11. Selectivity in Rhodium(II)-Catalyzed Rearrangements of Cycloprop-2-ene-1-carboxylates

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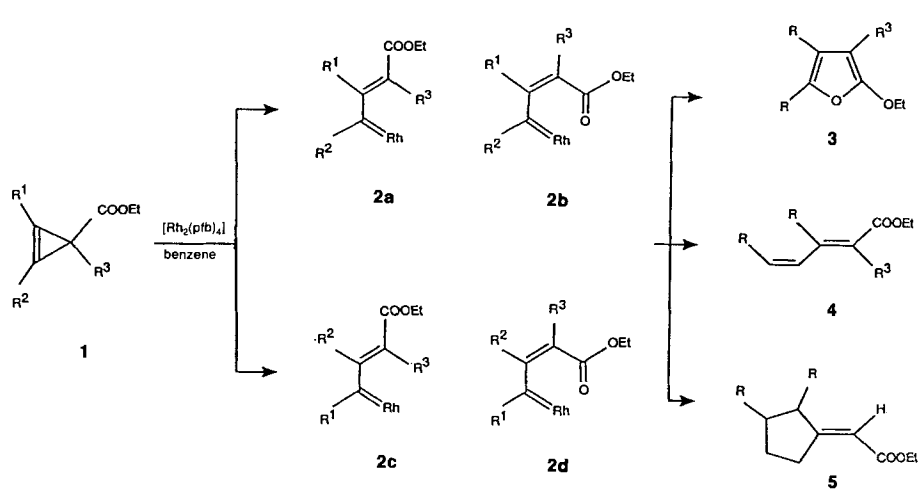
The course of the thermocatalytic rearrangement of cycloprop-2-ene-1-carboxylates in the presence of dirhodium(II) tetrakis(perfluorobutyrate) ($[Rh_2(pfb)_4]$) was investigated by varying the substituents of the cyclopropene ring. Product composition is markedly influenced by the number, nature, and position of the substituents, which determine the regio- and stereoselectivity of the cyclopropene-ring cleavage. A mechanism is proposed in which attack of the electrophilic Rh^{II} species is concerted with disrotatory ring opening of the incipient cyclopropyl cation and affords a metal-complexed vinylcarbene. The chemoselectivity of the latter is consistent with that of other carbenes generated in the presence of $[Rh_2(pfb)_4]$.

1. Introduction. – Substituted cycloprop-2-ene-1-carboxylates **1** isomerize in refluxing benzene in the presence of dirhodium(II) tetrakis(perfluorobutyrate) $[Rh_2(pfb)_4]$ to furans **3**, dienoates **4**, or cyclopentylideneacetates **5** [1] [2] (*Scheme 1*). These rearrangements were rationalized by a mechanism in which the cyclopropenecarboxylate undergoes ring opening to a rhodium-complexed vinylcarbene, which may occur as four regio- and stereoisomers (see **2a–d**).

The present study [3] was undertaken with the objective of establishing the factors which determine the regio- and stereoselectivity of the ring-opening process and the chemoselectivity of the intermediate vinylcarbenes in the hope of gaining insight in the

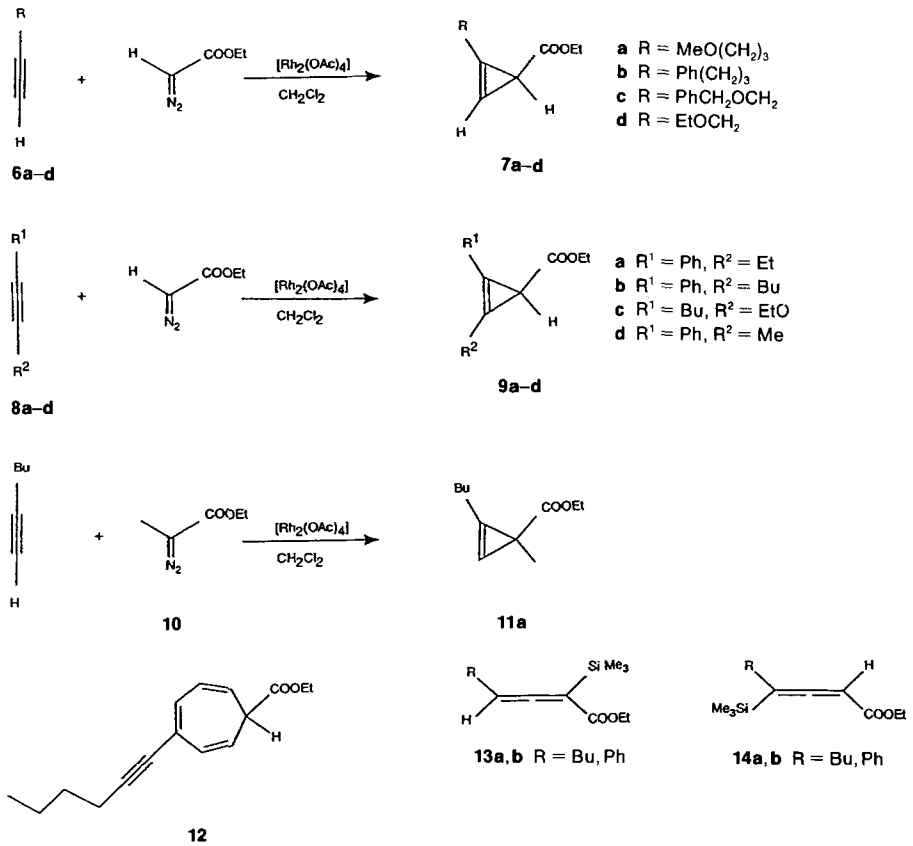
Scheme 1



reaction mechanism, and defining the structural parameters required for selective pathways.

2. Results. – 2.1. *Synthesis of Ethyl Cycloprop-2-ene-1-carboxylates.* The cyclopropenecarboxylates **7a–d** and **9a–d** were synthesized by addition of ethyl diazoacetate to the appropriate alkynes **6a–d** and **8a–d** in the presence of a catalytic amount of $[Rh_2OAc_4]$ [4] in 40–60% yield (*cf. Scheme 2* and *Exper. Part*). Since **8c** polymerized in the

Scheme 2



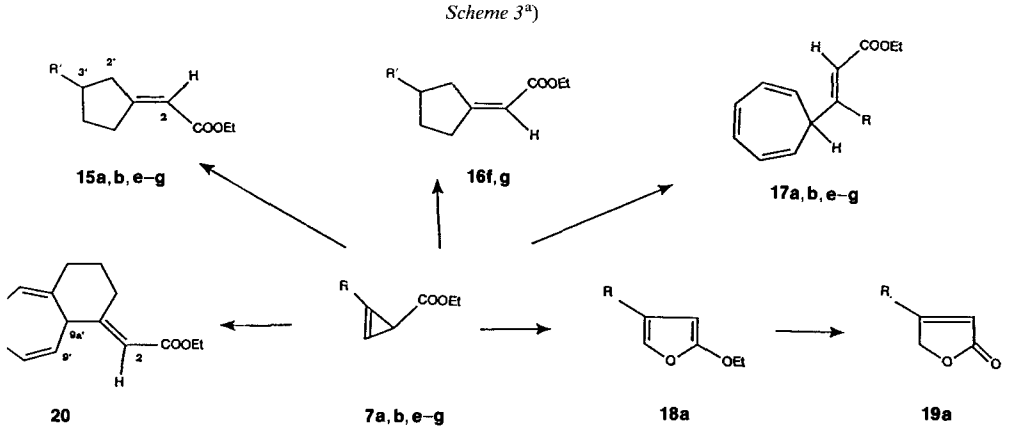
presence of $[Rh_2(OAc)_4]$, a less electrophilic catalyst, $[Rh_2\{(2S)\text{-mepy}\}_4]$ (= tetrakis-[μ-(*S*)-methyl 5-oxopyrrolidine-2-carboxylato-$\kappa N,\kappa O^5$]dirhodium(*Rh–Rh*)) [5] was used for this acetylene. The syntheses of the other cycloprop-2-ene-1-carboxylates (**7e–g** (*cf.* below, *Table 1*), **9e–h** (*cf.* below, *Table 2*), and **11b–d** (*cf.* below, *Scheme 5*)), which are included in the discussion, were reported previously [1] [2]. Ethyl 2-diazopropanoate (**10**), used for the synthesis of **11a**, was obtained *via* diazo transfer of ethyl 2-methylacetoacetate [6]. Principal by-products of the cyclopropenations were ethyl maleate and ethyl fumarate, the formal carbene dimers, which result from attack of the intermediate metallocarbene on unreacted diazoacetate [7]. When ethyl diazoacetate was added to **8b**,

addition of the carbene to the phenyl ring of the alkyne, leading to the cycloheptatriene-carboxylate **12**, occurred in a minor competing reaction (*ca.* 1%). The cyclopropenecarboxylates were purified by column chromatography. Purification by distillation was usually not possible owing to thermal cyclopropene decomposition, except when carried out under high vacuum, so that heating could be avoided. The alkoxyalkyl-substituted cyclopropenes **7c** and **7d** proved to be highly labile and could not be purified to the required degree, so that no rearrangements were investigated with these compounds.

In the course of this work, the structure of the allene by-products in the carbene addition of ethyl diazoacetate to 1-(trimethylsilyl)hex-1-yne and (trimethylsilyl)phenylacetylene were reexamined, and the previously assigned structures **13** had to be revised. NMR Experiments suggest that the *t* reported for the olefinic proton at 5.25 ppm (J = 5 Hz) for **13a** is due to a 5-bond coupling, typical for allenes [8], and not to coupling with an adjacent CH_2 group. The correct structure of the by-products is, therefore, **14** and not **13**, as previously suggested [2].

2.2. *Thermal Rearrangement of Cycloprop-2-ene-1-carboxylates in the Presence of [Rh_2(pfb)$_4$]. Monosubstituted Cycloprop-2-ene-1-carboxylates* **7a,b,e–g**. As previously reported, the 2-alkylcycloprop-2-ene-1-carboxylates such as **7e–g** rearranged in the pres-

Scheme 3[a])



a R = $MeO(CH_2)_3$; **b** R = $Ph(CH_2)_3$; **e** R = Bu; **f** R = hexyl; **g** R = octyl

[a]) For R′, see *Table 1*.

