33. Structural Effects on the Rh^{II}-Catalyzed Rearrangement of Cyclopropenes

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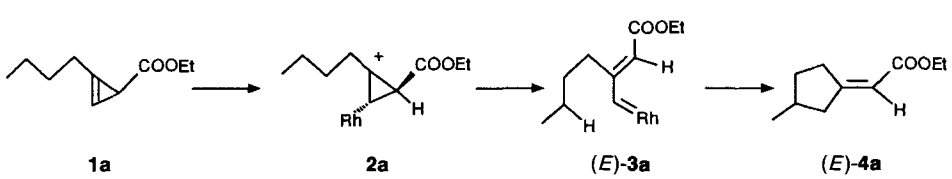
The thermocatalytic rearrangement of 2-alkylcycloprop-2-ene-1-carboxylates (**1**) in the presence of Rh^{II} perfluorobutyrate is regio- and stereospecific and leads to the less substituted metallocarbenes **3**. The latter undergo intramolecular C–H bond insertion to form cyclopentylidenes (**4**). In contrast, the metallocarbenes **19**, derived from 2,3-dialkylcycloprop-2-ene-1-carboxylates **6c**, **d**, react to dienes (*Z*)-**20**, *via* 1,2-H migration. The cyclopropenedicarboxylates **10**, in turn, rearrange exclusively to the more substituted metallocarbenes **26**, which cyclize to furans **28**. With **6e** and **12**, products derived from both modes of ring-opening are observed.

Introduction. – The product distribution of the thermocatalytic ring-opening of substituted cyclopropenes in the presence of Rh^{II} varies significantly with the substituents of the cyclopropene [1]. The reactions are often highly chemo-, regio-, and stereoselective. Mechanistically, they are believed to proceed *via* Rh-complexed vinylcarbenes [2] [3]. A rapid equilibrium between the possible regio- and stereoisomeric vinylcarbene intermediates has been proposed to account for the selectivity of the rearrangements.

Recently, we reported the stereospecific rearrangement of ethyl 2-butylcycloprop-2-enecarboxylate (**1a**) in the presence of Rh^{II} perfluorobutyrate, $Rh_2(PFB)_4$ [1]. The reaction proceeds *via* electrophilic attack of the catalyst *trans* to the EtOCO substituent at the less substituted center to the more stable cyclopropyl cation **2a** (*Scheme 1*). Disrotatory ring opening of **2a** leads to the Rh-complexed vinylcarbene (*E*)-**3a**. The latter undergoes insertion into one of the C–H bonds of the alkly substituent, which results in formation of the (*E*)-cyclopentylidene **4a**. The (*Z*)-isomer of **4a** is not observed upon rearrangement of **1a**.

Scheme 1

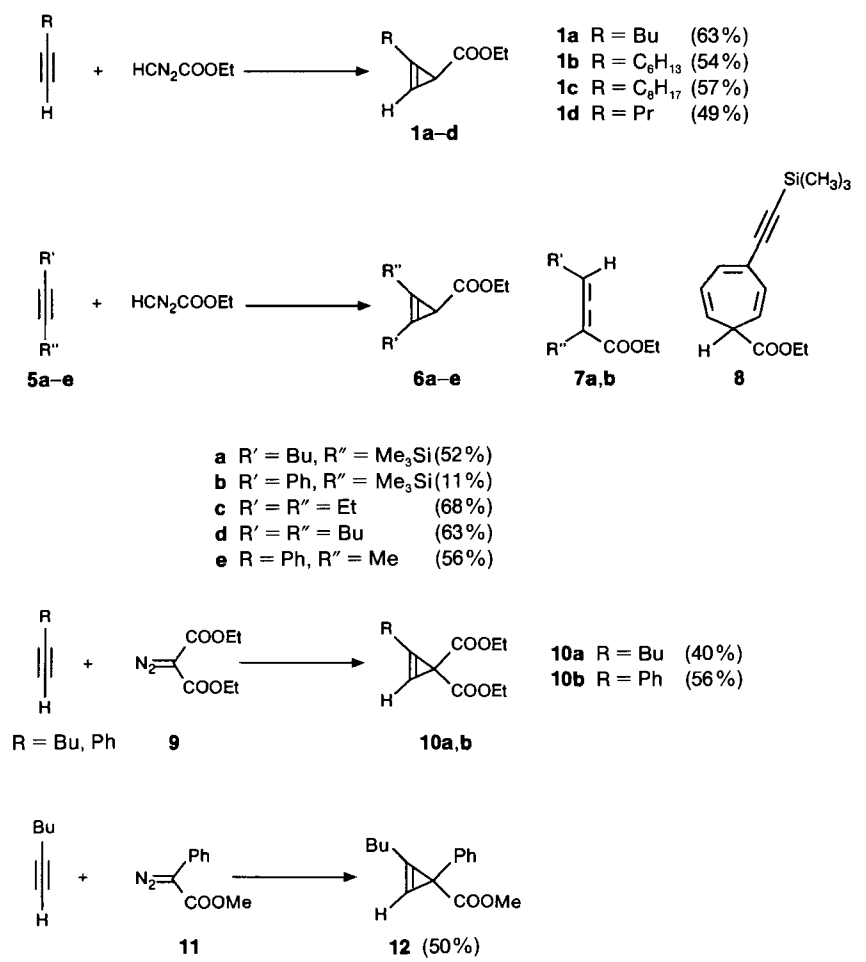


1a **2a** (*E*)-**3a** (*E*)-**4a**

The formation of a cyclopentylidene upon rearrangement of **4a** is of some mechanistic interest, because, contrary to other rearrangement products of cyclopropenes for which ionic mechanism may be invoked or, at least may not be ruled out [1] [4] [5], the cyclopentylidene **4a** *must* originate from a carbene. We have now investigated the Rh^{II}-catalyzed rearrangement of some other cyclopropenes in order to establish the preferred reaction pathways in function of their substituents.

Results and Discussion. – *Synthesis of Cyclopropenecarboxylates.* The cyclopropenes **1a–1d** and **6a–6e** were synthesized by slow addition of ethyldiazoacetate to an excess of the appropriate alkyne in dichloromethane, in the presence of a catalytic amount of $Rh_2(OAc)_4$ [6] (*Scheme 2*). Most of the compounds are known, and their synthesis by similar procedures is reported in the literature (see *Exper. Part*). The cyclopropanation of (phenyl)(trimethylsilyl)acetylene **5b** proceeded with mediocre yields and was accompanied by an unexpected secondary product, isolated in *ca.* 10% yield. The IR and ^{13}C-NMR spectra indicated the presence of an allene of structure **7b**. Allene **7a** was also observed upon cyclopropanation of 1-(trimethylsilyl)hex-1-yne (**5a**). In the case of **7a**, the olefinic proton resonates at 5.24 ppm as a *triplet*, which indicates that it must be adjacent to a methylene group and not attached to the C-atom bearing the EtOCO substituent, where it was in the ethyl diazoacetate. This product cannot be formed by direct reaction

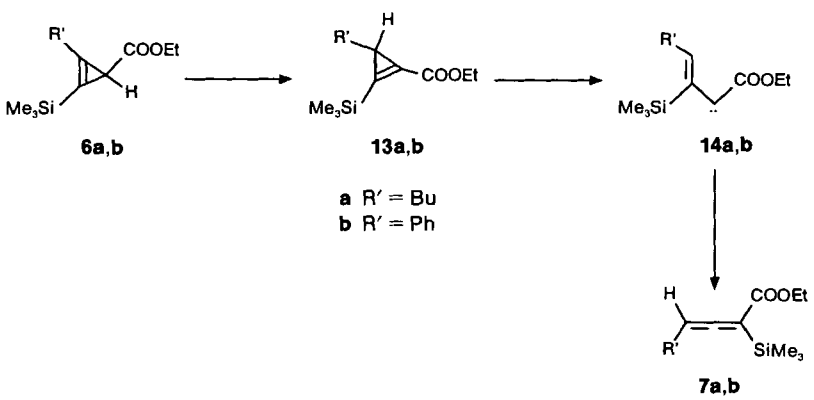
Scheme 2



of the carbene derived from ethyl diazoacetate with **5a**, but must originate from some rearrangement, whereby the H and the Me_3Si substituents exchange positions. The rearrangement does not require the presence of the Rh^{II} catalyst, since no allenes are formed in the Rh^{II}-catalyzed rearrangements of cyclopropenes (see below). The structure of the Ph-substituted allene **7b** is not unambiguously established but follows from the similarity of the ^1H- and ^{13}C-NMR data of the olefinic proton and the allenic C-atoms (see *Exper. Part*).

Allene formation upon Cu-catalyzed addition of ethyl diazoacetate to terminal acetylenes has been reported previously, and rationalized in terms of an 1,3-dipolar cycloaddition of the diazo compound to the C≡C bond leading to an intermediate pyrazoline [7]. This interpretation provides, however, no explanation of the rearrangement found in the case of **7**. Although we have made no mechanistic investigations in this direction, a plausible pathway may be proposed as depicted in *Scheme 3*. The initially

Scheme 3



formed cyclopropene **6** rearranges to the isomeric cyclopropene **13** which, in turn, undergoes ring-opening to a vinylcarbene **14**. The allene **7** is then obtained *via* 1,2-Me_3Si migration. Cyclopropene isomerizations analogous to that of **6** to **13** reportedly occur under very mild conditions (chromatography on silica gel) [3].

