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Rh^{II}-Catalyzed Reactions of Diazocarbonyl Compounds with Dicarboximides

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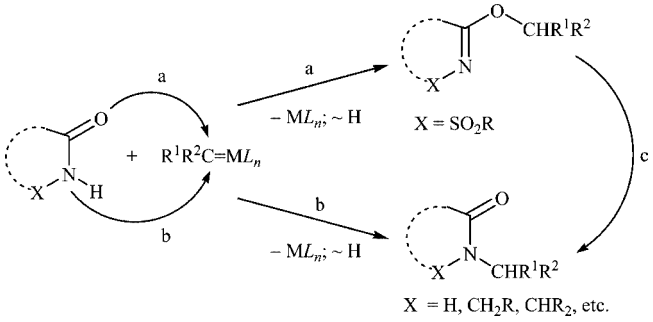
The reaction of Rh^{II}–oxocarbenoids derived from acyclic diazocarbonyl compounds with phthalimide and succinimide proceeds chemoselectively at the oxygen atom of the imidic carbonyl group, giving rise to the intermediate formation of carbonyl ylides. Intramolecular stabilization of these highly reactive species occurs in three different ways, and is controlled by the structure of the 2-oxocarbenoids. Carbonyl ylides from diazo esters mainly experience a [1,4]-hydrogen shift, and in this case, the corresponding *O*-alkylimidates are formed as the final products. These ylides may also be stabilized by 1,3-dipolar electrocyclization with intermediate formation of an oxirane. Carbonyl ylides with an acyl group in the carbene moiety undergo an intramolecular 1,5-dipolar electrocyclization to produce 1,3-dioxole derivatives.

Introduction

In recent years, the insertion reactions of carbene and carbenoid intermediates from diazo compounds have actively been used as a powerful method in organic synthesis.[1,2] When amides, lactams and carbamates are employed as starting compounds, the N–H insertion reaction is a familiar procedure for the preparation of a variety of nitrogen-containing natural products and heterocyclic compounds (Scheme 1, path b).[3,4]



Scheme 1.

Against this background, it is rather surprising that there is a lack of research and publications on carbenoid reactions with imidic substrates which have unsubstituted ("free") N–H groups in their structures.[5a,5b,6] To the best of our knowledge, the available information on this matter is limited to two remarks in recent publications, where it was mentioned that catalytic decomposition of diazomalonic and diethoxyphosphoryl diazoacetic esters by rhodium tetraacetate in the presence of phthalimide does not produce any insertion products.[7] On the other hand, catalytic decomposition of diazocarbonyl compounds in the presence of saccharins, which can be considered to be the sulfonyl analogues of phthalimide, gives rise to the corresponding *O*-alkylimidates with good yields (Scheme 1, path a).[8] Formally, these latter compounds are insertion products of the relevant oxocarbenes into the O–H bond of the enol form of the sulfonimidic group (SO_2–NH–CO) of the molecule.

The reason for such a drastic difference in the reactivity of the CO–NH group in the amidic and imidic substrates, as well as with phthalimide and sulfonamides (saccharines), remains as yet unclear. In this connection, we undertook a detailed investigation of the catalytic reactions of a series of diazocarbonyl compounds with the imides of dicarboxylic acids.[5a,5b] This paper is concerned with the results of the catalytic decomposition of diazocarbonyl compounds in the presence of dicarboximides.[5c]

Imides of dicarboxylic acids, along with the other substrates possessing a CO–NH framework, have two major potential centers for interaction with electrophilic metal–carbenes, namely the N and O atoms of the imidic and carbonyl groups. Based on the known carbenoid reactions with amide and sulfonimides substrates, one would expect that this electrophilic intermediate[1,2] would react either with the N atom of the imide group, to give *N*-alkyl derivatives (Scheme 1, path b), or with the O atom to give the *O*-alkylimidates (Scheme 1, path a).

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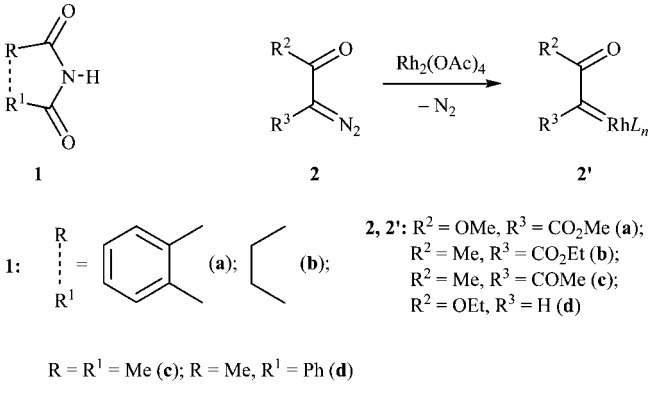
In the case of a catalytic reaction according to path a, one cannot a priori rule out the possible subsequent isomerisation of the *O*-alkyl derivative to an *N*-substituted isomer (Scheme 1, path c). It is well known that *O*-alkyl(aryl)-imidates are in general thermodynamically less stable than their *N*-substituted counterparts,[9] and, under specific conditions, oxygen-to-nitrogen 1,3-migration of the *O*-substituent can readily occur (Lander–Chapman rearrangement).[9a,10] The ease of this process increases when electron-withdrawing groups (EWG) or unsaturated bonds are in the structure of the migrating fragment,[9a] as well as when some metal salts are added to the reaction mixture.[10c,11] Thus, as a result of the catalytic decomposition of diazo compounds possessing EWGs in the presence of dicarboximides **1**, one could primarily expect the formation of *N*-alkylsubstituted imides.

Results and Discussion

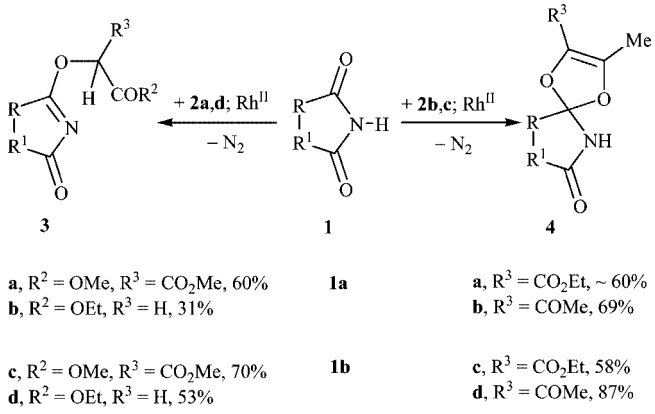
For the detailed investigation of the catalytic reactions with cyclic imides, i.e. phthalimide (**1a**) and succinimide (**1b**), and acyclic imides, i.e. *N*-acetylacetamide (**1c**) and *N*-acetylbenzamide (**1d**), a set of diazo compounds **2** was used as the precursors of Rh^{II}–oxocarbenoids **2′**, namely: methyl diazomalonate (**2a**), ethyl diazoacetoacetate (**2b**), diazoacetylacetone (**2c**) and ethyl diazoacetate (**2d**) (Scheme 2). These diazocarbonyl compounds fall into different classes of aliphatic diazo compounds (diazo esters, diazo oxo esters, diazo diketones), and as a rule, differ substantially in their reactivity.[1,12]



Scheme 2.

