF (5 mL). The mixture was allowed to react at the same temperature, with the progress of the reaction being monitored by TLC (eluent CH_2Cl_2/light petroleum ether, 8:2). It was seen to be complete after 12 h, whereupon the mixture was quenched by the addition of water (5 mL). Most of the organic solvent was then evaporated under reduced pressure. The crude oil was taken up in dichloromethane (50 mL) and the resulting solution was washed with water (2 × 10 mL). The organic phase was dried with Na_2SO_4, filtered through a Celite pad, and the solvent was removed under reduced pressure. The crude reaction mixture was purified by flash column chromatography; eluting with light petroleum ether/ethyl acetate (8:2) furnished 0.47 mg of **20** (10%); eluting with ethyl acetate/ethyl

ether (8:2) furnished 0.076 mg of **18** (25%). − **20:** (*E*)/(*Z*) mixture; red oil. − IR (neat): $\tilde{\nu}$ = 2051 [ν(CO) *trans*], 1968−1909 [broad, ν(CO) *cis*], 1609 cm^{-1} [ν(C=C)]. − ^1H NMR (300 MHz, $CDCl_3$): δ = 2.03−2.17 [m, 4 H, (*Z*)-CH_2CH_2N, (*E*)-NCH_2CH_2], 3.67 [m, 2 H, (*E*)-NCH_2CH_2], 4.17 [m, 2 H, (*Z*)-CH_2CH_2N], 5.87−5.96 [m, 1 H, CH, −(CH=CH)$_3$ *cis* + *trans*], 6.20−6.31 [m, 1 H, CH, −(CH=CH)$_3$ *cis* + *trans*], 6.46−6.52 [m, 1 H, CH, −(CH=CH)$_3$ *cis* + *trans*], 6.95−7.02 [m, 1 H, CH, −(CH=CH)$_3$ *cis* + *trans*], 7.32−7.41 [m, 1 H, CH, −(CH=CH)$_3$ *cis* + *trans*], 7.50 (d, 2 H, J_{ortho} = 8.8.Hz, arom.), 8.17 (d, 2 H, J_{ortho} = 8.8.Hz, arom.). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 25.0 [(*E*)-NC−*C*], 25.4 [(*Z*)-*C*−CN], 55.6 [(*E*)-N*C*−C], 59.1 [(*Z*)-C−*C*N], 124.0 (CH, arom.), 130.4, 133.1, 133.9, 135.2, 142.6, 126.6 [−(*C*H=*C*H)$_3$ *cis* + *trans*], 143.7 (C_q, arom.), 146.6 (C_q, arom.), 217.7 (CO_{cis}), 223.4 (CO_{trans}), 263.1 (Cr=*C*−C). − $C_{22}H_{18}N_2CrO_7$ (474.39): calcd. C 55.70, H 3.82, N 5.63; found C 55.98, H 4.09, N 5.63. − MS (FAB^+); *m*/*z*: 474 [M^+], 446 [M^+ − CO], 418 [M^+ − 2 CO], 362 [M^+ − 4 CO], 334 [M^+ − 5 CO], 282 [M^+ − 5 CO − Cr]. − **18:** Pale-yellow solid; m.p. 108−110 °C (from CH_2Cl_2/pentane). − IR (Nujol): $\tilde{\nu}$ = 3301 [ν(NH)], 1759 [ν(C=O)], 1683 [ν(C=O)], 1510 [$\nu(NO_2)_{asym.}$], 1344 cm^{-1} [$\nu(NO_2)_{sym.}$]. − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (m, 2 H, CH_2 cyclopropane), 1.37 (m, 1 H, MeOCONH−CO−CH_2C$H_{cyclopropane}$), 1.51 (m, 1 H, Ar−CH=CH−C$H_{cyclopropane}$), 2.82 (m, 2 H, CH_3OCONH−CO−CH_2-cyclopropane), 3.76 (s, 3 H, CH_3O), 5.98 (dd, 1 H, J_{trans} = 15.8 Hz, J_{vic} = 8.9 Hz, Ar−CH=C*H*−$CH_{cyclopropane}$), 6.49 (d, 1 H, J_{trans} = 15.8 Hz, Ar−C*H*=CH−$CH_{cyclopropane}$), 7.38 (d, 2 H, *J* = 8.8 Hz, arom.), 7.74 (br. s, 1 H, NH), 8.11 (d, 2 H, *J* = 8.8 Hz, arom.). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5 (CH_2 cyclopropane), 16.9 (CH cyclopropane), 22.2 (CH cyclopropane), 40.1 (CH_3OCONH−CO-*C*H_2-cyclopropane), 53.0 (CH_3O), 124.0 (CH, arom.), 125.9 (CH, arom.), 126.2 (Ar−CH=*C*H−$CH_{cyclopropane}$), 138.7 (Ar−*C*H=CH−$CH_{cyclopropane}$), 144.1 (C_q, arom.), 146.2 (C_q, arom.), 152.3 (C=O), 173.3 (C=O). − $C_{15}H_{16}N_2O_5$ (304.31): calcd. C 59.85, H 5.58, N 9.36; found C 59.60, H 5.42, N 9.24. − MS (EI); *m*/*z*: 304 [M^+].

Acknowledgments

We thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Rome) and the C.N.R. (Rome) for their financial support. We thank Mrs. Federica Zaccheria for her assistance with the experimental work.

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Received August 28, 2000
[O00442]