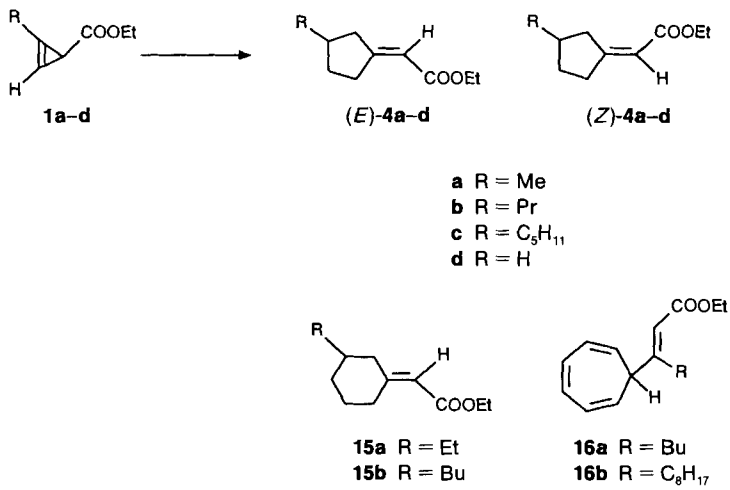
The cyclopropenation of **5b** affords, in addition, another secondary product, identified as the 4-substituted cyclopheptatriene-carboxylate **8**, which originates from Rh^{II}-catalyzed addition of ethyl diazoacetate to the Ph substituent of the acetylene. Cycloheptatriene formation *via* reaction of metal-complexed carbenes including Cu^I [8] and Rh^{II} [9] with benzene is a known reaction.

Diazomalonate (**9**) required for the synthesis of **10a** and **10b**, was prepared by diazo transfer from *p*-toluenesulfonyl azide to diethyl malonate in the presence of Et_2NH [10]. The diazoester **11**, used for the preparation of **12**, in turn was synthesized *via* diazo transfer from *p*-toluenesulfonyl azide to phenylacetate in the presence of LDA, a method developed by *Davies et al.* [11] for the preparation of vinyldiazomethanes.

Cyclopropene Rearrangements Catalyzed by $Rh_2(PFB)_4$. When ethyl 2-butylcycloprop-2-ene-1-carboxylate (**1a**) was heated in benzene with $Rh_2(PFB)_4$ (8%, added in three

portions), the (*E*)-cyclopentylidene **4a** was formed in 30–35% yield (*Scheme 4*). The yield of the reaction increased to 44%, when the cyclopropene was added to the catalyst (3.4 mol-%) in refluxing benzene by means of a syringe pump over 13 h. Other solvents such as $CHCl_3$, 1,2-dichloroethane, toluene, and xylene were found less effective. $Rh_2(OAc)_4$ (3.8%) in boiling benzene and $Rh_2(NHCOCH_3)_4$ (2%) in boiling xylene were significantly less efficient and afforded the cyclopentylidene **4a** in a yield of only 5 and 11%, respectively. No other volatile products were detected in the reaction mixture.

Scheme 4



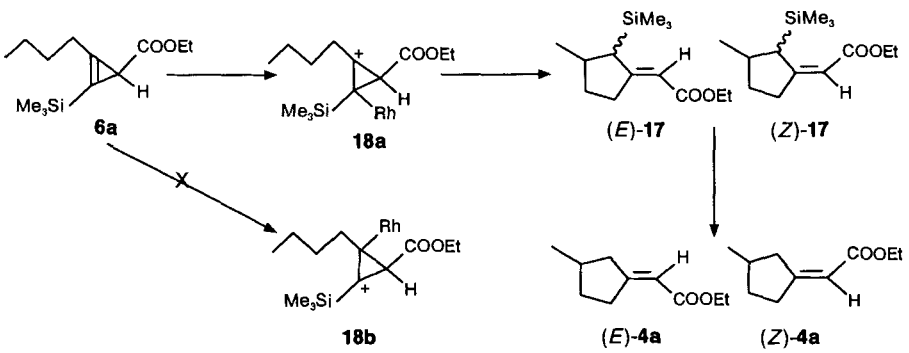
The rearrangement of ethyl 2-octylcycloprop-2-ene-1-carboxylate (**1c**) proceeded in analogy to that of the 2-butyl derivative **1b**, which has been reported previously [1]. The (*E*)-cyclopentylidene (**4c**) was the major product (19.5%). In addition, according to NMR analysis and MS, the volatile fraction of the reaction mixture contained the (*Z*)-isomer of **4c** (1%), the cyclohexylidene **15b** (6%), and the cycloheptatriene **16b** (20%). Compound **16b** originates from the reaction of the intermediate vinyl carbene with the solvent. The configuration of the C=C bond of **15b** and **16b** is not established, but is assumed to be (*E*). The cycloheptatriene **16a** has previously been isolated upon rearrangement of **1a** in benzene, but apparently escaped detection in the case of **1b** [1].

If the chain length of the alkyl substituent was reduced to Pr (see **1d**), the yield of the corresponding cyclopentylidene (**4d**) dropped to 15% at most. The low yield of **4d** precluded its isolation in pure form. The compound was, therefore, identified by comparison of the NMR spectrum of the reaction mixture with that of an authentic sample, prepared from cyclopentanone *via* a *Wittig-Horner* reaction [12], and the yield was determined by GC analysis. The low yield of insertion product from **1d** is consistent with the preference of metallocarbenes for insertion into secondary over primary C–H bonds.

With ethyl 2-butyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (**6a**), the rearrangement proceeded by analogy and led to a mixture of two inseparable, stereoisomeric,

silylated cyclopentylidenes (*E*)-**17** and (*Z*)-**17** in a 2.5:1 ratio (*Scheme 5*). Desilylation of the mixture with TBAF in moist THF afforded the corresponding mixture of (*E*)- and (*Z*)-cyclopentylidenes (**4a**). The latter were identified by co-injection of authentic (*E*)-**4a** and of an independently prepared (*E*)/(*Z*)-mixture in the capillary GC, and by comparison of the NMR data. This result is fully consistent with the mechanism proposed in *Scheme 1*. Attack of the cyclopropene by the Rh catalyst results in preferential formation of the tertiary carbenium ion **18a**, which is more stable than the isomeric, Me_3Si-substituted carbenium ion **18b**. No rearrangement occurred, when the (trimethylsilyl)(phenyl)-acetylene (**5b**) was heated in refluxing benzene in the presence of $Rh_2(PFB)_4$. The starting material was recovered unchanged even when heating was prolonged to 24 h. In refluxing xylene, **6b** decomposed, and no rearrangement products were isolated.

Scheme 5



Ring-opening of the symmetrically substituted diethylcyclopropene-carboxylate **6c** in either direction leads to the same metallocarbene **19** (*Scheme 6*). The latter suffers 1,2-H migration to afford a 7.5:1 mixture of (*Z*)- and (*E*)-dienes **20a** and **b** [1]. The metallocarbene **19** derived from the dibutyl derivative **6d** may undergo the same process to **20c, d** or insert into one of the C–H bonds of the alkyl substituent to give a cyclopentylidene **21**. Only H migration occurred upon rearrangement with $Rh_2(PFB)_4$ in benzene, leading to a 6:1 (*Z*)/(*E*)-mixture of dienes **20c, d** in 88% yield. The (*E*)-configuration of the α,β-C=C bond in **20** was assigned on the grounds of the chemical shift of the olefinic H-atom at C(1) and the CH_2 group of the Et and Bu substituent, respectively, at C(3) (*Table*). For comparison, the CH_2 group of methyl (2*E*,4*E*)-3-ethylhexa-2,4-dienoate resonates at 2.82 ppm and the olefinic proton at 5.72 ppm [4]. In the (2*Z*,4*E*)-isomer the corresponding signals are shifted to 2.36 and 5.58 ppm [4]. For **20a** and **20b**, the CH_2 group appears at 2.68 and 2.65 and the olefinic proton at 5.66 and 5.64 ppm, respectively, which is in agreement with the (2*E*)-configuration of the reference compound. If the intermediate metallocarbenes had (2*Z*)-configuration, they would probably react further to furans, rather than to dienes. The reasons for the preference for (*Z*)-configuration at the C(4)=C(5) bond has been discussed previously [1].

When ethyl 2-methyl-3-phenylcycloprop-2-ene-1-carboxylate (**6e**) was rearranged with Rh^{II}, products derived from both regioisomeric (*Z*)-metallocarbenes **22a** and **22b** were isolated, while no products derived from the (*E*)-stereoisomers could be detected.

