Reactions of (1*E*)-Buta-1,3-dien-1-yl Acetate with Diazocarbonyl Compounds

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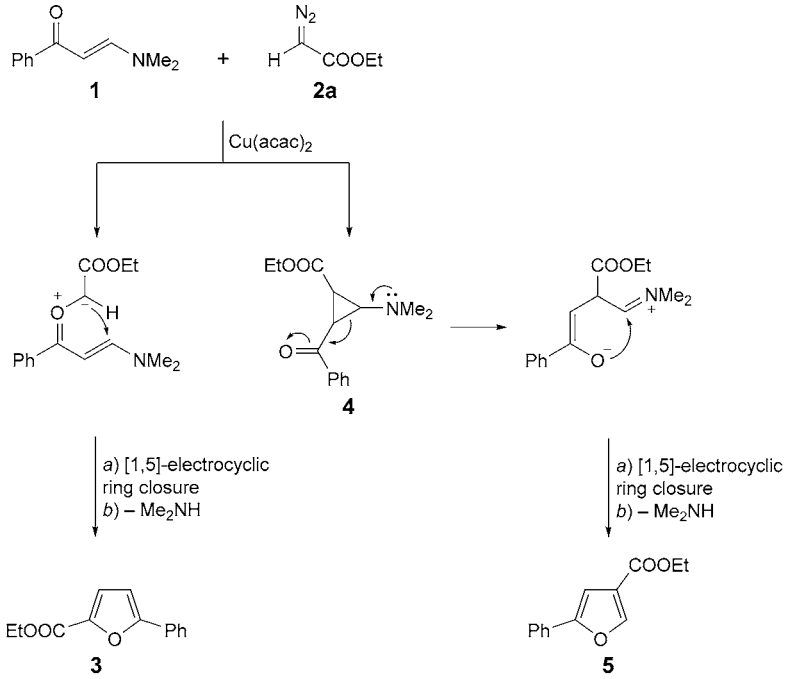
Carbene transfer to appropriate substrates is a highly versatile tool for the construction of carbon frameworks with increased functional and structural complexity. In this study, some novel cyclopropane derivatives were synthesized *via* carbenoid reactions and their further reactivities were investigated. (1*E*)-Buta-1,3-dien-1-yl acetate was reacted with four different diazocarbonyl compounds, ethyl diazoacetate, dimethyl diazomalonate, 1-diazo-1-phenylpropan-2-one, and methyl (3*E*)-2-diazo-4-phenylbut-3-enoate, in the presence of two catalysts. All synthesized substituted cyclopropanes were obtained chemoselectively with respect to less-hindered C=C bonds. Under the applied conditions, while cyclopropanes **7a** and **7d** underwent further reactions, cyclopropanes **7b** and **7c** were stable enough. Cyclopropanes **7a** and an additional equivalent of ethyl diazoacetate yielded polyfunctionalized cyclohexenes. Cyclopropanes from methyl (3*E*)-2-diazo-4-phenylbut-3-enoate yielded polyfunctionalyzed cycloheptadiene isomers by *Cope* rearrangement.

Introduction. – Cyclopropanes, donor-acceptor (DA) cyclopropanes, and their ring opening/addition/cyclization/expansion derivatives [1–4], that can be easily obtained due to the reactivities of some cyclopropyl ring bonds, are valuable building blocks for synthetic organic chemistry. Cyclopropanes are frequently synthesized by reaction of simple alkenes with chosen carbenes/metallo-carbenoids derived from corresponding diazo compounds. When the alkene contains additional competing heteroatom-bearing functional groups, carbenes/metallo-carbenoids may prefer to form corresponding carbonyl ylides to give further reactions [5][6].

Intra-/intermolecular carbenoid insertion(s) can also occur [6]. The choice of convenient combinations of diazo reactant and catalyst are highly important for the reactivity and the chemo-/stereoselectivity of the target reaction. A higher activity of the related carbene/carbenoids may result in the formation of undesirable carbene-dimers, -trimers, *etc.*, instead of the expected reactions. Based on the nature of the substituents (D and/or A) flanking the carbenoid center, different chemo-/stereoselectivities may be observed [7]. For example, carbenes/carbenoids functionalized with D/A groups have the advantage of chemoselective orientation to the target reaction(s) because of their relatively controllable activities and the consequent selectivities. The efficiency of the desired reaction is also noticeable determined by the convenient catalyst. There are several novel studies with Rh, Pd, Cu, and Ru catalysts that result in different selectivities [1–4].

In our laboratory, the parameters of ring closure reactions of α,β-conjugated carbonyl ylides have recently been studied to improve the yields and clarify the reaction mechanism in detail [8]. Moreover, the $Cu(acac)_2$-catalyzed reaction of a

Scheme 1. *Cu(acac)$_2$-Catalyzed Reaction of Tertiary Enaminone* **1** *and Ethyl Diazoacetate* **2a**



tertiary enaminone, **1** (a push-pull alkene), and ethyl diazoacetate (**2a**) having one A group was studied and an expected novel furan derivative, **3**, formed by 1,5-electrocyclization of the corresponding carbonyl ylide, was obtained [9]. However, the same reaction also gave another furan derivative, **5**, that reduced the yield of **3** (ratio of **3**:**5** = 1:1). Furan **5** was formed by ring opening closure reaction of initially formed DA cyclopropane **4** (ethyl 2-benzoyl-3-(dimethylamino)cyclopropanecarboxylate; *Scheme 1*). It was the first time that **5** could be formed under the studied conditions. In view of this finding, we aimed to gain more information about the formation and possible further reactions of various substituted cyclopropanes under two catalytic conditions.

