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2-Methoxy-Δ^3-1,3,4-oxadiazoline, a Multipurpose Precursor for the Generation of a Carbene, an Ylide, or a Diazo Compound[‡]

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In the course of our investigation of the *intermolecular* reactions of foiled carbenes of the norborn-2-en-7-ylidene type, we have investigated the decomposition of methoxyoxadiazoline **1** in alcohols. Most of the reactions performed lead to products with an *anti* configuration confirming the participation of the double bond to the stabilization of the transition states. The thermal behavior of spirooxadiazoline **1** is quite different from the behavior of the parent 2-methoxy-2,5,5-trimethyl-Δ^3-1,3,4-oxadiazoline. Photolysis of **1** leads to the carbene after prior formation of the diazo compound whereas thermolysis cleanly generates an extremely unstable carbonyl ylide **4** that immediately decomposes to the stabilized-nucleophilic carbene **5** and methyl acetate without generation of 1-methoxyethylidene. Both conformers of **4** do not interconvert and, therefore, they have different life times. Nevertheless, we were able to trap *syn* ylide **4a** with methanol. Calculations show that nonbonding interactions between an alkyl carbene and an ester are more significant than ylide formation. Synthetically, photolysis of oxadiazoline **1** in ethyl acetate has proven to give *anti* ethers in excellent yields. Moreover, we report the first reactions of a norbornenylidene derivative with O–H bonds in which no products resulting from a cationic rearrangement are formed.

Introduction

It is still a challenging task to find a convenient source of alkyl carbenes: for an efficient interception of the divalent species, the precursor has to be generated under mild conditions and no other reactive intermediate should be generated. Of course, the precursor should be readily available. In many cases, nitrogen-containing compounds are used like tosylhydrazone salts or diazirines but most of them have significant drawbacks. First of all, usually, a quite reactive diazo species is initially generated which decomposes only in a further step to a carbene. Diazirines often lead directly to the carbene but frequently, their preparation succeeds only with very low yields. Therefore, Δ^3-1,3,4-oxadiazolines have become very popular precursors. They are readily synthesized from the corresponding ketones and have been widely used for the generation of nucleophilic carbenes like dimethoxycarbene. And depending on their substitution pattern and their activation, their decomposition pathways vary considerably.[1] Especially, 2-alkoxy-Δ^3-1,3,4-oxadiazolines are very attractive since Warkentin has shown some 20 years ago that they are suitable for the generation of alkyl carbenes under photochemical conditions after prior formation of a diazoalkane.[2] Indeed, they have permitted numerous investigations.[3] In this work, we will show that the two diastereomers of oxadiazoline **1** differ significantly in their chemistry, that their thermal activation leads exclusively to the formation of the strained alkenylidene **5** without the intermediacy of a diazo species, and that the generated intermediates are very efficiently trapped by alcohols.

Results and Discussion

Tricyclo[6.2.1.0^{2,7}]undec-9-en-11-ylidene (**5**) is a typical foiled carbene based on a cyclopent-3-enylidene scaffold. In these reactive intermediates, stabilization occurs mainly through electron donation from the C=C double bond into the antibonding lone pair (LP*) of the divalent carbon atom, making the LUMO of carbene **5** less reactive. In other words, the electrophilicity of the carbene is strongly reduced and, overall, the nucleophilic character of **5** is determining its chemoselectivity. This led us to define norbornenylidene derivatives as stabilized-nucleophilic carbenes.[4] These electronic processes explain why foiled carbenes could not be trapped intermolecularly in synthetically use-

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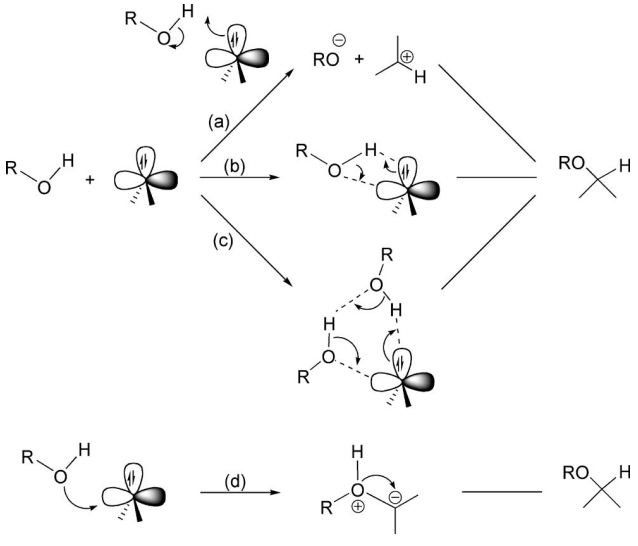
ful yields by alkenes or hydrocarbons. In fact, the only efficient intermolecular reactions known so far concerns the insertion into the N–H bond of diethylamine[5] and the O–H bond of methanol.[6] For the latter reaction, the ease of etherification can be related to the high proton affinity (PA) of **5**. Indeed, **5** still possesses the same high PA characteristic of nucleophilic and alkyl carbenes.[7]

In fact, it has already been proven by means of deuterium labels[6b,8] that bicyclo[2.1.1]hexan-2-ylidene is protonated by methanol and that in solvolysis experiments norbornen-7-ylidene reacts efficiently with the O–H bond of methanol through the carbocation mechanism.[6b] Indeed, three different mechanisms can be envisaged for this insertion reaction (Scheme 1):[8] (a) protonation to a carbenium ion, (b) a concerted cheletropic cycloaddition and (c) the OH group catalysis mechanism[9] in which alcohol (ether) formation occurs in only one step but in which the hydrogen atom and the hydroxy (alkoxy) group stem from two different molecules. The often discussed ylide mechanism (d) by which the carbene first attacks the oxygen atom and then rearranges by a proton transfer (Stevens rearrangement) is only relevant for reactive-electrophilic carbenes.[4,9,10] In this study, we have attempted to repeat this etherification with compounds **1** under less polar conditions in order to favor the concerted reaction pathway over the cationic mechanism. The large difference in pK_a for methanol and more generally for alcohols depending on the solvents used (pK_a = 15.54 in H_2O)[11] and (pK_a = 29 in DMSO)[12] suggests that the cationic mechanism may not occur in nonpolar organic solvents, since under these conditions a protonation of the carbene is less probable.



Scheme 1. Possible reaction mechanisms for the insertion of a carbene into an O–H bond.

Experimental Results

2-Methoxy-2-methyl-Δ^3-1,3,4-oxadiazolines are known to react photochemically via a 1,3-dipolar cycloreversion to methyl acetate and a diazo compound that then splits off nitrogen and generates the carbene.[2] The only drawback of precursor **1** was that the two diastereomers, which are formed in about equal amounts, decomposed differently, especially when photolyzed. Whereas diastereomer **1a** can be conveniently decomposed within two hours, diastereomer **1b** requires reaction times of more than one day. Therefore, in this special case, both compounds were separated by column chromatography and the photolysis was exclusively performed with **1a**. In control experiments, diastereomer **1b** has been shown to react in the same manner as **1a**, but just slower.