Scheme 6

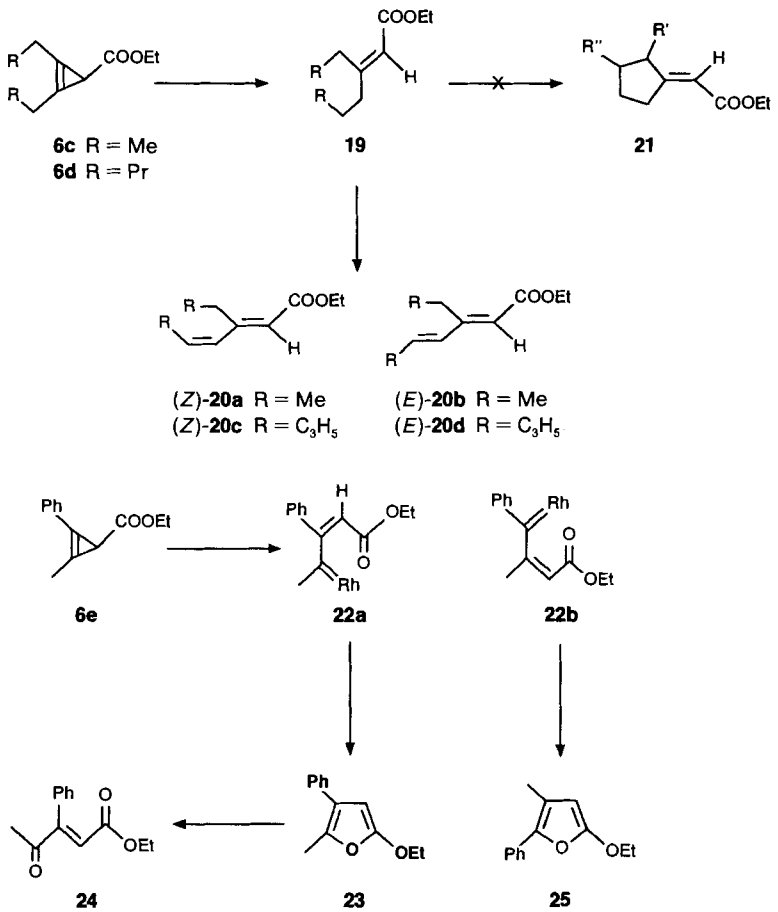
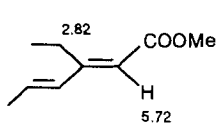
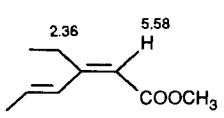
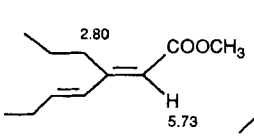
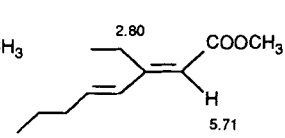
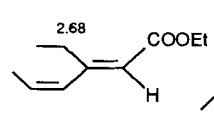
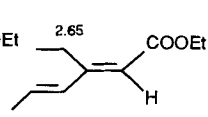
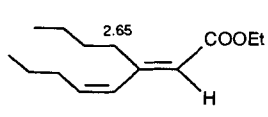
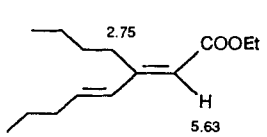


Table. *^{1}H-NMR Chemical Shifts* [ppm]

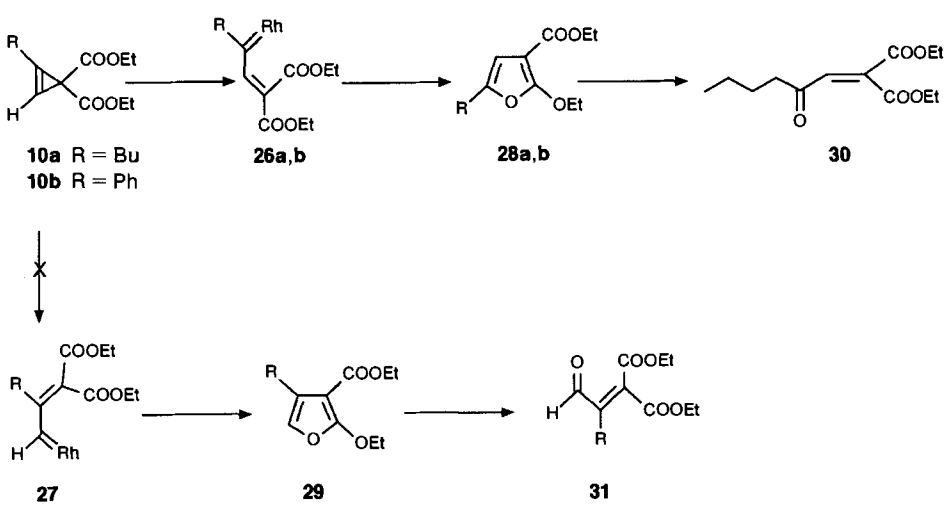
			
methyl (2*Z*,4*E*)-**20b**[a])	methyl (2*E*,4*E*)-**20b**[a])	(2*Z*,4*E*)[a])	(2*Z*,4*E*)[a])
			
(2*Z*,4*Z*)-**20a**	(2*Z*,4*E*)-**20b**	(2*Z*,4*Z*)-**20c**	(2*Z*,4*E*)-**20d**

[a]) From [4].

After simultaneous addition of cyclopropene **6e** and catalyst over 24 h to refluxing benzene, the reaction mixture contained 20% of unreacted **6e**, 2-ethoxy-5-methyl-4-phenylfuran (**23**; 10%), its oxidation product ethyl 4-oxo-3-phenylpent-2-eneoate [13] (**24**; 10%), and 2-ethoxy-4-methyl-5-phenylfuran (**25**; 20%), all identified by comparison of their NMR data with those reported in the literature [13]. That a furan is obtained from the Ph-stabilized vinylcarbene (**22b**) is plausible, since there is no pathway for formation of any other stable product available from **22b** except that for cyclization to the furan **25**. Furan formation requires (*Z*)-configuration of the metallocarbene and carboxylate groups, as in **22a** and **22b**. Although the Me-stabilized vinylcarbene (**22a**) or its (*E*)-isomer could suffer 1,2-H migration to a diene in competition with furan formation, the former pathway is not followed, and only products originating from **22a** and **22b** are obtained. 1,2-H migration is clearly not competitive with cyclization to a furan in this case. This is remarkable in the light of the high yield isomerization of cyclopropene carboxylates of structural type **6c** and **6d** to dienes, which proceeds *via* a vinylcarbene having (*E*)-configuration. In contrast, in the thermocatalytic rearrangement of **6e** with Cu^I reportedly [14] the furan **25**, which derives from the Ph-substituted carbene **22b**, is favored over **23** by *ca.* 20:1. It is worth mentioning in this context that the photochemical rearrangement of **6e**, which proceeds through an excited singlet state, produces only the furan **23**, which originates from the Me-substituted carbene **22a** [13].

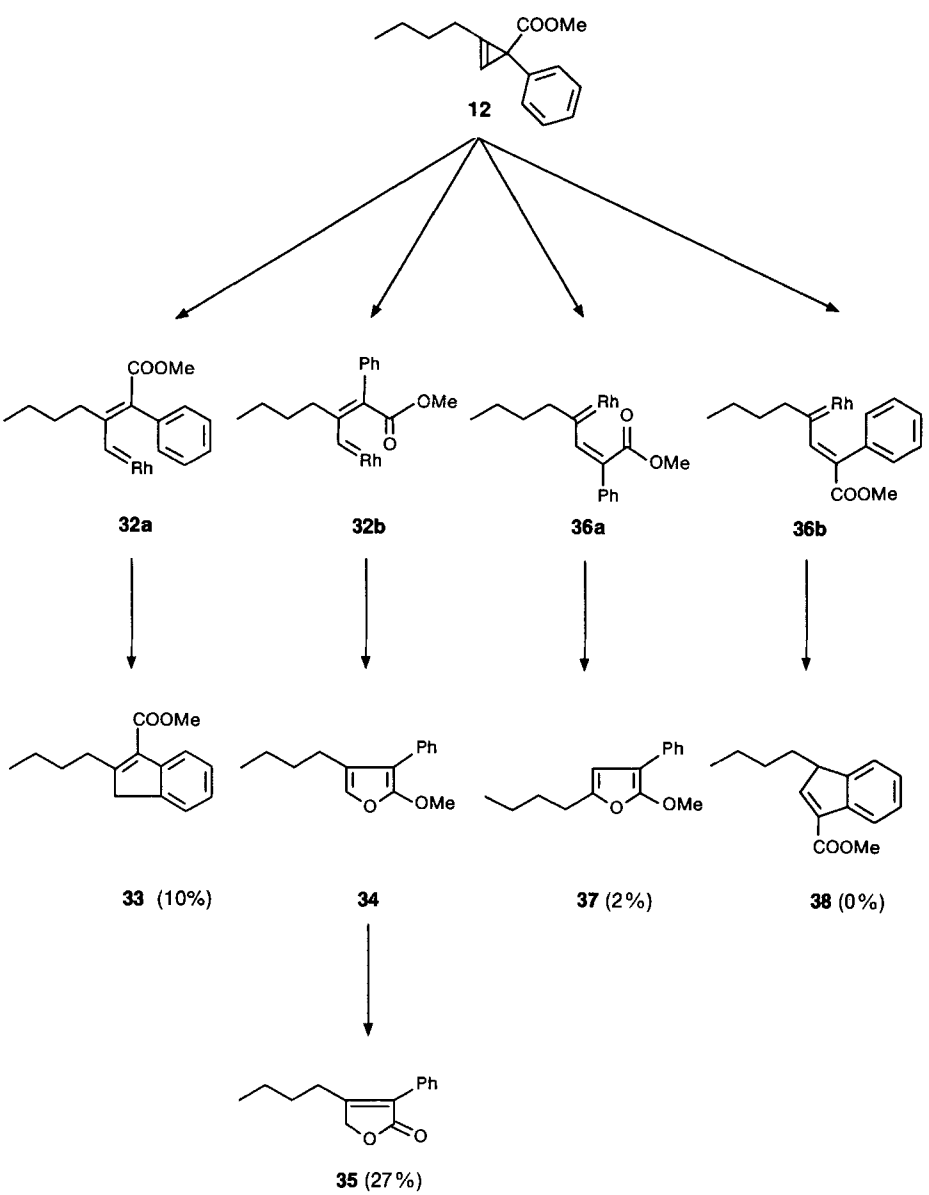
The products isolated from rearrangement of monosubstituted 2-alkyl-cyclopropene-carboxylates of type **1** with $Rh_2(PFB)_4$ are derived from cleavage of the less substituted cyclopropene σ-bond, which leads to the less substituted metallocarbene preferentially in the (*E*)-configuration. However, with the cyclopropene dicarboxylates **10a** and **10b**, the reactivity pattern changes (*Scheme 7*). The more substituted cyclopropene bond suffers cleavage, and this results in formation of the more substituted metallocarbenes **26** in preference of the less substituted isomeric **27**. Since, for structural reasons, these carbenes must have a carboxylate group in (*Z*)-configuration, they invariably cyclize to furans,

