122. Rh(II)-Catalyzed Isomerizations of Cyclopropenes

Evidence for Rh(II)-Complexed Vinylcarbene Intermediates

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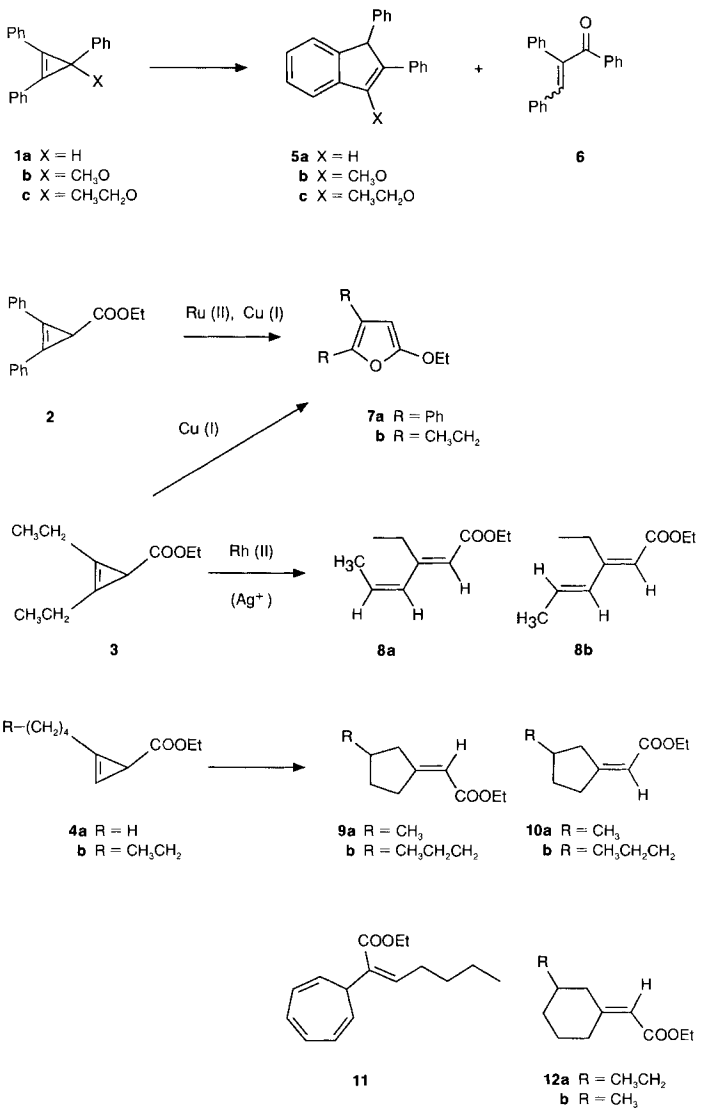
The thermocatalytic rearrangements of cyclopropenes **1**–**4** have been investigated in the presence of Rh(II) perfluorobutyrate. 1,2,3-Triphenylcyclopropene (**1a**) undergoes rearrangement to diphenylindene **5a** or, with alkoxycyclopropene derivatives, to α,β-unsaturated ketone **6**. Furan formation occurs with 2,3-diphenylcyclopropenecarboxylate **2**, but the diethyl counterpart **3** rearranges to dienoate **8**. 2-Alkylcyclopropenecarboxylates **4** afforded (*E*)-methylidenecyclopentane derivatives **9** as the only isolable product in yields of *ca.* 35%. A mechanism involving regio- and stereospecific cyclopropene ring opening to a Rh-complexed vinylcarbene and insertion of the latter into the C–H bond to give **9** is proposed. An analogous mechanism should account for the rearrangement products of **1** to **3**.

Introduction. – The photochemical and thermal rearrangements of cyclopropenes to vinylcarbenes and products derived from the latter are reasonably well understood [1] and have been exploited for synthetic applications [2]. Analogous reactions occur upon heating cyclopropenes in the presence of a transition-metal salt [3]. These thermocatalytic reactions may lead to identical products as those derived from thermal or photochemical pathways, but their mechanism is less clear. Complexed vinylcarbenes have been proposed as intermediates [4] [5], but proof for the intermediacy of such species is lacking, and often mechanisms that do not involve carbenes can equally well account for the observed products [6].