Photolysis of **1a** in pure methanol afforded two methyl ethers: 48% *anti*,*endo*-11-methoxytricyclo[6.2.1.0^{2,7}]undec-9-ene (**10me**) and 43% 3-methoxytricyclo[5.4.0.0^{2,6}]undec-4-ene (**12me**) (Table 1, Scheme 2). The presence of the rearrangement product **12me** suggests that *syn*-diazonium ion **3** has been generated as an intermediate[6b] and that the reaction mainly does not proceed through carbene **5**.

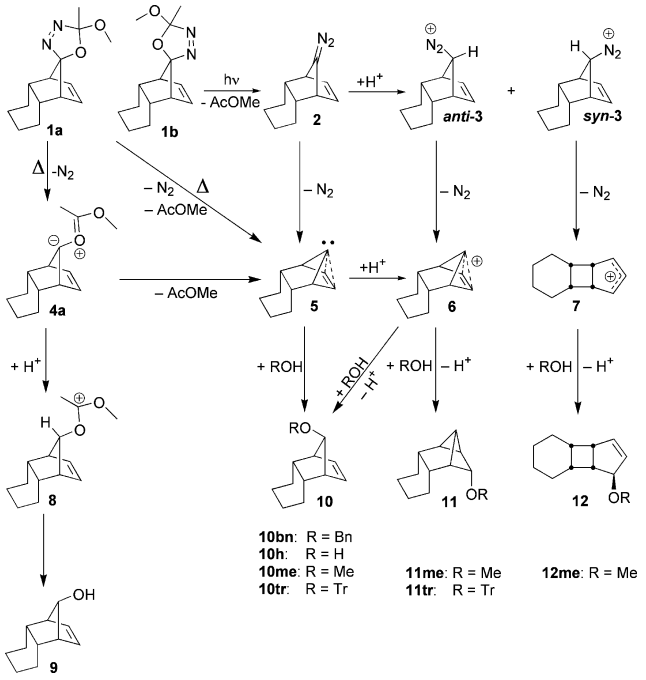
Table 1. Distribution (%) of the products (NMR integration) in the crude reaction mixtures obtained from the decomposition of 40 mg of oxadiazoline **1** in methanol.[a]

		9	**10me**	**11me**	**12me**
	Photolysis with **1a**:				
a)	MeOH, *hν*	–	48	–	43
b)	2 equiv. MeOH in EE, *hν*	–	82	–	11
c)	2 equiv. MeOH in benzene, *hν*	–	92	7	1
d)	2 equiv. MeOH in hexane, *hν*	–	85	–	15
	Thermolysis:				
e)	**1b**: MeOH, Δ	–	96	–	–
f)	**1a**: MeOH, Δ	26	71	–	–
g)	**1b**: THF/MeOH (10:1), Δ	–	80	15	–

[a] No methyl ether is obtained from the thermolysis of **1a** in a saturated solution of MeOH in hexane or with 10 equiv. of MeOH in benzene.

Under less polar conditions, the amount of **12me** is reduced but **12me** is still produced [11% 2 equiv. MeOH in ethyl acetate (EE) and even 15% 2 equiv. MeOH in hexane]. These results show that in solution some of the diazo compound **2** decomposes to carbene **5** before it can be protonated. In benzene, 7% of tetracycle **11me** is also formed, a compound whose formation is best explained by trapping of carbocation **6**. It is worth noticing that the corresponding capture of the closely related 7-norbornenyl cation proceeds even in methanol under methoxylation at the former double bond.[6b] Overall, even under the less polar conditions, protonation of **2** and **5**, respectively, plays a significant role in the formation of methyl ethers **10me**, **11me**, and **12me**. It is also worth noticing that the trapping of allyl cation **7** by methanol leads exclusively to *exo*-ether **12me** because the six-membered ring seems to prevent the approach of the nucleophile from the *endo*-side. In contrast, capture of the parent bicyclo[3.2.0]hept-3-en-2-yl cation by methanol leads to a mixture of *endo*- and *exo*-ethers.[6b]

Thermally, compound **1a** reacts faster than **1b**. Therefore, reactions of **1a** were performed at 155 °C while reactions with **1b** were carried out at 165 °C. However, the thermoly-



Scheme 2. Reaction mechanisms for the decomposition of oxadiazoline **12** under protic conditions.

ses in saturated solutions of methanol in hexane (20 mg of **1a** and **1b** in 4 mL) or with 10 equiv. of methanol in benzene were not successful. No volatile product was formed and etherification was only obtained under solvolytic conditions. Probably, carbene **5** rearranges intramolecularly by a 1,2 vinyl shift before it can be trapped and the resulting strained alkene polymerizes under the drastic reaction conditions. Thermal decomposition of oxadiazoline **1a** in dry methanol at 155 °C leads to formation of *anti* ether **10me** but in addition, *syn* alcohol **9** is formed. The presence of this compound is best explained by the capture of carbonyl ylide **4a** by methanol. Replacement of methanol by *t*BuOH, AcOH or dioxane/water as a trap does not lead to an increase in the formation of **9**. Only 2 M of NaOMe in methanol increased the production of **9** to 35%. Thermally, no other methyl ether is formed and no rearrangement is observed. This result suggests that no diazo compound is generated from **1a** and that the cycloreversion solely leads to the formation of a carbonyl ylide. Starting from diastereomer **1b** in pure methanol, *anti* methyl ether **10me** is formed exclusively in a particularly clean reaction. The absence of *syn* alcohol **9** indicates that the other carbonyl ylide conformer **4b** is formed and that it does not interconvert to **4a** before reacting further. Under less polar conditions, in THF/MeOH (10:1), tetracycle **11me** is also formed[13] from **1b** by an attack of the nucleophile on C(9) of cation **6** suggesting that the etherification proceeds through the cationic mechanism. It is worth noticing that tetracycle **11** has only been observed by reactions with methanol and not with other nucleophiles. Indeed, thermal hydrolysis of oxadiazoline **1b** in dioxane/water (5:1) exclusively leads to *anti* alcohol **10h** in a very good yield (Table 2).

Table 2. Distribution (%) of products in the crude reaction mixtures obtained from the decomposition of 40 mg of oxadiazoline **1** in presence of alcohols or water.[a]

	10	**11**
Photolysis with **1a**:		
1 equiv. TrOH in 1 mL of benzene, *hν*	**10tr**: 63	**11tr**: 2
1 equiv. TrOH in 1 mL of acetonitrile, *hν*	**10tr**: 59	**11tr**: 6
1 equiv. TrOH in 1 mL of EE, *hν*	**10tr**: 66	–
2 equiv. BnOH in 0.5 mL of EE, *hν*	**10bn**: 89	–
2 equiv. BnOH in 0.5 mL of THF, *hν*	**10bn**: 73	–
Thermolysis with **1b**:		
Dioxane/water (5:1), Δ	**10h**: 94	–

[a] Tr = trityl. Bn = benzyl.

