Reactions of α,β-Enones with Diazo Compounds

Part 3[1])

On the Nature of the 1,5-Ring Closure of α,β-Enone Ylides

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Carbonyl ylides arising from ethyl acetodiazoacetate/dimethyl diazomalonate and α,β-enones with mainly s-*cis* conformations underwent disrotatory cyclization to produce dihydrofuran derivatives. This process proved to be sensitive to steric effects. The corresponding ylides arising from rather s-*trans* α,β-enals yielded dioxole derivatives. The mechanisms of the reactions are discussed.

Introduction. – Furan derivatives are among the most-significant heterocycles in natural products, and, consequently, a wide range of methods for their syntheses has been developed [2]. In relation to dihydrofuran synthesis, we previously reported the reactions of three β-monosubstituted (*E*)-enones (α- and β-ionone, and benzalacetone) with two diazobis(carbonyl) compounds (dimethyl diazomalonate (DMDM) and ethyl acetodiazoacetate (EADA)) in the presence of copper(II) acetylacetonate ([Cu(acac)$_2$]) [1]. Those enones definitely adopt s-*cis* conformations in their ground states. The results of that former work are summarized in *Table 1* and showed interesting selectivities concerning both product distribution (initial dihydrofuran formation *vs.* furofuran formation) and diastereoselectivity in dihydrofuran formation[2]). It was mostly the product distribution that led us to further studies on this subject.

The only previous reports directly related to our work came from *Spencer* and co-workers [3–5]. They showed that in the case of a few cyclic α-methoxymethylene ketones, in which the carbonyl and olefin moieties are fixed in a s-*cis* arrangement, reactions with ethyl diazoacetate (EDA) had given furancarboxylates in moderate yields *via* carbonyl ylides after MeOH elimination. The configuration at alkenyl C=C bonds was not mentioned in their reports. On the other hand, *Alt* and *Maas*, and *Huisgen* and *March* have shown that it is possible to trap carbonyl-ylide adducts intermolecularly from the reactions of unsaturated aldehydes with some α-diazo-α-(trimethylsilyl)acetates [6–8], although they did not observe 1,5-cyclization reactions of carbonyl ylides.

Our focus in the present work has been the nature of the ring closure of the carbonyl ylides. The formation of the dihydrofuran derivatives in the first-step reactions should be realized by way of a 1,5-cyclization process of the related carbonyl ylides. At this

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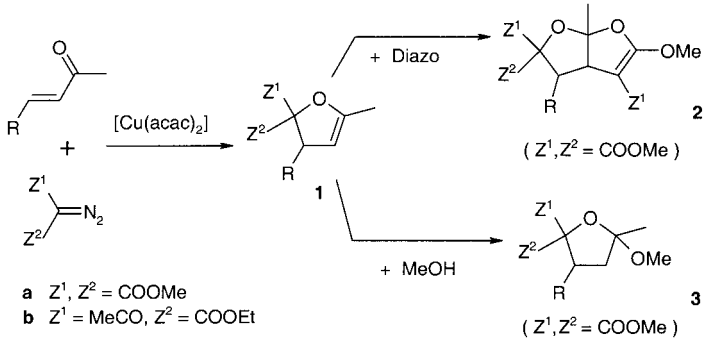
[1]) Part 2: [1].

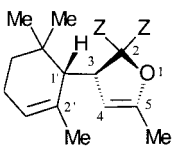
[2]) The initially formed dihydrofurans will be called 'first-step products' and the furofurans will be called 'second-step products' throughout this paper hereafter.