Scheme 7



although, in the case of the alkyl derivative **26a**, H migration to a diene could also occur. The structure of the furan **28a** was attributed by its quantitative air oxidation to ethyl 2-(ethoxycarbonyl)-4-oxooct-2-eneoate (**30**). The isomeric furan **29** would afford an aldehyde **31** upon oxidation. The structure of the Ph-substituted furan **28b** was deduced on the grounds of comparison of the ^{13}C- and ^{1}H-NMR data of the furan moiety with

Scheme 8



those of **28a** and other furans having similar substitution patterns described in the literature [15].

According to the mechanism outlined in *Scheme 1*, the 2-substituted cyclopropene carboxylates react *via* electrophilic attack at the less substituted center to the more substituted and, therefore, more stable carbenium ion **2a**, which undergoes ring-opening to the less substituted (*E*)-metallocarbene **3a**. We have invoked steric reasons for the preferential formation of the Rh-complexed terminal vinylcarbene. The cyclopropene-dicarboxylates, however, react with preferential cleavage of the more substituted bond to the more substituted metallocarbene **26** rather than to the terminal metallocarbene **27**. We believe that this change in regioselectivity is due to the presence of the second electron-withdrawing COOEt group which destabilizes the metallocarbene in such a way, that the steric preference for the terminal carbene **27** is overruled by the electronic stabilization of the more substituted carbene **26**. This requires that the product-determining step consists not in the formation of the cyclopropyl cation, but rather in formation of the metallocarbene.

This argument is corroborated by the results of the thermocatalytic rearrangement of methyl 2-butyl-1-phenylcyclopropene-1-carboxylate (**12**; *Scheme 8*). Replacement of one of the COOEt groups of **10a** by the less electron-attracting Ph group returns the reactivity pattern to the original one, and the main products occur *via* the less substituted carbene **32a**. C–H Insertion of the isomer **32a** which has the Ph group *cis* to the carbenic C-atom results in formation of a substituted indene **33** (10%), while the *trans*-stereoisomer **32b** affords the furan **34** (27%). The latter hydrolyzes very readily and was, therefore, characterized through its hydrolysis product, the lactone **35**, which is already present in the crude reaction mixture, and which was isolated in 27% yield. No products derived from C–H insertion in the aliphatic side chain could be observed, however. In addition, the isomeric furan **37** (2%) was detected spectroscopically in the crude mixture and separated by chromatography, but could not be purified owing to decomposition. Compound **37** originates from the regioisomeric carbene **36a**, and is clearly only a minor product. No indene **38** deriving from the stereoisomeric carbene **36b** was detected in the reaction mixture, and no products resulting from 1,2-H migration could be observed.

Conclusions. – In the presence of $Rh_2(PFB)_4$, 2-alkylcycloprop-2-ene-1-carboxylates rearrange thermally to cyclopentylidenes *via* ring-opening to the less substituted (*E*)-metallocarbenes. No cyclopentylidene is formed, however, if the intermediate vinylcarbenes can undergo 1,2-H migration. 2-Organylcycloprop-2-ene-1,1-dicarboxylates, in turn, undergo ring-opening to the more substituted metallocarbene, which react further to furans. The rearrangement of 2-methyl-3-phenylcycloprop-2-ene-1-carboxylate (**6e**) proceeds without regiospecificity to the corresponding furans, and 2-butyl-1-phenylcycloprop-2-ene-1-carboxylate (**12**) rearranges preferentially *via* the less substituted metallocarbene.

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Experimental Part

General. See [16].

Synthesis of Ethyl 2-Alkylcycloprop-2-ene-1-carboxylates (1a–d). – *General Procedure.* To the appropriate alkyne (*ca.* 50 mmol) and $Rh_2(OAc)_4$ (40 mg, 0.09 mmol) in CH_2Cl_2 (20 ml) was added, by means of a syringe pump, ethyl diazoacetate (3.50 g, 35 mol) in CH_2Cl_2 (5.0 ml) at a rate of 0.4 ml/h. After the addition, stirring was continued for 3 h, whereupon the soln. was filtered through a small column of silica gel, which was washed exhaustively with CH_2Cl_2 to remove the catalyst. The filtrate was evaporated and afforded a *ca.* 50% yield of crude cyclopropene, as an undistillable oil, contaminated by some diethyl maleate and fumarate (carbene dimers). The impurities were removed by column chromatography (silica gel).

Ethyl 2-Butylcycloprop-2-ene-1-carboxylate (**1a**) [6]. Yield 63%. IR (CH_2Cl_2): 3057*w*, 2961*m*, 2934*m*, 2873*m*, 1802*w*, 1715*s*, 1466*w*, 1370*w*, 1525*w*, 1289*s*, 1030*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.92 (*t*, *J* = 7.4, 3 H); 1.25 (*t*, *J* = 7.0, 3 H); 1.32–1.45 (*m*, 2 H); 1.53–1.62 (*m*, 2 H); 2.12 (*d*, *J* = 1.5, 1 H); 2.50 (*dt*, *J* = 7.4, *J* = 1.5, 2 H); 4.13 (*q*, *J* = 7.0, 2 H); 6.33 (*dd*, *J* = 1.4, 1,5, 1 H). ^{13}C-NMR ($CDCl_3$): 13.6 (*q*); 14.3 (*q*); 19.7 (*d*); 22.2 (*t*); 24.6 (*t*); 28.7 (*t*); 60.1 (*t*); 93.9 (*d*); 115.6 (*s*); 176.6 (*s*). MS: 168 (2.2, M^+), 139 (8), 125 (12), 111 (5), 98 (14), 97 (67), 95 (100), 81 (10), 67 (16), 53 (30).

Ethyl 2-Hexylcycloprop-2-ene-1-carboxylate (**1b**). See [1].

Ethyl 2-Octylcycloprop-2-ene-1-carboxylate (**1c**). The crude product was obtained upon two successive distillations (bulb-tube, 30°/1 Torr and 40°/0.05 Torr) to remove unreacted alkyne, followed by chromatography (CH_2Cl_2/hexane 1:1). Yield of **1c** 64% (90% pure), corresponding to a 57% yield of pure **1c**. IR (CH_2Cl_2): 2930*s*, 2850*m*, 1715*s*, 1470*w*, 1350*w*, 1320*w*, 1200*s*, 1040*w*, 880*w*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.88 (*t*, 3 H); 1.24 (*t*, 3 H); 1.23–1.41 (*m*, 10 H); 1.53–1.63 (*m*, 2 H); 2.12 (*d*, *J* = 1.6, 1 H); 2.49 (*dt*, *J* = 1.2, 7.2, 2 H); 4.09–4.15 (*m*, 2 H); 6.32 (*dd*, *J* = 1,2, 1.6, 1 H). ^{13}C-NMR ($CDCl_3$, 400 MHz): 14.0 (*q*); 14.3 (*q*); 19.7 (*d*); 22.6 (*t*); 24.9 (*t*); 26.6 (*t*); 29.7 (*t*); 29.10 (*t*); 29.2 (*t*); 31.8 (*t*); 60.1 (*t*); 93.9 (*d*); 115.6 (*s*); 176.6 (*s*). MS: 225 (14.4, $[M + 1]^+$), 224 (1), 179 (7), 152 (13), 151 (100), 137 (20), 125 (46), 111 (11), 109 (54), 81 (82), 80 (16), 67 (72), 52 (32). HR-MS: calc. for $C_{14}H_{24}O_2$: 224.1770; found: 224.1775.