Anyhow, these reaction conditions point to a formal concerted insertion of **5** into the O–H bond since rearrangement products **11** and **12** are not obtained. Moreover, this reaction represents a convenient synthetic procedure for the transformation of a ketone to an ether since both reaction steps, the formation and the decomposition of the oxadiazoline, take place in a cleanly manner. Whereas many carbenoids tend to insert into the O–H bonds as well as into the C–H bonds of alcohols,[14] here only ether formation has been observed.

From a synthetic point of view, photolysis is a more suitable method than thermolysis because oxadiazolines **1a** and **1b** react selectively with the O–H bond of alcohols even if only stoichiometric amounts are used. With BnOH and TrOH, no rearrangement is observed, only the *anti* ether is obtained (66% **10tr** and 89% **10bn** in ethyl acetate). The moderate yield of 66% achieved with the sterically hindered Ph_3COH is caused by reaction with water traces and formation of alcohol **10h** and of the corresponding symmetrical ether bis(*anti*,*endo*-tricyclo[6.2.1.$0^{2,7}$]undec-9-en-11-yl) ether. Slightly lower yields are obtained in acetonitrile (59%) and tetrahydrofuran (63%).

Investigation of the Reaction Mechanisms

In a next step, we took a closer look at the decomposition of precursor **1** in order to better understand in which reactions a carbene can be expected. As a multipurpose precursor, oxadiazolines may decompose either to a ketone, a diazo compound, or a carbonyl ylide.[1] Whereas the chemistry of ketones and diazo compounds is well understood, carbonyl ylides remain fascinating species with properties that are extremely dependant on their substitution.[15] For example, ylides formally derived from the addition of an electrophilic carbene to a carbonyl group are convenient intermediates to undergo 1,3-dipolar cycloadditions to double bonds.[15] Moreover, trapping of tetrakis(trifluoromethyl)cyclopentadienylidene by urea leads to a push-pull ylide, which is crystalline and melts at 200–202 °C.[16] In contrast, nucleophilic carbenes do not even add to the oxygen atom of C=O double bonds.[17]

In regard to the decomposition of oxadiazoline **13**, computations were performed at the B3LYP/6-31G(d) level of theory. It is found that diastereomer **13b** is more stable than **13a** by about 1.3 kcal/mol. This difference is observed again from the calculations of the transition states of the nitrogen liberating reactions for which the barriers are 1.2 to 1.3 kcal/mol higher for **13b** than for **13a** (Figure 1). Experimentally, diastereomer **13b** reacts slower, necessitating an increase of the reaction temperature from 155 °C to 165 °C in order to maintain a similar reaction time as for diastereomer **13a**.

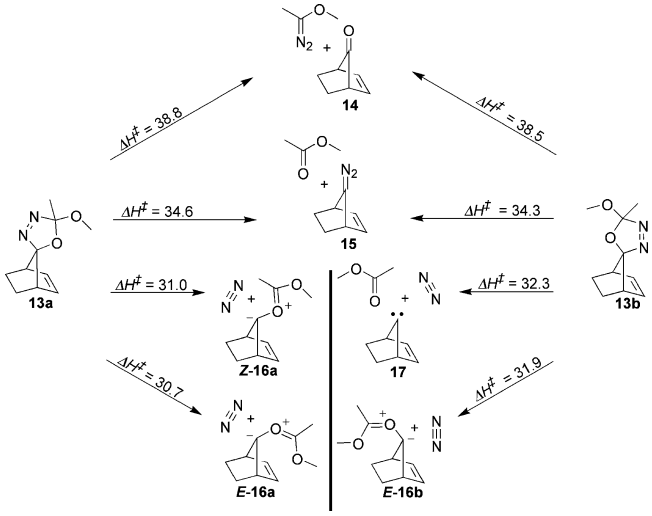


Figure 1. Potential cycloreversions for the decomposition of oxadiazolines **13a** and **13b**. Enthalpies in kcal/mol as given by B3LYP/6-31G(d).

Figure 1 shows the results of the computations for the decomposition of oxadiazoline **13**, which speak for reactions through carbonyl ylides **16**. The barrier for ylide formation (30.7 to 31.9 kcal/mol) is significantly lower then that leading to diazo species **15** (34.3 and 34.6 kcal/mol) or ketone **14** (38.5 and 38.8 kcal/mol). The differences in the decomposition rates between **13a** (overnight in a pressure tube at 155 °C; calculated barrier: $\Delta H^{\ddagger}$ = 30.7 kcal/mol, $\Delta G^{\ddagger}$ = 29.0 kcal/mol) and **13b** (overnight at 165 °C, calculated barrier: $\Delta H^{\ddagger}$ = 31.9 kcal/mol, $\Delta G^{\ddagger}$ = 29.7 kcal/mol) are also well reproduced. The absolute values are satisfactory but a little too low; according to the Eyring equation a free energy of activation of 32–33 kcal/mol would be expected. However, it is worth noticing that the back reactions **16a**→**13a** and **16b**→**13b**, respectively, occur with very low enthalpic barriers.

The decomposition of **13** requires 3–4 kcal/mol more energy than is necessary for the thermolysis of the smaller oxadiazoline **18** (Figure 2).[18] Indeed, **18** usually is decomposed under exclusive formation of ylide **21** at temperatures as low as 80 °C with rates ($k^{79.5}_{CD_3OD} = 5.3 \times 10^{-6}$ s^{-1} and $k^{79.5}_{CCl_4} = 1.4 \times 10^{-5}$ s^{-1})[19] in good agreement with our calculated values. The difference in the stability of oxadiazolines **13** and **18** probably is caused by the ring strain of polycyclic compound **13** and its decomposition products **14**, **15**, and **16**. In **13**, C(7) is about sp^3-hybridized (preferred angle in unstrained systems: 109.5°; actual angle from the crystal structure of **1b**[5] is 94.3°) whereas for the formation of the products a double bond has to be formed leading to sp^2 hybridization (preferred angle: 120°), a geometry requiring an even larger angle. A similar behavior is found for example for ketals of bicyclo[3.2.1]octan-8-one derivatives which are more stable than ketals of acyclic ketones.

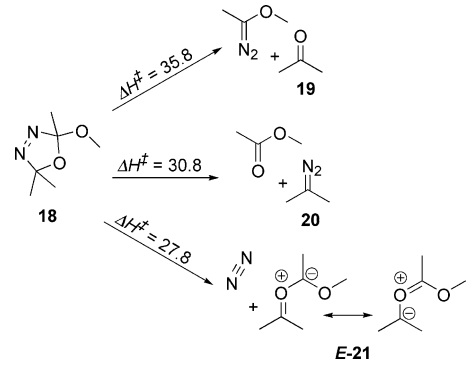


Figure 2. Potential cycloreversions for the decomposition of oxadiazoline **18**. Enthalpies in kcal/mol as given by B3LYP/6-31G(d).