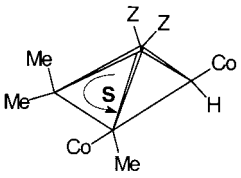
Table 1. *Reactions of Enones with DMDM and EADA* [1]



Entry	Enone	Diazo comp.	Products	Time [h][a])	Product distribution[b])
1	α-Ionone ($R+S$)	DMDM	**1a$_1$** (two diastereoisomers)[c]) **2a$_1$**	17	**1a$_1$′**[d])/**1a$_1$″**/**2a$_1$** 0.7 : 1.0 : 0.15
2	β-Ionone	DMDM	**1a$_2$** (1′*SR*,3*SR*); **2a$_2$**, **3a$_2$** (trace)	12	**1a$_2$**/**2a$_2$** 1.0 : 0.19
3	Benzal acetone	DMDM	**1a$_3$** (trace); **2a$_3$**; **3a$_3$** (trace)	5	
4	β-Ionone	EADA	**1b′** (1′*RS*)-*trans* **1b″** (1′*RS*)-*cis*	36	**1b′**/**1b″** 1.0 : 0.43

[a]) Time for complete consumption (> 99%) of the diazo compound determined by IR spectroscopy. [b]) Ratio of products determined by GC. [c]) **1a** formed as a mixture (*SR*)-(1′*RS*,3*SR*) (**1a$_1$′**)/(*RS*)-(1′*RS*,3*SR*) (**1a$_1$″**). [d]) The configuration and nomenclature of **1a$_1$** is given in detail as a pattern



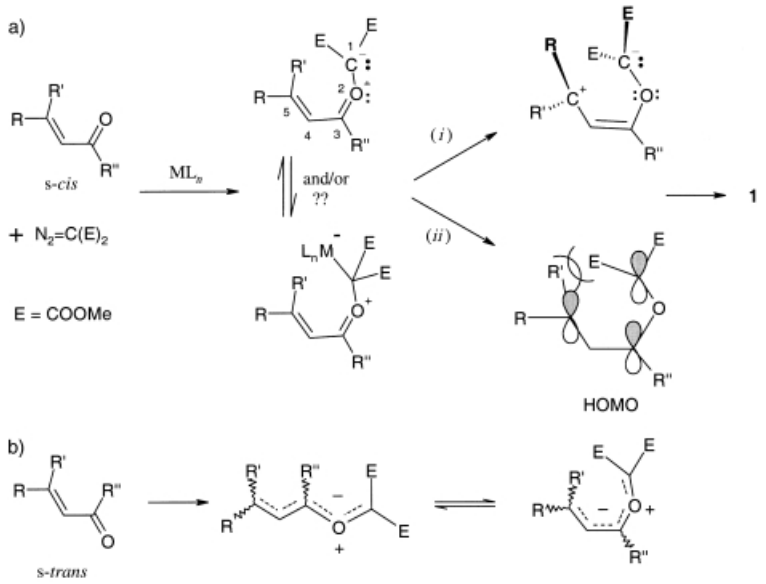


Highly restricted rotation around the C(1′)–C(3) bond at ambient temperature. Name: dimethyl (*S*)-(1′*R*, 3*S*)-2,3-dihydro-5-methyl-3-(2′,6′,6′-trimethylcyclohex-2-ene-1′-yl)furan.

point, one may think of two ways for the 1,5-ring-closure reactions of the formed carbonyl ylides: *i*) ionic coupling or *ii*) electrocyclic disrotatory ring closure (*Scheme 1*).

1,5-Electrocyclization of zwitterionic species is a well-recognized and established process in heterocyclic chemistry [9][10], and the reactions that the authors are interested in can well be rationalized by these mechanisms. On the other hand, if the reaction would proceed *via* 1,5-ionic coupling *i*), the electronic effects at C(5) (β-C-atom) would be predominant, and rotation about the C(4)–C(5) bond would be possible to some extent, which, in turn, would cause a decrease in the stereoselectivity

Scheme 1. *Two Ways for the 1,5-Ring-Closure Reactions of the Formed Carbonyl Ylides: i) Ionic Coupling, or ii) Disrotatory Electrocyclic Ring Closure*