Ethyl 2-Propylcycloprop-2-ene-1-carboxylate (**1d**) [17]. Purification of crude **1d** by column chromatography (silica gel; hexane/CH_2Cl_2 1:1) afforded 53% of product having a purity of 94% (yield of pure **1d** 49%). ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, 3 H); 1.15 (*t*, 3 H); 1.42–1.60 (*m*, 2 H); 2.02 (*d*, 1 H); 2.38 (*t*, 2 H); 4.02 (*q*, 2 H); 6.25 (*d*, 1 H).

Synthesis of Ethyl 1,2-Disubstituted Cycloprop-2-ene-1-carboxylates (6a–e). – *Ethyl 2-Butyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate* (**6a**) [18]. The compound was synthesized according to the *General Procedure* on a 4.5-mmol scale of ethyl diazoacetate. Most of the excess of alkyne was removed by distillation (bulb-tube, 50°/0.05 Torr). Distillation at 110°/0.05 Torr afforded a mixture composed mainly of **6a** (72%) and *ethyl 4-butyl-2-(trimethylsilyl)buta-2,3-dienoate* (**7a**) (14%). Flash chromatography with NH_3 neutralized silica gel with CH_2Cl_2/hexane 1:1 yielded **6a** (52%) and **7a** (10%).

Data of **6a**: IR (CH_2Cl_2): 2960*s*, 1825*m*, 1710*s*, 1350*m*, 1330*m*, 1250*s*, 880*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.16 (*s*, 9 H); 0.89 (*t*, *J* = 7.2, 3 H); 1.20 (*t*, *J* = 7, 3 H); 1.15–1.45 (*m*, 2 H); 1.50–1.70 (*m*, 2 H); 1.96 (*s*, 1 H); 2.49 (*t*, 2 H); 4.07 (*dq*, *J* = 7, 2.5, 2 H). ^{13}C-NMR ($CDCl_3$, 400 MHz): −1.5 (*q*); 13.7 (*q*); 14.4 (*q*); 20.9 (*d*); 22.2 (*t*); 26.1 (*t*); 29.1 (*t*); 103.2 (*s*); 126.7 (*s*); 177.1 (*s*). MS: 241 (2, $[M + 1]^+$), 240 (2, M^+), 211 (4), 197 (12), 169 (8), 167 (28), 122 (23), 121 (13), 107 (14), 94 (16), 85 (17), 79 (50), 75 (100), 59 (19), 45 (29). HR-MS: calc. for $C_{13}H_{24}O_2Si$: 240.1539; found: 240.1559.

Data of **7a**: IR (CH_2Cl_2): 2980*w*, 1930*s*, 1695*s*, 1260*s*, 1170*m*, 1130*m*, 840*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.14 (*s*, 9 H); 0.88 (*t*, 3 H); 1.24 (*t*, *J* = 7, 3 H); 1.3–1.5 (*m*, 4 H); 2.06–2.12 (*m*, 2 H); 4.06–4.22 (*m*, 4 H); 5,25 (*t*, 1 H). ^{13}C-NMR ($CDCl_3$, 400 MHz): −1.7 (*q*); 13.78 (*q*); 14.3 (*q*); 22.2 (*t*); 28.2 (*t*); 31.1 (*t*); 60.2 (*t*); 82.9 (*d*); 100.2 (*s*); 168.2 (*s*); 208.7 (*s*). MS: 241 (2, $[M + 1]^+$), 240 (2, M^+), 211 (4), 197 (11), 169 (7), 167 (11), 122 (25), 121 (12), 107 (13), 94 (17), 85 (17), 79 (49), 73 (100), 59 (10), 45 (30). HR-MS: calc. for $C_{13}H_{24}O_2Si$: 240.154, found: 240.159.

Ethyl 2-Phenyl-3-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (**6b**). The *General Procedure* with 5.1 mmol of ethyl diazoacetate and 25 mmol of 1-phenyl-2-(trimethylsilyl)acetylene (*Aldrich*) afforded, after flash chromatography (silica gel; CH_2Cl_2/hexane 1:1) 146 mg (11%) of **6b**, 7% of *ethyl 4-phenyl-2-(trimethylsilyl)buta-2,3-dienoate* (**7b**) and 10% of *ethyl 4-[2-(trimethylsilyl)ethynyl]cyclohepta-2,4,6-triene-1-carboxylate* (**8**).

Data of **6b**: IR ($CHCl_3$): 2950*m*, 2860*m*, 1820*m*, 1720*s*, 1250*m*, 1180*s*, 850*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.31 (*s*, 9 H); 1.23 (*t*, 3 H); 2.39 (*s*, 1 H); 4.06–4.22 (*m*, ABC_3 system, 2 H); 7.35–7.45 (*m*, 3 H); 7.52–7.57 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): −1.5 (*q*); 14.3 (*q*); 20.5 (*d*); 59.9 (*t*); 107.9 (*s*); 124.0 (*s*); 127.5 (*s*); 128.6 (*d*); 129.5 (*d*); 129.7 (*d*); 176.0 (*s*). MS: 260 (3.2, M^+), 231 (5), 187 (18), 142 (45), 114 (36), 105 (18), 77 (6), 73 (100), 59 (15), 53 (5), 45 (37). HR-MS: calc. for $C_{15}H_{20}O_2Si$: 260.1227; found: 260.1227.

Data of **7b**: IR ($CHCl_3$): 2970*w*, 2370*w*, 1925*m*, 1710*s*, 1250*m*, 1075*w*, 850*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.29 (*s*, 9 H); 1.29 (*t*, 3 H); 4.12–4.29 (*m*, ABC_3 system, 2 H); 5.56 (*s*, 1 H); 7.23–7.38 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$):

−0.69 (*q*); 14.3 (*q*); 60.5 (*t*); 84.0 (*d*); 104.0 (*s*); 127.1 (*d*); 128.0 (*d*); 128.7 (*d*); 134.5 (*s*); 167.4 (*s*); 212.1 (*s*). MS: 260 (5.5, M^+), 231 (6), 203 (5), 187 (11), 142 (48), 114 (36), 105 (15), 75 (24), 73 (100), 45 (36).

Data of **8**: IR ($CHCl_3$): 2950*m*, 2380*w*, 2150*m*, 1730*s*, 1200*m*, 860*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.21 (*s*, 9 H); 1.30 (*t*, 3 H); 2.57 (*tt*, 1 H); 4.25 (*q*, 2 H); 5.38 (*dd*, 1 H); 5.49 (*ddd*, 1 H); 6.22–6.29 (*m*, 2 H); 6.92 (*d*, 1 H). ^{13}C-NMR ($CDCl_3$): −0.1 (*q*); 14.2 (*q*); 43.2 (*d*); 61.2 (*t*); 95.0 (*s*); 105.8 (*s*); 115.7 (*d*); 117.3 (*d*); 125.3 (*s*); 125.4 (*d*); 127.6 (*d*); 135.9 (*d*); 172.5 (*s*). MS: 260 (8.8, M^+), 231 (6), 217 (6), 187 (100), 167 (15), 129 (12), 105 (13), 97 (12), 75 (29), 73 (44), 59 (31), 53 (13), 45 (19).

Ethyl 2,3-Diethylcycloprop-2-ene-1-carboxylate (**6c**). See [1].

Ethyl 2,3-Dibutylcycloprop-2-ene-1-carboxylate (**6d**). The cyclopropenation of *dec-5-yne* (**5d**) [19] (29 mmol) with ethyl diazoacetate and 19.3 mmol) afforded, after flash chromatography (silica gel; hexane/CH_2Cl_2 1:1), **6c** (12 mmol, 63%). IR ($CHCl_3$): 2940*s*, 1710*s*, 1450*m*, 1360*m*, 1190*s*, 960*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.88 (*t*, 3 H); 1.21 (*t*, 3 H); 1.3–1.6 (*m*, 8 H); 2.00 (*s*, 1 H); 2.38 (*t*, 4 H); 4.08 (*q*, 2 H). ^{13}C-NMR ($CDCl_3$): 13.6 (*q*); 14.3 (*q*); 22.1 (*d*); 22.2 (*t*); 24.1 (*t*); 29.0 (*t*); 59.6 (*t*); 105.6 (*s*); 176.9 (*s*). MS: 224 (5.2, M^+), 195 (7), 181 (14), 151 (100), 93 (5), 79 (7), 67 (10), 55 (11).

Ethyl 2-Methyl-3-phenylcycloprop-2-ene-carboxylate (**6e**). The cyclopropenation of phenylpropyne (24 mmol) with ethyl diazoacetate (6.7 mmol afforded, after flash chromatography (silica gel; CH_2Cl_2), **6e** in 56% yield. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.24 (*t*, *J* = 7.1, 3 H); 2.32 (*s*, 3 H); 2.42 (*s*, 1 H); 4.14 (*dq*, *J* = 7.1, 2 H); 7.2–7.5 (*m*, 5 H). For further data of **6e** (methyl ester), see [13].