For the decomposition of oxadiazolines **13**, formation of two different conformers of ylide **16** is predicted (Figure 1). The lowest pathway leads to ***E*-16a** and ***E*-16b**, respectively, in which the oxygen atoms are arranged in the same manner than in methyl acetate in its *E*-conformation. However, the difference in the activation energies is small and a significant amount of ***Z*-16** should be generated. Merely due to dipole-dipole and also to steric interactions, esters are better stabilized in the *Z*-conformation.[20] Therefore, ***Z*-16a** decomposes readily to norbornenylidene **17** by overcoming a low barrier of 0.6 kcal/mol [Figure 3, TS(***Z*-16a**/**17**), +10.7 kcal/mol in comparison to norbornenylidene and methyl acetate, +0.6 kcal/mol from ylide ***Z*-16a**]. Ylide ***Z*-16b** was not even found; instead oxadiazoline **13b** directly gives carbene **17** because the decomposition of ***Z*-16b** is further facilitated by anchimeric assistance from the double bond.

In contrast, for the decomposition of ***Z*-16a** to 1-methoxyethylidene and norbornenone **14** 10.6 kcal/mol [TS(***Z*-16a**/**14**)] are required. This prohibitively high energy barrier is at first surprising because the nucleophilic 1-methoxyethylidene is a more stable carbene than usual alkyl carbenes. However, the stability of the second compound formed is also important: liberation of norbornenylidene **17** leads to the release of an ester, i.e., methyl acetate, whereas generation of 1-methoxyethylidene leads to formation of strained ketone **14**. As a *syn* ylide, no participation of the neighboring double bond is expected. The preference for the generation of norbornenylidene **17** can already be seen in the geometry of ylide ***Z*-16a** (Figure 3): the C–O bonds are strongly asymmetric. The C(7)–O bond is relatively long with 1.474 Å (normal single C–O bond: 1.43 Å)[21] whereas the carboxylic C=O bond (1.266 Å) of the former methyl

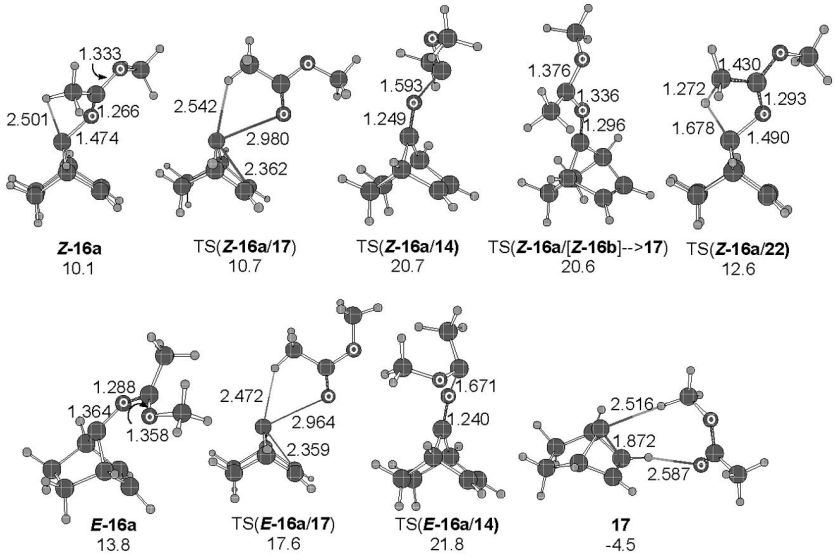


Figure 3. Stationary points describing ylides ***E*-16a** and ***Z*-16a** and their decomposition. Enthalpies at 298 K are in kcal/mol and distances in Ångstroms. Norbornenylidene and methyl acetate were taken as reference (0 kcal/mol).

acetate still has about the expected length of such a bond (normally 1.21 Å).[21] The carboxylic carbon is still planar whereas C(7) is sp^3-hybridized, suggesting the presence of a negative charge on C(7). This lone pair of electrons further interacts (d = 2.501 Å) with the C–H bonds in α-position to the carboxylic group.

In contrast, ***E*-16a** has the potential to have a more significant lifetime. The direct decompositions to norbornenylidene or 1-methoxyethylidene are correlated with high energy barriers [3.8 and 8.0 kcal/mol for TS(***E*-16a/17**) and TS(***E*-16a/14**), respectively] (Figure 3) when compared with ***Z*-16a**. However, rotation around the C–O bond is almost free of energy [TS(***E*-16a/Z_2-16a**), +0.5 kcal/mol] and leads to a second *Z*-conformer ***Z_2*-16a** which readily decomposes to norbornenylidene **17** [TS(***Z_2*-16a/17**), +1.5 kcal/mol] (Figure 4).

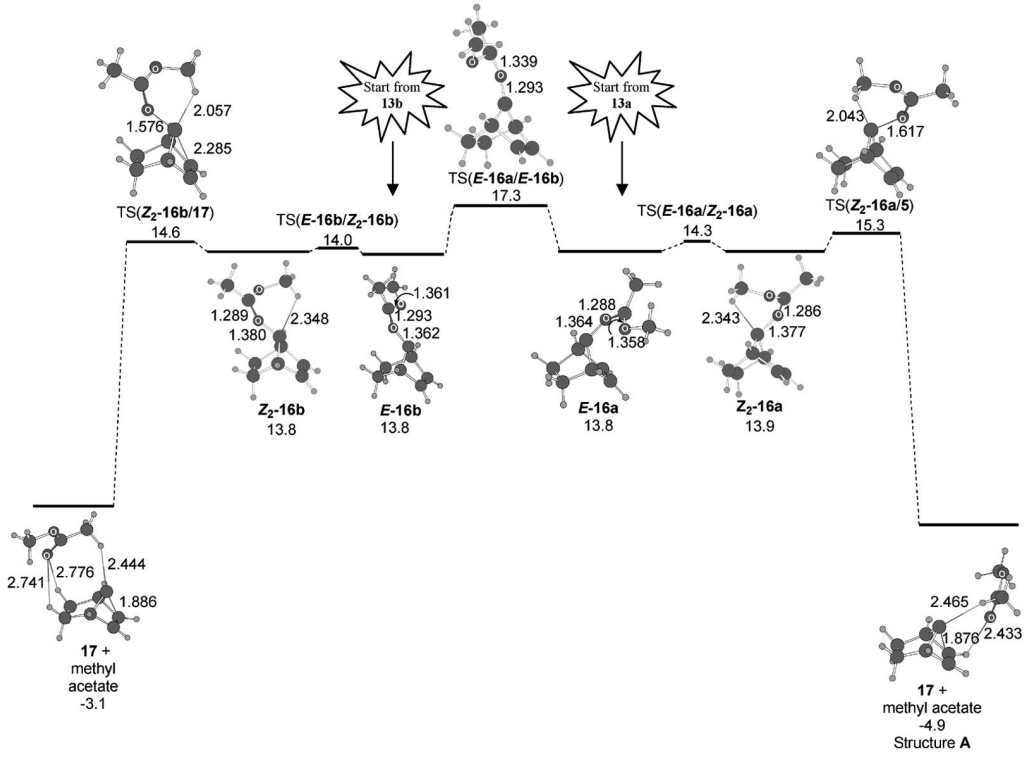


Figure 4. Energy diagram for the decomposition of ylides ***E*-16a** and ***E*-16b**. Enthalpies at 298 K are in kcal/mol and distances in Ångstroms. Norbornenylidene and methyl acetate were taken as reference (0 kcal/mol).