Results and Discussion. – In this study, (1*E*)-buta-1,3-dien-1-yl acetate (**6**), commercially available as (*E*)/(*Z*) mixture (2.4:1), was selected as model reactant [1h]. Firstly, we aimed to prepare corresponding mono-/biscyclopropane derivatives containing an acyloxy function similar to DA cyclopropanes (2-formyl-3-(methoxycarbonyl)cyclopropyl methyl oxalate) of *Böhm et al.* [4i] or containing an unsubstituted vinyl group similar to DA cyclopropanes of *Pohlhaus et al.* [4a]. Then, we investigated their possible further reactions under different catalytic conditions. The studied diazo compounds were ethyl diazoacetate (**2a**), dimethyl diazomalonate (**2b**) [10], 1-diazo-1-phenylpropan-2-one (**2c**) [11], and methyl (3*E*)-2-diazo-4-phenylbut-3-enoate (**2d**) [5]. Cu(acac)$_2$ and (AcO)$_4$Rh$_2$ were used as catalysts. Results including some further

reactions of the corresponding cyclopropanes are summarized in *Scheme 2* and in the *Table*.

As a first experiment, (*E*)/(*Z*)-**6** was reacted with ethyl diazoacetate (**2a**) in the presence of $Cu(acac)_2$ (*Scheme 2* and *Table*, *Entry 1*). The A-type carbenoid with one A group from diazo compound **2a** could react with both (*E*)-**6** and (*Z*)-**6**. The reaction showed that the ethoxycarbonylcarbenoid attack took place only at the less hindered

Scheme 2. *Reactions of* **6** *and Diazocarbonyl Compounds* **2a**–**2d**

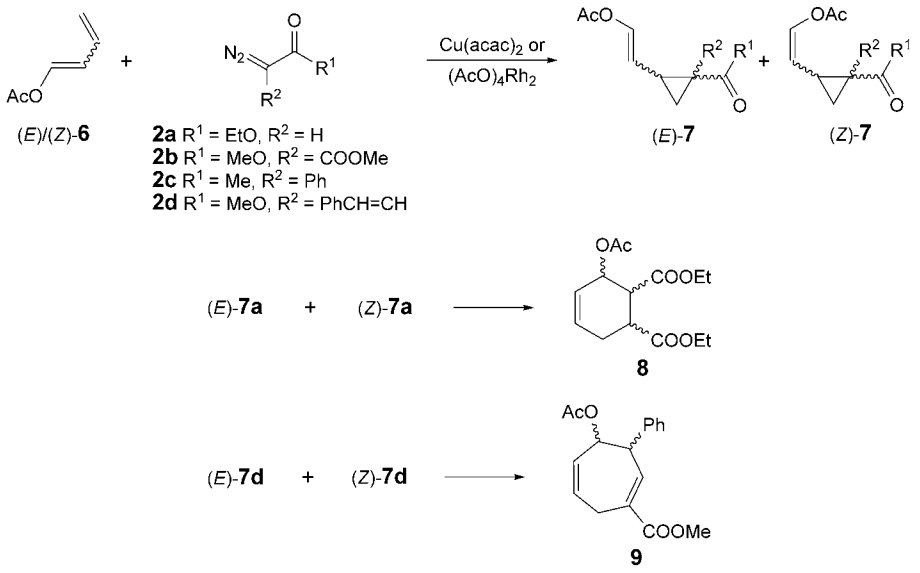


Table. *Reactions of* **6** *and Diazocarbonyl Compounds* **2a**–**2d**

Entry	**2**	Condition[a])	Product ratio[b])	Yield of **7** [%]	Yield of **8** [%]	Yield of **9** [%]
1	**2a**	Condition 1	**7a**/**8** 1 : 1	13 (**7a**)	15	–
2	**2a**	Condition 2	(1*R*,2*S*)-(*E*)-**7a**/(1*R*,2*R*)-(*E*)-**7a**/(1*R*,2*S*)-(*Z*)-**7a**/(1*R*,2*R*)-(*Z*)-**7a** 3 : 3 : 1.5 : 1	28 (**7a**)	1	–
3	**2b**	Condition 1	(*E*)-**7b**/(*Z*)-**7b** 2.3 : 1	32 (**7b**)	–	–
4	**2c**	Condition 1	(1*R*,2*S*)-(*E*)-**7c**/(1*R*,2*S*)-(*Z*)-**7c** 2.5 : 1	17 (**7c**)	–	–
5	**2c**	Condition 3	(1*R*,2*S*)-(*E*)-**7c**/(1*R*,2*S*)-(*Z*)-**7c** 2.4 : 1	21 (**7c**)	–	–
6	**2d**	Condition 1	–[c])	–	–	–
7	**2d**	Condition 3	Only **9** was formed.	–	–	30