Diethyl 2-Organylcycloprop-2-ene-1,1-dicarboxylates. – *Diethyl 2-Butylcycloprop-2-ene-1,1-dicarboxylate* (**10a**). To a mixture of hex-1-yne (5.11 g, 62 mmol), and $Rh_2(OAc)_4$ (55.7 mg, 0.6 mol-%) in CH_2Cl_2 (20 ml) was added diethyl diazomalonate [10] (3.79 g, 19.9 mmol) in CH_2Cl_2 (5 ml) in 18 h at r.t. After additional stirring (8 h), the mixture was filtered through silica gel. The solvent was evaporated and the crude product purified by distillation with a bulb-tube (120°/0.01 Torr) and column chromatography (NH_3-neutralized silica gel; CH_2Cl_2). Yield of **10a** [20] 40%. IR (CH_2Cl_2): 2960*s*, 1750*s*, 1360*m*, 1285*s*, 1240*s*, 1070*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.92 (*t*, *J* = 7, 3 H); 1.26 (*t*, *J* = 8, 6 H); 1.35–1.45 (*m*, 2 H); 1.55–1.64 (*m*, 2 H); 2.56 (*dt*, *J* = 8, 1.5, 2 H); 4.17 (*dq*, *J* = 8, 1.5, 4 H); 6.37 (*t*, *J* = 1.5 Hz, 1 H). ^{13}C-NMR ($CDCl_3$, 400 MHz): 13.5 (*q*); 14.0 (*q*); 22.0 (*t*); 23.6 (*t*); 28.4 (*t*); 60.7 (*t*); 93.5 (*d*); 114.6 (*s*); 171.4 (*s*). MS: 240 (1.7, M^+), 211 (3), 168 (11), 167 (100), 166 (88), 124 (38), 123 (28), 53 (10).

Diethyl 2-Phenylcycloprop-2-ene-1,1-dicarboxylate (**10b**). To phenylacetylene (4.4 ml, 40 mmol) and $Rh_2(OAc)_4$ (36.5 mg, 1 mol-%) in CH_2Cl_2 at reflux was added under N_2 in 30 min diethyl diazomalonate [10] (1.50 g, 8.06 mmol) in CH_2Cl_2. After the addition, heating was continued for 15 min. Column chromatography of the crude product (silica gel; pentane/Et_2O 8:2) afforded 1.18 g (56.4%) of **10b** [20]. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.23 (*t*, *J* = 7.2, 6 H); 4.18 (*q*, *J* = 7.2, 4 H); 6.88 (*s*, 1 H); 7.36–7.50 (*m*, 3 H); 7.55–7.65 (*m*, 2 H). For further data, see [20].

Methyl 2-Butyl-1-phenylcycloprop-2-ene-1-carboxylate. – *Methyl 2-Diazo-2-phenylacetate* (**11**) [21]. To lithium diisopropylamide (LDA; prepared from 22 mmol of $(i\text{-}Pr)_2NH$ and 20 mmol of BuLi) in Et_2O (15 ml) at −78° was added hexamethylphosphoric triamide (HMPA, 5.2 ml, 20 mmol). The soln. was stirred for 30 min, whereupon methyl phenylacetate (1.52 g, 10.1 mmol) in Et_2O (5 ml) was added dropwise. After stirring for 30 min at −78°, *p*-toluenesulfonyl azide [10] (4.00 g, 23.3 mmol) in Et_2O (6 ml) was added at −78°. The mixture was warmed to r.t. and stirred overnight. It was poured into cold water (120 ml) which was extracted 3 times with pentane. The org. layers were washed with H_2O (10 ml) and sat. NaCl soln., and dried ($MgSO_4$). After evaporation of the solvent, crude **11** was purified by flash chromatography (silica gel; CH_2Cl_2). Yield 0.97 g (55%). IR (CH_2Cl_2): 3062*w*, 2955*m*, 2092*s*, 1702*s*, 1702*s*, 1499*m*, 1436*m*, 1354*m*, 1251*s*, 1156*m*, 1053*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 3.86 (*s*, 3 H); 7.15–7.22 (*m*, 1 H); 7.35–7.41 (*m*, 2 H); 7.46–7.50 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 52.0 (*q*); 124.0 (*d*); 125.5 (*s*); 125.8 (*d*); 128.0 (*s*); 128.9 (*d*); 165.5 (*s*). MS: 176 (20.6, M^+), 148 (7), 118 (8), 105 (100), 90 (16), 89 (19), 77 (68), 63 (21), 51 (18).

Methyl 2-Butyl-1-phenylcycloprop-2-ene-1-carboxylate (**12**). To hex-1-yne (3 ml, 27 mmol) and $Rh_2(OAc)_4$ (16.4 mg, 1 mol-%) in CH_2Cl_2 (20 ml) was added dropwise, at r.t. and under N_2, **11** (0.623 g, 3.57 mmol) in CH_2Cl_2 (5 ml) during 19 h. After additional stirring at r.t. (4 h), the mixture was filtered through silica gel and concentrated. The crude product (0.613 g, 75%) was almost pure. Flash chromatography (silica gel; CH_2Cl_2) was accompanied by much decomposition and yielded pure **12** (0.40 g, 49%). IR (CH_2Cl_2): 3025*w*, 2986*m*, 2874*w*, 2360*w*, 1714*s*, 1494*w*, 1435*m*, 1270*m*, 1225*s*, 1023*m*, 826*w*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.90 (*t*, *J* = 7.4, 3 H); 1.30–1.45 (*m*, 2 H); 1.54–1.65 (*m*, 2 H); 2.57 (*dt*, *J* = 7.4, 1.5, 2 H); 3.70 (*s*, 3 H); 6.68 (*t*, *J* = 1.5, 1 H); 7.20–7.24 (*m*, 1 H); 7.26–7.34 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 13.6 (*q*); 22.2 (*t*); 24.2 (*t*); 28.8 (*t*); 52.0 (*q*); 96.9 (*d*); 120.9 (*s*); 126.2 (*d*); 128.0 (*d*); 128.8 (*s*); 141.8 (*s*); 176.0 (*s*). MS: 230 (27.3, M^+), 215 (41), 188 (27), 187 (50), 171 (84), 155 (52), 129 (100), 128 (91), 114 (73), 91 (33), 85 (65), 77 (33), 57 (45), 51 (19). HR-MS: calc. for $C_{15}H_{18}O_2$: 230.1307; found: 230.1306 [22].

Thermocatalytic Rearrangements of Ethyl 2-Alkylcycloprop-2-ene-1-carboxylates. – *Rearrangement of* **1a**. *(E)-Ethyl (3-methylcyclopentylidene)acetate* (**4a**). The cyclopropene **1a** (40.1 mg) in benzene (5.0 ml) was added dropwise, during 13 h under N_2 by means of a syringe pump, to $Rh_2(PFB)_4$ [22] (8.7 mg, 3.4 mol-%) in refluxing benzene (3.0 ml). After the addition, heating and stirring were continued for 1 h. The yield of **4a**, determined by GC, was 44%. The mixture contained, in addition, **1a** (2%) and polymeric material. For data of **4a**, see [1].

Rearrangement of **1b**. See [1].

Rearrangement of **1c**. *(E)- and (Z)-Ethyl (3-Pentylcyclopentylidene)acetate* (**4c**). To $Rh_2(PFB)_4$ (1.6 mg, 0.0015 mmol) in benzene (3.0 ml) were added, at 40°, simultaneously by means of a syringe pump **1c** (108 mg, 0.48 mmol) in benzene (5 ml) and $Rh_2(PFB)_4$ (6.6 mg, 0.0062 mmol) in benzene (5 ml) during 16 h. After the addition, the mixture was stirred for 2 additional h at 40°. It was filtered through silica gel. Flash chromatography (silica gel; CH_2Cl_2/hexane 1:1) afforded (*E*)-**4c** (21 mg, 19.4%) and 34 mg of a mixture composed of (*Z*)-**4c** (yield 1%), **15b** (6%), and **16b** (20%).

*Data of (E)-***4c**: IR (CH_2Cl_2): 2960*s*, 2930*s*, 1705*s*, 1640*m*, 1380*m*, 1210*m*, 1120*m*, 1030*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.89 (*t*, 3 H); 1.28 (*t*, *J* = 8, 3 H); 1.25–1.35 (*m*, 9 H); 1.85–2.00 (*m*, 2 H); 2.00–2.10 (*m*, 1 H); 2.55–2.68 (*m*, 2 H); 2.92–3.02 (*m*, 1 H); 4.15 (*q*, *J* = 8, 2 H); 5.75 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 14.1 (*q*); 14.4 (*q*); 22.6 (*t*); 28.1 (*t*); 32.0 (*t*); 32.2 (*t*); 32.5 (*t*); 34.9 (*t*); 39.3 (*d*); 42.5 (*t*); 59.4 (*t*); 111.7 (*d*); 166.9 (*s*); 169.0 (*s*). MS: 225 (7.5, $[M+1]^+$), 224 (10, M^+), 179 (16), 154 (12), 153 (100), 125 (76), 107 (45), 95 (13), 93 (14), 81 (27); 80 (14), 79 (44), 77 (23), 69 (18), 67 (28), 53 (52). HR-MS: calc. for $C_{15}H_{24}O_2$: 224.1770; found: 224.1789.

*Diagnostic Data of (Z)-***4c**: ^{1}H-NMR: 5.65 (*m*, 1 H). **15b**: ^{1}H-NMR: 5.60 (*s*, 1 H). **16b**: ^{1}H-NMR: 5.25 (*m*, 2 H); 5.92 (*s*, 1 H); 6.25 (*m*, 2 H); 6.68 (*m*, 2 H). MS: 302 (9, M^+), 91 (100).