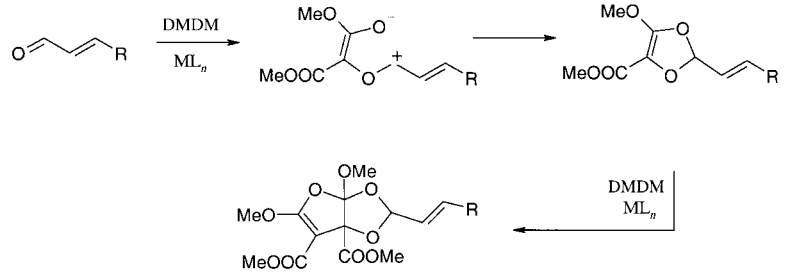


of the reaction. Although the present theories [11] introduced a large degree of predictability to clearly differentiate between allowed and forbidden processes in electrocyclic reactions (*e.g.*, *ii*), there can still exist stereoelectronic variants within an allowed transformation that have considerable differences in activation energy, the reasons for which are not always obvious [12]. In an ongoing investigation of 1,5-ring closure in s-*cis*/s-*trans* enones/enals, we reacted various starting compounds to gain information on substitutent and related effects.

Results and Discussion. – The main feature of an aromatic-like transition state must be securing a close proximity between the two termini. First of all, we aimed to view the absence of dihydrofuran-forming reactions of β-substituted (*E*)-enals that exist mainly in s-*trans* conformation [13].

For that purpose, we performed the reactions of two enals, crotonaldehyde (**4**) and cinnamaldehyde (**7**), as the first set (*Table 2*) of our experiments that was intended to probe the effects of the single-bond conformation between ene and carbonyl functions. The reactions of these two enals with DMDM under our standard procedure gave dioxole derivatives but no dihydrofuran compounds (*Scheme 2*). 'First-step' dioxoles were the minor, and the double adducts were the major products. So, the necessity of both termini being closest to each other (C(1) and C(5)) for an electrocyclic 1,5-ring closure reaction was verified. These data also pointed out the need for the presence of an aromatic-like transition state as illustrated in path *ii*. On the other hand, if the ionic path *i* for a s-*trans* starting compound like an enal were valid, and the electrocyclic way were invalid, the reaction should yield a dihydrofuran derivative following a possible

Scheme 2. *The Reaction of Crotonaldehyde and Cinnamaldehyde with DMDM* (R = Me, Ph)



rotation about the C(4)–C(3) bond (*Scheme 1*,*b*). The reaction of the enal ylide (which also should be a electrocyclic process) is illustrated in *Scheme 2*.

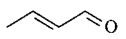
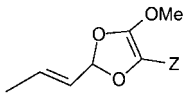
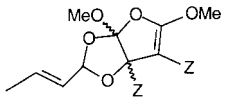
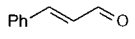
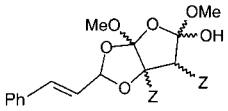
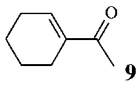
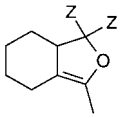
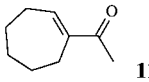
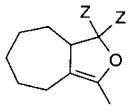
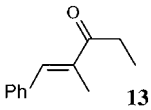
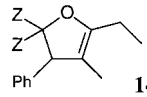
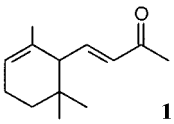
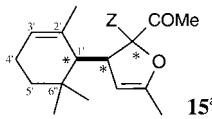
The analogous studies on the reactions of **4** with EADA and DMDM are present in the literature [8][14][15]. *Alonso* and *Chitty* [14] reported the reactions of **4** with EADA under [Cu(acac-F_6)$_2$] catalysis to give a dioxole as the major product. On the other hand, *Huisgen* and *March* [8][15] did not report any dioxole derivatives in their Cu^{II}-catalyzed reactions of DMDM with excess **4**. Instead, they claimed the occurence of dioxolane and oxirane derivatives. These different reaction routes with small differences in reaction conditions were somewhat surprising.