Catalytic decomposition of diazocompounds **2a**–**d** was performed by adding 1–2 mol-% of dirhodium tetraacetate as the catalyst at 10–20 °C to a suspension of imide **1** in dry dichloromethane. Upon completion of the reaction as indicated by TLC, the reaction mixture was separated on a column filled with neutral silica gel, and the isolated compounds were analysed by using ^1H, ^{13}C NMR spectroscopy, mass spectrometry, and X-ray crystal structure analysis. Since the catalytic reactions and isolated products were found to be very sensitive to traces of acids and moisture, the initial reagents were subjected to careful purification by sublimation in vacuo (**1a**–**d**) or by distillation of diazo compounds **2a**–**d** at reduced pressure, whereas the workup procedure was performed, where possible, under the exclusion of moisture.

These studies on the catalytic decompositions of diazocarbonyl compounds **2** in the presence of imides **1a**,**b** (Scheme 3) revealed that with continuous monitoring of the catalytic process and speedy workup of the reaction mixture after disappearance of the diazo compound, the initial reaction products could be isolated in moderate yields.



Scheme 3.

Furthermore, it was established that the structures of the resulting products depend strongly on the nature of the diazo compound **2**/Rh^{II}–carbenoid **2′**. Thus, decomposition of diazo esters **2a**,**d** with rhodium tetraacetate in the presence of phthalimide (**1a**) and succinimide (**1b**), as with oxoisothiazole 1,1-dioxides, leads to *O*-alkylation and formation of the imidates **3a**,**b** and **3c**,**d**, respectively. Low yields of compounds **3b** and **3d** are the result of side reactions (mostly formation of ethyl fumarate and maleate) which take place under the reaction conditions. On the other hand, the similar reaction of ethyl diazoacetoacetate (**2b**) and diazoacetylacetone (**2c**) produces spiro adducts **4** of the imides and the corresponding dioxocarbenes.

The structures of the isolated compounds **3** were assigned on the basis of an X-ray crystal structure determination of the adduct **3a**, and also by relying on the complete correlation of the key spectroscopic data of the new compounds **3a**,**b** with the corresponding parameters of the associated sulfonimide *O*-alkyl derivatives in the ^1H and ^{13}C NMR spectra.[8]

The results of the crystal structure analysis of **3a** unequivocally establish the structure of compounds **3** as *O*-alkylated phthalimide and succinimide (for **3a** see Figure 1). These data also testify that *O*-alkylimidate **3a**, analogous to the saccharin *O*-alkylation products,[8] has an s-*cis* conformation along the NC(9)–O(10)CH$(CO_2Me)_2$ single bond.

The ^1H and ^{13}C NMR spectra of the adducts **3a**,**b** contain a set of proton and carbon signals for carbenoid and phthalimide fragments in a 1:1 ratio, and their positions in the spectra as a whole are similar to those of the initial compounds. The main difference is the appearance of new sharp signals of the methine or methylene groups [O*CH*-$(CO_2Me)_2$ or OCH_2CO_2Et] at δ = 6.10 and 5.18 ppm (^1H

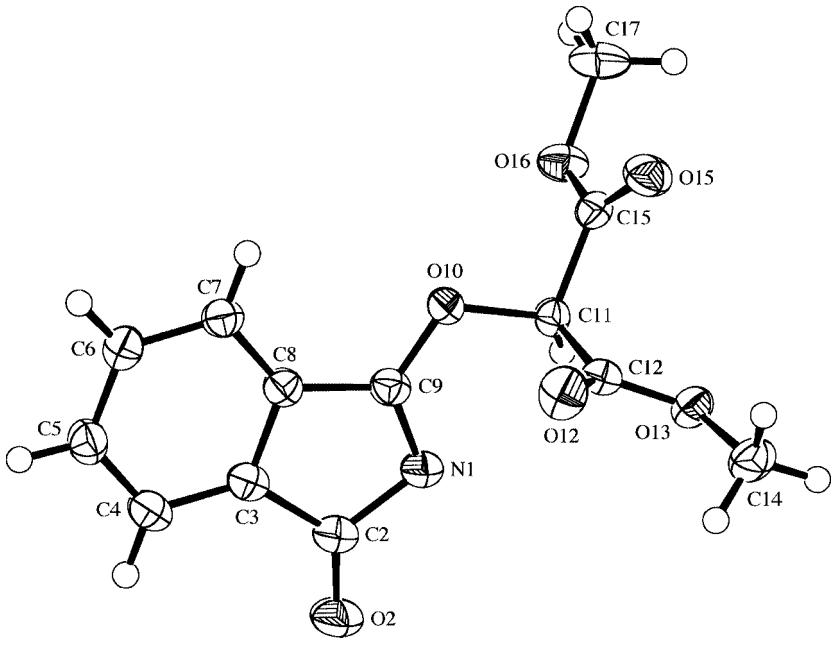
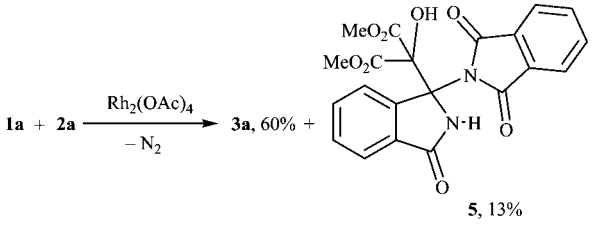


Figure 1. ORTEP plot[13] of the molecular structure of **3a** (arbitrary numbering of the atoms; displacement ellipsoids with 50% probability).

NMR) and at δ = 75.9 and 66.5 ppm (^{13}C NMR), respectively. In the NMR spectra of the analogous *O*-alkylated sulfonimides, these signals are positioned at δ = 5.96 and 5.10 ppm (^{1}H NMR) and at δ = 76.0 and 66.1 ppm (^{13}C NMR), respectively.[8]

Decomposition of **2a** in the presence of phthalimide (**1a**) also leads to the formation of the product **5** in 13% yield. In the ^{1}H NMR spectrum of **5**, along with signals of aromatic protons, one can observe signals of two different OMe groups, signals of OH and NH groups and the signal of CH_2Cl_2, which crystallizes with one molecule of **5** in a 1:1 ratio. The ^{13}C NMR spectrum of **5** contains signals of 21 C atoms and the signal of CH_2Cl_2. Mass spectrometry and CHN analysis data indicate that one molecule of **5** contains two molecules of phthalimide and one molecule of bis(methoxycarbonyl)carbene (Scheme 4).



Scheme 4.

The structure of **5** was confirmed by an X-ray crystal structure determination (Figure 2).