Rearrangement of **1d**. *Ethyl Cyclopentylideneacetate* (**4d**). To $Rh_2(PFB)_4$) (3.6 mg, 0.003 mmol) in refluxing benzene (5.0 ml) were added simultaneously, by means of a syringe pump, **1d** (65 mg, 0.42 mmol) in benzene (5.0 ml) and $Rh_2(PFB)_4$) (3.6 mg, 0.003 mmol) in benzene (5.0 ml) during 16 h. After the addition, heating was continued for 5 h. The mixture was filtered through silica gel; the filtrate was concentrated, and the volatiles were separated by bulb-to-bulb distillation (50–200°/15 Torr). The structure of the product **4d** was determined by comparison of its ^{1}H-NMR spectrum with that of an authentic sample, prepared from cyclopentanone *via Horner-Wittig* reaction [12]. The yield of **4d** was determined by GC to be 15%, using independently prepared material for calibration. IR (CH_2Cl_2): 2970*w*, 2840*w*, 2360*w*, 1705*s*, 1640*m*, 1360*m*, 1200*s*, 1120*m*, 1030*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.27 (*t*, *J* = 7, 3 H); 1.60–1.70 (*m*, 2 H); 1.70–1.80 (*m*, 2 H); 2.41–2.47 (*m*, 2 H); 2.74–2.80 (*m*, 2 H); 4.12 (*q*, *J* = 7, 2 H); 5.78–5.81 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 14.3 (*q*); 25.4 (*t*); 26.4 (*t*); 32.5 (*t*); 35.8 (*t*); 59.3 (*t*); 111.6 (*d*); 166.8 (*s*); 168.9 (*s*). MS: 155 (24, $[M+1]^+$), 154 (44, M^+), 126 (48), 125 (19), 109 (100), 108 (33), 97 (32), 83 (10), 81 (74), 80 (45), 77 (26), 69 (12), 67 (99), 66 (58), 65 (10), 53 (61).

Rearrangement of **6a**. *(E)-Ethyl [3-Methyl-2-*cis/trans*-(trimethylsilyl)cyclopentylidene]acetate* (**17**). To $Rh_2(PFB)_4$ (6.2 mg, 0.006 mmol) in toluene (3.0 ml) were added, at 100°, simultaneously, by means of a syringe pump, **6a** (151.6 mg, 0.63 mmol) in toluene (5.0 ml) and $Rh_2(PFB)_4$ (24.6 mg, 0.023 mmol) in toluene (5.0 ml). The mixture was heated to 100° for additional 21 h after the addition. It was then filtered through silica gel under N_2, and the silica gel was eluted with CH_2Cl_2. The solvents were evaporated, and the volatiles were separated by bulb-tube distillation (180°/0.05 Torr). Flash chromatography (silica gel; CH_2Cl_2/hexane 1:1) afforded 29.7 mg (19.5%) of a 1:2.5 mixture of *cis*/*trans*-isomers of **17**. IR (CH_2Cl_2): 2970*s*, 1690*m*, 1630*w*, 1100*s*, 1000*s*, 810*s*. *trans*-**17** (major component): ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.08 (*s* 9 H), 0.97 (*d*, *J* = 6.4, 3 H); 1.27 (*t*, 3 H); 1.40–3.20 (*m*, 6 H); 4.14 (*q*, 2 H); 5.59 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 1.01 (*q*); 14.4 (*q*); 22.7 (*q*); 32.2 (*t*); 33.9 (*t*); 34.7 (*d*); 47.2 (*d*); 59.3 (*t*); 109.1 (*d*); 167.0 (*s*); 173.0 (*s*). MS: obtained with GC-MS: 240 (1, M^+), 225 (2), 195 (2), 137 (3), 122 (14), 121 (10), 108 (8), 107 (100), 77 (12), 75 (16), 73 (61), 45 (19). *cis*-**17** (minor component): ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.05 (*s*, 9 H); 1.11 (*d*, *J* = 6.8, 3H); 1.28 (*t* 3 H), 1.40–3.20 (*m*, 6 H); 4.14 (*q*, *J* = 6.8, 2 H); 5.60 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): −2.39 (*q*); 14.1 (*q*); 22.7 (*q*); 32.6 (*t*); 33.7 (*t*); 37.7 (*d*); 45.9 (*d*); 59.3 (*t*); 110.0 (*d*); 167 and 173 not detectable. MS: obtained with GC-MS: 240 (M^+, not detectable), 225 (4), 208 (4), 137 (5), 123 (4), 108 (10), 107 (100), 77 (13), 75 (20), 73 (60), 45 (20).

Thermocatalytic Rearrangement of Ethyl 2,2-Diorganylcycloprop-2-ene-1-carboxylates. – *Rearrangement of* **6c**. See [1].

Rearrangement of **6d**. *Ethyl (2E,4Z)- and (2E,4E)-3-Butylocta-2,4-dienoate* **20c, d**). To $Rh_2(PFB)_4$ (10.5 mg,, 0.0099 mmol) in refluxing benzene was added dropwise and under N_2 **6d** (166.7 mg, 0.75 mmol) in 5.0 ml of benzene during 22 h. After the addition, heating was continued for 8 h. The mixture was filtered through silica gel, which was extracted with CH_2Cl_2. After concentration, the crude product was purified by bulb-tube distillation (150°/0.1 Torr) to afford 146.3 mg (88%) of a 6:1 mixture of (4*Z*)-**20c** and (4*E*)-**20d**.

*Data of (4Z)-***20c**: IR (CH_2Cl_2): 2940*s*, 1708*s*, 1620*m*, 1460*m*, 1370*m*, 1200*s*, 1140*s*, 1040*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6.7, 3 H); 0.90 (*t*, *J* = 7.0, 3 H); 1.27 (*t*, *J* = 7.1, 3 H); 1.25- 1.50 (*m*, 6 H); 2.19 (*dq*, *J* = 7.0,

1.6, 2 H); 2.65 (*t*, *J* = 7.5, 2 H); 4.15 (*q*, *J* = 7.1, 2 H); 5.59 (*dt*, *J* = 11.8, 7.2, 1 H); 5.65 (*s*, 1 H); 5.84 (*dq*, *J* = 11.8, 1.6, 1 H). ^{13}C-NMR ($CDCl_3$): 13.7 (*q*); 13.8 (*q*); 14.2 (*q*); 22.7 (*t*); 23.0 (*t*); 30.6 (*t*); 30.7 (*t*); 31.9 (*t*); 59.5 (*t*); 117.4 (*d*); 130.8 (*d*); 135.3 (*d*); 157.5 (*s*); 166.5 (*s*). MS: 224 (16, M^+), 195 (14), 181 (100), 167 (7), 153 (83), 136 (7), 121 (14), 107 (18), 95 (25), 79 (25), 67 (20), 55 (26).

*Data of (4E)-***20d**: ^{1}H-NMR ($CDCl_3$, 200 MHz; determined with (*E*/*Z*)-mixture): 0.82–1.0 (*t*, 6 H); 1.26 (*t*, *J* = 7.2, 3 H); 1.25–1.50 (*m*, 6 H); 2.13 (*q*, *J* = 8, 2 H); 2.75 (*t*, *J* = 8, 2 H); 4.14 (*q*, *J* = 7.2, 2 H); 5.63 (*s*, 1 H); 5.96 (*dq*, *J* = 16, 1 H); 6.11 (*dt*, *J* = 15.8, 6, 1 H).

Rearrangement of **6e**. *2-Ethoxy-5-methyl-4-phenylfuran* (**23**) *and 2-Ethoxy-4-methyl-5-phenylfuran* (**25**). To $Rh_2(PFB)_4$ (7.5 mg, 0.007 mmol) in refluxing benzene (5.0 ml) were added simultaneously by means of a syringe pump, **6e** (116.5 mg, 0.58 mmol) in benzene (5.0 ml) and $Rh_2/PFB)_4$ (7.5 mg, 0.007 mmol) in benzene (5.0 ml) during 24 h. After the addition, heating was continued during 29 h. The mixture was filtered through silica gel under N_2. NMR analysis of the crude product revealed the presence of unreacted **6e** (20%), **23** (10%), **24** (10%), and **25** (20%). The spectroscopic data of these compounds are reported in [13].