Next, we tried the second set of experiments to observe the stereoelectronic variants of the substituents at C(5) (β-C-atom) within this allowed process. For this purpose, we attempted at the reactions of 1-(cyclohex-1-enyl)ethanone (**9**), 1-(cyclohept-1-enyl)ethanone (**11**), 1-(2-methylcyclopent-1-enyl)ethanone, 4-methylpent-3-en-2-one, and 2-methyl-1-phenylpent-1-en-3-one (**13**), all of which adopt mainly s-*cis* conformations in their ground states (*Table 2*). 1-(2-Methylcyclopent-1-enyl)ethanone and 4-methylpent-3-en-2-one constituted another subset with an additional Me substituent at C(5) (β-C-atom). Except for these two enones, which did not give any dihydrofuran derivatives, the other three smoothly yielded the expected products. It was found that enones with a second substitutent at the β-C-atom might cause steric inhibition for the allowed 1,5-electrocyclic ring closure (see *Scheme 1*, *ii*). This must be the reason why 4-methylpent-3-en-2-one yielded a cyclopropane instead of any ylide-originated products previously reported by our group [16].

Another set of experiments that did not provide any furofuran derivatives (second-step products) was also notable. These cases are *Entry 4* in *Table 1* and *Entries 5* and *6* in *Table 2*. Related explanations might be derived either from electronic (*Entry 4* in *Table 1*, and *Entry 6* in *Table 2*) or steric (*Entry 5* in *Table 2*) effects of both enones and diazo compounds. While α- and β-ionones gave high yields of first-step reactions with remarkable follow-up of the second-step transformations in their reactions with DMDM (*Entries 1* and *2* in *Table 1*), similar follow-ups were not observed in the reactions of the same ionones with EADA (*Entry 4* in *Table 1*, and *Entry 6* in *Table 2*).

So, one can assume that the yield of the dihydrofuran product should theoretically increase in the range: diazomalonic ester (DMDM) < α-diazo-β-oxo ester (EADA)

Table 2. *Reactions of Enals/Enones with DMDM and EADA* (Z = COOMe)

Entry	Enal/Enone	Diazo compound	Time [h]	Product(s)
1	 **4**	DMDM	17	 **5**  **6** **5 / 6** 1.0 : 0.52
2	 **7**	DMDM	29	 **8**
3	 **9**	DMDM	5	 **10**
4	 **11**	DMDM	6	 **12**
5	 **13**	DMDM	11	 **14**
6	 **1**	EADA	23	 **15**[a])

[a]) Mixture of all possible isomers. Rotation about the bold bond highly restricted at ambient temperature.

with respect to the electrophilic character of the related carbenes to form an ylide structure. This preference of EADA, attachment to the carbonyl O-atom instead of reacting with the enol ether moiety, may be explained by a favored harder acid – harder base like relationship. Furthermore, probably higher stabilization of the aromatic-like transition structure of the vinylcarbonyl ylide by additional conjugation may be another contribution.

To test the steric effects on the formation of the furofuran 'second-step' products, we reacted the ketone **13** with DMDM (*Entry 5* in *Table 2*). As expected, the increased bulk around the newly formed double bond seemed to have prevented its further reaction with DMDM to yield a furofuran.

At this point, we might also make another assumption by invoking similar electronic and steric arguments represented above for the reaction of benzalacetone with DMDM in *Entry 3* (*Table 1*). In this reaction, we obtained the second-step product predominantly within the shortest reaction time (5 h). For this specific enone pattern, with a Ph group at the β-C-atom, one could claim that the reaction rates of both steps were rather fast, the second step being even faster. The presence of this Ph substituent at the β-C-atom that can interact by conjugation with one terminus of the aromatic-like transition state probably caused an additional stabilization in the first-step reaction. Then, the lack of hindrances in the newly formed dihydrofuran to react with another carbene allowed the formation of the second-step product mainly and rapidly. The reaction of the other enone with a Ph group in β-position, namely compound **13** mentioned above, was somewhat slower, probably due to the inhibition of the second-step.