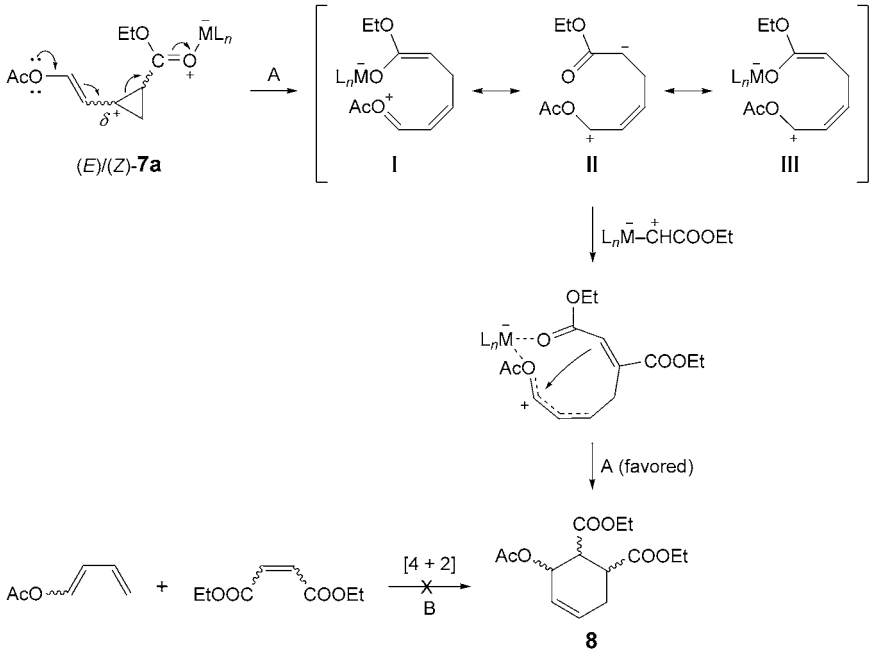
[a]) Condition 1: the reaction was performed in the presence of $Cu(acac)_2$ using 1.5 equiv. of **6** with the standard adding rate of **2** (addition over 2.5 h). Condition 2: the reaction was performed in the presence of $Cu(acac)_2$ using 1.5 equiv. of **6** with addition of **2** over 24 h. See the *Exper. Part*. Condition 3: the reaction was performed in the presence of $(AcO)_4Rh_2$. [b]) The ratio was determined by ^{1}H-NMR of the crude products. [c]) The diazo compound was reacted with itself and formed a pyrazol derivative. No other products were detected.

C=C bond to form cyclopropanes as reported for its analogs [4f–4h][12–14]. All four theoretical cyclopropane stereoisomers, (1*R*,2*S*)-(*E*)-**7a**, (1*R*,2*R*)-(*E*)-**7a**, (1*R*,2*S*)-(*Z*)-**7a**, and (1*R*,2*R*)-(*Z*)-**7a**, were spectroscopically observed at a ratio of 3:3:1.5:1 ((*E*)-**7a**/(*Z*)-**7a** 6:2.5), respectively. The (*E*)/(*Z*) ratio was the same as that of dieneester **6** ((*E*)/(*Z*)-**6** 2.4:1).

In this experiment, another compound, **8** (two stereoisomers), was also found at the same ratio as cyclopropane derivatives **7a** (The amount of **8** decreased when the reaction condition was modified to a slower addition rate of **2a** to **6** (*Table*, *Entry 2*)). The structure of **8** was determined by ^{1}H-NMR, COSY, and HSQC data. This compound was a novel cyclohexene derivative formed by ring opening of vinylcyclopropane derivative (*E*)/(*Z*)-**7a** with another equiv. of carbenoid by a formal [5 + 1] cycloaddition. The proposed mechanism of the reaction is depicted in *Scheme 3*, *Path A*: the catalyst activates the cyclopropane ring opening, a second equiv. of carbenoid adds to **I**–**III**. The intermediate adduct seems to prefer the more stable conformer with a *cis* orientation of the vicinal acetyloxy and ethoxycarbonyl substituents. The other pathway, *Diels–Alder* reaction of possible carbene dimers (dimethyl maleate and/or dimethyl fumarate) and dieneester (*E*)/(*Z*)-**6** (*Path B*), seems not possible, because *Diels–Alder* reaction under the same conditions gave all possible isomers, whereas *Path A* yielded only two isomers of **8**. We also confirmed *Path A* by reacting isolated **7a** with **2a** and found only the same two isomers of **8**.

Metal-catalyzed intermolecular formal [5 + 2] cycloadditions of vinylcyclopropanes and π-systems has been reported [14c][14d]. New reactivity types for dimethyl 2-

Scheme 3. *Reaction Mechanism and Origin of the Diastereoselectivity for the Formation of* **8**



phenylcyclopropane-1,1-dicarboxylate as 1,2- or 1,4-dipoles instead of the established 1,3-dipoles have also been reported [15]. But in the present study, a new [5 + 1]-like behavior was observed.