Table 1. *Rearrangement of Ethyl 2-Alkylcycloprop-2-ene-1-carboxylates* **7a,b,e–g**

	Cyclopropene-carboxylate **7**	Cyclopentylidene acetates **15** and **16**			Cycloheptatrienyl-alkenoate **17**		Other [%]	Comment
	R	R′	yield [%] of **15**	yield [%] of **16**	R	yield [%]		
a	$MeO(CH_2)_3$	MeO	53	–	$MeO(CH_2)_3$	3	**19** (7)	this work
b	$Ph(CH_2)_3$	Ph	15	–	$Ph(CH_2)_3$	6	**20** (44)	this work
e	Bu	Me	44	–	Bu	5–40	–	[1]
f	hexyl	Pr	33	2	hexyl	–	–	[1]
g	octyl	pentyl	20	1	octyl	20	–	[2]

ence of $[Rh_2(pfb)_4]$ in refluxing benzene to (*E*)-cyclopentylideneacetates **15e–g** in yields of up to 44% under optimized conditions [1] [2] (*Scheme 3*, *Table 1*). By-products were (*Z*)-cyclopentylideneacetates (**16f,g**, 1–2%) and, if the side chain of the cyclopropene ring was sufficiently long as in the case of **7f** or **7g**, the corresponding cyclohexylideneacetates (**7f**, 8%; **7g** 6% [1] [2]). In addition, interception of the intermediate vinylcarbene by the solvent, benzene, occurred and provided the corresponding cycloheptatrienylalkenoate **17e,g** in varying amounts [1] [2].

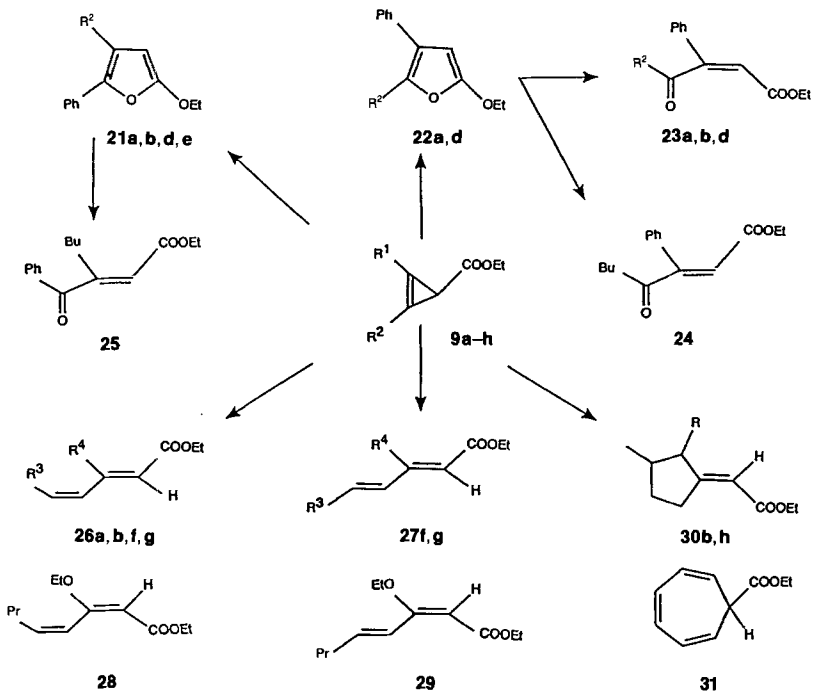
The rearrangement of the methoxypropyl-substituted cyclopropenecarboxylate **7a** was investigated, because the presence of an O-atom adjacent to the insertion site reportedly increases the yields of insertion products [9] in comparison to insertions into hydrocarbon chains. Indeed, rearrangement of **7a** with $[Rh_2(pfb)_4]$ provided the expected (*E*)-cyclopentylideneacetate **15a** in 53% yield. In addition to **15a**, a small amount of furan **18a** (7%), isolated after its hydrolysis to the lactone **19a**, and of the cycloheptatrienylhexenoate **17a** (3%) were also present. The configuration of **15a** was assigned by ^{1}H-NMR spectroscopy (NOE between olefinic proton and the *cis*-$CH_2(2')$ of the cyclopentane ring; unambiguous assignment of $CH_2(2')$ by coupling to *H*–C(3′) [3]). No (*Z*)-cyclopentylideneacetate **16a** was present, however. The configuration of the double bond in **17a** was not determined owing to an insufficient amount of sample.

Rearrangement of **7b**, where the MeO group is replaced by Ph, resulted in a reduced yield of 15% of the (*E*)-cyclopentylideneacetate **15b**. The low yield of insertion product **15b** was compensated by a new product which originates from a competing intramolecular cycloaddition of the carbene to the Ph group of the side chain, leading to the cycloheptatriene derivative **20** (44%), together with 6% of the solvent adduct **17b**. The (*E*)-configuration of the double bonds of both **15b** and **20** was assigned by ^{1}H-NMR spectroscopy (^{1}H,^{1}H correlation and NOESY [3]; **20**: strong NOE for H–C(2)/H–C(9′) and weak NOE for H–C(2)/H–C(9′a)). These stereochemical assignments are consistent with those of other stereoisomers of benzosuberone derivatives of known relative configuration [10]. The preference of **7b** to react *via* aromatic cycloaddition rather than CH insertion is consistent with the general reactivity trend of carbenoid reactions in the presence of $[Rh_2(pfb)_4]$ [11]. Insertion into benzylic CH bonds is usually less efficient than insertion into CH bonds of saturated alkyl chains, an observation originally attributed to the electron-attracting inductive effect of the Ph groups [12]. This explanation is, however, not very convincing since in **7a** the MeO group, which also has an electron-attracting inductive effect, actually enhances the yield of CH insertion product in comparison to alkyl, and it is difficult to see, why the inductive effect should enhance the yield of insertion products in one case, but reduce it in the other. In the rearrangement of **7b**, the low yield of cyclopentylidene **15b** is essentially due to the competing intramolecular cycloaddition, and it is not directly related to the electronic effect of the Ph group.

2.3. *Rearrangement of 2,3-Disubstituted Ethyl Cycloprop-2-ene-1-carboxylates* **9a–d**. The rearrangement of ethyl 2-methyl-3-phenylcycloprop-2-ene-1-carboxylate (**9d**; R^1 = Ph, R^2 = Me) was described previously [2]. It led to the regioisomeric furans **21d** and **22d** (or its degradation product **23d**) in a ratio of *ca.* 1:1 (*Scheme 4*, *Table 2*) [2].

The main rearrangement products of **9a** (R^1 = Ph, R^2 = Et) was the (*Z,Z*)-dienoate **26a** (37%). It derives from [1,2]-H migration of the alkyl-substituted vinylcarbene corresponding to **2a** or **2c**, with (*E*)-configuration. Although analogous dienoates were found in the thermocatalytic rearrangement of 2,3-diethyl- and 2,3-dibutylcycloprop-2-ene-1-

Scheme 4[a])



a R^1 = Ph, R^2 = Et; **b** R^1 = Ph, R^2 = Bu; **c** R^1 = Bu, R^2 = EtO; **d** R^1 = Ph, R^2 = Me; **e** $R^1 = R^2$ = Ph; **f** $R^1 = R^2$ = Et; **g** $R^1 = R^2$ = Bu; **h** R^1 = Bu, R^2 = Me_3Si

[a]) For R, R^3, and R^4, see *Table 2*.

Table 2. *Rearrangement of 2,3-Disubstituted Ethyl Cycloprop-2-ene-1-carboxylates* **9a–h**

	Cyclopropene-carboxylate **9**		Furan **21**		Furan **22**		Oxoenoate **23**		Dienoate **26** (**28**)			Other [%]	Com-ment
	R^1	R^2	R^2	yield [%]	R^2	yield [%]	R^2	yield [%]	R^3	R^4	yield [%]		
a	Ph	Et	Et	19	Et	7	Et	3	Me	Ph	37		this work
b	Ph	Bu	Bu	17			Bu	6	Pr	Ph	31	**24** (3)	this work
												30b R = Ph (9)	
c	Bu	EtO							Pr	OEt	49 (**28**)	**29** (22)	this work
												31 (26)	
d	Ph	Me	Me	20	Me	10	Me	10					[2]
e	Ph	Ph	Ph	83									[1]
f	Et	Et							Me	Et	65	**27f** (9)	[1]
g	Bu	Bu							Pr	Bu	75	**27g** (13)	[2]
h	Bu	Me_3Si										**30h** R = Me_3Si (20)	[2]

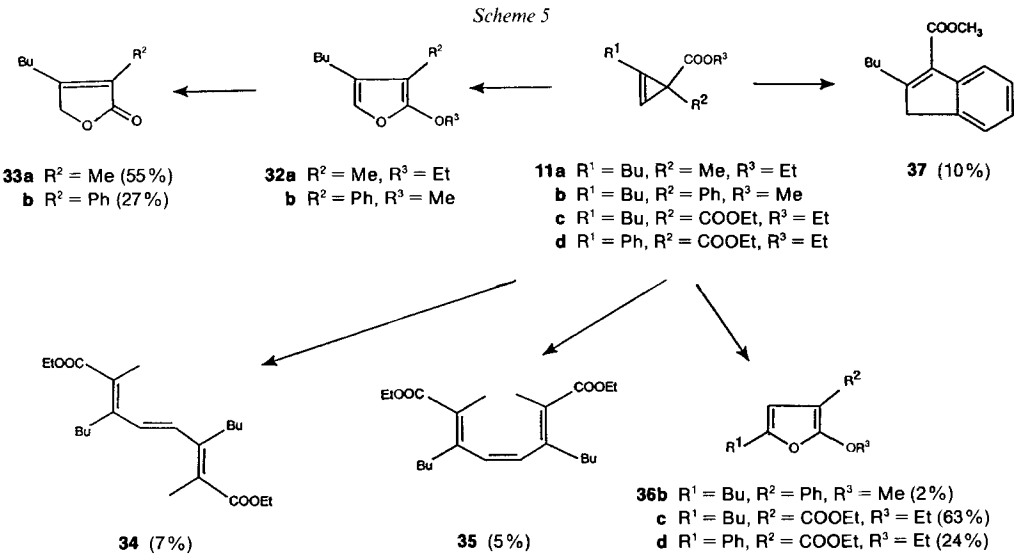
carboxylates **9f** and **9g**, respectively (see **26f,g** and **27f,g**) [1] [2], **9d** affords no dienoates. The other rearrangement products of **9a** were the furan **21a** (19%) and the isomeric furan **22a** (7%) and its degradation product **23a** (7%). No cyclopentylidene derivatives was formed, however.