Like 4-methylpent-3-en-2-one, methyl vinyl ketone, the smallest member of enones, preferred self-condensation reactions and did not give any dihydrofuran or dioxole derivatives. The only identifiable carbene-based products in the complex mixtures were carbene dimers.

Probable Oxirane Intermediates? Recently, *Hamaguchi et al.* [17] presented new examples of vinylcarbonyl ylide cyclization reactions. In that work are reported the formations of oxiranes and dihydrofurans, as well as the transformations of the oxiranes to dihydrofurans. Our studies did not reveal any oxirane products that may be due to: *i*) favored[3]) [17] cyclization to dihydrofurans, and/or *ii*) facile thermal conversion of probably formed oxiranes to dihydrofurans. The latter possibility cannot be tested because of the high temperatures required by the Cu-catalyzed reaction. The proposed preference[3]) of cyclization to a five-membered ring seems valid enough to us for now. Furthermore, *Doyle et al.* [19] reported that 3-aryl-2-(2-phenylethenyl)oxirane 2-carboxylates would not convert to the relevant furans, unless the aryl group was replaced by another 2-phenylethenyl group.

Conclusions. – It has been shown that pericyclic reactions of properly chosen s-*cis*-enones proceed under mild conditions clearly and predominantly. Substituents from both enones and diazocarbonyl compounds that can stabilize the concerted transition state of the initially formed enone ylide by conjugation have a beneficial influence on the reaction rate. On the other hand, while steric inhibitions at the terminus (β-C-atom) retard the reaction, steric crowdings at the remaining part (α-C-atom) of the enone provides a beneficial effect of preventing the possible follow-up reactions. Reactions of α-diazo-β,β'-diones and α,β-disubstituted s-*cis* enones (with R = aryl, alkenyl, and with R′,R″ = rotable crowded substituents), which may cleanly yield dihydrofuran derivatives, are under study.

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[3]) See the reference of *Hamaguchi et al.* to a study by *Crawford et al.* [18].

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Experimental Part

General: DMDM and EADA were prepared according to literature procedures. IR Spectra: *JASCO FT-IR 5300* apparatus. ^{1}H-NMR: 250-MHz *Bruker* apparatus, TMS as internal standard, δ in ppm, J in Hz, at 25°. ^{13}C-NMR: at 60 MHz. GC/MS: *Hewlett-Packard* instrument with *HP-1* cap. column (24 m, packed with cross-linked (phenylmethyl)siloxane), EI-MS detector; column conditions: 150° (7′ isothermal), heat to 280° with 5°/min.; 0.54 bar He. MS: *VG-Zabspec* double-focusing spectrometer; EI-MS at 70 eV, CI-MS in isobutane.

General Procedure for the Reactions of Enones with DMDM. A soln. of 1 equiv. of DMDM in benzene (4 mmol, 1 ml) was added very slowly to a refluxing benzene soln. of 1.5 equiv. of the substrate (2 mmol, 1 ml) and 0.007 equiv. of $[Cu(acac)_2]$ under N_2. Consumption of DMDM was monitored by IR. After the complete disappearance of the band at 2130 cm^{-1}, the mixture was filtered (gravity), and the soln. was passed rapidly through a short column of neutral aluminum oxide to remove the highly colored impurities and the catalyst.

Methyl 5-Methoxy-2-(prop-1-enyl)[1,3]dioxole-4-carboxylate (**5**). The minor product (14%) in the GS/MS analysis; not isolated in pure form. GC and GC/MS data (from crude fractions) are provided only: CI-MS: 218 (9, $[M+18]^+$), 201 (100, $[M+1]^+$), 185 (53), 183 (95), 153 (54), 141 (64), 133 (23), 113 (34), 101 (19), 88 (59), 72 (90), 70 (94).