In recent years, Rh(II) acetate [7] and other binuclear Rh compounds have found increasing use for the generation of carbenes from diazo compounds, often giving better results than the traditional Cu(I) salts [8]. We reasoned that the higher efficiency of the Rh(II) catalyst over Cu(I) could be of interest for cyclopropene rearrangements, at least, if they proceed *via* carbenes. Accordingly, we have carried out a series of thermocatalytic rearrangements with cyclopropenes **1**–**4** in the presence of rhodium perfluorobutyrate dimer ($Rh_2(PFB)_4$) [9], which is more active than Rh(II) acetate for carbenoid transformations [10] (*Scheme 1*). In the course of this investigation, we found some similarities between Cu- and Rh-catalyzed cyclopropene rearrangements, but also some striking differences. More importantly, several reaction products could be isolated from the Rh(II)-catalyzed reactions which can only be derived from vinylcarbenes.

Scheme 1



Results and Discussion. – As the *Table* shows, the products of the Rh-catalyzed cyclopropene rearrangements depend, in a surprising way, on the substituents of the cyclopropene. Thus, 1,2,3-triphenylcyclopropene (**1a**) reacted with $Rh_2(PFB_4)$ to yield 1,2-diphenylindene (**5a**) in 95% yield. This latter product is also formed upon reaction of **1a** with $[(C_2H_4)PtCl_2]_2$ [11] or with an acid catalyst [12]. 3-Alkoxy-substituted triphenylcyclopropenes **1b** [13] and **1c** undergo the same transformation and afford the substituted indenes **5b** and **5c**, but in this case only the Cu(I) catalysts are effective. With **1b**, $Rh_2(PFB)_4$ produced only the unsaturated ketone **6**, which originates from ring opening

Table. *Catalyzed Rearrangements of Cyclopropenes*

Cyclo-propene	Catalyst	T [°C]	Product (yield [%])	Other products	Ref.
1a	$Rh_2(PFB)_4$	60°	**5a** (95)	–	–
1a	$[(C_2H_4)PtCl_2]_2$	25°	**5a**[c])	–	[10]
1a	H^+	–	**5a**	–	[11]
1b	$CuIP(OCH_3)_3$	80°	**5b** (30)	(*E*/*Z*)-**6** (67)	–
1b	$Rh_2(PFB)_4$	60°	–	(*E*/*Z*)-**6** (94)	–
1c	CuBr	65°	**5c** (85)	–	[12]
2	$Rh_2(PFB)_4$	100°	**7a** (89)	–	–
2	Cu(I) stearate	90°	**7a** (87)	–	[14]
3	$Rh_2(PFB)_4$	80°	**8a** (65)[a])	**8b** (9)	–
3	$AgClO_4$	40°	–	**8b** (55)[b])	[4]
3	Cu(I)	70°	**7b** (90)[c])	–	[14]
4a	$Rh_2(PFB)_4$	80°	**9a** (~ 35)	(**11**; 6.5)[d])	–
4b	$Rh_2(PFB)_4$	80°	**9c** (33)	**10b** (2), **12a** (8)	–

[a]) Isolated yield. [b]) Analytical yield. [c]) For R = Bu. [d]) See text. [e]) No yield given.

of **1b**. When the 3-Ph group of **1a** was replaced by COOEt, the course of the reaction changed, and the substituted furan **7a** was formed from **2** in high yield. The same reaction reportedly takes place with Cu(I) [14]. 2,3-Dialkylcyclopropenecarboxylates undergo the same transformation in the presence of Cu(I) salts and furnish 2,3-dialkylfurans, as exemplified by the conversion of **3** to **7b** [15], but when **3** was heated with $Rh_2(PBF)_4$, an entirely different reaction, leading exclusively to a 7.5:1 mixture of isomeric dienes **8a** and **8b** [16] in essentially quantitative yield, took place. No reaction occurred, when **3** was refluxed in benzene in the absence of catalyst. The transformation of 2,3-dialkylcyclopropenecarboxylates to dienes has already been effected with $AgClO_4$ as catalyst, but the yield is lower, the stereoselectivity for the diene product is not the same, and partial decomposition of the cyclopropene takes place [4].