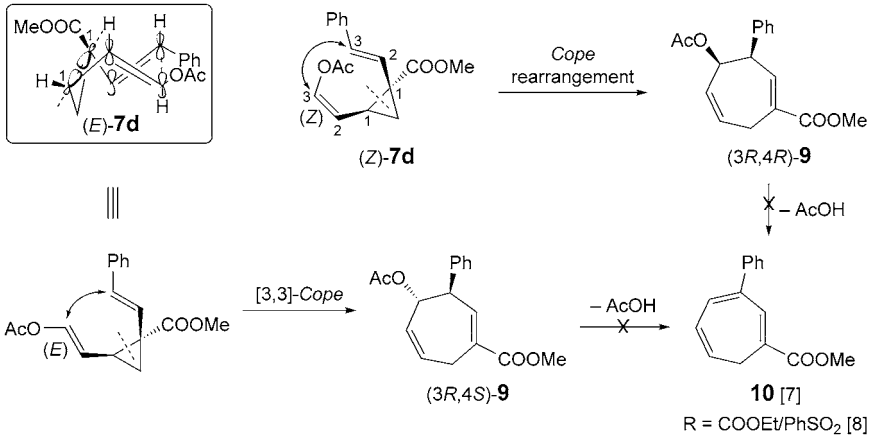
To check the reproducibility of regioselective addition to the less-substituted C=C bonds of (*E*)-**6** and (*Z*)-**6**, the reaction was repeated using dimethyl diazomalonate (**2b**; an AA carbenoid) under the same $Cu(acac)_2$ catalytic conditions (*Table*, *Entry 3*). The products also were terminal cyclopropanes. Furthermore, their ratio ((*E*)-**7b**/(*Z*)-**7b** 2.3 : 1) mirrored the isomer ratio of the starting material again (*Scheme 2*).

Then, reactions of 1-diazo-1-phenylpropan-2-one (**2c**; DA substituents) with (1*E*)-buta-1,3-dien-1-yl acetate ((*E*)-**6** and (*Z*)-**6**) with two catalysts were studied (*Table*, *Entries 4* and *5*). In each experiment, only two isomeric terminal cyclopropanes, (1*R*,2*S*)-(*E*)-**7c** and (1*R*,2*S*)-(*Z*)-**7c**, were determined as main compounds. (*E*)-**7c** and (*Z*)-**7c** also represented approximately the same isomer ratio than that of **6**.

Finally, another DA diazo compound, methyl (3*E*)-2-diazo-4-phenylbut-3-enoate (**2d**), was reacted with **6** with two different catalysts (*Table*, *Entries 6* and *7*). While $Cu(acac)_2$ was not effective (*Entry 6*), $(AcO)_4Rh_2$ yielded product **9** (*Entry 7*). ^{1}H-NMR and HSQC spectra showed that the obtained two compounds, diastereoisomers (3*R*,4*S*)-**9** and (3*R*,4*R*)-**9**, were products of a tandem-cyclopropanation/*Cope* rearrangement (*Scheme 4*). In the first step of this reaction, (*E*)-**7d** and (*Z*)-**7d** were formed with excellent chemo- and stereoselectivities, which favored the more accessible C=C bond and represented only *cis*-divinyl orientation. Then, these cisoid compounds, (*E*)-**7d**/(*Z*)-**7d**, underwent stereospecific *Cope* rearrangements yielding the corresponding cycloheptadiene isomers (3*R*,4*S*)-**9** and (3*R*,4*R*)-**9** (*Scheme 4*) [14–16]. In this reaction, the further cycloheptatriene derivative **10** could not be observed, possibly because of steric hindrance by the phenyl substituent.

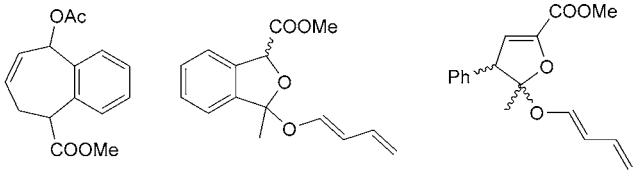
Conclusions. – In this study, the reactions of (1*E*)-buta-1,3-dien-1-yl acetate (**6**) with four different diazocarbonyl compounds, ethyl diazoacetate (**2a**), dimethyl diazomalonate (**2b**), 1-diazo-1-phenylpropan-2-one (**2c**), and methyl (3*E*)-2-diazo-4-phenylbut-

Scheme 4. *Further Reactions of* (E)/(Z)-**7d**: *Cope Rearrangement*



3-enoate (**2d**), were investigated in the presence of Cu/Rh catalysts. Except for *Entry 6* in the *Table*, in all other experiments cyclopropanation reactions could be observed. *Entries 1–5* yielded corresponding stable cyclopropane derivatives **7a**–**7c**. All cyclopropanations were chemospecific with respect to the less-substituted C=C bond.

Cyclopropanes **7b** and **7c** did not show any further reactivity. Analogous to the present literature, vinylcyclopropanes **7c** and **7d** showed *cis*-orientation [17–19]. (*E*)/(*Z*)-**7c** were stable *cis*-vinyloid cyclopropane derivatives and no corresponding *Cope* rearrangement product **11** could be determined.