The spirocyclic structures of the adducts **4a**,**b**, presented in Scheme 3, were established by comparison of their ^{13}C NMR spectroscopic data with the related spectroscopic parameters of dioxoles obtained upon catalytic decomposition of diazo compounds **2b**,**c** in the presence of succinimide (Scheme 5).[5c] From mass spectrometry and elemental

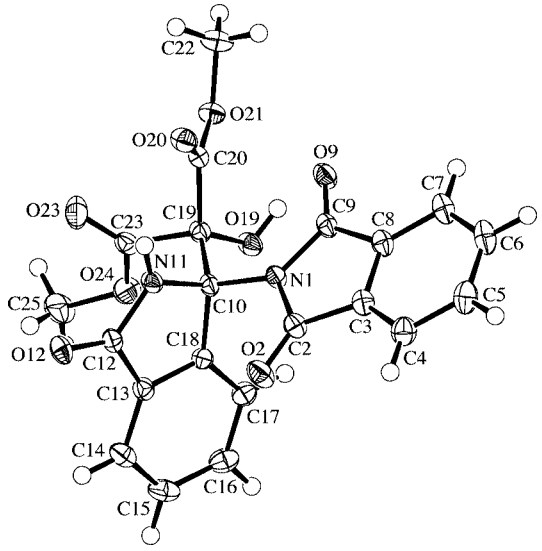
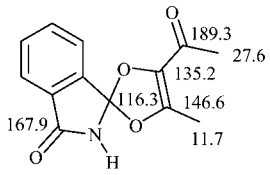


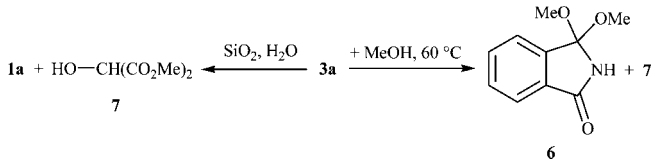
Figure 2. ORTEP plot[13] of the molecular structure of **5** (arbitrary numbering of the atoms; displacement ellipsoids with 50% probability).

analysis data, the molecular formula of compound **4b** ($C_{13}H_{11}NO_4$ $[M]^{+\cdot}$; *m*/*z* = 245) corresponds to the adduct of phthalimide (**1a**) and diacetylcarbene in the ratio 1:1. In the ^{13}C NMR spectrum of compound **4b**, thirteen signals were observed, whereas in the case of *N*- or *O*-alkylation products of **1a**, one might expect only 7 or 11 C signals. Additionally, in the spectra of compound **4b**, diagnostic signals of the O–*CH* group, typical for *O*-alkylimidates, and the products of *N*-alkylation in the dioxo form,[14] were absent.[8] Therefore, the adduct **4b** does not have the structure of an *O*-alkylimidate or an *N*-alkyl derivative of phthalimide.



4b **4c**

Scheme 5.



Scheme 6.

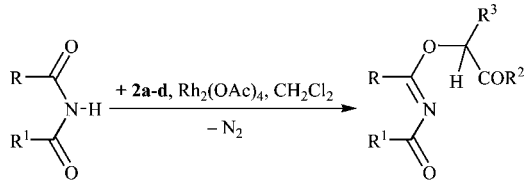
Furthermore, according to the ^1H and ^{13}C NMR spectra for **4b**, two nonequivalent CH_3 groups (signals at δ = 2.29 and 2.36 ppm) were present. The chemical shift of the C atom of one of these methyl groups (at δ = 27.65 ppm) was rather close to the relevant parameter of the initial diazoacetylacetone (**2c**) at δ = 28.4 ppm, while for the other CH_3 group a considerable shift of the C atom signal was observed (δ =11.73 ppm) compared with that from the original diazo substrate. It was evident that this shift resulted from the chemical transformation during the reaction of one of the α-carbonyl groups ($CH_3C{=}O$) of the diacylcarbene. The same conclusion could be also made regarding one of the former phthalimide (**1a**) carbonyl groups, since in the ^{13}C NMR spectrum of **4b**, only two carbonyl signals (at δ = 167.9 and 189.3 ppm) remained of the four in the structure of the initial substrates, and the chemical shifts in the new structure at δ = 135.2 and 146.6 ppm indicated that they were the C atoms of the double bond.

One can conclude that the spectroscopic data of the phthalimide–diacylcarbene adduct are in closest agreement with the structure **4b**. For comparison, Scheme 5 shows the data from the ^{13}C NMR spectra for adducts **4b** and **4c** obtained from phthalimide (**1a**) and succinimide (**1b**), respectively (for the latter, the structural assignment was confirmed by a crystal structure analysis of the adduct[5c]), and demonstrate the complete correspondence of the chemical shifts for the key C atoms of both compounds. This analogy provides strong evidence that the major product of the catalytic reaction of **2c** with phthalimide (**1a**) has the spirocyclic structure of dioxole **4b**.

Whereas the adducts **4b** and **4c**,**d** were isolated in moderate yields, we were unable to isolate its analogue **4a** in pure form, although the occurrence of this compound in the reaction mixture was clearly demonstrated by TLC during the reaction and by ^1H NMR of the crude reaction mixture. This is apparently due to the easy hydrolysis of the adducts **4** with the formation of the corresponding imide and 1,3-dicarbonyl-2-hydroxy compounds when they are exposed to moisture in the air or during the workup procedure using silica gel. A similar instability and easy hydrolysis in the presence of water (or alcohols) and catalytic amounts of acids are also characteristic for *O*-alkyl-substituted phthalimide derivatives **3**. Thus, it was established by using imidate **3a** that slow chromatography of the reaction mixture on a column with silica gel (or short-time heating of **3a** in methanol) gives rise to its complete hydrolysis and the formation of phthalimide (**1a**) [or 3,3-dimethoxyisoindol-1-one (**6**)] and 2-hydroxymalonate **7** (Scheme 6).

This enhanced tendency of phthalimide *O*-alkylimidates to hydrolyze was probably the main reason for the unsuccessful attempts to isolate the products of Rh^{II}–oxocarbenoid reactions with phthalimide (**1a**) in the course of the initial investigations.[7]

Catalytic decomposition of compounds **2a**–**d** in the presence of acyclic imides **1c**,**d** was performed under the same conditions as for cyclic imides **1a**,**b**. In all experiments, soon after addition of $Rh_2(OAc)_4$ to the reaction mixture, its color changed from green to brown-red, and decomposition of the diazo compound stopped. Addition of a new portion of the catalyst resumed decomposition, but only for a very short period of time. Analysis of the obtained reaction mixtures by means of mass spectrometry showed that in all cases an adduct is formed from one molecule of imide and one molecule of carbene in a ratio of 1:1. In the ^1H NMR spectra of the crude reaction mixtures one can observe a characteristic signal between δ = 4.52 and 5.63 ppm, which belongs to the OCH group of the *O*-alkylation product. On the basis of earlier results[5a–5c] and those discussed above, we suggest that decomposition of diazo compounds **2a**–**d** in the presence of acyclic imides **1c**,**d** leads to *O*-alkylation products **8a**–**h** (Scheme 7).

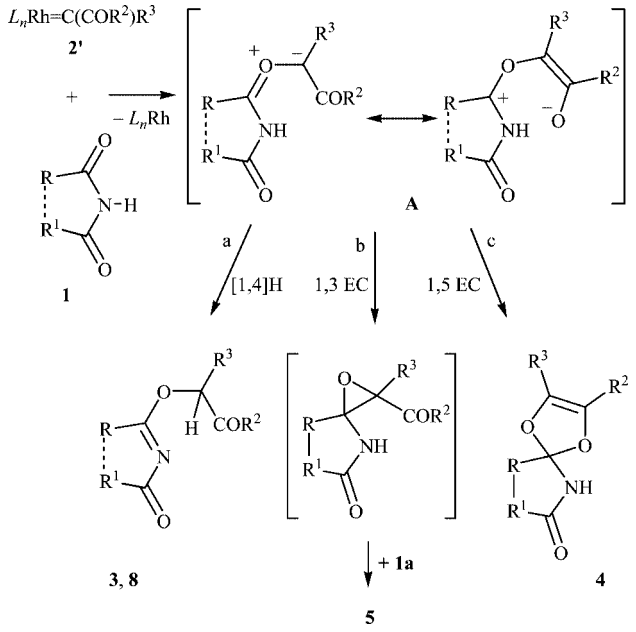


Scheme 7.