When 2-butylcyclopropene carboxylate **4a** was exposed to $Rh_2(PFB)_4$ in refluxing benzene, the cyclopentylidene derivative **9a** was formed in 30–35% yield as the only volatile product, together with polymeric material. Capillary GC showed that only one stereoisomer had been formed. The structure of **9a** was deduced by comparison of the NMR data with those of the parent compound, lacking the Me substituent at the 5-membered ring of some substituted analogues [17]. Independent synthesis from 3-methylcyclopentanone *via* a modified *Wittig* reaction [18] afforded a *ca.* 1:1 mixture of diastereoisomers **9a**/**10a**, clearly distinguishable by NMR and partially separable by column chromatography. The (*E*)-configuration of **9a** was established by NMR using a shift reagent [19] ($Eu(fod)_3$). Under these conditions, the signals of the cyclopentane protons are well separated. Compound **9a** has two sets of 2 allylic protons (H–C(2) and H–C(5)). A COSY experiment allowed identification of those adjacent to the C-atom carrying the Me group (C(3)). Since complexation of the COOEt group by the shift reagent produced a smaller shift with these protons (24.4% of the shift of CH_2O) than with the allylic protons at C(5) (76.7%), the former must be *trans* to the ester function. It follows that **9a** has (*E*)-configuration. This assignment was confirmed by repeating the shift experiment with a mixture of **10a** (80%) and **9a** (20%). When **4a** was exposed to the same reaction conditions, but with $CuCl(i\text{-}PrO)_3$ or $PtCl_2(PhCN)_2$ instead of Rh(II), only

slow decomposition occurred. Under different conditions, cyclopropenes do, however, rearrange with Cu(I) [6].

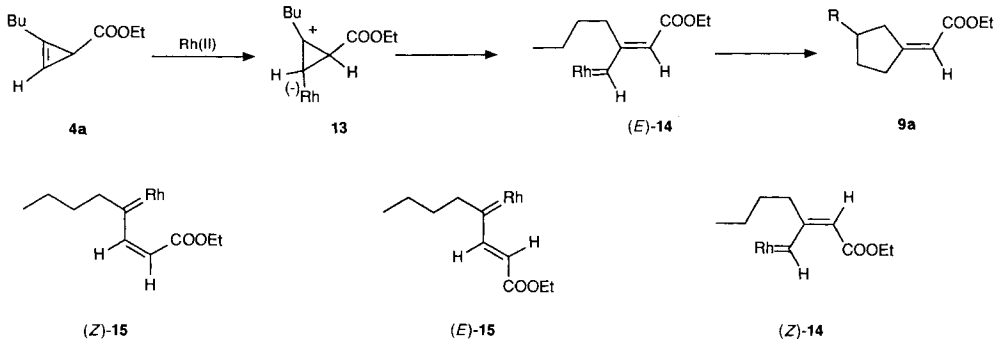
In one run, when a fresh batch of $Rh_2(PFB)_4$ was used for rearrangement of **4a**, a side product, identified as cycloheptatriene derivative **11** was isolated in 6.5% yield. The olefinic protons of the cycloheptatriene moiety of **11** resonate in the usual range at 5.25, 6.25, and 6.68 ppm, while that of the side-chain appears as *singlet* at 5.93. H–C(7) of the cycloheptatriene gives rise to a *triplet* at 2.28 and the allylic CH_2 group to one at 2.71 ppm. The configuration in the side chain of **11** is assumed to be (*Z*), in analogy to that of **9a**. The MS of **11** indicates a molecular weight of 246, corresponding to formal addition of the cyclopropene to benzene. The cycloheptatriene structure is further indicated by the base peak of *m*/z 91, corresponding to the tropylium ion.

Reaction of the hexyl derivative **4b** with $Rh_2(PFB)_4$ resulted in a 43% yield of volatile compounds. Capillary GC/MS showed the presence of three components with the molecular ion at *m*/z 196 in the ratio of 5:1:12 (order of increasing retention times). ^{1}H- and ^{13}C-NMR spectra were obtained from the mixture. To the major component was attributed the structure of **9b** by comparison with the spectra of **9a**. The MS of the minor component **10b** was almost identical to that of **9a** and showed in particular, the base peak at *m*/z 153, corresponding to loss of C_3H_7. No NMR data could be obtained for this compound, which is probably the (*Z*)-stereoisomer of **9b**. In the MS of the intermediate fraction, the base peak is not at *m*/z 153, but at 139, and an intense signal (87%), corresponding to loss of C_2H_5 appears at *m*/z 167. The ^{1}H-NMR exhibits a broad *singlet* at 5.60 and two *multiplets* in the range of 2.25–2.45 ppm. The other peaks are covered by those of **9b**. Based on this fragmentary evidence, the cyclohexylidene structure **12a** appeared likely. For confirmation, the model compound **12b** was synthesized from commercial 3-methylcyclohexanone by the procedure used for **9a**. Comparison of the NMR data confirmed the proposed structure. The configuration of **12a** is assumed to be (*E*) in analogy to that of **9a**.