11 **12** **13**

In the case of *Entry 1* in the *Table*, cyclopropane **7a** was obtained along with **8**. This polysubstituted cyclohexene derivative might be formed by ring opening of **7a**, which contained an acetyloxyvinyl-substituent having a weak D effect, and then a formal [5 + 1] cycloaddition with another equiv. of **2a** (*Scheme 3*, *Path A*). Contrary to our results, *Reißig et al.* [1a] reported no conversion of their cyclopropane ((1*S*,2*S*,3*S*)-2-formyl-3-(methoxycarbonyl)cyclopropyl methyl oxalate) to a cyclohexene derivative.

On the other hand, *cis*-orientations of divinylcyclopropanes (*E*)-**7d**/(*Z*)-**7d** led to *Cope* rearrangements in a clear way to form polyfunctionalized cycloheptadiene derivatives (3*R*,4*S*)-**9** and (3*R*,4*R*)-**9**, which failed to eliminate AcOH to form cycloheptatriene **10**. In an analogous work [14a] that aimed to obtain cycloheptadienes starting from the two different vinylated diazo compounds, no identifiable products could be observed. Moreover, any reaction pathway that led to [1,5]-ring closure to **12** or **13** *via* carbonyl ylides could not be observed.

As a result, di-/trisubstituted cyclopropanes **7a**–**7d** were synthesized by a chemospecific way. Compounds **7b** and **7c** were stable enough under the reaction conditions used in this study, whereas **7a** showed a further formal [5 + 1] cycloaddition to **8**. Compound **7d** underwent *Cope* rearrangement to give **9**.

Experimental Part

General. Thin layer chromatography (TLC): aluminum sheets precoated with silica gel *60* F_{254} (SiO_2; *Merck*); visualized by UV light (at 254 nm). Column chromatography (CC): SiO_2 *60* (40–63 μm). FT-IR Spectra: *PerkinElmer Spectrum One* with an ATR accessory (ZnSe, *PIKE MIRacle®* accessory) and a CdTe (MCT) detector; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Agilent VNMRS* (500 and 125 MHz, resp.); in $CDCl_3$; δ in ppm rel. to Me_4Si or $CDCl_3$ as internal standard, *J* in Hz. GC/MS: *Hewlett–Packard* instrument equipped with a flame ionization detector. A cross-linked (phenylmethyl)siloxane capillary column (30 m × 0.32 mm, 0.25 μm) was used with He as carrier gas (column head pressure, 25 psi). Temp. program as follows: start at 100°, then 5 min isothermal, ramp 20°/min; final 290° and then 10 min isothermal. EI-MS: *Thermo Finnigan Trace DSQ*; in *m*/*z* (rel. %). HR-MS: *Agilent 6230B* TOF LC/MS; in *m*/*z*.

Materials. All solvents and reactants are commercially available. (1*E*)-Buta-1,3-dien-1-yl acetate (**6**) and ethyl diazoacetate (**2a**) were purchased. Dimethyl diazomalonate (**2b**) [10], 1-diazo-1-phenylpropan-2-one (**2c**) [11], and methyl (3*E*)-2-diazo-4-phenylbut-3-enoate (**2d**) [5] were prepared as described in the literature.

*General Procedure for the Reaction of (1*E*)-Buta-1,3-dien-1-yl Acetate with Diazo Compound. Condition 1.* To a soln. of **6** (8.9 mmol, 1.5 equiv.) in benzene (15 ml) was added $Cu(acac)_2$ ($4.16 \cdot 10^{-2}$ mmol, 0.007 equiv.), and the mixture was heated under reflux. A soln. of diazo compound (5.9 mmol, 1 equiv.) in benzene (1.5 ml) was added to this mixture over 2.5 h under N_2 atmosphere. When the IR spectrum of the mixture indicated total consumption of the diazo compound (absence of the characteristic diazo band), the mixture was filtered, evaporated, and purified by CC or prep. TLC.

Condition 2. To a soln. of **6** (8.9 mmol, 1.5 equiv.) in benzene (30 ml) was added $Cu(acac)_2$ ($4.16 \cdot 10^{-2}$ mmol, 0.007 equiv.), and the mixture was heated under reflux. A soln. of diazo compound (5.9 mmol, 1 equiv.) in benzene (5 ml) was added to this mixture over 24 h under N_2 atmosphere. When the IR spectrum of the mixture indicated total consumption of the diazo compound, the mixture was filtered, evaporated, and purified by CC or prep. TLC.

Condition 3. To a soln. of **6** (3.3 mmol, 1.5 equiv.) in CH_2Cl_2 (15 ml) was added $(AcO)_4Rh_2$ ($1.53 \cdot 10^{-2}$ mmol, 0.007 equiv.), and the mixture was heated at 40°. A soln. of diazo compound (2.2 mmol, 1 equiv.) in CH_2Cl_2 (1.5 ml) was added to this mixture over 2.5 h under N_2 atmosphere. When the IR spectrum of the mixture indicated total consumption of the diazo compound, the mixture was filtered, evaporated, and purified by CC or prep. TLC.