Rearrangement of 2-butyl-3-phenylcyclopropenecarboxylate **9b** (R^1 = Ph, R^2 = Bu) resulted in a similar product distribution (**21b**, characterized as its oxidation product **25**, 17%; **23b**, 6%; **24**, 3%; **26b**, 31%), but in addition, a (*E*)-cyclopentylideneacetate **30b** appeared in 9% yield (*cf.* **9h**→**30h** [2]).

Introduction of an EtO group at C(3) (see **9c**) resulted in a regioselective ring opening and led to a 2.2:1 mixture of (2*E*,4*Z*)- and (2*E*,4*E*)-dienoates **28** and **29**, respectively, in 71% total yield, while neither furans nor cyclopentylideneacetates were found. The double-bond configurations of **28** and **29** were again attributed by ^{1}H-NMR spectroscopy (**28**: strong NOE for H–C(2)/MeCH_2O–C(3) (3.88 ppm); $^3J(4,5)$ = 11.8 Hz; **29**: $^3J(4,5)$ = 15.4 Hz). In addition, a secondary product was isolated in 26% yield, identified as **31**, the formal adduct of (ethoxycarbonyl)carbene to benzene. The origin of this product was not investigated. However, since **9c** was synthesized by carbenoid addition of ethyl diazoacetate to **8c** in the presence of $[Rh_2(OAc)_4]$ at 25°, the reverse process at higher temperature, leading to carbene extrusion and transfer of the carbene to the solvent provides a plausible rationale.

2.4. *Rearrangement of 1-Substituted 2-Butylcycloprop-2-ene-1-carboxylates* **11a,b**. The rearrangement of **11a** provided mainly furan **32a**, isolated as its hydrolysis product **33a** in 55% yield (*Scheme 5*). Small amounts of formal carbene dimers **34** and **35** were also formed. Their configuration followed from comparison of their ^{1}H-NMR spectra with those of similar trienes in the literature [13]. The dimers most likely originate from attack of an intermediate vinylcarbene on unreacted cyclopropene to yield a bicyclobutane, which then breaks down to the trienes **34** and **35**. This pathway was proposed in Cu^{II}-catalyzed carbenoid additions to cyclopropenes [14].

Scheme 5



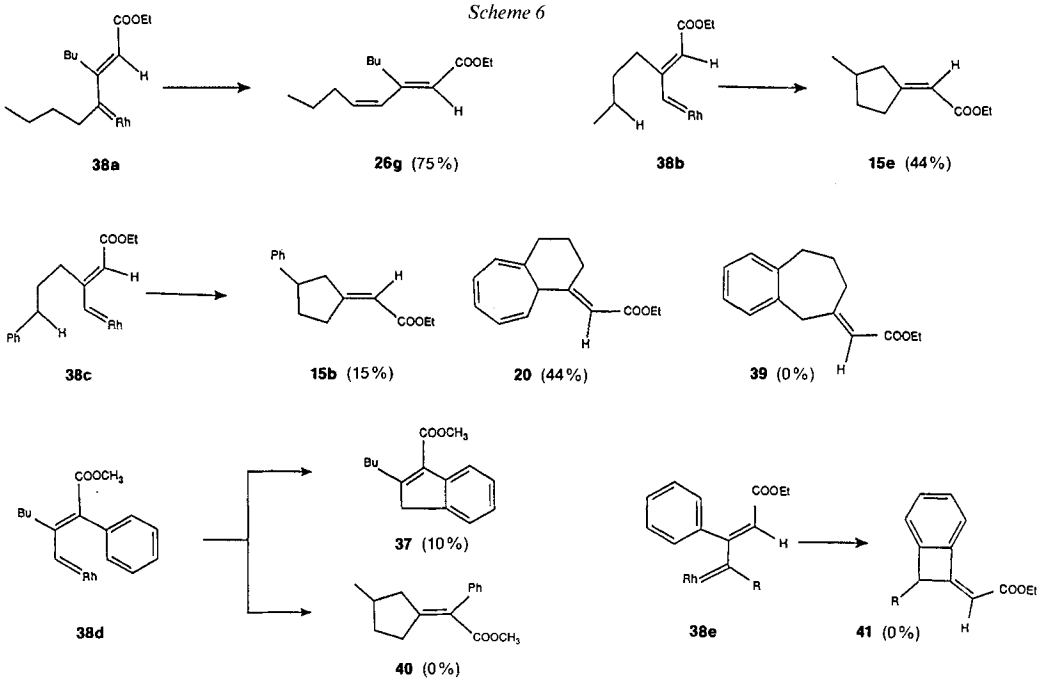
As reported previously, the isomerization of **11b** led also mainly to furan **32b** and, subsequently, to lactone **33b** (27%). The isomeric furan **36b** was formed in 2% yield only. In addition, an aromatic substitution product, **37**, resulting from intramolecular attack of the carbene on the Ph substituent was also formed (10% yield) [2]. The presence of a second carboxy group at C(1) changed the regioselectivity of the ring opening. Thus only furans of structure **36c** and **36d** were formed from **11c** and **11d**, respectively.

3. Discussion. – 3.1. *Preamble.* The interpretation of the above results must be considered preliminary. In several rearrangements, the material balance was far from 100%. We repeatedly observed darkening of the reaction mixture during rearrangement, a phenomenon which we ascribe to partial polymerization rather than to rearrangement of the cyclopropenecarboxylates. In addition, some of the rearrangement products were found to be highly labile and decomposed partially during workup. Although all precautions were taken to account for all of the rearrangement products, we cannot rigorously rule out some undetected ones.

3.2. *Product Distribution.* The product distribution of the rearrangements changes significantly with the substitution pattern of the cyclopropene ring. Some cyclopropenecarboxylates investigated rearrange in a highly specific fashion and give only one product, but other yield products derived from all four possible regio- and stereoisomeric vinylcarbenes. Apparently, the vinylcarbenes having the carboxy group and the carbenic center in *cis*-configuration (**2b,d** in *Scheme 1*) lead mainly to furans or their hydrolysis or oxidation products, irrespective of other pathways which the carbenes could in principle choose. The major exception to this occurs with **9c** where H-migration to **28**/**29** rather than furan formation takes place. Minor exceptions are provided by the (*Z*)-cyclopentylideneacetates **16f** and **16g**, which are formed as secondary products upon rearrangement of **7f** and **7g**, where the furans are absent, and by the cyclopentylideneacetate **30h** which occurs as a 2.5:1 (*E*)/(*Z*)-mixture in the rearrangement of **9h** [2]. It should be noted, however, that the structures of **16f** and **16g** are not rigorously established [2], whereas the selectivity of the silyl-substituted carbene derived from **9h** is not directly comparable with that of the unsubstituted ones.

The carbenes with (*E*)-configuration (**2a,c** in *Scheme 1*) afford products derived from competing [1,2]-H migration, aromatic substitution, aromatic cycloaddition, and aliphatic CH insertion. *E.g.*, carbene **38a** derived from **9g** reacts only with H migration to dienoate **26g** (and **27g**), and no CH insertion into the aliphatic chain occurs, but **38b** (from **7e**), which may not undergo H migration, reacts by insertion to **15e** (*cf. Scheme 6*). Carbene **38c** (from **7b**) may react by CH insertion to **15b** or by intramolecular aromatic cycloaddition to **20**, and the latter pathway is favored by *ca.* 3:1. Aromatic substitution is only observed with carbene **38d**, where it leads to the indenecarboxylate **37**. Aliphatic CH insertion is clearly not competitive with this process. The absence of any insertion product makes an estimate of the relative rates of the processes difficult, however. Intramolecular aromatic substitution with the other carbenes having Ph substituents (**38c**, **38e**) would require formation of cycloheptenylideneacetates (**39**) or cyclobutenylideneacetates (**41**), and this process is disfavored for reasons of strain. From the various competing pathways, the approximate order for carbene selectivities is furan formation $\approx$ [1,2]-H migration > aromatic substitution > aromatic cycloaddition > aliphatic CH insertion. This sequence compares favorably with the reactivity sequence for

Scheme 6

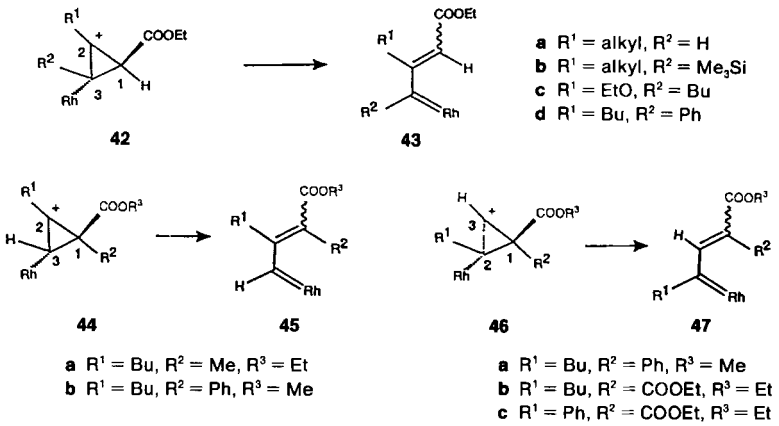


carbenoid reactions with $[Rh_2(pfb)_4]$ which, for diazoketones and diazoamides is: aromatic substitution > tertiary CH insertion > cyclopropanation > aromatic cycloaddition > secondary CH insertion [11].

If the carbenes were in rapid equilibrium, as previously suggested [1] [2] then the product composition would be determined by the differences in the activation energies between the various pathways. The observation that the least favorable pathway (CH insertion) occurs only when no other pathway is available to the carbene suggests that carbene interconversion must be slow relative to the product-forming step.

3.3. *Regioselectivity of Ring Cleavage.* The 2-alkylcycloprop-2-ene-1-carboxylates **7a**, **b**, **e**–**g** undergo ring cleavage in a fully regioselective manner and form the less substituted vinylcarbene **43a** (*cf. Scheme 7*). This has been interpreted by a mechanism in which the cyclopropene undergoes electrophilic attack by the Rh^{II} at the less substituted center (C(3)), so that the more substituted (tertiary) cyclopropyl cation **42a** results. Electrocyclic ring opening of the cation affords then the less substituted vinylcarbene **43a**. The Me_3Si group, in turn, is known to stabilize a positive charge in β, but to destabilize it, when it occurs in α position [15]. The regioselectivity of 2-butyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (**9h**) is consistent with this. Attack occurs only at C(3) leading to the alkyl-stabilized cyclopropyl cation **42b** and, ultimately, to carbene **43b**, which has the Me_3Si substituent at the carbenic center. Introduction of an EtO substituent at C(3) inverts the regioselectivity. Electrophilic attack of **9c** at C(2) results in a cyclopropyl cation **42c**, in which the positive charge is stabilized by the adjacent EtO group. The resulting vinylcarbene **43c** carries the EtO substituent at the double bond, and not at the carbenic center. With a Ph group at C(3), the 2-butylcyclopropenecarboxylate **9b** rear-

Scheme 7



ranges without clear regioselectivity. Products are derived from attack at C(3) *via* the alkyl-substituted cyclopropyl cation **42d** and the phenylcarbene **43d**, a pathway accounting for 26% of the products. The isomeric Ph-stabilized cation, in turn, accounts for 40% of the products. The remaining 34% of the products are undetected. Replacement of the Bu group of **9b** by Et (**9a**) shifts the balance in favor of the products derived from the Ph-substituted cation to 47% and those originating from the alkyl-substituted cation to 19%. When the Bu group of **9b** is replaced by Me (**9c**), the corresponding product percentages are 20% for each pathway.