Depending upon the substituents of the cyclopropene, three different products may be isolated from their Rh(II)-catalyzed rearrangements, namely furans, dienes, or methylidenecyclopentanes. While furans and dienes have previously been obtained from cyclopropene rearrangements with other metal ions, there is, to our knowledge, no precedent for formation of a methylidenecyclopentane. The latter compound is of particular interest, because it is a typical product of a carbene insertion into a C–H bond, and it would be difficult to propose a mechanism not involving a vinyl carbene in order to account for its formation. Intramolecular C–H insertion of carbenes or metallocarbenes resulting from decomposition of diazo compounds in presence of Rh acetate is, however, well documented, and is known to lead preferentially to cyclopentane derivatives [20] [21]. The cycloheptatriene **11** in turn results from intermolecular interception of the same carbene by the solvent. Again, there is ample precedent for this reaction [22]. Rh(II)-Catalyzed decomposition of diazo compounds and their carbenoid addition to substituted benzenes is, indeed, an efficient route to cycloheptatrienes [23]. The results obtained with **4b** are consistent with those of **4a**, except that the stereoselectivity is less clean, and some insertion to a methylenecyclohexane occurs, which is impossible with **4a**.

The ring opening of the cyclopropenes **4a** or **4b** may lead to two regioisomeric vinylcarbenes **14** and **15**, respectively, and each of those can occur as two (*E*)(*Z*)-stereoisomers (*Scheme 2*). However, only products derived from the less substituted

Scheme 2

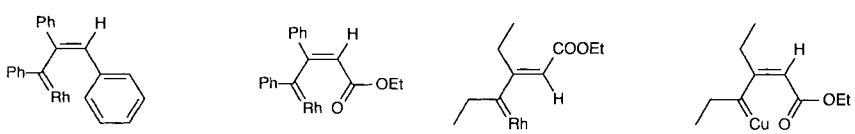


carbene (*E*)-**14** are isolated. If a free carbene were involved, one would expect (*E*)-**15** to be favored. The regio- and stereoselectivity of the reaction suggests that the intermediate is not a free, but a complexed metallocarbene. A plausible mechanism for regioselective cyclopropene opening consists in electrophilic attack of $Rh_2(PFB)_4$ *trans* to the COOEt group leading to the more substituted cyclopropyl cation **13**. Disrotatory ring opening of **13** leads to the complexed carbene (*E*)-**14**. Formation of the stereoisomer (*Z*)-**14** is less favorable, presumably for steric reasons.

Rh-Carbene complexes have been proposed to occur in Rh(II)-catalyzed decomposition of diazo compounds [24], but to our knowledge, no evidence has been presented in the past for the occurrence of such species in cyclopropene rearrangements.

Alternatively, the selectivity observed in the cyclopropene ring opening can be accounted for by rapid equilibrium between the stereo- and regioisomeric vinylcarbenes, in analogy to the equilibration occurring in thermal [22] and photochemical cyclopropene-vinylcarbene rearrangements [25], but only the carbene that yields **9a**, and not the one related to (*Z*)-**14**, is reactive towards C–H insertion.