For the generation of a carbene, with 18.8 kcal/mol, this reaction is quite exothermic and can be considered as irreversible because **17** has the possibility to react intramolecularly by a 1,2-vinyl shift to bicyclo[3.2.0]hepta-1,6-diene.[7,22] Because of the low barrier toward decomposition of ylide 7-(1-methoxyethylideneoxonio)bicyclo[2.2.1]hept-2-en-7-ide (**16**), inversion of the configuration at C(7) of *syn* ylide ***E*-16a** to *anti* ylide ***E*-16b** should not occur [TS(***E*-16a**/***E*-16b**): barrier 3.5 kcal/mol]. Despite its low kinetic stability, we were able to trap **16a** with methanol. Interestingly, the noncovalent interactions between the stabilized nucleophilic carbene **17** and methyl acetate are quite significant (4.9 kcal/mol, see structure **A** in Figure 4). The main interaction results from electron donation from the LP at the carbenic center toward the slightly acidic C–H bond of methyl acetate (second order perturbation theory analysis of the Fock matrix in the NBO basis: E = 5.4 kcal/mol) assisted by electron donation from the carboxylic oxygen into an alkenic C–H antibond (1.1 kcal/mol). It all sums up to a small charge transfer of 0.01 e from carbene **17** to methyl acetate. Dipole-dipole interactions between the carbenic center and the C=O double bond should also provide an important contribution to the stabilization of the structure.

Whereas these calculations show that 2-methoxy-2-methyl-Δ^3-1,3,4-oxadiazolines generated from strained ketones should be a convenient thermal source of alkyl carbenes, the computational results obtained for ylide **21** generated from the monocyclic oxadiazoline **18** lead to a more complex picture (Figure 5). Once again, two conformers with different reactivities have to be considered.[23] In contrast to bicyclic ylide **16**, **21** is almost planar (a 0°, 0° conformation)[24] and therefore should possess more diradical character and be less polar than **16**.[9,24,25] The heterocycle **18** is predicted to almost exclusively give ylide ***E*-21** which lies in a relatively deep well with reasonable barriers toward formation of propan-2-ylidene [TS(***E*-21**/**24**), 12.4 kcal/mol], 1-methoxyethylidene [TS(***E*-21**/**25**), 7.3 kcal/mol], and 2-(1-methoxyethoxy)propene (**27**) [TS(***E*-21**/**27**), 7.1 kcal/mol] (start on the right side of Figure 5). Calculations at the CCSD(T) level confirm the validity of the B3LYP results but also show that the stabilities of the carbonyl ylides **21** are slightly underestimated. These relatively high activation energies explain why ylide ***E*-21** could be trapped by acetone[26] or chloroform.[27] This scanning of the energy surface also means that thermally **18** is predicted not to be a source of alkyl carbene, in contrast to the experimental results which speak for the generation of about equal amounts of both carbenes.[19,28] The second relevant conformer, ***Z*-21**, can neither be obtained from ***E*-21** nor from oxadiazoline **18**. It is predicted to be in equilibrium with the complex between propan-2-ylidene and methyl acetate. The barrier between both structures is quite low [TS(***Z*-21**/**24**), 0.9 and 1.2 kcal/mol, respectively; start on the left side of Figure 5]. The next higher transition states represent a 1,4-H shift to 2-(1-methoxyvinyloxy)propane (**26**) [TS(***Z*-21**/**26**), 2.3 kcal/mol] or to **27** [TS(***Z*-21**/**27**), 3.1 kcal/mol, see Supporting Information], and the decomposition of ***Z*-21** to acetone and 1-methoxyethylidene [TS(***Z*-21**/**25**), 2.9 kcal/mol]. These results suggest that carbene **25** may be obtained through generation of an alkyl carbene in the corresponding ester. This process can be coined a transcarbenation. This kind of reaction could be particularly useful for the generation of carbenes for which

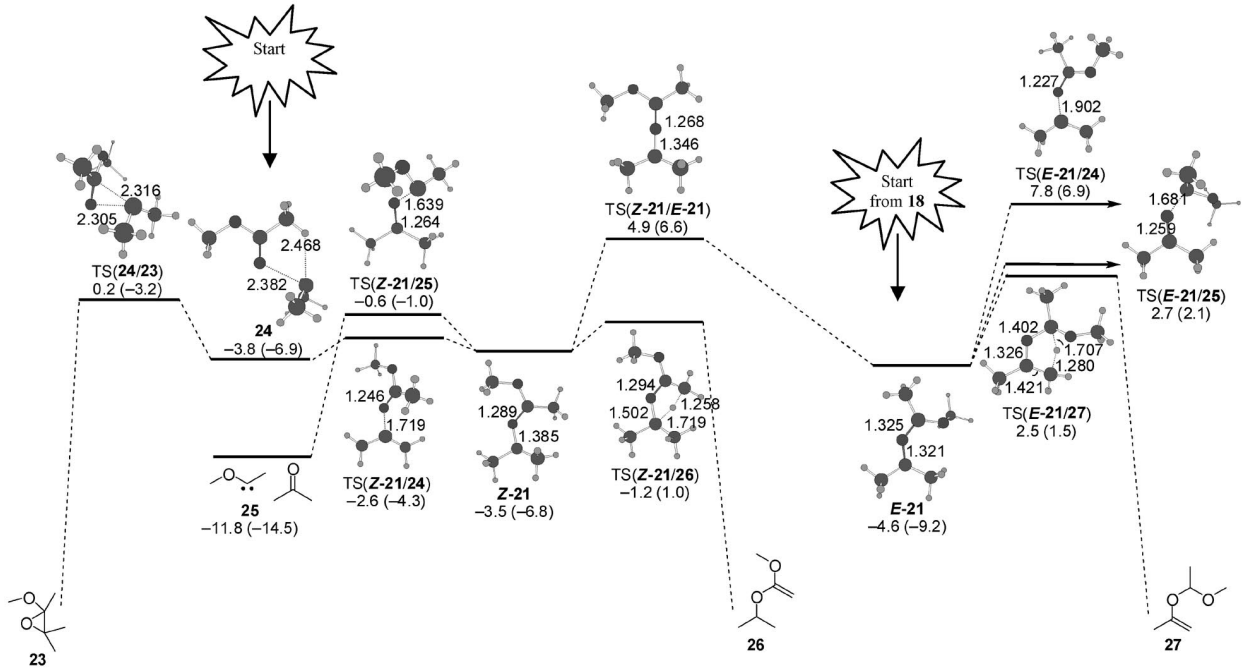


Figure 5. Main stationary points on the potential energy surface of ylides ***E*-21** and ***Z*-21**. Energies in kcal/mol as given by B3LYP/6-31G(d); values in parentheses represent CCSD(T)/6-31G(d)//B3LYP/6-31G(d) computations. Propan-2-ylidene and methyl acetate were taken as reference (0 kcal/mol).