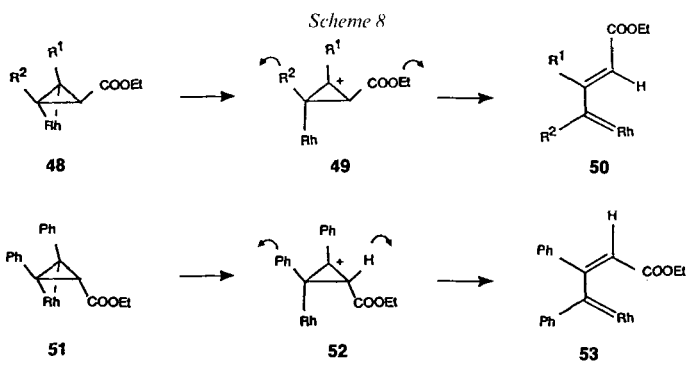
The regioselectivity of the ring opening of the cyclopropene-1-carboxylates is unaffected by introduction of a Me group at C(1) as shown in the case of **11a**. Only products derived from attack at C(3) *via* **44a** and **45a** are observed. A Ph group at C(1) (see **11b**) is similar. The main products (37%) derive from the cation **44b** and the corresponding vinyl carbene **45b**, but a small amount (2%) from the isomeric cation **46a** and carbene **47a** are also formed [2]. However, with two carboxy substituents at C(1), the regioselectivity is inverted and only products derived from the cations **46b, c** and carbenes **47b, c** result from **11c, d**.

The change in regioselectivity for ring opening as observed for the cyclopropene-1,1-dicarboxylates **11c, d** requires adjustment of the reaction mechanisms. The proposition of a cyclopropyl cation intermediate originating from electrophilic attack of the Rh^{II} on the cyclopropene should not be taken literally. In fact cyclopropyl cations are not generally observable species, but usually rearrange during their formation to allyl cations. Typically, in solvolysis reactions of allylic derivatives, leaving-group departure is assisted by σ-participation on the backside of the incipient cation, and ring opening is concerted with the ionization process [16]. If the transition state for the reaction of the cyclopropene with $[Rh_2(pfb)_4]$ lies intermediate between the cyclopropyl cation and the vinylcarbene, the substituent effects on the regioselectivity of the ring-opening process can be accommodated. The strong electron-withdrawing effect of the 1,1-dicarboxy substituents will favor the more substituted carbene **47**, since the substituent stabilizes the partial positive charge at the carbenic center. However, in the absence of strong electron-attracting

substituents at C(1), stabilization of positive charge at the cyclopropyl-cation stage determines the regioselectivity. A transition-state intermediate between cyclopropyl cation and vinylcarbene, rather than a cyclopropyl cation appears, therefore, to be a more appropriate description.

3.4. *Stereoselectivity of Ring Opening.* Some of the cyclopropene rearrangements are not only fully regioselective, but also stereoselective. The most striking examples in this respect are provided by **9e**. The reaction leads in 83% yield to the furan **21e** derived from a vinylcarbene with (*Z*)-configuration, while **9f** or **9g** provide dienoates from (*E*)-configurated carbenes in yields of 74 and 88%, respectively [1] [2] (see *Table 2*). Originally, we proposed a reversible ring-opening process, with all isomeric vinylcarbenes **2a–d** in a rapid pre-equilibrium. In the light of the more recent data on the selectivity of the rearrangements (see above), this hypothesis appears no longer justified. A mechanism for the cyclopropene-vinylcarbene rearrangement may be formulated in analogy to that proposed for rearrangement of 3,3-disubstituted cyclopropenes in the presence of $[WCl_2(NAr)(PX_3)_3]$ [17], or $[W(CO)_5]$ [18], or with $[Ti(Cp)_2(PMe_3)_2]$ [19], *via* vinylcarbene complexes. In some cases, η^2-complexes are isolable [17]. Coordination of the double bond from the less hindered side of the cyclopropene with the Rh^{II} affords a metallacyclopropane **48** or a π complex (*Scheme 8*). Ring opening of the latter to a cyclopropyl cation **49** is accompanied by disrotatory ring opening. A similar disrotatory ring opening upon electrophilic attack was reported for alkylidenecyclopropanes [20]. Backside stabilization of the incipient positive charge is possible in that disrotatory mode in which the carboxy group rotates outwards and leads to the (*E*)-vinylcarbene **50**. The presence of bulky substituents such as Ph destabilizes the transition state leading to **50**. Attack from the opposite side will then pass by analogy through **51** to **53**, where the interactions between one of the Ph groups and the ethoxycarbonyl substituent are avoided. Rearrangement products from (*Z*)-configurated vinylcarbenes occur typically with disubstituted cyclopropenecarboxylates, where at least one of the substituents is Ph, and they are almost entirely absent with monosubstituted cyclopropenecarboxylates. That attack from the more hindered face of the cyclopropene is feasible is demonstrated by the behavior of the cyclopropene-1,1-dicarboxylates **11c,d** which exhibit normal reactivity towards $[Rh_2(pfb)_4]$, although attack must occur on the side of a carboxylate. The above argument based on steric effects is, however, not the final answer. It fails to account for the observation that the 2,3-dialkylcyclopropenecarboxylates **9f,g** open to (*E*)-vinylcar-

Scheme 8



benes, while the EtO-substituted cyclopropenecarboxylate **9c** gives a (*Z*)-vinylcarbene. Several other questions are still open: the reversibility of the ring opening, although unlikely on the grounds of the present results, and the (*Z*)/(*E*)-isomerization of the vinylcarbenes, which was established with other metals [21], have yet to be formally ruled out. Similarly, the possible involvement of metallacyclobutenes [22] as intermediates on the reaction coordinate may not be ruled out at the present time.

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Experimental Part

1. *General.* See [23]. FC = Flash chromatography.

2. *Synthesis of Ethyl Cycloprop-2-ene-1-carboxylates. General Procedure.* To a soln. of the appropriate alkyne (5.5 mmol) and $[Rh_2(OAc)_4]$ (45 mg, 0.10 mmol) in dry CH_2Cl_2 (20 ml) was added, at 20° and under N_2, a soln. of ethyl diazoacetate (3.50 g, 31 mmol) in dry CH_2Cl_2 (1.8 ml), within 16 h by means of a syringe pump. After the addition, stirring was continued for 3 h at 20°. The mixture was filtered through a small column of silica gel to remove the catalyst. After evaporation of the solvent, the cyclopropenecarboxylate was isolated as an oil, contaminated with carbene dimers (diethyl fumarate and maleate). The impurities were removed by FC (silica gel, CH_2Cl_2/hexane 1:1).

Ethyl 2-(3-Methoxypropyl)cycloprop-2-ene-1-carboxylate (**7a**). *5-Methoxypent-1-yne* (**6a**) [24]: To a mixture of MeI (7.78 g, 56.2 mmol) and NaH (2.1 g, 52.5 mmol) in dry THF (50 ml) was added, dropwise within 15 min under N_2 and at 20°, pent-4-yn-1-ol (2.72 g, 32.5 mmol). The mixture was then heated to 50° for 1 h, then cooled, and poured into 70 ml of H_2O. The aq. layer was extracted with Et_2O, the extract dried ($MgSO_4$) and evaporated, and the residue distilled (b.p. 107–115°): **6a** (1.87 g, 59%). IR (CH_2Cl_2): 3305*s*, 3054*w*, 2930*m*, 2877*m*, 1118*s*, 1063*m*, 642*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.72–1.80 (*m*, 2 H); 1.92 (*t*, *J* = 2.7, 1 H); 2.26 (*dt*, *J* = 2.7, 7.0, 2 H); 3.32 (*s*, 3 H); 3.44 (*t*, *J* = 6.2, 2 H).

7a: The *General Procedure*, starting with **6a** (1.76 g, 18 mmol), $[Rh_2(OAc)_4]$ (91.7 mg, 0.21 mmol), and ethyl diazoacetate (2.75 g, 24.1 mmol) afforded, after bulb-to-bulb distillation (b.p. 20°/10^{-3} Torr), crude **7a** (2.08 g, 64% pure). Repeated FC (silica gel, CH_2Cl_2/hexane 2:1 and CH_2Cl/AcOEt 40:3) afforded **7a** in low yield with a purity of 90%. IR (CH_2Cl_2): 3140*w*, 3058*w*, 2983*m*, 2930*m*, 2870*w*, 1715*s*, 1446*w*, 1370*m*, 1329*m*, 1191*s*, 1117*m*, 1029*m*, 805*w*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.25 (*t*, *J* = 7.0, 3 H); 1.82–1.89 (*m*, 2 H); 2.14 (*d*, *J* = 1.5, 1 H); 2.59 (*dt*, *J* = 1.1, H = 7.4, 2 H); 3.33 (*s*, 3 H); 3.40–3.46 (*m*, 2 H); 4.10–4.20 (*m*, 2 H); 6.36–6.37 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 14.3 (*q*); 19.7 (*d*); 21.7 (*t*); 26.7 (*t*); 58.5 (*q*); 60.1 (*t*); 71.4 (*t*); 94.5 (*d*); 115.1 (*s*); 176.4 (*s*). MS: 184 (5, M^+), 183 (43), 169 (18), 137 (9), 125 (9), 124 (24), 123 (37), 111 (14), 97 (23), 96 (15), 95 (28), 89 (14), 79 (100), 69 (19), 68 (20), 67 (34), 66 (10), 65 (11), 61 (54), 57 (12), 55 (33), 52 (43), 51 (21), 45 (80). HR-MS: 184.1122 ($C_{10}H_{16}O_3^+$, calc. 184.1100).