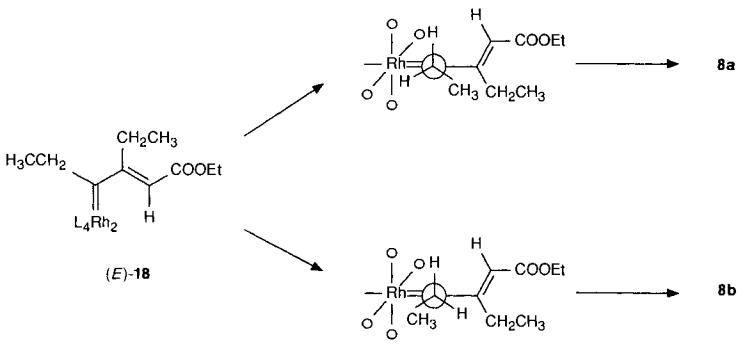
Although the mechanism of the other Rh(II)-catalyzed cyclopropene rearrangements (*Scheme 1*) is not unambiguously established, it appears justified, in the light of the results with **4a** and **4b**, to formulate them to occur also *via* complexed vinylcarbenes. With this assumption, some interesting observations can be accomplished: since the cyclopropenes **1**–**3** are symmetrically substituted at the double bond, there exists no problem of regioselectivity in the ring-opening process. The metallocarbenes derived from **1** and **2** can only cyclize to **5** and **7a** from the (*Z*)-configuration ((*Z*)-**16** and (*Z*)-**17**), where the carbenic center is *cis*-oriented to the Ph and COOEt groups, respectively. The dienes **8a** and **8b** formed in the Rh(II)-catalyzed reaction of **3**, however, result from a metallocarbene ((*E*)-**18**) with the (*E*)-configuration. With Cu(I), the stereochemistry again changes, since



(*Z*)-**16** (*Z*)-**17** (*E*)-**18** (*Z*)-**19**

the furan **7b** is derived from **19** with (*Z*)-configuration, in which coordination by the carbonyl O-atom with copper would be possible. Predominant formation of the thermodynamically less stable **8a** from catalytic decomposition with **3** with $Rh_2(PFB)_4$ is surprising in view of the results from the comparable $AgClO_4$-catalyzed reaction [4]. However, this result is consistent with the stereoselectivity observed for olefin formation in the $Rh_2(PFB)_4$-catalyzed decomposition of 1-phenyl-1-diazopentane, where (*Z*)-1-phenylpent-1-ene was the main product. The preference for the (2*E*,4*Z*)-diene **8a** (*Scheme 3*) can be attributed to constraints by the face of the rhodium carboxylate on orientation of the Et group for H migration in the metal-carbene intermediate [26].

Scheme 3



It is also noteworthy that, with **1a** and **2**, both Rh(II) and Cu(I) lead to the same reaction products, while the products are different in the case of **3**. This implies that the intermediates obtained with Rh(II) and Cu(I) must be different. An obvious hypothesis is that in both cases metallocarbenes are involved. Cu-Complexed carbenes from catalyzed decomposition of diazo compounds, indeed, show different reactivities than those exhibited with Rh(II) [27]. Further work to elucidate these reaction mechanisms is in progress.

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Experimental Part

General. See [28].

Synthesis of Cyclopropenes. – 1,2,3-Triphenylcyclopropene (**1a**) was synthesized following the procedure of *Breslow* and *Dowd* [29], and *3-methoxy-1,2,3-triphenylcyclopropene* (**1b**) according to *Breslow* and *Yuan* [30]. The synthesis of *ethyl 2,3-diphenylcycloprop-2-ene-1-carboxylate* (**2**) by the Cu-catalyzed decomposition of ethyl diazoacetate in presence of diphenylacetylene has been described [31]. *Ethyl 2,3-diethylcycloprop-2-ene-1-carboxylate* (**3**) and *ethyl 2-butylcycloprop-2-ene-1-carboxylate* (**4a**) were obtained by reaction of hex-3-yne and hex-1-yne, respectively with ethyl diazoacetate in presence of $Rh_2(OAc)_4$ [32]. The same procedure was used for **4b**.

Ethyl 2-Hexylcycloprop-2-ene-1-carboxylate (**4b**). To oct-1-yne (6.0 g, 54.5 mmol) and $Rh_2(OAc)_4$ (40 mg, 0.09 mmol) in CH_2Cl_2 (20 ml) under N_2 was added, by means of a syringe pump, ethyl diazoacetate (3.50 g, 35 mmol) in CH_2Cl_2 (5 ml) at a rate of 0.4 ml/h. After the addition, the soln. was filtered through a small column of silica gel, and extracted exhaustively with CH_2Cl_2. The filtrate was evaporated and afforded a 54% (by GC) yield of **4b** as an undistillable liquid, contaminated with some dimeric material. The latter was removed by column chromatography (silica gel, cyclohexane/CH_2Cl_2 1:1). ^{1}H-NMR: 0.93 (*t*, 3 H); 1.26 (*t*, 3 H); 1.22–1.42 (*m*, 6 H); 1.58 (*m*, 2 H); 2.13 (*d*, 1 H); 2.50 (*t*, 2 H); 4.14 (*q*); 6.33 (*d*, 1 H). ^{13}C-NMR: 14.0 (*q*); 14.4 (*q*); 19.8 (*d*); 22.5 (*t*); 25.0 (*t*); 26.7 (*t*); 28.8 (*t*); 28.9 (*t*); 31.5 (*t*); 60.1 (*t*); 94.0 (*t*). CO, not identified.