no readily available precursors exist. The exclusive generation of ylide ***E*-21** from the oxadiazoline **18** is also reflected in the gas phase chemistry of **18** where for steric reasons **27** is the sole 1,4 H-shift product.[28] In contrast, in a carbon tetrachloride solution one half of ylide **21** decomposes to propan-2-ylidene and the rest generates 1-methoxyethylidene.[28] There are two reasons for the different behavior in the gas phase and in solution: firstly, thermal fragmentation of carbonyl ylides occurs from the more zwitterionic 0°, 90° conformation and their transition states are more polar than the H-shift and should therefore be disfavored in the gas phase and favored in solution. Secondly, the H-shift is even more favored at higher temperatures (69% at 380 °C).[28,29] This observation suggests that dynamic effects[30] may play a role in the formation of vinyl ether **27**.

Mechanism of the Carbene Insertion into the O–H Bond

Finally, we have also analyzed the reaction mechanism of the formal carbene insertion into O–H bonds. For this, methanol and 7-norbornenylidene were taken as model compounds. We investigated the approach between the two reactants and found that a moderately strong hydrogen bond (structure **30**, –11.2 kcal/mol) is predicted between the lone pair (LP) of the divalent carbon C(7) and the O–H bond of methanol (Figure 6). This value is consistent with the distance calculated between C(7) and the hydroxylic hydrogen atom (1.932 Å). Of course, other complexes with different arrangements can be found but they are all higher in energy. Our attempts to find an ylide-like structure,[10,31] lead only to the weakly associated structure **28** in which four donor-acceptor interactions result in an energy gain of 3.5 kcal/mol. The relevant interaction energies from the carbene to methanol resulting from a NBO analysis are: LP(1) C(7)→BD*(1) C(A)–H: 2.47 kcal/mol and LP*(2) C(7)→BD*(1) C(A)–H: 1.27 kcal/mol and from methanol to the carbene: BD(1) C(A)–H→LP*(2) C(7): 0.83 kcal/mol and BD(1) C(A)–H→BD*(1) C(5)–H: 0.35 kcal/mol.[32] We also found structure **29** which really presents the characteristics of a weak ylide, with a short C–O distance of 1.712 Å but which is high in energy (+4.8 kcal/mol) because it is based on a poorly stabilized norbornenylidene conformer.

Next, we examined the transition states **32**–**35** leading to formation of methyl ether (Figure 7). For an efficient reaction, the hydroxy group should be well oriented with the hydrogen atom pointing toward the LP of the divalent carbon and the oxygen atom directed toward the LP*. We found that the concerted insertion into methanol is indeed predicted to be specific, since the *syn*-TS **33** is 6.0 kcal/mol higher in energy than the *anti*-TS **32**. This is due to the fact that the reaction proceeds via an early transition state, a fact that is reflected in the relatively short C(2)–C(7) distance (2.141 Å). The first part of the reaction being nucleophilic, the approach of the hydrogen is accompanied by the formation of a partial positive charge on the norbornenylidene unit which is efficiently stabilized by the double bond. The energy barrier for this *anti* approach is calculated to be 0.5 kcal/mol. This value is increased to 11.7 kcal/mol after consideration of the hydrogen-bridged structure **30**. For the reaction of an alkyl carbene, this is a really high value and therefore, it is unlikely that the reaction occurs through this concerted pathway. In fact, the insertion is better described with two methanol molecules than with one, as is depicted in **35**.

Norbornenylidene is predicted to be significantly better stabilized by a methanol dimer (structure **31**, –14.9 kcal/mol). From this structure, two transition states leading to an *anti* methyl ether can be found. The first one, structure **34**, corresponds to a concerted insertion of the carbene into one molecule of methanol during which the breaking of the O–H bond is assisted by a hydrogen bond pointing from the second methanol molecule. With 7.2 kcal/mol (–7.7 kcal/mol if norbornenylidene and a methanol dimer are taken as reference), the energy barrier already is substantially reduced. However, reaction through the OH group catalysis mechanism[9] is even more favored (structure **35**, energy barrier: +3.3 kcal/mol from complex **31** and –11.6 kcal/mol from the reactants). Here, the hydrogen atom and the methoxy group stem from two different methanol molecules. This mechanism is especially efficient because it allows a good overlap of the orbitals and optimal interactions between the carbene and the two alcohol molecules. Here, the hydrogen transfer energy wise is undemanding because the donor, the acceptor, and the hydrogen atom are all aligned. Concomitantly, the oxygen atom of the

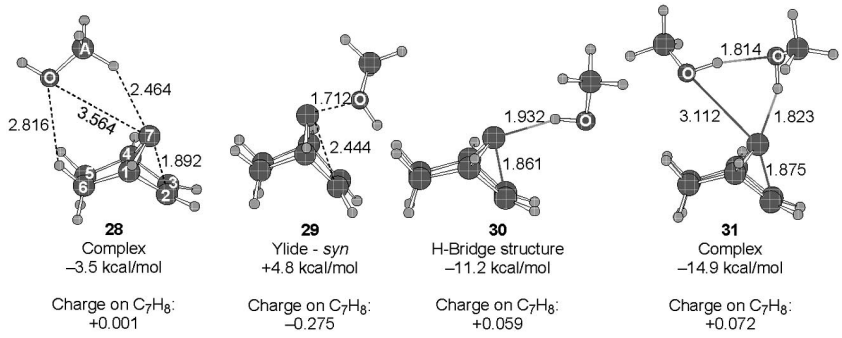


Figure 6. Geometries and relative energies of the most relevant complexes between norbornen-7-ylidene and methanol. The resulting charge on the carbene unit C_7H_8 as given by NPA analyses.