Ethyl 2-(3-Phenylpropyl)cycloprop-2-ene-1-carboxylate (**7b**). The crude product, obtained by the *General Procedure*, was first purified by bulb-to-bulb distillation (40°/5·10^{-4} Torr), then by FC (silica gel, CH_2Cl_2/hexane 3:2): 0.66 g (41%) of **7b**. IR (CH_2Cl_2): 3056*m*, 2982*m*, 2940*m*, 1716*s*, 1603*w*, 1454*m*, 1370*m*, 1190*s*, 1038*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.24 (*t*, *J* = 7, 3 H); 1.87–1.95 (*m*, 2 H); 2.14 (*d*, *J* = 1.5, 1 H); 2.51 (*dt*, *J* = 1.5, 7.0, 2 H); 2.68 (*t*, *J* = 7.7, 2 H); 4.1–4.2 (*m*, 2 H); 6.36 (*d*, *J* = 1.5, 1 H); 7.1–7.2 (*m*, 3 H); 7.2–7.3 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 14.3 (*q*); 19.7 (*d*); 24.3 (*t*); 28.3 (*t*); 35.8 (*t*); 60.2 (*t*); 94.4 (*d*); 115.2 (*s*); 125.9 (*d*); 128.3 (*d*); 128.4 (*d*); 141.5 (*s*); 176.5 (*s*). MS: 230 (1, M^+), 202 (3), 201 (9), 184 (10), 157 (48), 155 (17), 129 (15), 105 (15), 104 (28), 97 (16), 91 (100), 77 (15), 63 (21).

Ethyl 2-[(Benzyloxy)methyl]cycloprop-2-ene-1-carboxylate (**7c**). Prepared in 18% yield from 3-(benzyloxy)prop-1-yne (**6c**) [25] according to the *General Procedure*. After elimination of the excess acetylene by bulb-to-bulb distillation, **7c** (92% purity) was isolated by CC (neutralized silica gel (NH_3), CH_2Cl_2/hexane 1:1). IR (CH_2Cl_2): 3150*w*, 2982*m*, 2867*w*, 1719*s*, 1454*m*, 1370*m*, 1194*s*, 1094*m*, 1028*m*, 909*w*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.25 (*t*, *J* = 7, 3 H); 2.31 (*d*, *J* = 1.5, 1 H); 4.14 (*dq*, *J* = 3, 7, 2 H); 4.55 (*d*, *J* = 1.5, 2 H); 4.61 (*d*, *J* = 2, 2 H); 6.67 (*dd*, *J* = 2, 1.5 1 H); 7.30–7.36 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): 14.3 (*q*); 20.1 (*d*); 60.4 (*t*); 63.5 (*t*); 72.5 (*t*); 97.6 (*d*); 112.3 (*s*); 127.9 (*d*); 128.1 (*d*); 128.4 (*d*); 137.4 (*s*); 175.5 (*s*). MS: 232 (0.5, M^+), 105 (9), 92 (26), 86 (50), 84 (76), 77 (11), 49 (100).

Ethyl 2-(Ethoxymethyl)cycloprop-2-ene-1-carboxylate (**7d**). Prepared from ethyl propargyl ether [25] according to the *General Procedure*. Dimeric and polymeric material was separated from the crude mixture by bulb-to-bulb distillation (50°/0.001 Torr). The compound decomposed when subjected to CC (silical gel), and it could not be purified further. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.1–1.4 (*2t*, 6 H); 2.26 (*d*, *J* = 1.4, 1 H); 3.50–3.65 (*q*, 2 H); 4.1–4.3 (*q*, 2 H); 4.47 (*d*, *J* = 1.6, 2 H); 6.62 (*q*, *J* = 1.6, 1 H).

Ethyl 2-Ethyl-3-phenylcycloprop-2-ene-1-carboxylate (**9a**). Prepared from 1-phenyl-but-1-yne (**8a**) according to the *General Procedure* in 56% yield and 95% puritiy after FC (silica gel, CH_2Cl_2/hexane 1:1). IR (CH_2Cl_2): 3060*w*, 2979*m*, 2940*m*, 2360*w*, 1714*s*, 1490*w*, 1447*w*, 1369*m*, 1336*m*, 1247*m*, 1107*s*, 1019*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.24 (*t*, *J* = 7.0, 3 H); 1.33 (*t*, *J* = 7.4, 3 H); 2.25 (*s*, 1 H); 2.68 (*q*, *J* = 7.4, 2 H); 4.10–4.20 (*m*, 2 H); 7.26–7.33 (*m*, 1 H); 7.35–7.40 (*m*, 2 H); 7.45–7.49 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 12.0 (*q*); 14.3 (*q*); 19.1 (*t*); 22.1 (*d*); 60.0 (*t*); 104.5 (*s*); 111.5 (*s*); 127.0 (*s*); 128.5 (*d*); 128.6 (*d*); 129.3 (*d*); 175.8 (*s*). MS: 217 (4, $[M + 1]^+$), 216 (9), 203 (14), 188 (15), 187 (46), 175 (10), 143 (67), 131 (10), 128 (38), 115 (24), 105 (100), 102 (19), 91 (16), 77 (42), 69 (10), 65 (11), 63 (13), 57 (32), 51 (25). HR-MS: 216.1124 ($C_{14}H_{16}O_2^+$, calc. 216.1151).

Ethyl 2-Butyl-3-phenylcycloprop-2-ene-1-carboxylate (**9b**). Prepared from 1-phenylhex-1-yne (**8b**) [26] and ethyl diazoacetate according to the *General Procedure*. Yield 62.5% after FC (silica gel, CH_2Cl_2/hexane 2:3). B.p. 110°/0.05 Torr. Side-product **12**, 1%.

9b: IR (CH_2Cl_2): 3063*w*, 2965*m*, 2932*m*, 1878*w*, 1714*s*, 1622*w*, 1600*w*, 1447*m*, 1333*m*, 1186*s*, 1017*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.96 (*t*, *J* = 7.4, 3 H); 1.24 (*t*, *J* = 7.0, 3 H); 1.40–1.50 (*m*, 2 H); 1.68–1.76 (*m*, 2 H); 2.43 (*s*, 1 H); 2.67 (*dt*, *J* = 1.5, 7.4, 2 H); 4.10–4.20 (*m*, 2 H); 7.29–7.48 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): 13.6 (*q*); 14.3 (*q*); 22.1 (*d*); 22.4 (*t*); 25.1 (*t*); 29.4 (*t*); 60.0 (*t*); 104.6 (*s*); 110.4 (*s*); 127.1 (*s*; 128.4 (*d*); 128.5 (*d*); 129.2 (*d*); 175.8 (*s*). MS: 245 (5, $[M + 1]^+$), 244 (20), 216 (18), 215 (71), 203 (5), 173 (19), 172 (15), 171 (100), 159 (10), 141 (11), 129 (19), 128 (25), 105 (87), 91 (37), 77 (35), 57 (14), 59 (16).

Ethyl 4-(Hex-1-ynyl)cyclohepta-2,4,6-triene-1-carboxylate (**12**): IR (CH_2Cl_2): 3053*w*, 2960*m*, 2934*m*, 2873*w*, 2224*w*, 1734*s*, 1616*w*, 1466*w*, 1303*m*, 1193*m*, 1042*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.92 (*t*, *J* = 7.0, 3 H); 1.29 (*t*, *J* = 7.2, 3 H); 1.40–1.50 (*m*, 2 H); 1.50–1.60 (*m*, 2 H); 2.34 (*t*, *J* = 6.6, 2 H); 2.59 (*t*, *J* = 5.5, 1 H); 4.24 (*q*, *J* = 7.2, 2 H); 5.39 (*dd*, *J* = 5.5, 4.0, 1 H); 5.45 (*dd*, *J* = 5.5, 3.0, 1 H); 6.10–6.25 (*m*, 2 H); 6.81 (*d*, *J* = 6.2, 1 H). ^{13}C-NMR ($CDCl_3$): 13.6 (*q*); 14.2 (*q*); 19.1 (*t*); 22.0 (*t*); 30.8 (*t*); 43.3 (*d*); 61.1 (*t*); 81.5 (*s*); 91.5 (*s*); 115.8 (*d*); 116.7 (*d*); 125.5 (*d*); 126.1 (*s*); 127.9 (*d*); 134.4 (*d*); 172.7 (*s*). MS: 245 (4, $[M + 1]^+$), 244 (21), 215 (13), 172 (15), 171 (100), 142 (6), 141 (11), 129 (27), 128 (30), 115 (23), 91 (14), 77 (9), 49 (18).

Ethyl 2-Butyl-3-ethoxycycloprop-2-ene-1-carboxylate (**9c**). Synthesized in 37% yield from 1-ethoxyhex-1-yne [27] in the presence of $[Rh_2\{(2S)\text{-mephy}\}_4]$ [5]. Purification by FC (silica gel, CH_2Cl_2). IR (CH_2Cl_2): 3054*w*, 2984*m*, 2935*m*, 2873*w*, 2114*s*, 1922*m*, 1717*s*, 1378*m*, 1187*s*, 1027*m*, 909*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.90 (*t*, *J* = 7.4, 3 H); 1.25 (*t*, *J* = 7.3, 3 H); 1.36 (*t*, *J* = 7.0, 3 H); 1.30–1.40 (*m*, 2 H); 1.42–1.52 (*m*, 2 H); 2.30 (*t*, *J* = 7.7, 2 H); 2.63 (*s*, 1 H); 4.0–4.2 (*m*, 2 H); 4.22 (*q*, *J* = 7.0, 2 H). ^{13}C-NMR ($CDCl_3$): 13.7 (*q*); 14.3 (*q*); 15.0 (*q*); 22.25 (*t*); 22.5 (*t*); 29.5 (*t*); 29.7 (*d*); 60.1 (*t*); 69.3 (*t*); 121.3 (*s*); 133.6 (*s*); 175.1 (*s*). MS: 212 (13, M^+), 183 (27), 171 (14), 169 (24), 155 (38), 139 (12), 115 (21), 113 (16), 111 (14), 109 (14), 99 (12), 97 (18), 91 (15), 87 (21), 84 (100), 81 (26), 71 (18), 69 (29), 57 (52), 55 (23), 54 (15), 49 (26). HR-MS: 212.1400 ($C_{14}H_{20}O_3^+$, calc. 212.1413).

Ethyl 2-Methyl-3-phenylcycloprop-2-ene-1-carboxylate (**9d**). See [2].