Catalyzed Ring Opening of Cyclopropenes. – *1,2,3-Triphenylcyclopropene* (**1a**). To a soln. of **1a** (58 mg, 0.22 mmol) in dry toluene (20 ml) was added, under Ar, rhodium(II)-perfluorobutyrate dimer (3.2 mg, 1.4%). The mixture was stirred at 60° for 48 h. The solvent was evaporated, the residue dissolved in Et_2O, and filtered through *Celite*. After evaporation of the solvent and recrystallization of the crude product, 55.1 mg (95%) of *1,2-diphenylindene* (**5a**) was isolated. M.p. 180.5–181° ([11]: 178°). IR ($CHCl_3$): 3080*w*, 3060*m*, 3030*w*, 3010*m*, 1600*m*, 1490*s*, 1450*m*, 1180*w*, 1070*w*, 880*m*. ^{1}H-NMR (360 MHz): 5.01 (*s*, 1 H); 7.10–7.32 (*m*, 11 H); 7.38–7.41 (*m*, 1 H); 7.42–7.48 (*m*, 1 H); 7.50–7.56 (*m*, 2 H). ^{13}C-NMR: 56.2 (*d*); 121.0 (*d*); 123.8 (*d*); 125.4 (*d*); 126.6 (*d*); 126.7 (*d*); 127.0 (*d*); 127.3 (*d*); 127.8 (*d*); 128.0 (*d*); 128.4 (*d*); 128.8 (*d*); 135.0 (*s*); 140.0 (*s*); 143.2 (*s*); 149.1 (*s*); 149.8 (*s*). MS: 268 (100, M^+), 252 (10), 191 (16), 165 (9), 126 (8).

Ethyl 2,3-Diphenylcycloprop-2-ene-1-carboxylate (**2**). To **4** (9.5 mg, 0.036 mmol) in dry toluene (1.0 ml) was added, at 100°, $Rh_2(PFB)_4$ (2.5 mg, 6.5%). After stirring of the mixture for 19 h, the crude product was purified by prep. TLC (Al_2O_3 hexane/Et_2O 5:1) and afforded 8.5 mg (85%) of *2,3-diphenyl-5-ethoxyfuran* (**7a**) as a colorless oil (M.p. [33]: 38–39°). ^{1}H-NMR (360 MHz): 1.54 (*t*, *J* = 7, 3 H); 4.25 (*q*, *J* = 7, 2 H); 5.42 (*s*, 1 H); 7.18–7.54 (*m*, 10 H). IR ($CHCl_3$): 3010*w*, 2985*w*, 2930*m*, 2855*w*, 1620*m*, 1600*s*, 1590*s*, 1570*m*, 1505*w*, 1480*w*, 1450*w*, 1390*m*, 1310*m*, 1045*m*, 1025*m*, 950*m*, 905*w*, 696*s*. MS: 264 (36, M^+), 235 (47), 205 (16), 191 (7), 105 (100), 77 (34), 57 (19).

Ethyl 2,3-Diethylcycloprop-2-ene-1-carboxylate (**3**). Compound **3** (125 mg, 0.74 mmol) was heated to reflux in benzene (7.0 ml) in the presence of $Rh_2(PFB)_4$ (10.5 mg, 1.3 mmol) under N_2 and stirring for 24 h. GC of the reaction soln. showed that the reaction was complete and, following removal of the solvent under reduced pressure, ^{1}H-NMR of the residue (132 mg, 97% yield) showed a mixture of *ethyl (2*E*,4*Z*)-3-ethylhexa-2,4-dienoate* (**8a**, major product) and *ethyl (2*E*,4*E*)-3-ethylhexa-2,4-dienoate* (**8b**, minor product) in a 7.5:1 molar ratio and > 90% purity. Bulb-to-bulb distillation (120°, 10 mm) afforded 91 mg of the mixture **8a**/**8b** (74% yield) as a colorless liquid.