*Dimethyl 3a,6a-Dihydro-3a,5-dimethoxy-2-(prop-1-enyl)furo[2,3-*d*][1,3]dioxole-6,6a-dicarboxylate* (**6**). This compound was the main product (86%) in the GS/MS analysis. The oily compound was purified by column chromatography (CC) (neutral aluminum oxide; CCl_4/AcOEt 7:10). Yield 43%. ^{1}H-NMR ($CDCl_3$): 6.10 (*dd* with some distortion, J = 6.6, 15.4, MeC*H*); 5.93 (*d*, J = 7.5, H–C(2)); 5.60 (*ddq*, J = 15.2, 7.5, 1.3, MeCH=C*H*); 3.87–3.77 (4 MeO); 1.76 (*dd*, J = 6.5, 1.2, M*e*CH). ^{13}C-NMR($CDCl_3$): 166.3 (CO_2Me), 136.7 (Me*C*H); 125.5 (MeCH=*C*H); 108.7 (CH–O); 17.6 (*Me*CH); signals for four MeO groups appear between 53.1 and 55.6, partially overlapped, which are not assigned individually. CI-MS: 331 (16, $[M+1]^+$), 287 (12), 263 (38), 231 (10), 201 (7), 185 (3), 173 (5), 145 (4), 133 (7), 113 (3), 86 (12), 72 (30). Anal. calc. for $C_{14}H_{20}O_{10}$ (348.3): C 48.27, H 5.78; found: C 48.57, H 5.96.

Methyl 5-Methoxy-2-(2-phenylethenyl)[1,3]dioxole-4-carboxylate. This compound was the minor product (21%) in the GS/MS analysis; not isolated in pure form. GC and GC/MS data (from crude fractions) are provided only for reference: GC/MS: t_R 18.07 min. EI-MS: 246 (31), 231 (4), 214 (76), 186 (13), 155 (50), 147 (7), 128 (62), 115 (57), 102 (16), 77 (21), 59 (30), 44 (100), 32 (46).

*Dimethyl 3a,6a-Dihydro-5-hydroxy-3a,5-dimethoxy-2-(2-phenylethenyl)furo[2,3-*d*][1,3]dioxole-6,6a-dicarboxylate* (**8**). This compound was the main product (74%) in the GS/MS analysis. The purification of the oily compound was attempted by CC (neutral aluminium oxide; CCl_4/AcOEt 20:1), but the resulting product was still impure. On the other hand, its structure could be identified by ^{1}H-NMR and MS: Yield *ca.* 38%. CI-MS: 392 (71, M^+), 391 (93, $[M-1]^+$), 377 (15 $[M-15]^+$), 297 (15), 279 (51), 263 (100), 247 (71), 215 (21), 203 (31), 175 (10), 149 (57), 133 (74). ^{1}H-NMR ($CDCl_3$): 7.75–7.20 (*m*, Ph); 6.72 (*d*, J = 16.0, PhC*H*); 6.23 (*dd*, J = 16.0, 7.0, PhCH=C*H*); 5.0 (*d*, J = 7.0, CH=CHC*H*); 3.87–3.78 (4 MeO).

*Dimethyl 5,6,7,7a-Tetrahydro-3-methyl-4*H*-isobenzofuran-1,1-dicarboxylate* (**10**). This compound was the main product (72%) in the GS/MS analysis. The starting enone was removed under reduced pressure. The residue was product **10**, which could be further purified by prep. TLC. Yield 47%. GC/MS: t_R 13.62 min. ^{1}H-NMR ($CDCl_3$): 3.79 (*s*, COOMe); 3.78 (*s*, COOMe); 3.49 (*m*, H–(7a)); 2.30–2.10 (*m*, CH_2(4)); 1.79 (*s*, Me); 2.00–0.80 (other H-atoms). ^{13}C-NMR ($CDCl_3$): 168.7, 167.9 (2 *C*OOMe); 142.5 (MeC); 108.8 (C(4)); 89.0 (C(1)); 53.4, 52.4 (2 MeO); 49.6 (C(7a)); 29.7 (C(5)); 26.1, 25.2, 23.7 (other C-atoms); 10.9 (Me). EI-MS: 254 (2, M^+), 225 (14), 201 (21), 195 (85), 185 (100), 162 (75), 142 (16), 125 (81), 105 (24), 95 (40), 91 (31), 79 (37), 59 (17). Anal. calc. for $C_{13}H_{18}O_5$ (254.3): C 61.40, H 7.13; found: C 61.22, H 7.15.