*Ethyl 2-[(*E*)-2-(Acetyloxy)ethenyl]cyclopropanecarboxylate* ((*E*)-**7a**) *and Ethyl 2-[(*Z*)-2-(Acetyloxy)ethenyl]cyclopropanecarboxylate* ((*Z*)-**7a**). Compound **7a** was obtained by reaction of **6** and **2a** according to *Condition 2*. Compound **7a** was purified by prep. TLC (SiO_2; petroleum ether (PE)/Et_2O 80:28). Compounds (1*R*,2*S*)-(*E*)-**7a**, (1*R*,2*R*)-(*E*)-**7a**, (1*R*,2*S*)-(*Z*)-**7a**, and (1*R*,2*R*)-(*Z*)-**7a** were obtained together (3:3:1.5:1, resp., from ^{1}H-NMR). Total yield of **7a**: 28%. Yellow oil. t_R 9.23, 9.27, 8.91, 9.01 min, resp.

*Data of (1*R*,2*S*)-(*E*)-***7a***.* ^{1}H-NMR: 7.23 (*d*, *J* = 12.4, OCH=C); 5.12 (*dd*, *J* = 12.4, 8.5, OCH=C*H*); 4.14 (*q*, *J* = 6.9, MeCH_2O); 2.11 (*s*, MeC=O); 1.99–1.94 (*m*, C*H*CH=CH); 1.39–1.37 (*m*, C*H*COOEt); 1.26 (*t*, *J* = 6.9, COOCH_2*Me*); 1.23–1.18 (*m*, 1 H, CH_2); 0.97–0.93 (*m*, 1 H, CH_2). ^{13}C-NMR: 173.2; 167.9; 136.6; 114.0; 60.7; 21.5; 20.2; 16.9; 14.3; 14.2. *Data of (1*R*,2*R*)-(*E*)-***7a***.* ^{1}H-NMR: 7.25 (*d*, *J* = 12.1, OCH=C); 5.50 (*dd*, *J* = 12.1, 9.5, OCH=C*H*); 4.14 (*q*, *J* = 6.9, COOCH_2Me); 2.10 (*s*, MeC=O); 1.94–1.84 (*m*, C*H*CH=CH); 1.39–1.37 (*m*, C*H*COOEt); 1.26 (*t*, *J* = 6.9, COOCH_2*Me*); 1.23–1.18 (*m*, 1 H, CH_2); 0.97–0.93 (*m*, 1 H, CH_2). ^{13}C-NMR: 173.4; 168.0; 136.6; 114.9; 60.7; 21.9; 20.6; 18.5; 14.4; 14.2. *Data of (1*R*,2*S*)-(*Z*)-***7a***.* ^{1}H-NMR: 7.12 (*d*, *J* = 6.5, 0.5 H, OCH=C); 4.97 (*dd*, *J* = 9.9, 6.5, 0.5 H, OCH=C*H*); 4.14 (*q*, *J* = 6.9, 1 H, MeCH_2O); 2.38–2.30 (*m*, 0.5 H, C*H*COOEt); 2.17 (*s*, 1.5 H, MeC=O); 1.45–1.42 (*m*, 0.5 H, C*H*CH=CHO); 1.26 (*t*, *J* = 6.9, 1.5 H, COOCH_2*Me*); 1.23–1.18 (*m*, 0.5 H, CH_2); 0.97–0.93 (*m*, 0.5 H, CH_2). ^{13}C-NMR: 172.0; 167.8; 135.3; 110.7; 60.6; 20.7; 19.4; 15.3; 14.2; 14.1. *Data of (1*R*,2*R*)-(*Z*)-***7a***.* ^{1}H-NMR: 7.01 (*d*, *J* = 6.5, 0.34 H, OCH=C); 4.37 (*dd*, *J* = 9.9, 6.5, 0.34 H, OCH=C*H*); 4.14 (*q*, *J* = 6.9, 0.68 H, MeCH_2O); 2.38–2.30 (*m*, 0.34 H, C*H*COOEt); 2.15 (*s*, 1.02 H, MeC=O); 1.45–1.42 (*m*, 0.34 H, C*H*CH=CHO); 1.26 (*t*, *J* = 6.9, 1.02 H, COOCH_2*Me*); 1.23–1.18 (*m*, 0.34 H, CH_2); 0.97–0.93 (*m*, 0.34 H, CH_2). ^{13}C-NMR: 172.0; 167.8; 135.8; 112.4; 60.6; 20.7; 20.2; 15.7; 14.3; 14.1. *Data of Mixture of* **7a**. IR (CH_2Cl_2): 2981, 1757, 1724, 1672, 1371, 1221, 1180, 1097. EI-MS: 198 (5, M^+), 155 (65), 128 (99), 110 (60), 82 (100), 55 (66). HR-MS: 198.0901 (M^+, $C_{10}H_{14}O_4^+$; calc. 198.0892).