Data of **8a**: ^{1}H-NMR: 1.05 (*t*, *J* = 7.5, 3 H); 1.29 (*t*, *J* = 7.1, 3 H); 1.82 (*dd*, *J* = 6.9, 1.6, 3 H); 2.68 (*q*, *J* = 7.5, 2 H); 4.17 (*q*, *J* = 7.1, 2 H); 5.66 (*s*, 1 H); 5.75 (*dq*, *J* = 11.7, 6.9, 1 H); 5.88 (*dq*, *J* = 11.7, 1.6, 1 H). MS: 168 (1, M^+), 140 (7), 139 (8), 125 (14), 96 (7), 95 (100), 77 (9), 67 (20), 57 (16), 55 (27), 53 (11).

Data of **8b**: ^{1}H-NMR: 1.07 (*t*, *J* = 7.6, 3 H); 1.28 (*t*, *J* = 7.1, 3 H); 1.85 (*dd*, *J* = 6.6, 1.4, 3 H); 2.78 (*q*, *J* = 7.6, 2 H); 4.16 (*q*, *J* = 7.1, 2 H); 5.62 (*s*, 1 H); 6.01 (*dq*, *J* = 15.6, 1.4, 1 H); 6.18 (*dq*, *J* = 15.6, 6.6, 1 H). Heating **3** at reflux in benzene without $Rh_2(PFB)_4$ for 24 h did not cause any measurable decomposition.

Ethyl (3-Methylcyclopentylidene)acetate (**9a**). Compound **4a** (550 mg, 3.3 mmol) was heated to reflux in benzene (12 ml) in presence of $Rh_2(PFB)_4$ (40.5 mg, added in 3 equal portions after 0, 4, and 12 h) under N_2 and stirring for 24 h. The mixture was filtered through silica gel, washed with CH_2Cl_2, then concentrated and purified by column chromatography (silica gel, hexane/CH_2Cl_2 1:1) and bulb-to-bulb distillation (120°, 10 mm): **9a** in 34% yield. IR ($CHCl_3$): 3050*w*, 2970*m*, 2950*s*, 2920*m*, 2870*m*, 2820*w*, 1710*s*, 1650*s*, 1455*m*, 1425*w*, 1375*w*, 1350*m*, 1325*m*, 1275*m*, 1225*m*, 1200*s*, 1190*s*, 1100*w*, 1050*m*. ^{1}H-NMR: 1.01 (*d*, *J* = 6.5, 3 H); 1.27 (*t*, 3 H); 1.32 (*m*, 1 H); 1.95 (*m*, 1 H); 2.05 (*m*, 2 H); 2.60 (*m*, 2 H); 2.95 (*dd*, 1 H); 4.14 (*q*, 2 H); 5.77 (*s*, 1 H). ^{13}C-NMR: 14.3 (*q*); 19.3 (*q*); 33.6 (*t*); 34.3 (*t*); 44.2 (*d*); 59.3 (*t*); 111.8 (*d*); 166.8 (*s*); 168.9 (*s*). MS: 168 (43, M^+), 153 (23), 140 (16), 125 (100), 123 (423), 122 (14), 121 (13), 111 (13), 107 (22), 98 (11), 97 (16), 95 (33), 94 (13), 93 (20), 91 (12), 81 (30), 80 (31), 79 (44), 77 (27), 67 (36), 67 (36), 65 (11), 55 (40), 53 (33).

Ethyl 2-(Cyclohepta-2,4,6-trienyl)hept-2-enoate (**11**) *from Rearrangement of* **4a**. Compound **4a** (250 mg, 1.50 mmol) was heated to reflux with freshly prepared $Rh_2(PFB)_4$ (31 mg, 0.03 mmol) in benzene (10 ml) for 2.5 h. The mixture was worked up as described above. The crude product was purified by column chromatography (silica gel, hexane/AcOEt 10:1). The first isolated material was 16 mg (6.5%) of **11**, which was followed by **9a** (30%).