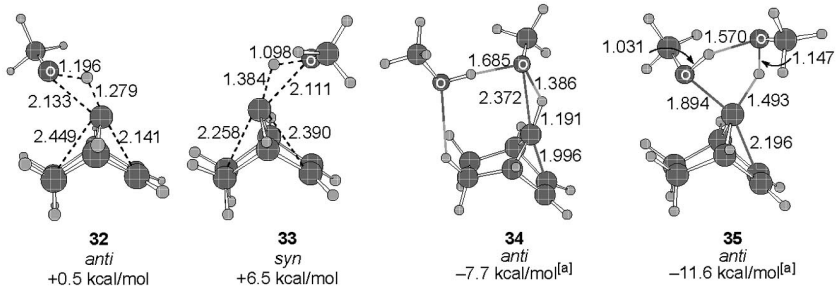


Figure 7. Geometries and relative energies of the most relevant transition states for the insertion of norbornen-7-ylidene into methanol. [a] Energy based on norbornenylidene and the methanol dimer (–5.5 kcal/mol).

second methanol molecule is directed from the beginning of the reaction toward the empty *p*-orbital of the carbene. In our opinion this mechanism describes best the reaction between a carbene and an O–H bond. Indeed, as expected, the stepwise mechanism in which the carbene is protonated and an ion pair is formed cannot be found computationally. This is due to the high nucleophilicity of the methoxide ion; in this compound, the negative charge remains mostly located on the oxygen atom and this species is still very reactive as long as it is not solvated.

Conclusions

In conclusion, it has been shown in this study that carbonyl ylides resulting from the addition of alkyl carbenes to esters are extremely unstable species. Their decomposition occurs usually before rotation around a single bond takes place and therefore, each conformer has to be investigated on its own. This means that depending on the generation method, different conformers with different stabilities are produced, leading to different product distributions. For example, decomposition of oxadiazoline **6** leads to "long-lived" ylide ***E*-21**, whereas the other conformer ***Z*-21** disaggregates rapidly and is an interesting intermediate for performing transcarbenations. Overall, noncovalent interactions (mainly a hydrogen bond from the acidic C–H bond and the carbon lone pair) between an alkyl carbene and an ester lead to a complex which has a similar stability than the carbonyl ylide. Ylide **16**, resulting from the addition of a stabilized-nucleophilic carbene to methyl acetate is even less stable. Nevertheless, we were able to trap *syn* ylide **16a** with methanol, resulting in the isolation of *syn* alcohol **9**. This represents an experimental evidence for the thermal generation of an ylide from a methoxylated oxadiazoline. Oxadiazoline **1** is shown to be a very convenient carbene precursor due to the simplicity of its synthesis and the clean thermal generation of alkyl carbene **4** without prior formation of a reactive diazo species. Every thermolysis led exclusively to the *anti* ether confirming the active participation of the double bond in the stabilization of the intermediates and the transition states. In the same way, the experimental results show that ether formation from oxadiazoline **1** proceeds at least partly through the intermediacy of a carbenium ion even under apolar conditions. From calculations of this reaction in the gas phase the insertion is best described by the OH group catalysis mechanism because the negative charge in the alkoxylate is not delocalized and therefore, no contact ion pair can be computed. This mechanism also nicely explains why the kinetics of the reaction between alcohol and carbenes is strongly dependant on the concentration of the alcohol. From a synthetic point of view, the synthesis of the oxadiazoline followed by photolysis is a very convenient method to transform norbornenone derivatives to the corresponding *anti* ether.

Computational Methods

The Gaussian 03 program[33] was used for density functional theory calculations, employing Becke's[34] three-parameter hybrid method, and the exchange functional of Lee, Yang and Parr (B3LYP).[35] Geometries were optimized at the B3LYP/6-31G(d) level of theory. The stationary points were characterized by vibrational analysis. The values discussed in the text represent enthalpies at 298 K (H_{298}). Unless otherwise stated, all values in the text refer to B3LYP/6-31G(d) calculations. Quantification of donor/acceptor interactions has been made by second-order perturbation analysis as incorporated in the Natural Bond Orbital (NBO) method.[36] The results concerning the reactions of ylide **21** were confirmed using single point calculations at the CCSD(T)/6-31G(d) level of theory. This method represents a coupled cluster calculation using single and double substitutions augmented by a non-iterative treatment of triple excitations.[37]

Experimental Section

General: Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. The chemical shifts at δ = 7.26 ppm and 77.0 ppm of $CHCl_3$ were used as internal standards for ^{1}H and ^{13}C spectra. Conventional 2D COSY, NOESY, HMBC, and HMQC spectra were used to derive proton and carbon assignments.

The synthesis of oxadiazoline **1** has already been described.[5]

***endo*,*syn*-Tricyclo[6.2.1.0^{2,7}]undec-9-en-11-ol (9):** Oxadiazoline **1a** (302 mg, 1.22 mmol) was thermolyzed overnight in 4 mL of methanol in a pressure tube at 155 °C. After removal of the solvent, *syn* alcohol **9** was separated from the main product, *anti* methyl ether **10me** by preparative TLC with hexane/2-propanol (39:1). Yield 40 mg (0.244 mmol, 20%); m.p. 81–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.14–6.12 (m, 2 H), 3.87 (d, J = 11.0 Hz, 1 H), 2.72 (q, J = 1.6 Hz, 2 H), 2.14 (d, J = 11.3 Hz, 1 H), 2.02–1.95 (m, 2

H), 1.58–1.51 (m, 2 H), 1.35–1.26 (m, 4 H), 0.90–0.77 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.7, 87.7, 53.2, 36.4, 22.1, 19.9 ppm. IR: $\tilde{\nu}$ = 3316, 3061, 2926, 1416, 1330, 1288, 1248, 1194, 1040, 986, 908, 884, 836, 772 cm^{-1}. MS (70 eV): *m*/*z* (%) = 164 (24) [M$^+$], 146 (79), 135 (100), 133 (79), 121 (43), 107 (50), 91 (96), 79 (41), 67 (18). HRMS (70 eV): calcd. for $C_{11}H_{16}O$ 164.1201, found 164.1198.

***anti*,*endo*-11-Benzoxytricyclo[6.2.1.0^{2,7}]undec-9-ene (10bn):** Oxadiazoline **1a** (200 mg, 0.81 mmol) was photolyzed overnight in 2 mL of dry ethyl acetate in the presence of benzyl alcohol (87.1 mg, 0.81 mmol). After removal of the solvent, the product was submitted to preparative TLC with hexane/CH_2Cl_2 (95:5). Yield 102 mg (0.402 mmol, 50%) oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36–7.31 (m, 4 H), 7.30–7.26 (m, 1 H), 6.01 (t, *J* = 2.2 Hz, 2 H), 4.45 (s, 2 H), 3.39 (t, *J* = 1.9 Hz, 1 H), 2.73–2.70 (m, 2 H), 2.24–2.17 (m, 2 H), 1.63–1.58 (m, 2 H), 1.45–1.36 (m, 4 H), 0.99–0.90 (m, 2 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 138.7, 133.8, 128.3, 127.5, 127.4, 89.8, 70.4, 48.6, 36.0, 22.7, 20.4 ppm. MS (70 eV): *m*/*z* (%) = 254 (1) [M$^+$], 225 (9), 162 (2), 145 (4), 133 (13), 91 (100), 77 (15), 65 (30). HRMS (70 eV): calcd. for $C_{18}H_{22}O$ 254.1671, found 254.1667.