Ethyl 2-Butyl-1-methylcycloprop-2-ene-1-carboxylate (**11a**). *Ethyl 2-Diazopropanoate* (**10**) [6]: To a dispersion of NaH (60%; 0.57 g, 14.2 mol) in dry THF (15.0 ml) was added dropwise, at 20°, under N_2, ethyl 2-methyl-3-oxobutanoate (1.0 ml, 6.9 mol) in THF (4.0 ml). *p*-Toluenesulfonyl azide [28] (2.1 g, 10.7 mol) was added within 30 min at 0°. The mixture was stirred at 0° for 30 min and then filtered. Two portions of pentane were added to the filtrate to complete precipitation. The filtrate was washed (sat. NaCl soln.) and dried ($MgSO_4$). After concentration, **10** was purified by distillation (b.p. 20°/0.01 Torr): 0.69 g (78%) of **10**. IR (CH_2Cl_2): 2982*m*, 2085*s*, 1685*s*, 1465*s*, 1371*m*, 1327*m*, 1309*m*, 1137*m*, 1064*w*, 1028*w*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.25 (*t*, *J* = 7.1, 3 H); 1.94 (*s*, 3 H); 4.20 (*q*, *J* = 7.1, 2 H).

11a: To a mixture of hex-1-yne (10.95 g, 133.5 mmol) and $[Rh_2OAc_4]$ (90.1 mg, 0.2 mol) in dry CH_2Cl_2 (30 ml) was added, dropwise within 15 h and under N_2, **10** (1.69 g, 13.2 mmol) in CH_2Cl_2 (4.0 ml). The soln. was stirred for 4 additional h after the addition, then filtered through a silica-gel column. Distillation (60°/0.01 Torr) afforded crude **11a** (44%), which was further purified by FC (silica gel, hexane/Et_2O 1:1) with partial decomposition. Yield 0.55 g (23%). IR (CH_2Cl_2): 3045*w*, 2960*m*, 2932*m*, 2873*w*, 1705*s*, 1466*w*, 1377*w*, 1277*m*, 1115*m*, 1028*w*, 864*w*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.92 (*t*, *J* = 7.4, 3 H); 1.21 (*t*, *J* = 7.0, 3 H); 1.34 (*s*, 3 H); 1.38–1.44 (*m*, 2 H); 1.51–1.58 (*m*, 2 H); 2.46 (*dt*, *J* = 1.1, 7.4, 2 H); 4.05–4.15 (*m*, 2 H); 6.40–6.42 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 13.6 (*q*); 14.3 (*q*); 20.5 (*q*); 22.2 (*t*); 23.9 (*t*); 24.1 (*s*); 28.9 (*t*); 60.1 (*t*); 99.8 (*d*); 121.3 (*s*); 177.5 (*s*). MS: 183 (1, $M + 1]^+$), 182 (0.7), 155 (9), 154 (7), 153 (18), 139 (9), 126 (6), 125 (7), 112 (16), 111 (67), 110 (10), 109 (100), 107 (9), 97 (30), 83 (11), 81 (35), 79 (36), 77 (15), 73 (14), 69 (17), 66 (17), 55 (46), 53 (38), 45 (23).

3. *Rearrangement of Cycloprop-2-ene-1-carboxylates.* 3.1. *General Procedure.* To a mixture of $[Rh_2(pfb)_4]$ (0.01 mmol) in dry refluxing benzene (5.0 ml) were added simultaneously within 15 h solns. of cyclopropenecarboxylate (0.5 mmol) in benzene (5.0 ml) and $[Rh(pfb)_4]$ (0.005 mmol) in benzene (5.0 ml). After the addition, the mixture was heated for 4 additional h to reflux and then filtered under N_2 through a silica-gel column with CH_2Cl_2. ^{1}H-NMR Spectra were obtained with degassed (under N_2) solvents, and GC analyses were effected from the crude reaction mixture to determine the product composition. The rearrangement products were separated by distillation and FC.

3.2. *Rearrangement of* **7a**. According to the *General Procedure*, with **7a** (150 mg, 0.92 mmol). The crude product was filtered though silica gel with CH_2Cl_2 (40 ml) followed by AcOEt (100 ml). The AcOEt fraction (162.7 mg) contained **15a** (79%, by GC). FC (silica gel, CH_2Cl_2/AcOEt 20:1) afforded **15a** (79 mg, 53%), **19a** (10 mg, 7%), and **17a** (6.5 mg, 3%).

*Ethyl (*E*)-(3-Methoxycyclopentylidene)acetate* (**15a**): IR (CH_2Cl_2): 3046*w*, 2982*m*, 2933*m*, 1705*s*, 1654*m*, 1464*w*, 1373*m*, 1347*m*, 1209*s*, 1122*s*, 1090*m*, 1038*m*, 909*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.27 (*t*, *J* = 7.0, 3 H); 1.8–1.9 (*m*, 1 H); 1.9–2.0 (*m*, 1 H); 2.53–2.68 (*m*, 2 H); 2.82–2.95 (*m*, 2 H); 3.23 (*m*, 3 H); 3.87 (*quint.*, *J* = 4.2, 1 H); 4.14 (*q*, *J* = 7.0, 2 H); 5.81 (*quint.*, *J* = 2.2, 1 H). ^{13}C-NMR ($CDCl_3$): 14.3 (*q*); 29.6 (*t*); 31.0 (*t*); 41.5 (*t*); 56.3 (*q*); 59.5 (*t*); 80.4 (*d*); 113.2 (*d*); 165.3 (*s*); 166.5 (*s*). MS: 184 (3, M^+), 153 (9), 152 (54), 139 (24), 138 (22), 126 (16), 125 (13), 124 (33), 123 (24), 107 (34), 106 (15), 98 (13), 95 (23), 80 (22), 79 (100), 78 (18), 77 (26), 67 (20), 53 (25), 51 (10). HR-MS: 184.1084 ($C_{10}H_{10}O_3^+$, calc. 184.1099).

Ethyl 3-(Cyclohepta-2,4,6-trienyl)-6-methoxyhex-2-enoate (**17a**): IR (CH_2Cl_2): 3054*s*, 2927*m*, 1711*s*, 1423*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.28 (*t*, *J* = 7.1, 3 H); 1.65–1.90 (*m*, 2 H); 2.2–2.4 (*m*, 2 H); 2.70–2.85 (*m*, 2 H); 3.30 (*s*, 3 H); 3.39 (*t*, *J* = 6.5, 1 H); 4.16 (*q*, *J* = 7.1, 2 H); 5.20–5.30 (*m*, 2 H); 5.94 (*s*, 1 H); 6.20–6.30 (*m*, 2 H); 6.64–6.68 (*m*, 2 H). MS: 262 (2, M^+), 216 (5), 203 (7), 171 (6), 158 (31), 157 (22), 156 (25), 155 (17), 143 (21), 142 (39), 141 (22), 131 (17), 130 (16), 129 (51), 128 (36), 117 (13), 116 (12), 115 (43), 91 (100), 79 (16), 77 (19), 71 (18), 65 (25), 57 (17), 55 (22), 45 (76). HR-MS: 262.1592 ($C_{16}H_{22}O_3^+$, calc. 262.1569).

*4-(3-Methoxypropyl)furan-2-(5*H*)-one* (**19a**): IR (CH_2Cl_2): 3052*w*, 2927*m*, 2856*w*, 2360*m*, 1779*w*, 1750*s*, 1421*w*, 1115*w*, 896*w*. ^{1}H-NMR (CDCl, 400 MHz): 1.83–1.91 (*m*, 2 H); 2.51 (*t*, *J* = 7.7, 2 H); 3.34 (*s*, 3 H); 3.43 (*t*, *J* = 5.9, 2 H); 4.74–4.76 (*m*, 2 H); 5.83–5.90 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 25.4 (*t*); 27.3 (*t*); 58.7 (*q*); 71.2 (*t*); 73.1 (*t*); 115.5 (*d*); quaternary C's not detected. MS: decomposition.

3.3. *Rearrangement of* **7b**. According to the *General Procedure*, with **7b** (146 mg, 0.64 mmol) and $[Rh_2(pfb)_4]$ (21.6 mg, 0.02 mmol; 3 h reflux after addition). CC of the crude product (CH_2Cl_2/hexane 2:3) afforded **15b** (16 mg, 11%), **17b** (5 mg, 3%), and **20** (56 mg, 38%). Product composition according to GC analysis with internal standard was 15% of **15b**, 6% of **17b**, and 44% of **20**.

*Ethyl (*E*)-(3-Phenylcyclopentylidene)acetate* (**15b**): IR (CH_2Cl_2): 3056*s*, 2962*m*, 2360*m*, 1703*s*, 1652*w*, 1421*m*, 1372*m*, 1212*m*, 1096*m*, 1036*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.29 (*t*, *J* = 7.0, 3 H); 1.77–1.87 (*m*, 1 H); 2.22–2.30 (*m*, 1 H); 2.55–2.65 (*m*, 1 H); 2.71–2.83 (*m*, 1 H); 2.85–2.92 (*m*, 1 H); 3.10–3.20 (*m*, 2 H); 4.17 (*q*, *J* = 7.0, 2 H); 5.86 (*s*, 1 H); 7.19–7.35 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): 14.4 (*q*); 32.4 (*t*); 34.0 (*t*); 43.3 (*t*); 44.3 (*d*); 59.5 (*t*); 112.2 (*d*); 126.3 (*d*); 126.9 (*d*); 128.4 (*d*); 143.7 (*s*); 166.9 (*s*); 167.5 (*s*). MS: 231 (14, $[M + 1]^+$), 230 (81), 201 (7), 185 (27), 158 (13), 157 (100), 156 (30), 155 (18), 142 (19), 129 (28), 128 (18), 115 (23), 98 (20), 91 (60), 77 (20), 53 (17). HR-MS: 230.1320 ($C_{15}H_{18}O_2^+$, calc. 230.1307).

Ethyl 3-(Cyclohepta-2,4,6-trienyl)-6-phenylhex-2-enoate (**17b**): IR (CH_2Cl_2): 3056*w*, 2927*s*, 2855*m*, 1710*s*, 1644*m*, 1454*w*, 1299*w*, 1216*m*, 1161*s*, 1041*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.29 (*t*, *J* = 7.0, 3 H); 1.73–1.82 (*m*, 2 H); 2.31 (*t*, *J* = 5.9, 1 H); 2.66 (*t*, *J* = 8.1, 2 H); 2.78 (*t*, *J* = 7.8, 2 H); 4.17 (*q*, *J* = 7.0, 2 H); 5.20–5.24 (*m*, 2 H); 5.95 (*s*, 1 H); 6.21–6.25 (*m*, 2 H); 6.67 (*t*, *J* = 3.3, 2 H); 7.14–7.18 (*m*, 3 H); 7.23–7.28 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 14.3 (*q*); 30.5 (*t*); 32.4 (*t*); 36.2 (*t*); 46.2 (*d*); 59.7 (*t*); 116.1 (*d*); 122.3 (*d*); 125.3 (*d*); 127.7 (*d*); 128.2 (*d*); 128.4 (*d*); 130.7 (*d*); 142.2 (*s*); 163.4 (*s*); 166.6 (*s*). MS: 309 (1, $[M + 1]^+$), 308 (4), 204 (8), 158 (28), 129 (24), 104 (19), 91 (100), 77 (9), 65 (12). HR-MS: 308.1796 ($C_{21}H_{24}O_2^+$, calc. 308.1776).