Products **8** cannot be isolated in reasonable yields, either because the imidic substrates **1c**,**d** react with the catalyst as ligands and totally destroy its catalytic activity, or because inhibition of the catalyst is due to the product of the reaction or to a secondary product. In either case, decomposition of diazo compounds cannot be performed to completion.

These results suggest that the attack of Rh^{II}–oxocarbenoids **2′** is primarily directed at the O atom of phthalimide, giving rise to intermediate formation of the highly reactive carbonyl ylides **A**,[1,2a,2b,6,15,16] whereas interaction of **2′** with the heterocyclic N atom and generation of cycloimmonium ylides is evidently not effective or does not occur at all.[5a] The subsequent stabilization of carbonyl ylides **A**

occurs in three different pathways, a, b and c (Scheme 8), which are controlled by the structure of the initial diazo compound **2** and the corresponding oxocarbenoid **2′**.



Scheme 8.

(a) Imidic carbonyl ylides **A** generated from diazo esters **2a**,**b** undergo intramolecular hydrogen transfer[6c,6d,15a,15c–15f] and *O*-alkylimidates **3** and **8** are formed as the final reaction products (Scheme 8, path a). In the series of oxoisothiazol 1,1-dioxides, a similar sulfonimidic [1,4]-hydrogen shift has been observed with all carbonyl ylides, independent of the structure of the initial diazo esters and diazo ketones.[8]

The "oxonium" mechanism for the formation of the imidates **3**, which assumes the reaction of the ketocarbenoids **2′** with the enol form of phthalimide **1a** and intermediate formation of the appropriate oxonium ylides, is less likely.[8a]

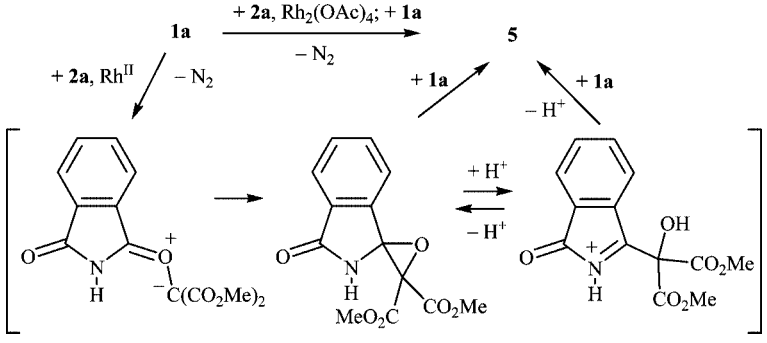
(b) Stabilization of ylide **A** generated from diazo ester **2a** and imide **1a** may also occur by 1,3-dipolar electrocyclization and intermediate formation of an oxirane (Scheme 8, path b). Further reaction of **1a** with the oxirane gives product **5**. The proposed formation of an oxirane is based on literature analogies.[17] Carbonyl ylides and oxiranes are valence isomers, they easily turn one into another, and epoxides are often used in thermal and photochemical reactions to generate carbonyl ylides.[18]

The mechanism of the second step, the formation of **5**, may include direct reaction of the oxirane with **1a**, or protonation of the O atom of the oxirane, followed by ring opening as a result of nucleophilic attack of phthalimide (**1a**) (Scheme 9).

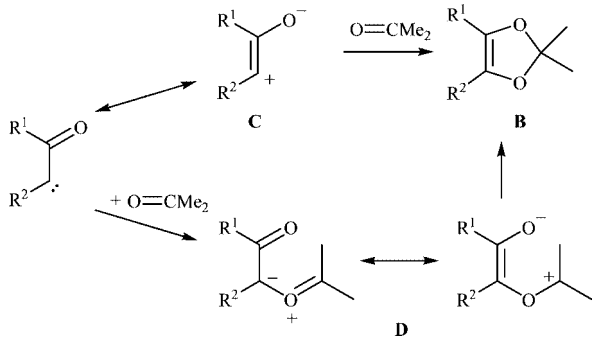
In both cases, the regioselectivity of this second step depends on the nature of the substituents of the oxirane. It is known that electron-withdrawing substituents in the oxirane ring prevent nucleophilic attack on the atom they are attached to, but this attack easily occurs on the atom with substituents which can stabilize a positive charge.[18b] In our case, the preferred direction of the nucleophilic attack is the spiro C atom, because it has two substituents (an aromatic system and an N–H group), which stabilize the positive charge much better than the two ester groups attached to the other C atom of the oxirane ring. As a result, the regioisomer **5** is to be expected.

(c) The carbonyl ylides with at least one acyl group in the carbene fragment experience an intramolecular 1,5-dipolar electrocyclization, which produces 1,3-dioxole derivatives, i.e., the spiro adducts **4** (Scheme 8, path c). The implementation of this pathway is apparently possible only with diazo compounds possessing an α-acyl carbonyl group adjacent to the diazo functionality. The same dependence on the nature of the carbonyl group has been observed in thiocarbonyl ylides.[19]

A few examples are known in which 1,3-dioxoles **B** are formed during the decomposition of diazocarbonyl compounds in the presence of simple aldehydes and ketones,[1,20] but a similar reaction with the imidic carbonyl group was revealed only recently.[5c] Originally, it was suggested that dioxoles **B** arise from a 1,3-dipolar cycloaddition reaction of the carbene or metal–carbene complex, induced to operate as a 1,3-dipole **C**, with the C=O bond of a carbonyl substrate[20] (Scheme 10). However, the current commonly accepted mechanism of the formation of 1,3-dioxoles **B** from diazocarbonyl compounds and C=O-containing substrates implies the intermediate occurrence of the associated carbonyl ylides **D** (Scheme 10).[1,2]



Scheme 9.



Scheme 10.

Conclusions

The interaction of dicarboximides with Rh^{II}–oxocarbenoids generated from acyclic diazocarbonyl compounds proceeds chemoselectively with the O atom of the imidic carbonyl group, followed by intermediate formation of highly reactive carbonyl ylides. *Intramolecular* stabilization of these transient species occurs in three different ways, which are controlled by the structure of the diazo compound and associated oxocarbenoid: (a) carbonyl ylides derived from diazo esters are stabilized by an intramolecular [1,4]-hydrogen shift, and imide *O*-alkyl ethers (*O*-alkylimidates) are formed as the final products; b) ylides obtained from the same diazo compounds may also be stabilized by 1,3-dipolar electrocyclization with intermediate formation of oxiranes; c) carbonyl ylides with at least one acyl group in the "carbene" fragment of this intermediate undergo 1,5-dipolar electrocyclization to yield 1,3-dioxole derivatives. Thus, reactions of Rh^{II}–oxocarbenoids with phthalimide and succinimide can serve as a new synthetic approach to the labile and otherwise not readily accessible imidic derivatives [*O*-alkylimidates and spirocyclic 5-acyl- or 5-(alkoxycarbonyl)-4-methyl-1,3-dioxoles], while the carbonyl units provide additional opportunities for versatile functionalization of these nitrogen-containing heterocycles.