***anti*,*endo*-Tricyclo[6.2.1.0^{2,7}]undec-9-en-11-ol (10h):** In a pressure tube, oxadiazoline **1b** (205 mg, 0.825 mmol) was thermolyzed overnight at 165 °C in 6 mL of dioxane/water (5:1). After removal of the solvent, 127 mg (0.774 mmol, 94%) of alcohol **10h** were obtained. Crystals suitable for structure analysis were obtained by recrystallization from hexane;[38] m.p. 85–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.98 (t, *J* = 2.2 Hz, 2 H), 3.62 (t, *J* = 1.8 Hz, 1 H), 2.54 (q, *J* = 1.8 Hz, 2 H), 2.20–2.09 (m, 2 H), 1.97 (br. s, 1 H), 1.66–1.53 (m, 2 H), 1.45–1.30 (m, 4 H), 1.02–0.87 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.0, 83.2, 50.7, 35.7, 22.5, 20.4 ppm. IR: $\tilde{\nu}$ = 3265, 3060, 2926, 2861, 1458, 1321, 1248 cm^{-1}. MS (70 eV): *m*/*z* (%) = 164 (23) [M$^+$], 146 (33), 135 (87), 133 (60), 121 (26), 107 (40), 91 (100), 82 (73), 67 (33). HRMS (70 eV): calcd. for $C_{11}H_{16}O$ 164.1201, found 164.1203.

***anti*,*endo*-11-Methoxytricyclo[6.2.1.0^{2,7}]undec-9-ene (10me):** In a pressure tube, oxadiazoline **1b** (200 mg, 0.81 mmol) was thermolyzed for 24 h at 165 °C in 5 mL of methanol. After removal of the solvent, 138 mg (0.778 mmol, 96%) of oily **10me** were obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.00 (t, *J* = 2.2 Hz, 2 H), 3.26 (s, 3 H), 3.18 (t, *J* = 1.8 Hz, 1 H), 2.68 (sextet, *J* = 1.8 Hz, 2 H), 2.12–2.03 (m, 2 H), 1.62–1.56 (m, 2 H), 1.44–1.32 (m, 4 H), 0.98–0.86 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.8, 91.6, 56.0, 48.2, 35.9, 22.6, 20.4 ppm. IR: $\tilde{\nu}$ = 3071, 2934, 2856, 1427, 1302, 1112 cm^{-1}. MS (70 eV): *m*/*z* (%) = 178 (7) [M$^+$], 146 (75), 131 (30), 121 (44), 117 (18), 105 (27), 96 (18), 91 (100), 77 (19), 67 (13). HRMS (70 eV): calcd. for $C_{12}H_{18}O$ 178.1358, found 178.1350.

***anti*,*endo*-11-Trityloxytricyclo[6.2.1.0^{2,7}]undec-9-ene (10tr):** Oxadiazoline **1a** (200 mg, 0.81 mmol) was photolyzed overnight in 2 mL of dry ethyl acetate in the presence of trityl alcohol (209.7 mg, 0.81 mmol). After removal of the solvent, the product was submitted to column chromatography with hexane/CH_2Cl_2 (95:5). The product could also be recrystallized from ethanol. Yield 199 mg (0.49 mmol, 60%); m.p. 156–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.43 (m, 6 H), 7.30–7.18 (m, 9 H), 5.77 (t, *J* = 2.2 Hz, 2 H), 3.35 (t, *J* = 1.6 Hz, 1 H), 2.31–2.23 (m, 2 H), 1.83–1.79 (m, 2 H), 1.59–1.53 (m, 2 H), 1.45–1.35 (m, 2 H), 1.30 (br. d, *J* = 13.5 Hz, 2 H), 0.88–0.75 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.1, 133.5, 128.7, 127.7, 126.8, 86.5, 85.6, 49.7, 36.5, 22.7, 20.5 ppm. IR: $\tilde{\nu}$ = 3057, 2933, 2862, 1489, 1448 cm^{-1}. MS (70 eV): *m*/*z* (%) = 406 (0.3) [M$^+$], 243 (100), 165 (51), 91 (28), 77 (18), 67 (18).

***rac*-(1R,2R,3S,4R,5R,6S,7S)-5-Methoxytetracyclo[5.4.0.0^{2,4}.0^{3,6}]undecane (11me):** ^{1}H NMR (400 MHz, $CDCl_3$, main peaks): δ = 3.87 (dd, *J* = 7.2, 3.8 Hz, 1 H), 3.20 (s, 3 H), 2.29–2.21 (m, 2 H), 1.95–1.90 (m, 1 H), 1.81–1.75 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, main peaks): δ = 72.3, 54.5, 44.1, 36.4, 24.9, 22.9, 22.3, 22.2, 21.7, 17.6 ppm.

***rac*-(1R,2R,3R,6S,7S)-3-Methoxytricyclo[5.4.0.0^{2,6}]undec-4-ene (12me):** Oxadiazoline **1** (300 mg, 1.21 mmol) was dissolved in 4 mL of methanol and photolyzed overnight. The solvent was rotary-evaporated. The crude product contained 48% of **10me** and 43% of **12me**. **12me** was obtained from repeated chromatography with hexane/Et_2O (90:10) as eluent. Yield 68 mg (32%, 0.382 mmol) oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.22 (ddd, *J* = 5.6, 2.4, 0.8 Hz, 1 H), 6.07–6.03 (m, 1 H), 4.34 (t, *J* = 2.5 Hz, 1 H), 3.48–3.41 (m, 1 H), 3.26 (s, 3 H), 2.85 (dd, *J* = 8.9, 6.3 Hz, 1 H), 2.65–2.49 (m, 2 H), 1.55–1.44 (m, 2 H), 1.43–1.21 (m, 5 H), 1.15–1.04 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.2, 132.9, 86.8, 55.2, 48.9, 42.5, 33.6, 32.7, 22.2, 21.8, 20.8, 20.7 ppm. IR: $\tilde{\nu}$ = 3046, 2930, 2864, 2815, 1461, 1449, 1371, 1190 cm^{-1}. MS (70 eV): *m*/*z* (%) = 178 (19) [M$^+$], 146 (20), 131 (11), 117 (15), 105 (11), 96 (100), 91 (27), 81 (34), 67 (15), 53 (22). HRMS (70 eV): calcd. for $C_{12}H_{18}O$ 178.1358, found 178.1354.

Supporting Information (see also the footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra for the new compounds, Cartesian coordinates and energies for all relevant stationary points.

Acknowledgments

Calculations were performed on the Schrödinger III cluster at the University of Vienna.

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[38] CCDC-693658 (for **10h**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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