*Ethyl (*E*)-(2,3,4,9a-Tetrahydro-1*H*-benzocyclohepten-1-ylidene)acetate* (**20**): IR (CH_2Cl_2): 3005*w*, 2983*m*, 2940*m*, 1706*s*, 1645*m*, 1372*m*, 1269*s*, 1226*s*, 1188*s*, 1149*s*, 1052*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.28 (*t*, *J* = 7.0, 3 H); 1.65–1.75 (*m*, 1 H); 1.75–1.85 (*m*, 1 H); 2.18 (*d*, *J* = 6.0, 1 H); 2.42 (*t*, *J* = 6.0, 2 H); 2.65–2.80 (*m*, 1 H); 3.5–3.6 (*m*, 1 H); 4.16 (*q*, *J* = 7.0, 2 H); 5.10 (*dd*, *J* = 6.0, 9.0, 1 H); 5.73 (*s*, 1 H); 6.0–6.04 (*m*, 1 H); 6.12–8.18 (*m*, 1 H); 6.60 (*t*, *J* = 5.0, 2 H). ^{13}C-NMR ($CDCl_3$): 14.3 (*q*); 24.1 (*t*); 27.4 (*t*); 30.2 (*t*); 47.9 (*d*); 59.6 (*t*); 116.8 (*d*); 119.5 (*d*); 122.5 (*d*); 123.9 (*d*); 128.8 (*d*); 130.2 (*d*); 136.2 (*s*); 161.8 (*s*); 166.6 (*s*). MS: 231 (9, $[M + 1]^+$), 230 (53), 202 (30), 201 (60), 185 (44), 184 (68), 173 (20), 157 (38), 156 (32), 155 (83), 143 (24), 142 (48), 141 (59), 130 (19), 129 (100), 128 (89), 127 (26), 126 (25), 117 (32), 116 (21), 115 (72), 91 (73), 77 (31), 65 (21), 63 (19), 51 (25). HR-MS: 230.1317 ($C_{15}H_{18}O_2^+$, calc. 230.1307).

3.4. *Rearrangement of* **9a**. According to the *General Procedure*, with **9a** (155 mg, 0.72 mmol) and $[Rh(pfb)_4]$ (45.6 mg, 0.043 mmol; 5 h reflux after addition). The crude product was bulb-to-bulb distilled (100–170°/$1 \cdot 10^{-4}$

Torr): 115 mg of an oil. ^{1}H-NMR with benzaldehyde as internal standard revealed the following product composition: **21a** 19%, **22a** 7%, **23a** 3%, and **26a** 37%. FC (silica gel, CH_2Cl_2/hexane 1:1) afforded **26a** (43 mg, 28%). The other compounds decomposed upon attempted isolation.

Ethyl (2Z,4Z)-3-Phenylhexa-2,4-dienoate (**26a**): IR (CH_2Cl_2): 3050*w*, 3000*w*, 2983*w*, 1715*s*, 1594*w*, 1444*w*, 1368*w*, 1270*s*, 1223*m*, 1164*s*, 1035*w*, 879*w*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.09 (*t*, *J* = 7.3, 3 H); 1.49 (*dt*, *J* = 7.4, 1.8, 3 H); 4.01 (*q*, *J* = 7.3, 2 H); 5.83 (*dq*, *J* = 11.8, 7.4, 1 H); 5.93 (*s*, 1 H); 6.06–6.10 (*dm*, *J* = 11.8, 1 H); 7.20–7.23 (*m*, 2 H); 7.30–7.38 (*m*, 3 H). ^{13}C-NMR ($CDCl_3$): 13.9 (*q*); 14.7 (*q*); 59.8 (*t*); 119.7 (*d*); 127.6 (*d*); 127.7 (*d*); 127.8 (*d*); 131.2 (*d*); 132.3 (*d*); 139.3 (*s*); 153.1 (*s*); 166.1 (*s*). MS: 218 (10, $[M+2]^+$), 217 (65), 216 (52), 202 (10), 201 (65), 187 (32), 173 (48), 172 (10), 171 (55), 170 (10), 169 (38), 144 (11), 143 (58), 142 (51), 141 (58), 129 (33), 128 (100), 127 (18), 116 (11), 115 (64), 102 (17), 91 (32), 89 (11), 77 (25), 65 (26), 51 (33), 50 (11). HR-MS: 216.1167 ($C_{14}H_{16}O_2^+$, calc. 216.1150).

Characteristic ^{1}H-NMR signals of the other products in crude mixture: *5-Ethoxy-3-ethyl-2-phenylfuran* (**21a**): 2.64 (*q*, *J* = 7.5, 2 H); 5.18 (*s*, 1 H). *5-Ethoxy-2-ethyl-3-phenylfuran* (**22a**): 5.28 (*s*, 1 H). *Ethyl 4-Oxo-3-phenylhex-2-enoate* (**23a**): 6.83 (*s*, 1 H).

3.5. *Rearrangement of* **9b**. According to the *General Procedure*, with **9b** (218.5 mg, 0.90 mmol) and $[Rh_2(pfb)_4]_4$ (36.6 mg, 0.035 mmol; 3 h reflux after addition). The filtrate was bulb-to-bulb distilled (150–250°/2 · 10^{-3} Torr). An oil (183 mg) containing 7 components was collected which were separated by repeated FC (silica gel, CH_2Cl_2/hexane 1:1): **9b** (17.5 mg, 8%), **21b** and its oxidation product, **25** (37.9 mg, 17%), **23b** (13.8 mg, 6%), **24** (6.9 mg, 3%), **30b** (18.5 mg, 9%), and **26b** (66.6 mg, 31%). Furan **21b** was isolated after conversion *via* air oxidation to **25**, which was purified by prep. TLC (silica gel, CH_2Cl_2/hexane 4:1).

3-Butyl-5-ethoxy-2-phenylfuran (**21b**): ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.7–0.9 (*t*, 3 H); 1.2–1.7 (*m*, 4 H); 1.42 (*t*, *J* = 7.0, 3 H); 2.60 (*t*, *J* = 7.3, 2 H); 4.11 (*q*, *J* = 7.0, 2 H); 5.15 (*s*, 1 H); 7.1–7.6 (*m*, 5 H).

Ethyl 3-Benzoylhept-2-enoate (**25**): IR (CH_2Cl_2): 3054*s*, 2928*s*, 1713*s*, 1672*m*, 1421*m*, 1197*m*, 1034*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.90 (*t*, *J* = 7.4, 3 H); 1.03 (*t*, *J* = 7.2, 3 H); 1.30–1.42 (*m*, 2 H); 1.48–1.55 (*m*, 2 H); 2.40 (*dt*, *J* = 1.6, 7.8, 2 H); 3.97 (*q*, *J* = 7.2, 2 H); 5.98 (*t*, *J* = 1.6, 1 H); 7.44–7.49 (*m*, 2 H); 7.55–7.60 (*m*, 1 H); 7.87–7.92 (*m*, 2 H). MS: 261 (4, $[M+1]^+$), 260 (15), 232 (14), 215 (30), 214 (47), 187 (22), 186 (15), 185 (23), 172 (21), 105 (100), 77 (45). HR-MS: 260.1398 ($C_{16}H_{20}O_3^+$, calc. 260.1412).

Ethyl (Z)-3-Phenyl-4-oxooct-2-enoate (**23b**): IR (CH_2Cl_2): 3065*w*, 2960*m*, 2940*m*, 2320*w*, 1711*s*, 1610*m*, 1370*m*, 1185*s*, 1028*m*, 808*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.89 (*t*, *J* = 7.4, 3 H); 1.30 (*t*, *J* = 7.2, 3 H); 1.2–1.4 (*m*, 2 H); 1.68 (*quint.*, *J* = 7.7, 2 H); 2.66 (*t*, *J* = 7.7, 2 H); 4.21 (*q*, *J* = 7.2, 2 H); 6.15 (*s*, 1 H); 7.3–7.6 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): 13.9 (*q*); 14.1 (*q*); 22.2 (*t*); 25.2 (*t*); 42.5 (*t*); 60.9 (*t*); 115.8 (*d*); 126.7 (*d*); 129.1 (*d*); 130.4 (*d*); 133.3 (*s*); 158.4 (*s*); 165.4 (*s*); 206.6 (*s*). MS: 261 (2, $[M+1]^+$), 260 (7), 245 (16), 215 (19), 214 (12), 204 (11), 203 (62), 187 (34), 176 (13), 175 (100), 172 (20), 148 (11), 147 (47), 131 (23), 105 (28), 103 (29), 102 (45), 85 (31), 77 (27), 69 (24), 57 (56). HR-MS: 260.1423 ($C_{12}H_{20}O_3^+$, calc. 260.1412).

Ethyl (E)-3-Phenyl-4-oxooct-2-enoate (**24**): ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.84 (*t*, *J* = 7.0, 3 H); 1.06 (*t*, *J* = 7.0, 3 H); 1.17–1.40 (*m*, 2 H); 1.56 (*quint.*, *J* = 7.4, 2 H); 2.55 (*t*, *J* = 7.4, 2 H); 4.03 (*q*, *J* = 7.0, 2 H); 6.69 (*s*, 1 H); 7.15–7.20 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): 13.8 (*q*); 13.9 (*q*); 22.2 (*t*); 26.0 (*t*); 40.1 (*t*); 60.8 (*t*); 125.6 (*d*); 128.4 (*d*); 128.5 (*d*); 134.8 (*s*); 151.4 (*s*); 165.5 (*s*); 201.7 (*s*).