Experimental Section

General Remarks: ^1H and ^{13}C NMR spectra were measured with VARIAN "Gemini 200", "Gemini 300" and BRUKER DRX-600 "AVANCE" spectrometers, with working frequencies of 200, 300 and 600 MHz for ^1H NMR and 50.3, 75.45 and 150.92 MHz for ^{13}C NMR spectra, respectively. Solutions were in $CDCl_3$ or [D_6]-DMSO, with an internal standard of Me_4Si (δ, ppm). *J* values are given in Hz. Infrared spectra were obtained using ATI Mattson "Genesis Series FTIR" or Specord IR-75 instruments. Mass spectra were determined by electron impact ionization at 70 eV with a Quadrupol-MS VG 12-250 spectrometer (VG. Instruments GmbH, Manchester Analytical). Microanalyses were performed on a Heraeus CHNS Rapid Analyser. Melting points were determined with a Boetius micro melting point apparatus and are uncorrected. All reactions were carried out in carefully dried and distilled solvents. Rhodium acetate, phthalimide (**1a**) and succinimide (**1b**) were commercially available (Fluka). Diazodicarbonyl compounds **2a**–**c** were prepared from the corresponding 1,3-dicarbonyl compounds and arenesulfonyl azides by diazo transfer reactions[1,12] followed by distillation in vacuo. Commercially available ethyl diazoacetate (**2d**) (Fluka) was distilled just before catalytic reaction, b.p. 58–60 °C/1 Torr. All reactions were monitored by thin-layer chromatography (TLC) on Silufol UV/Vis 254 plates using UV light and I_2 as the visualizing agents. Neutral silica gel (MERCK 70–230 mesh or CHEMAPOL L 40/100) was used for column chromatography.

Dimethyl 2-[(3-Oxo-3*H*-isoindol-1-yl)oxy]malonate (3a) and Dimethyl 2-Hydroxy-2-(3,1′,3′-trioxo-2,3,1′,3′-tetrahydro[1,2′]biisoindol-1-yl)malonate (5): Rhodium catalyst (13 mg, 0.029 mmol) was added at room temperature to a stirred mixture of phthalimide (**1a**) (0.79 g, 5.4 mmol) and dimethyl diazomalonate (**2a**) (1.0 g, 6.3 mmol) in dichloromethane (20 mL). After complete decomposition of the diazo compound (monitored by TLC, ca. 7 h), the solvent was removed in vacuo to reach a volume of 5–6 mL. Addition of 2.5 mL of Et_2O crystallized product **5**. After filtration and evaporation of the solvents from the mother liquor, the residue was dissolved in CH_2Cl_2 (5 mL) and addition of Et_2O (4 mL) crystallized product **3a**.

3a: Yield 0.9 g (60%); colorless crystals; m.p. 113–115 °C (CH_2Cl_2/Et_2O); R_f = 0.30 (CH_2Cl_2/hexane, 2:1). ^1H NMR ($CDCl_3$): δ = 3.90 (s, 6 H, 2 OCH_3), 6.10 (s, 1 H, OCH), 7.60–7.76 (m, 4 H, CH-arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 53.6 (OCH_3), 75.9 (OCH), 121.6, 124.1, 133.3, 133.4, 134.3, 135.0 (C-arom.), 163.5 (CO_2), 180.0 (O–C=N), 184.7 (CONH) ppm. IR (KBr): $\tilde{\nu}$ = 1754 (90), 1544 (90), 1409 (78), 1241 (65) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 277 (28) $[M]^{+\cdot}$, 261 (17), 246 (11), 220 (56), 174 (11), 162 (63), 147 (31), 130 (100), 103 (45), 76 (35), 69 (51), 59 (30). $C_{13}H_{11}NO_6$ (277.24): calcd. C 56.33, H 3.99, N 5.05; found C 56.32, H 4.09, N 5.11.

5: Yield 0.17g (13%); colorless crystals; m.p. 140–141 °C (CH_2Cl_2/Et_2O); R_f = 0.30 (CH_2Cl_2/EtOAc, 10:1). ^1H NMR ($CDCl_3$): δ = 3.54 (s, 3 H, OCH_3), 3.96 (s, 3 H, OCH_3), 4.90 (s, 1 H, OH), 7.47–7.86 (m, 8 H, CH-arom.), 7.87 (s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 53.9, 54.2 (OCH_3), 77.6 (CN_2), 81.3 (C-2), 123.3, 123.7 (2 C), 126.0, 130.3, 131.2 (2 C), 131.9, 132.1, 134.7 (2 C), 142.4 (C-arom.), 166.7 (CO_2Me), 167.8 (2 CON), 168.6 (CO_2Me), 169.1 (CONH) ppm. IR (KBr): $\tilde{\nu}$ = 3415 (55), 1785 (52), 1706 (81), 1612 (29), 1468 (45), 1364 (63), 1304 (73), 1276 (69), 1041 (54), 720 (65) cm^{-1}. MS (ESI): *m*/*z* (%) = 479 (2.65×10^{-6}) $[M + CH_3OH + Na]^+$. $C_{21}H_{16}N_2O_8 \cdot CH_2Cl_2$ (509.30): calcd. C 51.88, H 3.56, N 5.50; found C 51.96, H 4.21, N 5.60.

Ethyl [(3-Oxo-3*H*-isoindol-1-yl)oxy]acetate (3b): At room temperature, a solution of diazoacetic ester (**2d**) (1.54 g, 13.5 mmol) in dichloromethane (30 mL) was added over 4 h to a stirred suspension of phthalimide (**1a**) (1.0 g, 6.8 mmol) and $Rh_2(OAc)_4$ (10 mg, 0.022 mmol) in dichloromethane (10 mL). The mixture was stirred for an additional 20 min, and the solvent was removed in vacuo to reach a volume of 5–7 mL. The remaining **1a** was filtered, and the product **3b** was crystallized from dichloromethane. The mother liquor was subjected to column chromatography to give **1a** (0.25 g) and a mixture of ethyl maleate and ethyl fumarate (0.53 g; ca. 10:1) which were identified by ^1H NMR spectroscopy. Yield of **3b** 0.3 g (31% based on consumed **1a**); colorless crystals; m.p. 109–111 °C (CH_2Cl_2); R_f = 0.32 (CH_2Cl_2/hexane, 1:1). ^1H NMR ($CDCl_3$): δ = 1.31 (t, $J_{H,H}$ = 6.9 Hz, 3 H, OCH_2CH_3), 4.28 (q, $J_{H,H}$ = 6.9 Hz, 2 H, OCH_2CH_3), 5.18 (s, 2 H, CH_2), 7.51–7.81 (m, 4 H, CH-arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.4 (OCH_2CH_3), 62.2 (OCH_2CH_3), 66.5 (OCH_2), 121.7, 124.3, 133.5, 133.6, 135.1, 135.5 (C-arom.), 166.5 (CO_2Et), 181.2 (O–C=N), 186.1 (CONH) ppm. IR (KBr): $\tilde{\nu}$ = 1710 (72), 1462 (54), 1200 (73), 1120 (85), 1032 (79) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 233 (23) $[M]^{+\cdot}$, 204 (8), 180 (14), 176 (28),

174 (14), 161 (20), 159 (8), 148 (48), 130 (100), 103 (100), 102 (54), 90 (11), 76 (40), 75 (25), 70 (17), 50 (25) 42 (28). $C_{12}H_{11}NO_4$ (233.22): calcd. C 61.81, H 4.75, N 6.00; found C 61.90, H 4.84, N 6.09.