*Dimethyl 2-[(*E*)-2-(Acetyloxy)ethenyl]cyclopropane-1,1-dicarboxylate* ((*E*)-**7b**) *and Dimethyl 2-[(Z)-2-(Acetyloxy)ethenyl]cyclopropane-1,1-dicarboxylate* ((*Z*)-**7b**). Compound **7b** was obtained by reaction of **6** and **2b** according to general procedure of *Condition 1*. The mixture was purified by prep. TLC (SiO_2; hexane/AcOEt 80:20). Compounds (*E*)-**7b** and (*Z*)-**7b** were obtained together ((*E*)-**7b**/(*Z*)-**7b** 2.3:1 from ^{1}H-NMR). Total yield of **7b**: 32%. Pale-yellow oil. t_R 10.66 and 10.25 min, resp.

*Data of (*E*)-***7b***.* ^{1}H-NMR: 7.31 (*d*, *J* = 13.2, OCH=C); 5.14 (*dd*, *J* = 12.7, 8.8, OCH=C*H*); 3.76 (*s*, COOMe); 3.75 (*s*, COOMe); 2.54 (*dd*, *J* = 17.1, 8.8, OCH=CHC*H*); 2.11 (*s*, MeC=O); 1.71–1.66 (*m*, CH_2). ^{13}C-NMR: 169.8; 167.8; 138.8; 109.8; 52.8; 52.7; 35.4; 26.7; 21.5; 20.7. *Data of (*Z*)-***7b***.* ^{1}H-NMR: 7.2 (*d*, *J* = 5.9, 0.44 H, OCH=C); 4.47 (*dd*, *J* = 9.7, 6.3, 0.44 H, OCH=C*H*); 3.77 (*s*, 1.32 H, COOMe); 3.76 (*s*, 1.32 H, COOMe); 2.94 (*dd*, *J* = 9.7, 7.9, 0.44 H, OCH=CHC*H*); 2.19 (*s*, 1.32 H, MeC=O); 1.63–1.60 (*m*,

0.88 H, CH_2). ^{13}C-NMR: 169.8; 167.8; 137.5; 108.5; 52.8; 52.7; 35.2; 24.5; 21.5; 20.6. *Data of Mixture of* **7b**. IR (CH_2Cl_2): 2956, 1757, 1720, 1672, 1437, 1327, 1202. EI-MS: 242 (4, M^+), 199 (70), 168 (100), 136 (83), 108 (87), 59 (18). HR-MS: 242.0792 (M^+, $C_{11}H_{14}O_6^+$; calc. 242.0790).

*(*E*)-2-[(1*S*,2*R*)-2-Acetyl-2-phenylcyclopropyl]ethenyl Acetate* ((*E*)-**7c**) *and (*Z*)-2-[(1*S*,2*R*)-2-Acetyl-2-phenylcyclopropyl]ethenyl Acetate* ((*Z*)-**7c**). Compound **7c** was obtained by reaction of **6** and **2c** according to general procedure of *Condition 3*. The mixture was purified by CC (SiO_2; PE/Et_2O 80:28). (1*R*,2*S*)-(*E*)-**7c** and (1*R*,2*S*)-(*Z*)-**7c** were obtained together ((*E*)-**7c**/(*Z*)-**7c** 2.4:1 from ^{1}H-NMR). Total yield of **7c**: 21%. t_R 11.87 and 11.65 min, resp.

*Data of (1*R*,2*S*)-(*E*)-**7c**.* ^{1}H-NMR: 7.40–7.25 (*m*, 5 arom. H); 7.20 (*d*, *J* = 12.4, OCH=C); 4.59 (*dd*, *J* = 12.4, 9.7, OCH=C*H*); 2.52 (*dddd*, *J* = 9.7, 9.2, 6.9, 2.8, OCH=CHC*H*); 2.04 (*s*, MeC=O); 1.97 (*s*, MeC=O); 1.90 (*dd*, *J* = 9.2, 4.2, 1 H, CH_2); 1.27 (*dd*, *J* = 6.5, 4.2, 1 H, CH_2). *Data of (1*R*,2*S*)-(*Z*)-**7c**.* ^{1}H-NMR: 7.40–7.25 (*m*, 2.1 arom. H); 7.04 (*d*, *J* = 6.9, 0.42 H, OCH=C); 3.96 (*dd*, *J* = 10.3, 6.9, 0.42 H, OCH=C*H*); 2.93 (*dddd*, *J* = 10.3, 9.3, 6.4, 2.5, 0.42 H, OCH=CHC*H*); 2.19 (*s*, 1.26 H, MeC=O); 1.99 (*s*, 1.26 H, MeC=O); 1.94 (*dd*, *J* = 9.3, 3.5, 0.42 H, CH_2); 1.28 (*dd*, *J* = 6.4, 3.5, 0.42 H, CH_2). ^{13}C-NMR: 207.7; 167.7; 137.3; 136.3; 131.6; 128.7; 127.6; 114.0; 43.0; 29.7; 28.4; 24.8; 20.6. *Data of Mixture of* **7c**. IR (CH_2Cl_2): 2926, 1755, 1691, 1421, 1371, 1217, 1151, 931, 704. EI-MS: 244 (33, M^+), 202 (100), 159 (93), 142 (87), 91 (53), 77 (18). HR-MS: 244.1105 (M^+, $C_{15}H_{16}O_3^+$; calc. 244.1099).