Ethyl (E)-(3-Methyl-2-phenylcyclopentylidene)acetate (**30b**): ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.68 (*d*, *J* = 7.0, 3 H); 0.86 (*t*, *J* = 7.4, 3 H); 1.60–1.75 (*m*, 1 H); 1.9–2.1 (*m*, 1 H); 2.3–2.4 (*m*, 1 H); 2.9–3.2 (*m*, 2 H); 3.8–3.9 (*m*, 1 H); 4.14 (*dq*, *J* = 1.8, 7.4, 2 H); 5.66–5.68 (*m*, 1 H); 7.05–7.15 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): 14.3 (*q*); 15.7 (*q*); 31.7 (*t*); 32.0 (*t*); 38.8 (*d*); 57.9 (*d*); 59.5 (*t*); 114.5 (*d*); 127.7 (*d*); 127.8 (*d*); 128.1 (*d*); 139.3 (*s*); 166.8 (*s*); 170.5 (*s*).

Ethyl (2Z,4Z)-3-Phenylocta-2,4-dienoate (**26b**): IR (CH_2Cl_2): 3105*w*, 2961*m*, 1715*s*, 1620*w*, 1593*w*, 1369*w*, 1283*w*, 1226*m*, 1163*s*, 1035*w*, 882*w*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.79 (*t*, *J* = 7.1, 3 H); 1.08 (*t*, *J* = 7.1, 3 H); 1.2–1.4 (*m*, 2 H); 1.83 (*dq*, *J* = 1.6, 7.5, 2 H); 4.01 (*q*, *J* = 7.1, 2 H); 5.71 (*dt*, *J* = 11.6, 7.5, 1 H); 5.91 (*s*, 1 H); 6.06 (*dq*, *J* = 11.6, 1.7, 1 H); 7.18–7.38 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): 13.6 (*q*); 13.9 (*q*); 22.8 (*t*); 30.6 (*t*); 59.9 (*t*); 119.5 (*d*); 127.78 (*d*); 127.82 (*d*); 127.95 (*d*); 130.3 (*d*); 138.4 (*d*); 139.4 (*s*); 153.5 (*s*); 166.2 (*s*). MS: 245 (4, $[M+1]^+$), 244 (20), 201 (100), 173 (56), 155 (11), 141 (23), 129 (15), 128 (11), 115 (13), 91 (16), 77 (6). HR-MS: 244.1454 ($C_{16}H_{20}O_2^+$, calc. 244.1463).

3.6. *Rearrangement of* **9c**. According to the *General Procedure*, with **9c** (95.8 mg, 0.45 mmol) and $[Rh_2(pfb)_4]$ (24 mg, 0.023 mmol; 2 h reflux after addition). GC analysis of the crude mixture revealed the presence of 3 products which were separated by FC (silica gel, CH_2Cl_2/hexane 1:1): **28** (48 mg, 50%), **29** (22 mg, 22%), and **31** (20 mg, 26%). The structure of **31** was confirmed by independent synthesis [29].

Ethyl (2E,4Z)-3-Ethoxyocta-2,4-dienoate (**28**): IR (CH_2Cl_2): 3058*w*, 2984*m*, 2932*m*, 1700*s*, 1643*m*, 1577*s*, 1393*w*, 1147*s*, 1055*s*, 909*m*, 814*w*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.92 (*t*, *J* = 7.7, 3 H); 1.26 (*t*, *J* = 7.0, 3 H); 1.39 (*t*, *J* = 7.0, 3 H); 1.35–1.45 (*m*, 2 H); 2.35–2.41 (*m*, 2 H); 3.88 (*q*, *J* = 7.0, 2 H); 4.13 (*q*, *J* = 7.0, 2 H); 5.02 (*s*, 1 H); 5.85

(*dt*, *J* = 11.8, 7.5, 1 H); 6.95 (*d*, *J* = 11.8, 1 H). ^{13}C-NMR ($CDCl_3$): 13.8 (*q*); 14.3 (*q*); 14.4 (*q*); 22.7 (*t*); 32.0 (*t*); 59.4 (*t*); 63.7 (*t*); 92.3 (*d*); 121.5 (*d*); 140.5 (*d*); 167.3 (*s*); 168.4 (*s*). MS: 212 (16, M^+), 160 (100), 167 (28), 141 (34), 139 (12), 113 (24), 97 (31), 96 (61), 95 (25), 91 (15), 86 (20), 84 (33), 81 (33), 69 (25), 55 (22), 53 (21). HR-MS: 212.1421 ($C_{12}H_{20}O_3^+$, calc. 212.1413).

*Ethyl (2*E*,4*E*)-3-Ethoxyocta-2,4-dienoate* (**29**) from mixture with **28**: ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.93 (*t*, *J* = 7.4, 3 H); 1.27 (*t*, *J* = 7.0, 3 H); 1.38 (*t*, *J* = 7.0, 3 H); 1.43–1.53 (*m*, 2 H); 2.14–2.22 (*m*, 2 H); 3.87 (*q*, *J* = 7.0, 2 H); 4.14 (*q*, *J* = 7.0, 2 H); 4.98 (*s*, 1 H); 6.54 (*dt*, *J* = 15.4, 7.1, 1 H); 7.33 (*d*, *J* = 15.4, 1 H). ^{13}C-NMR ($CDCl_3$): 13.7 (*q*); 14.2 (*q*); 14.4 (*q*); 21.9 (*t*); 34.8 (*t*); 59.3 (*t*); 63.6 (*t*); 90.9 (*d*); 122.5 (*d*); 139.0 (*d*); quaternary C's not observed.

Ethyl Cyclohepta-2,4,6-triene-1-carboxylate (**31**): IR (CH_2Cl_2): 3091*w*, 2983*w*, 1733*s*, 1369*m*, 1303*m*, 1216*m*, 1192*m*, 1173*m*, 1090*m*, 860*w*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.31 (*t*, *J* = 7.0, 3 H); 2.54 (*t*, *J* = 5.5, 1 H); 4.26 (*q*, *J* = 7.0, 2 H); 5.42–5.46 (*dd*, 2 H); 6.2–6.3 (*m*, 2 H); 6.66 (*t*, *J* = 3.1, 2 H). ^{13}C-NMR ($CDCl_3$): 14.2 (*q*); 44.1 (*d*); 61.0 (*t*); 117.2 (*d*); 125.6 (*d*); 130.9 (*d*); 173.0 (*s*). MS: 164 (6, M^+), 118 (4), 92 (9), 91 (100), 90 (6), 77 (13). HR-MS: 164.0823 ($C_{10}H_{12}O_3^+$, calc. 164.0837).

3.7. *Rearrangement of* **11a**. According to the *General Procedure*, with **11a** (57 mg, 0.31 mmol) and $[Rh_2(pfb)_4]$ (8 mg, 0.008 mmol; 2 h reflux after addition). ^{1}H-NMR analysis of the crude product revealed the following composition: **32a** 55.2%, **34** 6.8%, and **35** 5.2%. Bulb-to-bulb distillation of the crude product afforded pure **33a** (hydrolysis product of **32a**; 22.1 mg, 46%). The products were separated by chromatography (silica gel, CH_2Cl_2/hexane 3:2) in low yield owing to partial decomposition.

*4-Butyl-3-methylfuran-2-(5*H*)-one* (**33a**): IR (CH_2Cl_2): 3066*w*, 2932*w*, 2865*w*, 2360*w*, 1749*s*, 1676*w*, 1449*w*, 1340*w*, 1268*m*, 1083*m*, 1030*m*, 762*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.94 (*t*, *J* = 7.4, 3 H); 1.34–1.40 (*m*, 2 H); 1.45–1.52 (*m*, 2 H); 1.82 (*s*, 3 H); 2.41 (*t*, *J* = 7.7, 2 H); 4.66 (*s*, 2 H). ^{12}C-NMR ($CDCl_3$): 8.5 (*q*); 13.7 (*q*); 22.6 (*t*); 26.8 (*t*); 29.7 (*t*); 71.4 (*t*); 122.8 (*s*); 160.5 (*s*); 175.5 (*s*). MS: 154 (8, M^+), 126 (11); 125 (78), 112 (4), 98 (5), 97 (5), 81 (10), 69 (5), 56 (5), 55 (100), 53 (16). HR-MS: 154.1017 ($C_9H_{14}O_2^+$, calc. 154.0993).

*Diethyl (2*E*,4*E*,6*E*)-3,6-Dibutyl-2,7-dimethylocta-2,4,6-trienedioate* (**34**): IR (CH_2Cl_2): 2959*m*, 2361*m*, 1704*s*, 1221*s*, 1099*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.93 (*t*, *J* = 7.0, 6 H); 1.34 (*t*, *J* = 7.4, 6 H); 1.22–1.35 (*m*, 4 H); 1.35–1.45 (*m*, 4 H); 2.00 (*s*, 6 H); 2.36 (*t*, *J* = 8.1, 4 H); 4.22 (*q*, *J* = 7.0, 4 H); 7.14 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$): 13.9 (*q*); 14.3 (*q*); 16.5 (*q*); 23.0 (*t*); 28.9 (*t*); 30.7 (*t*); 60.4 (*t*); 127.3 (*s*); 129.2 (*d*); 144.4 (*s*); 169.9 (*s*). MS: 365 (20, $[M + 1]^+$), 364 (88), 335 (16), 290 (22), 289 (100), 273 (26), 261 (75), 233 (16), 175 (20), 119 (17), 105 (17), 95 (22), 91 (26), 55 (39), 53 (16). HR-MS: 364.2594 ($C_{22}H_{36}O_4^+$, calc. 364.2613).

*Diethyl (2*E*,4*Z*,6*E*)-3,6-Dibutyl-2,7-dimethylocta-2,4,6-trienedioate* (**35**): IR (CH_2Cl_2): 2960*m*, 2360*w*, 1703*s*, 1465*w*, 1367*w*, 1276*m*, 1212*m*, 1095*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.85 (*t*, *J* = 7.3, 6 H); 1.27 (*t*, *J* = 7.0, 6 H); 1.20–1.40 (*m*, 8 H); 1.91 (*s*, 6 H); 2.25 (*t*, *J* = 8.1, 4 H); 4.15 (*q*, *J* = 7.0, 4 H); 6.39 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$): 13.8 (*q*); 14.2 (*q*); 15.2 (*q*); 22.8 (*t*); 30.3 (*t*); 33.9 (*t*); 60.2 (*t*); 124.7 (*s*); 130.3 (*d*); 147.9 (*s*); 168.9 (*s*). MS: 365 (23, $[M + 1]^+$), 364 (95), 291 (21), 290 (22), 289 (100), 273 (31), 262 (19), 261 (91), 233 (20), 175 (30), 119 (23), 105 (25), 95 (29), 91 (36), 79 (20), 77 (24), 67 (20), 57 (26), 55 (58), 53 (24). HR-MS: 364.2623 ($C_{22}H_{36}O_4^+$, calc. 364.2613).

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