Dimethyl 2-[(5-Oxo-4,5-dihydro-3*H*-pyrrol-2-yl)oxy]malonate (3c): $Rh_2(OAc)_4$ (28 mg, 0.063 mmol) was added to a mixture of succinimide (**1b**) (0.198 g, 2.0 mmol) and dimethyl diazomalonate (**2a**) (0.332 g, 2.1 mmol) in dichloromethane (10 mL). The progress of the reaction was monitored by TLC, and it was complete after 24 h. The solvent was removed in vacuo, and the residue was passed through a plug of silica gel to give the crude product **3c**, which was then crystallized from benzene/Et_2O (1:1). Yield 0.321 g (70%); colorless crystals; m.p. 102–103 °C (benzene/Et_2O, 1:1); R_f = 0.30 (CH_2Cl_2/hexane, 1:1). ^1H NMR ($CDCl_3$): δ = 2.77–2.81 (m, 2 H, CH_2), 2.95–2.99 (m, 2 H, CH_2), 3.87 (s, 6 H, 2 OCH_3), 5.89 (s, 1 H, OCH) ppm. ^{13}C NMR ($CDCl_3$): δ = 28.9 (C-4), 32.8 (C-3), 53.7 (OCH_3), 76.3 (OCH), 163.7 (CO_2), 190.5 (C-2), 194.6 (C-5) ppm. MS (70 eV, EI): *m*/*z* (%) = 229 (45) $[M]^{+\cdot}$, 114 (100), 100 (60), 82 (54), 69 (37). $C_9H_{11}NO_6$ (229.19): calcd. C 47.16, H 4.85, N 6.11; found C 47.14, H 4.91, N 5.98.

Ethyl [(5-Oxo-4,5-dihydro-3*H*-pyrrol-2-yl)oxy]acetate (3d): A solution of ethyl diazoacetate (**2d**) (2.0 g, 17.0 mmol) in CH_2Cl_2 (20 mL) was added over 3 h to a suspension of succinimide (**1b**) (0.86 g, 8.7 mmol) and $Rh_2(OAc)_4$ (10 mg, 0.0226 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for an additional 30 min, and then the solvent was removed in vacuo and the residue was passed through a plug of silica gel using hexane/CH_2Cl_2 (1:1) as the eluent to give the product **3d**. Yield 0.86 g (53%); colorless oil, which becomes yellow on standing; R_f = 0.42 (CH_2Cl_2/hexane, 1:1). ^1H NMR ($CDCl_3$): δ = 1.24 (t, $J_{H,H}$ = 7.2 Hz, 3 H, OCH_2CH_3), 2.71 (m, 2 H, CH_2), 2.84 (m, 2 H, CH_2), 4.19 (q, $J_{H,H}$ = 7.2 Hz, 2 H, OCH_2CH_3), 4.93 (s, 2 H, OCH_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.3 (CH_3), 29.2 (C-3), 32.8 (C-4), 62.1 (OCH_2CH_3), 66.7 (OCH_2), 166.8 (CO_2Et), 191.8 (C-2), 196.1 (C-5) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2880 (65), 1652 (43), 1558 (18), 1322 (36), 810 (53), 601 (77) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 185 (49) $[M]^{+\cdot}$, 140 (46), 128 (70), 112 (27), 100 (49), 99 (40), 88 (100), 82 (92), 70 (67), 60 (86), 54 (92), 49 (67), 43 (51). $C_8H_{11}NO_4$ (185.18): calcd. C 51.89, H 5.98, N 7.56; found C 51.95, H 6.04, N 7.59.

4′-Acetyl-2,3-dihydro-5′-methylspiro[isoindole-1,2′-[1′,3′]dioxol]-3-one (4b): At room temperature, a solution of diazoacetylacetone (**2c**) (2.5 g, 0.02 mol) in dichloromethane (70 mL) was added over 3 h to a stirred mixture of phthalimide (**1a**) (3.0 g, 0.02 mol), $Rh_2(OAc)_4$ (20 mg, 0.045 mmol) and dichloromethane (20 mL). The mixture was stirred for an additional 0.5 h, the solvent was removed in vacuo to reach a volume of 8–10 mL, the remaining **1a** was filtered off, and the residue was passed through a small plug of silica gel using CH_2Cl_2 as the solvent. The obtained solution was dried with $MgSO_4$, and after evaporation of the solvent, the product **4b** was crystallized from acetone/Et_2O (1:4). Yield 2.3 g (69%, based on consumed phthalimide); colorless crystals; m.p. 150–170 °C (dec.); R_f = 0.40 (CH_2Cl_2/hexane, 2:1). ^1H NMR ($CDCl_3$): δ = 2.29 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 7.57–7.83 (m, 4 H, CH-arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.7 (=C–CH_3), 27.6 ($COCH_3$), 116.25 (C-spiro), 122.7, 123.6, 130.7, 131.8, 133.6, 141.1 (C-arom.), 135.2 (C-5′), 146.6 (C-4′), 167.9 (CONH), 189.3 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 1724 (94), 1633 (90), 1425 (50), 1365 (62), 1263 (73), 1072 (75) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 245 (16) $[M]^{+\cdot}$, 174 (12), 160 (10), 147 (100), 130 (29), 104 (59), 76 (66), 50 (26), 43 (68). $C_{13}H_{11}NO_4$ (245.23): calcd. C 63.68, H 4.52, N 5.71; found C 63.83, H 4.59, N 5.69.

Ethyl 2,3-Dihydro-5′-methyl-3-oxospiro[isoindole-1,2′-[1′,3′]dioxole]-4′-carboxylate (4a): $Rh_2(OAc)_4$ (14 mg, 0.031 mmol) was added to a mixture of phthalimide (**1a**) (1.1 g, 7.5 mmol) and ethyl diazoacetoacetate (**2b**) (1.21 g, 7.75 mmol) in dichloromethane (14 mL). The reaction was monitored by TLC and was complete after 5 h. The appearance of the desired product in the mixture was indicated by the appearance of the characteristic "white" spot after visualizing the chromatographic plate with iodine vapor. The solvent was removed in vacuo. Attempts to crystallize the product from acetone/CH_2Cl_2 (1:1) before and after passing the reaction mixture through a plug of silica gel failed, probably, because the desired product has a low melting point or is even liquid at standard conditions. Furthermore, the presence of hydrolysis products complicated the crystallization. The ^1H NMR spectrum of the reaction mixture and that of the fractions, obtained after quick purification of the reaction mixture by column chromatography showed that about 60% of the desired product had been isolated.