Rearrangement of Diethyl 2-Organylcycloprop-2-ene-1,1-dicarboxylates. – *Rearrangement of* **10a**. *Ethyl 5-Butyl-2-ethoxyfuran-3-carboxylate* (**28a**). To $Rh_2(PFB)_4$ (11 mg, 0.01 mmol) in refluxing benzene (5.0 ml) were added, simultaneously by means of a syringe pump, **10a** (474.6 mg, 1.82 mmol) in benzene (5.0 ml) and $Rh_2(PFB)_4$ (11 mg, 0.01 mmol) in benzene (5.0 ml) during 18 h. After the addition was complete, heating was continued for 6 h. The mixture was filtered through silica gel under N_2, and the gel was extracted with CH_2Cl_2. After evaporation of the solvent, the crude product was purified by bulb-to-bulb distillation (110°/0.1 Torr) to afford 299.6 mg (63%) of **28a**. IR (CH_2Cl_2): 2960*m*, 1700*s*, 1600*s*, 1440*m*, 1280*m*, 1090*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.92 (*t*, *J* = 7.2, 3 H); 1.31 (*t*, *J* = 7.3, 3 H); 1.33–1.41 (*m*, 2 H); 1.43 (*t*, *J* = 7.3, 3 H); 1.52–1.61 (*m*, 2 H); 2.49 (*dt*, *J* = 7.5, 1.5, 2 H); 4.24 (*q*, *J* = 7.3, 2 H); 4.40 (*q*, *J* = 7.3, 2 H); 6.16 (*t*, *J* = 1.5, 1 H). ^{13}C-NMR ($CDCl_3$): 13.7 (*q*); 14.4 (*q*); 15.0 (*q*); 22.0 (*t*); 27.2 (*t*); 29.6 (*t*); 59.6 (*t*); 67.9 (*t*); 92.7 (*s*); 105.6 (*d*); 146.0 (*s*); 160.8 (*s*); 163.3 (*s*). MS: 240 (15.7, M^+), 212 (7), 195 (9), 167 (15), 166 (100), 124 (37), 123 (24), 86 (21), 84 (32), 49 (42).

Ethyl 2-(Ethoxycarbonyl)-4-oxooct-2-enoate (**30**). A soln. of **28a** (50 mg, 0.21 mmol) in CH_2Cl_2 (5.0 ml) was saturated with air and stirred during 30 min. After evaporation of the solvent pure **30** was isolated quantitatively. IR (CH_2Cl_2): 2960*m*, 2925*m*, 1738*s*, 1690*m*, 1240*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.91 (*t*, *J* = 7, 3 H); 1.24–1.30 (*m*, 2 H); 1.32 (*t*, *J* = 7.5, 3 H); 1.34 (*t*, *J* = 7, 3 H); 1.58–1.66 (*m*, 2 H); 2.60 (*t*, *J* = 7.5, 2 H); 4.30 (*q*, *J* = 7.5, 2 H); 4.36 (*q*, *J* = 7, 2 H); 7.14 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 13.7 (*q*); 13.8 (*q*); 14.0 (*q*); 22.1 (*t*); 25.4 (*t*); 43.4 (*t*); 62.0 (*t*); 62.4 (*t*); 135.4 (*d*); 135.5 (*s*); 162.8 (*s*); 164.7 (*s*); 198.7 (*s*). MS: 257 (11.5, $[M + 1]^+$), 256 (0.7, M^+), 211 (57), 210 (11), 200 (7), 199 (15), 186 (17), 171 (31), 164 (14), 143 (100), 127 (18), 123 (13), 99 (21), 98 (14), 81 (25), 71 (24), 57 (85), 53 (75), 45 (17). HR-MS ($[M - 45]^+$): calc. for $C_{11}H_{15}O_4$: 211.0970; found: 211.0978.

Rearrangement of **10b**. *Ethyl 2-Ethoxy-5-phenylfuran-3-carboxylate* (**28b**). To $Rh_2(PFB)_4$ (4.4 mg, 0.004 mmol) in refluxing benzene (5.0 ml) were added, simultaneously by means of a syringe pump, **10b** (163.5 mg, 0.63 mmol) in benzene (5.0 ml) and $Rh_2(PFB)_4$ (4.4 mg, 0.004 mmol) in benzene (5.0 ml) during 21 h. After the addition, heating was continued for 2 h. The mixture was then filtered through silica gel under N_2, and the gel eluted with CH_2Cl_2. After evaporation of the solvent, the crude product was purified by flash chromatography (silica gel; Et_2O/pentane 2:3), which afforded 31.6 mg of unreacted **10b** (19%) and 38.8 mg of **28b** (24%) as colorless oil. IR (CH_2Cl_2): 2980*m*, 1710*s*, 1615*s*, 1600*s*, 1560*s*, 1240*s*, 1095*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.35 (*t*, *J* = 7.2, 3 H); 1.52 (*t*, *J* = 6.8, 3 H); 4.29 (*q*, *J* = 7.2, 2 H); 4.55 (*q*, *J* = 6.8, 2 H); 6.85 (*s*, 1 H); 7.21–7.26 (*m*, 1 H); 7.31–7.39 (*m*, 2 H); 7.52–7.56 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 14.4 (*q*); 15.0 (*q*); 60.0 (*t*); 68.2 (*t*); 94.3 (*s*); 106.1 (*d*); 122.8 (*d*); 127.1 (*d*); 128.7 (*d*); 129.9 (*s*); 143.4 (*s*); 161.5 (*s*); 163.1 (*s*). MS: 260 (22.3, M^+); 231 (19), 215 (5), 186 (100), 159 (9), 131 (9), 105 (65), 77 (30). HR-MS: calc. for $C_{15}H_{16}O_4$: 260.1044; found: 260.1052.

Rearrangement of **12**. To $Rh_2(PFB)_4$ (11.7 mg, 0.011 mmol) in refluxing benzene (5.0 ml) were added under N_2, simultaneously by means of a syringe pump, **12** (115.4 mg, 0.50 mmol) in benzene (5.0 ml) and $Rh_2(PFB)_4$ (11.7 mg, 0.011 mol) in benzene (5.0 ml) during 18 h. After the addition, heating was continued for 2 h. The mixture was filtered through silica gel which was eluted with CH_2Cl_2. After evaporation of the solvent the residue was purified by column chromatography (silica gel; CH_2Cl_2) which afforded *methyl 2-butylindene-3-carboxylate* (**33**; 11.3 mg, 10%), *4-butyl-2,5-dihydro-3-phenylfuran-2-one* (**35**; 29.1 mg, 27%), hydrolysis product of *4-butyl-2-methoxy-3-phenylfuran* (**34**), and *5-butyl-2-methoxy-3-phenylfuran* (**37**; *ca.* 2%, impure). The furans decomposed upon attempted purification.

Data of **33**: oil. IR (CH_2Cl_2): 2957*m*, 2360*m*, 1707*s*, 1214*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.94 (*t*, *J* = 7.4, 3 H); 1.37–1.46 (*m*, 2 H); 1.56–1.64 (*m*, 2 H); 2.88–2.95 (*m*, 2 H); 3.53 (*s*, 2 H); 3.91 (*s*, 3 H); 7.18 (*dt*, *J* = 6.3, 1.1, 1 H); 7.30 (*dt*, *J* = 6.6, 1.1, 1 H); 7.39 (*dd*, *J* = 7.4, 1.1, 1 H); 7.87 (*d*, *J* = 7.7, 1 H). ^{13}C-NMR ($CDCl_3$): 13.9 (*q*); 22.8 (*t*); 30.1 (*t*); 31.8 (*t*); 42.6 (*t*); 51.1 (*q*); 121.9 (*d*); 123.2 (*d*); 124.6 (*d*); 125.6 (*d*); 128.7 (*s*); 141.1 (*s*); 142.5 (*s*);

163.1 (*s*); 165.5 (*s*). MS: 230 (88, M^+), 199 (20), 188 (52), 171 (67), 155 (20), 141 (29), 129 (100), 115 (52), 108 (10), 91 (13), 77 (18), 55 (10). HR-MS: calc. for $C_{15}H_{18}O_2$: 230.1302; found: 230.1284.

Data of **34**: ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.80–1.00 (*t*, 3 H); 1.10–1.70 (*m*, 4 H); 2.40–2.60 (*dt*, 2 H); 3.88 (*s*, 3 H); 6.77 (*t*, J = 1.3, 1 H); 7.10–7.60 (*m*, 5 H).

Data of **35**: oil. IR (CH_2Cl_2): 3061*w*, 2961*m*, 2992*m*, 2864*m*, 2360*w*, 1754*s*, 1660*w*, 1496*w*, 1446*w*, 1340*w*, 1130*m*, 1037*m*, 961*w*, 910*w*, 790*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.91 (*t*, J = 7.4, 3 H); 1.32–1.42 (*m*, 2 H); 1.49–1.61 (*m*, 2 H); 2.61 (*t*, J = 8.1, 2 H); 4.83 (*s*, 2 H); 7.35–7.40 (*m*, 1 H); 7.41–7.45 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 13.7 (*q*); 22.7 (*t*); 27.5 (*t*); 30.0 (*t*); 71.2 (*t*); 126.6 (*s*); 128.5 (*d*); 125.54 (*d*); 128.9 (*d*); 130.0 (*d*); 162.1 (*s*); 173.6 (*s*). MS: 217 (15.5, $[M + 1]^+$), 216 (94.8, M^+), 187 (15), 159 (13), 130 (51), 128 (28), 117 (100), 102 (13), 91 (83), 85 (34), 55 (23). HR-MS: calc. for $C_{14}H_{16}O_2$: 216.1146; found: 216.1122.

Data of **37**: ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.80–1.00 (*t*, 3 H); 1.10–1.70 (*m*, 4 H); 2.55 (*dt*, J = 6.8, 0.9, 2 H); 3.98 (*s*, 3 H); 6.16 (*t*, J = 0.9, 1 H); 7.10–7.60 (*m*, 5 H).

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