*Trimethyl 6,7,8,9-Tetrahydro-2-methoxy-3a-methyl-5a*H*-3,4-dioxacyclopenta[*c*]indene-1,5,5-tricarboxylate.* This compound was the minor product (28%) in the GS/MS analysis; not isolated in pure form. GC and GC/MS data (from crude fractions) are provided only. GC/MS: t_R 23.24 min. EI-MS: 384 (15, M^+), 341 (17), 331 (19), 320 (21), 299 (30), 279 (15), 253 (85), 221 (95), 193 (100), 189 (98), 161 (44), 147 (59), 131 (33), 123 (33), 105 (70), 91 (71), 75 (88), 59 (18).

*Dimethyl 4,5,6,7,8,8a-Hexahydro-3-methyl-cyclohepta[*c*]furan-1,1-dicarboxylate* (**12**). This compound was the main product (65%) in the GS/MS analysis. The oily compound was purified by CC (neutral aluminum

oxide; hexane/AcOEt 10:1). Yield 32%. GC/MS: t_R 14.50 min. ^{1}H-NMR ($CDCl_3$): 3.84 (*s*, COOMe); 3.81 (*s*, COOMe); 3.60 (*m*, H–C(8a)); 1.25 (*s*, Me); 1.80–1.50 (other H-atoms). ^{13}C-NMR ($CDCl_3$): 169.4 (*C*OOMe); 145.0 (C(3)); 100.1 (C(3a)); 87.0 (C(1)); 55.5, 54.2 (MeO); 48.2 (C(8a)); 29.8 (C(4)), 29.7, 29.0, 25.1 (other C-atoms); 14.3 (Me). EI-MS: 269 (4, $[M+1]^+$), 241 (100), 223 (19), 209 (47), 181 (9), 162 (25), 149 (15), 139 (4), 121 (8), 93 (7), 79 (9), 59 (11). Anal. calc. for $C_{14}H_{20}O_5$ (268.3): C 62.67, H 7.51; found: C 62.95, H 7.27.

Trimethyl 5a,6,7,8,9,10-hexahydro-2-methoxy-3a-methyl-3,4-dioxacyclopenta[c]azulene-1,5,5-tricarboxylate. This compound was the minor product (35%) in the GS/MS analysis; not isolated in pure form. GC and GC-MS data (from crude fractions) are provided only. GC/MS: t_R 16.57 min. EI-MS: 398 (4, M^+), 268 (60), 224 (6), 208 (74), 181 (100), 148 (50), 121 (18), 93 (52), 79 (21), 59 (17).

The Reaction of 1-(2-Methylcyclopent-1-enyl)ethanone with DMDM. The only isolated product was dimethyl 2,3-bis(methoxycarbonyl)succinate.

The Reactions of 4-Methylpent-3-en-2-one and Methyl Vinyl Ketone with DMDM and EADA. The reactions gave oligomers, and likely carbene-originated products could not be identified. The crude reaction mixtures were extracted with hot hexane to discard polymeric material, but it was unsuccessful. The only isolated products were saturated and unsaturated dimerization products of DMDM and EADA.