Ethyl 3-Methyl-7-oxo-1,4-dioxa-6-azaspiro[4.4]non-2-ene-2-carboxylate (4c): $Rh_2(OAc)_4$ (14 mg, 0.031 mmol) was added to a mixture of succinimide (**1b**) (0.74 g, 7.5 mmol) and ethyl diazoacetoacetate (**2b**) (1.21 g, 7.75 mmol) in dichloromethane (14 mL). The reaction progress was monitored by TLC; the reaction was complete after 5 h. The solvent was removed in vacuo, and product **4c** was crystallized from acetone/CH_2Cl_2 (1:1). Yield 1.0 g (58%); colorless crystals; m.p. 117–118 °C (dec); R_f = 0.34 (CH_2Cl_2/hexane, 1:1). ^1H NMR ($CDCl_3$): δ = 1.30 (t, $J_{H,H}$ = 7.2 Hz, 3 H, OCH_2CH_3), 2.19 (s, 3 H, C=C–CH_3), 2.49–2.61 (m, 4 H, 2 CH_2), 4.24 (q, $J_{H,H}$ = 7.2 Hz, 2 H, OCH_2CH_3), 8.20 (s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.23 (C=C–CH_3), 14.3 (OCH_2CH_3), 29.4 (C-8), 33.1 (C-9), 60.9 (OCH_2CH_3), 120.7 (C-5), 126.1 (C-2), 146.5 (C-3), 160.1 (CO_2), 175.3 (CONH) ppm. IR (KBr): $\tilde{\nu}$ = 1716 (84), 1669 (75), 1379 (68), 1148 (78), 1100 (77), 786 (71) cm^{-1}. HRMS: *m*/*z* = 477.14887 $[2M+Na]^+$. $C_{10}H_{13}NO_5$ (477.14): calcd. C 52.87, H 5.76, N 6.16; found C 52.91, H 5.79, N 6.21.

2-Acetyl-3-methyl-1,4-dioxa-6-azaspiro[4.4]non-2-en-7-one (4d): $Rh_2(OAc)_4$ (14 mg, 0.031 mmol) was added to a mixture of succinimide (**1b**) (0.74 g, 7.5 mmol) and diazoacetylacetone (**2c**) (1.0 g, 7.9 mmol) in dichloromethane (12 mL). The reaction progress was monitored by TLC; the reaction was complete after 1.5 h. The solvent was removed in vacuo and the product **4d** was crystallized from acetone/CH_2Cl_2 (1:1). Yield 1.28 g (87%); colorless crystals; m.p. 155–156 °C (dec.); R_f = 0.4 (CH_2Cl_2/hexane, 1:1). ^1H NMR ($CDCl_3$): δ = 2.21 (s, 6 H, 2 CH_3), 2.54 (s, 4 H, 2 CH_2), 7.94 (s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.6 (CH_3–C=C), 27.5 (CH_3–C=O), 29.6 (C-8), 33.1 (C-9), 120.6 (C-5), 134.4 (C-2), 145.6 (C-3), 175.4 (CONH), 188.9 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 1714 (87), 1623 (85), 1444 (72), 1372 (80), 1254 (82), 1191 (83), 1134 (85), 1100 (81), 941 (77) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 197 (100) $[M]^{+\cdot}$, 154 (53), 126 (33), 116 (11), 98 (42), 82 (76), 55 (30), 43 (87). $C_9H_{11}NO_4$ (197.19): calcd. C 54.83, H 5.62, N 7.01; found C 54.84, H 5.65, N 7.08.

Methanolysis of Dimethyl 2-[(3-Oxo-3*H*-isoindol-1-yl)oxy]malonate (3a): A solution of imidate **3a** (1.0 g, 3.6 mmol) in methanol (10 mL) was heated under reflux until complete disappearance of the starting compound in the reaction mixture (monitored by TLC, 2 h). Methanol was removed by distillation at atmospheric pressure and then in vacuo (1–2 Torr). Preparative separation of the reaction mixture was accomplished by addition of diethyl ether to crystallize compound **6**, followed by column chromatography of the residue from the mother liquor on silica gel to obtain dimethyl 2-hydroxymalonate (**7**).

3,3-Dimethoxyisoindol-1-one (6): Yield 0.52 g (74%), colorless crystals, m.p. 119 °C. ^1H NMR ($CDCl_3$): δ = 3.34 (s, 6 H, 2 OCH_3), 7.54–7.88 (m, 4 H, CH-arom), 8.40 (br. s, 1 H, NH) ppm. ^{13}C

NMR ($CDCl_3$): δ = 51.0 (OCH_3), 109.3 (O–C–O), 123.0, 123.3, 130.7, 132.4, 132.9, 143.1 (C-arom.), 168.0 (C=O) ppm. MS (70 eV, EI): *m/z* (%) = 194 (1) $[M+H]^+$, 192 (2) $[M-H]^+$, 162 (100), 130 (78), 130 (40), 91 (7), 76 (24), 50 (13), 32 (5).

Dimethyl 2-Hydroxymalonate (7): Yield 0.16 g (30%); colorless crystals; m.p. 44–45 °C;[21] R_f = 0.5 (CH_2Cl_2/hexane, 3:1). ^1H NMR ($CDCl_3$): δ = 3.52 (d, $J_{H,H}$ = 4.15 Hz, 1 H, OH), 3.87 (s, 6 H, 2 OCH_3), 4.70 (d, $J_{H,H}$ = 4.15 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 53.4 (OCH_3), 71.3 (CH), 169.0 (CO_2Me) ppm.

Hydrolysis of Dimethyl 2-[(3-Oxo-3*H*-isoindol-1-yl)oxy]malonate (3a) on Silica Gel: Silica gel (2.0 g) was added to a solution of **3a** (0.4 g, 1.44 mmol) in dichloromethane (8 mL), and the mixture was stirred at room temperature for 72 h. The silica gel was filtered off, washed with dichloromethane and the solution was concentrated at atmospheric pressure to reach a volume of ca. 4 mL. After addition of diethyl ether (3 mL), phthalimide (**1a**) (0.14 g, 1.0 mmol, 70%) crystallized. The mother liquor was concentrated at atmospheric pressure and passed through a small plug of silica gel to give 0.14 g (68%) of dimethyl 2-hydroxymalonate (**7**), the physical properties of which were identical with those given above.

General Procedure for Catalytic Decomposition of Diazo Compounds 2a–d in the Presence of Acyclic Imides 1c,d: $Rh_2(OAc)_4$ (20 mg, 0.045 mmol) was added to a solution of imide **1c** (1.96 g, 0.02 mol) and diazo compound **2a** (3.16 g, 0.02 mol) in dichloromethane (10 mL). Within 30 min, the color of the reaction mixture changed from deep green to brown-red, and the decomposition of the diazo compound stopped (monitored by TLC and visually, no evolution of N_2 observed). The solvent was removed in vacuo, and the residue was analyzed by ^1H NMR spectroscopy and mass spectrometry.

Dimethyl 2-[1-(Acetylimino)ethoxy]malonate (8a): ^1H NMR ($CDCl_3$): δ = 2.05 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 3.76 (s, 6 H, 2 OCH_3), 5.46 (s, 1 H, OCH) ppm. MS: *m/z* = 254 $[M+Na]^+$.