The favored stereoisomers (*E*)-**7c**/(*Z*)-**7c** had minimum energies (Desktop Molecular Modelling) and they were also in accordance with π-interactions.

Diethyl 3-(Acetyloxy)cyclohex-4-ene-1,2-dicarboxylate (**8**). Compound **8** was obtained by reaction of **6** and **2a** according to general procedure of *Condition 1* and purified by prep. TLC (SiO_2; PE/Et_2O 80:28). Compound **8** was obtained as two isomers (3:1 from ^{1}H-NMR). Total yield of **8**: 15%. t_R 11.51 and 11.63 min.

Isomer 1. ^{1}H-NMR: 5.93–5.89 (*m*, CH=C*H*CH_2); 5.89–5.85 (*m*, C*H*=CHCH_2); 5.62–5.61 (*m*, CH–O); 4.17 (*q*, *J* = 7.3, 2 COOCH_2Me); 3.09–3.00 (*m*, C*H*COOEt); 2.92 (*dd*, *J* = 11.6, 8.5, OCHC*H*); 2.45 (*ddd*, *J* = 13.2, 5.4, 1.0, 1 H, CH_2); 2.30–2.24 (*m*, 1 H, CH_2); 2.06 (*s*, MeC=O); 1.29 (*t*, *J* = 7.3, 2 COOCH_2*Me*). ^{13}C-NMR: 171.4; 169.0; 127.5; 122.6; 65.1; 60.0; 59.9; 45.8; 39.8; 26.3; 20.0; 13.1. *Isomer 2.* ^{1}H-NMR: 5.98 (*ddd*, *J* = 7.7, 5.4, 2.4, CH=C*H*CH_2); 5.60 (*dd*, *J* = 7.7, 4.6, OCHC*H*=C); 5.61 (br. *d*, *J* = 8.6, CH–O); 4.20–4.14 (*m*, MeCH_2O); 4.14–4.09 (*m*, MeCH_2O); 3.09–3.00 (*m*, C*H*COOEt); 2.54 (*dtd*, *J* = 13.2, 4.2, 1.6, 1 H, CH_2); 2.16–2.09 (*m*, 1 H, CH_2); 1.98 (*s*, MeC=O); 1.28 (*t*, *J* = 7.3, COOCH_2*Me*); 1.23 (*t*, *J* = 7.3, COOCH_2*Me*). ^{13}C-NMR: 174.0; 169.3; 130.0; 124.9; 69.2; 59.9; 59.8; 45.6; 35.8; 27.8; 19.8; 13.1; 13.2. IR (CH_2Cl_2): 2962, 2359, 2341, 1736, 1371, 1234, 1021, 688. EI-MS: 281 (1, M^+), 238(6), 168 (62), 151 (89), 123 (66), 95 (54), 79 (100), 77 (31). HR-MS: 284.1252 (M^+, $C_{14}H_{20}O_6^+$; calc. 284.1260).

Methyl 4-(Acetyloxy)-3-phenylcyclohepta-1,5-diene-1-carboxylate (**9**). Compound **9** was obtained by reaction of **6** and **2d** according to general procedure of *Condition 3*. The mixture was purified by CC (SiO_2; PE/Et_2O 70:30). Compounds (3*R*,4*S*)-**9** and (3*R*,4*R*)-**9** were obtained together (11:0.7 from ^{1}H-NMR). Total yield of **9**: 30%. t_R 13.32 for (3*R*,4*S*)-**9** and 13.53 min for (3*R*,4*R*)-**9**.

IR (CH_2Cl_2): 2948, 2359, 2341, 1717, 1437, 1371, 1235, 1031, 669. ^{1}H-NMR: 7.31 (*d*, *J* = 7.7, 2 arom. H); 7.34–7.29 (*m*, 1 arom. H); 7.28–7.25 (*m*, 2 arom. H); 7.15 (*dd*, *J* = 6.1, 2.6, C*H*=CCOOMe); 5.96 (*dddd*, *J* = 10.6, 6.9, 3.9, 1.3, CH_2C*H*=C*H*); 5.72–5.70 (*m*, CH=C*H*CH); 5.65 (*ddd*, *J* = 10.6, 5.1, 2.6, C*H*OC=O); 4.12 (*dd*, *J* = 6.0, 3.0, C*H*CH=CH); 3.75 (*s*, COOMe); 3.44 (*dd*, *J* = 19.3, 7.7, 1 H, CH_2); 3.26 (*ddd*, *J* = 19.3, 5.6, 2.6, 1 H, CH_2); 2.02 (*s*, MeC=O). ^{13}C-NMR: 170.3; 167.6; 160.2; 141.6; 138.9; 129.9; 129.2; 128.3; 127.4; 126.9; 72.1; 52.2; 47.4; 26.4; 20.5. EI-MS: 286 (14, M^+), 245 (64), 212 (99), 195 (69), 183 (100), 167 (94), 162 (89), 115 (67), 91 (60), 77 (22). HR-MS: 286.1220 (M^+, $C_{17}H_{18}O_4^+$; calc. 286.1205).

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Received February 17, 2015