Data of **11**: ^{1}H-NMR: 0.90 (*t*, 3 H); 1.32 (*t*, 3 H); 1.20–1.50 (*m*, 6 H); 2.18 (*t*, 1 H); 2.71 (*t*, 2 H); 4.15 (*q*, 2 H); 5.25 (*m*, 2 H); 5.93 (*s*, 1 H); 6.25 (*m*, 2 H); 6.68 (*m*, 2 H). MS: 246 (28, M^+), 217 (29), 201 (27), 200 (72), 175 (24), 171 (34), 158 (55), 157 (30), 143 (44), 132 (35), 131 (31), 130 (56), 129 (69), 128 (56), 127 (25), 117 (59), 116 (33), 115 (75), 127 (25), 117 (59), 116 (33), 115 (75), 91 (100).

Ethyl (E)- and (Z)-(3-Propylcyclopentylidene)acetate (**9b** and **10b**, resp.) *and Ethyl (E)-(8-Ethylcyclohexylidene)acetate* (**12a**). Compound **4b** (1.18 mmol) in benzene (5.0 ml) was added to $Rh_2(PFB)_4$ (25 mg, 0.023 mmol)

in refluxing benzene during 8 h by means of a syringe pump. The mixture was filtered through silica gel and extracted with CH_2Cl_2. After evaporation of the solvent, the volatile fraction (130 mg) was separated by bulb-to-bulb distillation (120–190°/10 mm). GC: **9b** (33%), **10b** (2%), and **12a** (8%).

Data of **9b**: ^{1}H-NMR (300 MHz): 0.9 (*m*, 3 H); 1.30 (*t*, *J* = 7.2, 3 H); 1.10–1.50 (*m*, 5 H); 1.89–2.15 (*m*, 3 H); 2.50–2.75 (*m*, 2 H); 2.90–3.10 (*m*, 1 H); 4.13 (*q*, *J* = 7.2, 2 H); 5.76 (*s*, 1 H). ^{13}C-NMR: 14.3 (*q*); 14.4 (*q*); 21.5 (*t*); 32.2 (*t*); 32.5 (*t*); 37.2 (*t*); 39.1 (*d*); 42.5 (*t*); 59.4 (*t*); 111.8 (*d*); 166.9 (*s*); 168.9 (*s*). MS: 196 (17, M^+), 153 (100), 151 (26), 125 (95), 107 (41), 81 (31), 79 (51), 77 (24), 67 (29).

Data of **10b**: MS: 196 (29, M^+), 154 (34), 153 (100), 151 (62), 95 (18), 93 (36), 91 (18), 83 (18), 81 (61), 79 (65), 69 (30), 68 (22), 67 (56).

Data of **12a**: ^{1}H-NMR: 5.60 (*s*). ^{13}C-NMR: 11.3 (*q*); 14.1 (*q*); 22.6 (*t*); 26.5 (*t*); 29.3 (*t*); 29.6 (*t*); 41.5 (*d*); 43.9 (*t*); 59.4 (*t*); 113.1 (*d*), 162.5 (not identified); 166.8 (*s*). MS: 196 (51, M^+), 167 (81), 154 (15), 151 (50), 139 (100), 128 (28), 121 (62), 111 (23), 108 (41), 107 (35), 95 (24), 93 (63), 91 (32), 83 (20), 82 (27), 79 (80), 77 (41), 69 (35), 68 (42), 67 (74), 66 (24), 65 (25).

*Synthesis of (*E/Z*)-Mixtures of* **9a** *and* **10a**. The procedure of *Wolinsky* and *Erickson* [18] was applied to triethyl phosphonoacetate and 3-methylcyclopentanone. The crude product was separated on a chromatography column (hexane/CH_2Cl_2 1:5). The first fractions consisted in a 1:4 mixture **9a**/**10a**, which was distilled (bulb-to-bulb, 140°/0.2 mm).

Data of **10a**: ^{1}H-NMR (200 MHz, $CDCl_3$): 0.96 (*d*, *J* = 7.2, 3 H); 1.21 (*t*, *J* = 7.2, 3 H); 1.25 (*m*, 1 H); 1.95 (*m*, 3 H); 2.50 (*m*, 2 H); 3.05 (*m*, 1 H); 4.12 (*q*, *J* = 7.2, 2 H); 5.70 (*s*, 1 H). ^{13}C-NMR: 14.3 (*q*); 19.7 (*q*); 33.4 (*t*); 34.7 (*t*); 35.2 (*d*); 41.0 (*t*); 59.3 (*t*); 111.7 (*d*); 166.8 (*s*); 168.8 (*s*).

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