Dimethyl 5-Ethyl-2,3-dihydro-4-methyl-3-phenyl-furan-2,2-dicarboxylate (**14**). This compound was the main product (92%) in the GS/MS analysis. The oily compound was purified by prep. TLC (silica gel; hexane/AcOEt/$CHCl_3$ 4:1:1; extraction of zone around R_f *ca.* 0.6). Yield 35%. GC/MS: t_R 15.04 min. ^{1}H-NMR ($CDCl_3$): 7.35–7.14 (*m*, 5 arom. H); 4.71 (br. *s*, H–C(3)); 3.52 (*s*, COOMe); 3.16 (*s*, COOMe); 2.30 (*m*, CH_2); 1.45 (*s*, Me); 1.17 (*t*, $J=7.5$, *Me*CH_2). ^{13}C-NMR ($CDCl_3$): 169.04, 166.78 (2 COOMe); 152.69 (C(5)); 137.23 (C(1) of Ph); 129.13, 128.12, 127.52 (arom. C-atoms); 105.07 (C(4)); 90.80 (C(2)); 59.06 (C(3)); 53.23, 51.98 (2 MeO); 19.02 (CH_2); 11.78 (*Me*CH_2); 9.78 (Me). EI-MS: 304 (2, M^+), 272 (12), 244 (100), 229 (65), 213 (40), 171 (16), 128 (28), 115 (19), 91 (7), 77 (8), 59 (21). Anal. calc. for $C_{17}H_{20}O_5$ (304.3): C 67.09, H 6.62; found: C 67.54, H 6.60.

Methyl 2-Acetyl-2,3-dihydro-5-methyl-3-(2,6,6-trimethylcyclohex-2-enyl)-furan-2-carboxylate (**15**). Not isolated in pure form; GC and GC/MS data (from crude fractions) are provided only. GC/MS showed 8 different peaks all with same molecular weight and similar fragmentation pattern. This may be attributed to the presence of 8 possible diastereoisomers (3 apparent stereogenic centers and one for the rotational barrier). GC/MS: t_R 14.09 min: EI-MS: 320 (2, M^+), 253 (0.5), 193 (14), 183 (57), 165 (21), 125 (78), 124 (74), 109 (24), 105 (7), 91 (11), 56 (21), 43 (100). GC/MS: t_R 15.21 min. EI-MS: 320 (2, M^+), 283 (2), 254 (6), 193 (8), 183 (7), 165 (6), 125 (77), 109 (60), 105 (15), 91 (13), 44 (100), 43 (96). GC/MS: t_R 16.09 min. EI-MS: 320 (3, M^+), 278 (2), 262 (4), 190 (25), 121 (19), 105 (13), 93 (31), 91 (51), 44 (100), 43 (72). GC/MS: t_R 16.30 min. EI-MS: 320 (3, M^+), 276 (3), 175 (7), 155 (93), 127 (38), 109 (38), 91 (17), 81 (10), 44 (100), 43 (64). GC/MS: t_R 17.03 min. EI-MS: 320 (2, M^+), 264 (4), 221 (26), 165 (20), 149 (16), 125 (7), 121 (26), 107 (17), 93 (49), 91 (41), 77 (26), 44 (100), 43 (69). GC/MS: t_R 17.30 min. EI-MS: 320 (2, M^+), 256 (18), 155 (100), 127 (45), 125 (23), 109 (29), 107 (58), 105 (11), 91 (28), 44 (41). GC/MS: t_R 17.52 min. EI-MS: 320 (2, M^+), 282 (2), 278 (11), 259 (5), 247 (3), 155 (18), 125 (59), 111 (17), 109 (26), 107 (36), 91 (20), 44 (100). GC/MS: t_R 19.49 min. EI-MS: 320 (2, M^+), 295 (1), 293 (2), 254 (79), 239 (30), 197 (12), 183 (92), 153 (19), 128 (37), 91 (17), 44 (100). ^{1}H-NMR ($CDCl_3$): 6.40–5.80 (H–C(3′)); 4.50–4.10 (MeC*H*$_2$, H–C(3), H–C(4)); 2.29, 2.27, 2.18 (COOMe); 1.88, 1.77, 1.54 (CH_2(4′), Me(2′), Me–C(5), H–C(1′)); 1.26 (CH_2(5′)); 1.06, 0.90, 0.83 (*Me*CH_2, 2 Me(6′)).

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