Ethyl 2-[1-(Acetylimino)ethoxy]-3-oxobutyrate (8b): ^1H NMR ($CDCl_3$): δ = 1.27 (t, $J_{H,H}$ = 7.4 Hz, 3 H, OCH_2CH_3), 1.97 (s, 3 H, CH_3), 2.12 (s, 3 H, $COCH_3$), 2.41 (s, 3 H, CH_3), 4.22 (q, $J_{H,H}$ = 7.4 Hz, 2 H, OCH_2CH_3), 5.42 (s, 1 H, OCH) ppm. MS: *m/z* = 230 $[M+H]^+$.

***N*-[1-(1-Acetyl-2-oxopropoxy)ethyliden]acetamide (8c):** ^1H NMR ($CDCl_3$): δ = 1.93 (s, 3 H, CH_3), 1.98 (s, 3 H, CH_3), 2.25 (s, 6 H, 2 $COCH_3$), 5.23 (s, 1 H, OCH) ppm. MS: *m/z* = 200 $[M+H]^+$.

Ethyl [1-(Acetylimino)ethoxy]acetate (8d): ^1H NMR ($CDCl_3$): δ = 1.24 (t, $J_{H,H}$ = 7.2 Hz, 3 H, OCH_2CH_3), 1.96 (s, 3 H, CH_3), 2.09 (s, 3 H, CH_3), 4.52 (s, 2 H, OCH), 4.17 (q, $J_{H,H}$ = 7.2 Hz, 2 H, OCH_2CH_3) ppm. MS: *m/z* = 210 $[M+Na]^+$.

Dimethyl 2-[1-(Benzoylimino)ethoxy]malonate (8e): ^1H NMR ($CDCl_3$): δ = 2.11 (s, 3 H, CH_3), 3.78 (s, 6 H, 2 OCH_3), 5.63 (s, 1 H, OCH), 7.31–7.88 (m, 5 H, CH-arom.) ppm. MS: *m/z* = 316 $[M+Na]^+$.

Ethyl 2-[1-(Benzoylimino)ethoxy]-3-oxobutyrate (8f): ^1H NMR ($CDCl_3$): δ = 1.22 (t, $J_{H,H}$ = 7.4 Hz, 3 H, OCH_2CH_3), 2.04 (s, 3 H, CH_3), 2.59 (s, 3 H, $COCH_3$), 4.21 (q, $J_{H,H}$ = 7.4 Hz, 2 H, OCH_2CH_3), 5.57 (s, 1 H, OCH), 7.32–7.87 (m, 5 H, CH-arom.) ppm. MS: *m/z* = 292 $[M+H]^+$.

***N*-[1-(1-Acetyl-2-oxopropoxy)ethylidene]benzamide (8g):** ^1H NMR ($CDCl_3$): δ = 1.95 (s, 3 H, CH_3), 2.27 (s, 6 H, 2 $COCH_3$), 5.22 (s, 1 H, OCH), 7.31–7.86 (m, 5 H, CH-arom.) ppm. MS: *m/z* = 262 $[M+H]^+$.

Ethyl [1-(Benzoylimino)ethoxy]acetate (8h): ^1H NMR ($CDCl_3$): δ = 1.21 (t, $J_{H,H}$ = 7.4 Hz, 3 H, OCH_2CH_3), 2.03 (s, 3 H, CH_3), 4.17 (q, $J_{H,H}$ = 7.4 Hz, 2 H, OCH_2CH_3), 4.68 (s, 2 H, OCH), 7.13–8.02 (m, 5 H, CH-arom.) ppm. MS: *m/z* = 272 $[M+Na]^+$.

X-ray Crystal Structure Determination of 3a and 5:[22] All measurements were performed with a Nonius KappaCCD area-detector diffractometer[23] using graphite-monochromated Mo-K_α radiation (λ 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. The data collection and refinement parameters are given below, and views of the molecules are shown in Figures 1 and 2. Data reduction was performed with HKL Denzo and Scalepack.[24] The intensities were corrected for Lorentz and polarization effects. In the case of **5**, an absorption correction based on the multiscan method[25] was applied. The structures were solved by direct methods using SIR92,[26] which revealed the positions of all non-H atoms. The non-H atoms were refined anisotropically. The asymmetric unit of **5** contains one molecule of the heterocyclic compound plus one molecule of CH_2Cl_2. The N–H and hydroxy H atoms of **5** were placed in the positions indicated by difference electron density maps, and their positions were allowed to refine together with individual isotropic displacement parameters. All remaining H atoms in the structure were placed in geometrically calculated positions and refined using a riding model, where each H atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C atom (1.5 U_{eq} for the methyl groups). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. Corrections for secondary extinction were applied. In **3a**, one reflection, whose intensity was considered to be an extreme outlier, was omitted from the final refinement. Neutral atom scattering factors for non-H atoms were taken from ref.[27] and the scattering factors for H atoms were taken from ref.[28] Anomalous dispersion effects were included in F_c;[29] the values for f' and f'' were those of ref.[30] The values of the mass attenuation coefficients were those of ref.[31] All calculations were performed using the SHELXL97[32] program.

Crystal Data for 3a: $C_{13}H_{11}NO_6$, M = 277.23, colorless, prism, crystal dimensions 0.20 × 0.25 × 0.25 mm, monoclinic, space group $P2_1/c$, Z = 4, a = 18.8795(8), b = 4.8901(2), c = 13.7785(6) Å, β = 97.071(2)°, V = 1262.39(9) Å^3, D_X = 1.459 g cm^{-3}, T = 160 K, μ(Mo-K_α) = 0.117 mm^{-1}, 2θ(max) = 50°, total reflections measured 19639, symmetry-independent reflections 2229, reflections with $I > 2\sigma(I)$ 1787, reflections used in refinement 2228, parameters refined 184, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0435, $wR(F^2)$ (all reflections) = 0.1163 $\{w = [\sigma^2(F_o^2) + (0.0535P)^2 + 0.4818P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3\}$, goodness of fit 1.092, secondary extinction coefficient 0.016(3), final Δ_{max}/σ = 0.001, $\Delta\rho$(max/min) = 0.19/–0.20 e·Å^{-3}.

Crystal Data for 5: $C_{22}H_{18}Cl_2N_2O_8$, M = 509.30, colorless, plate, crystal dimensions 0.05 × 0.15 × 0.22 mm, triclinic, space group $P\bar{1}$, Z = 2, a = 9.7436(2), b = 11.2921(3), c = 11.5093(3) Å, α = 70.816(2), β = 84.056(2), γ = 67.102(1)°, V = 1101.32(5) Å^3, D_X = 1.536 g cm^{-3}, T = 160 K, μ(Mo-K_α) = 0.348 mm^{-1}, transmission factors (min/max) 0.926/0.983, 2θ(max) = 60°, total reflections measured 34416, symmetry-independent reflections 6431, reflections with $I > 2\sigma(I)$ 4737, reflections used in refinement 6431, parameters refined 318, final $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0527, $wR(F^2)$ (all reflections) = 0.1365 $\{w = [\sigma^2(F_o^2) + (0.0702P)^2 + 0.3072P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3\}$, goodness of fit 1.061, secondary extinction coefficient 0.094(5), final Δ_{max}/σ = 0.001, $\Delta\rho$(max/min) = 0.52/–0.43 e·Å^{-3}.

Acknowledgments

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