Palladium-Catalyzed Bicyclization of 2-Bromo-1,6-dienes and -1,6-enynes to 5-Membered-Ring-Annelated Vinylcyclopropane Derivatives

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Palladium-catalyzed cyclizations of the 2-bromo-1,6-diene **6** with an acetoxymethyl substituent on the bromoalkenyl moiety did not only lead to the expected 1-acetoxymethyl-1,3-diene **40** but also to the bicyclic vinylcyclopropane **35**, the 1,3-diene **36** and the triene **37** (a dendralene). All these compounds result from an initial 5-*exo-trig* cyclization of the 2-bromo-1,6-diene. By proper choice of the reaction conditions (ligand, base, allylic leaving group) each of these compounds could be formed selectively. Small amounts (3–5%) of the isomerized 1-acetoxymethyl-1,3-diene **38** and the 6-*endo* product **39** were also isolated. With the acetoxymethyl substituent on the alkenyl moiety (compound **27**) only the 1,4-diene **44** was formed. The related 1,6-enyne **57** with a methoxycarbonyloxymethylene substituent on the triple bond gave in 36% yield the 2,3-bis(bicyclo[3.1.0]hex-1-yl)-substituted 1,3-butadiene **63**, which can be regarded as a dehydrodimer of the vinylcyclopropane **35**. The presumption that the formation of **63** involves the alkenylpalladium species **65** was supported by its successful inter- as well as intramolecular trapping with formate as a hydride source to yield the vinylcyclopropane **35**. The reaction pathways leading to the vinylcyclopropane derivatives **35** and **63** have in common that an alkylpalladium species rather undergoes a 3-*exo-trig* cyclization than an internal rotation followed by a β-hydride elimination.

Introduction

Among the various methods of preparing cyclopropanes, transition-metal-catalyzed and -mediated reactions have gained an increasingly important role.[1] Cyclopropanes frequently also occur as intermediates in transition-metal-catalyzed reactions even if the three-membered ring does not show up in the final product. For example, Negishi et al. proved that a formal 6-*endo-trig* cyclization of a 2-halo-1,6-diene occurs with inversion of configuration around the double bond, and therefore must proceed in a sequence of 5-*exo*- and 3-*exo-trig* cyclizations to yield a cyclopropylmethylpalladium intermediate which, after an internal rotation, undergoes opening of the cyclopropane ring to yield a six-membered ring compound via a homoallylpalladium intermediate.[2] We here report on palladium-catalyzed bicyclizations of 2-bromo-1,6-dienes and -1,6-enynes with certain substituents on the double bond and the triple bond to yield bicyclo[3.1.0]hexane derivatives.[3−5]

Cyclization of 1-Substituted 2-Bromo-1,6-dienes

As was previously observed, intramolecular Heck reactions of 2-bromo-1,6-dienes with any substituents on the bromoalkenyl moiety *cis* to bromine, except for compounds with a cyclopropane ring directly attached in a methylenecyclopropane moiety, did not take place in the presence of silver or thallium salts.[3] Since substituents with oxygen functionalities such as hydroxymethyl or acetoxymethyl might coordinate the catalytically active palladium species and thereby facilitate the oxidative addition of the carbon−bromine bond, the 1-substituted 2-bromo-1,6-dienes **6**, **7**, **9**−**11**, and for comparison the bromodiene **27** with the bromine and acetoxy moieties on two different double bonds were synthesized according to standard protocols[6−9] (Schemes 1−4; for details see the electronic Supporting Information) and tested with respect to their palladium-catalyzed transformations.

The alcohol (*Z*)-**7** did not cyclize in the presence of palladium acetate (5−10 mol-%), triphenylphosphane (10−25 mol-%) and silver carbonate in acetonitrile at 85 °C, regardless whether methyl acrylate (**28**), to trap the cyclization product **31**, was present or not. When potassium carbonate was used, (*Z*)-**7** in the presence of methyl acrylate was converted into a new product which, surprisingly, was neither the expected Diels−Alder adduct **29** nor the lactone **30**, but the aldehyde **34** (30%). Its formation can be rationalized in terms of a 5-*exo-trig* cyclization and subsequent β-hydride elimination to yield alcohol **31** which then undergoes a 1,5-hydrogen shift (thermal[10] or palladium-catalyzed[11]) to the enol **32**. Tautomerization of **32** to the corresponding aldehyde must be followed by a twofold base-catalyzed Michael addition to methyl acrylate (**28**) (Scheme 5). Most probably, the (*Z*) configuration of the exocyclic double bond in **31** prevents the system from undergoing the [4 + 2] cycloaddition with acrylate, and the 1,5-hydrogen shift can successfully compete with the Diels−Alder reaction.

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Supporting Information for this article is available on the WWW under http://www.wiley-vch.de/home/eurjoc or from the author.

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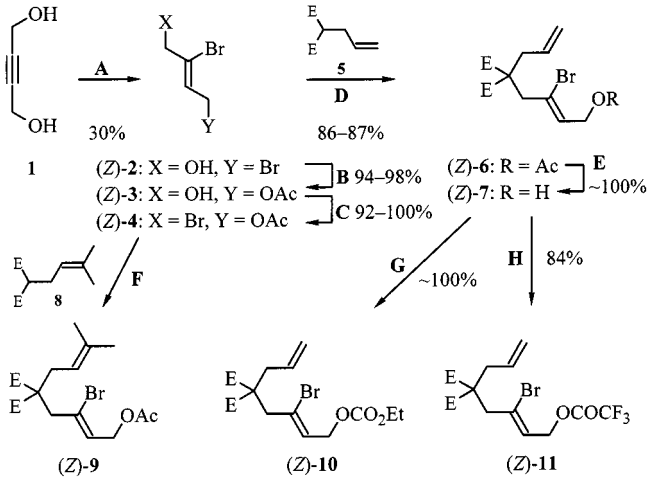
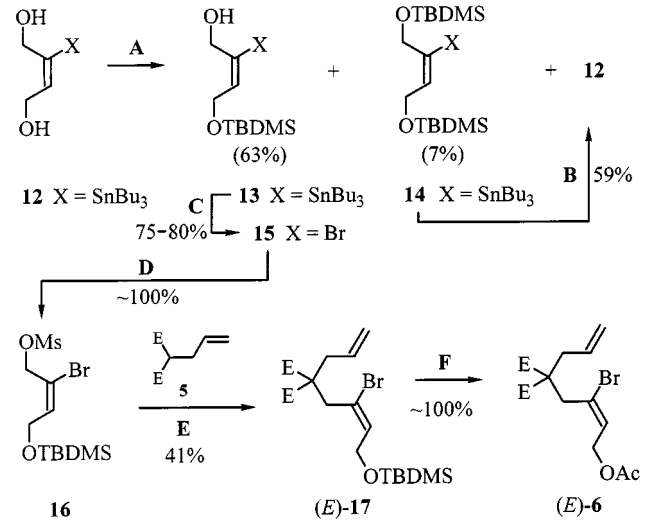
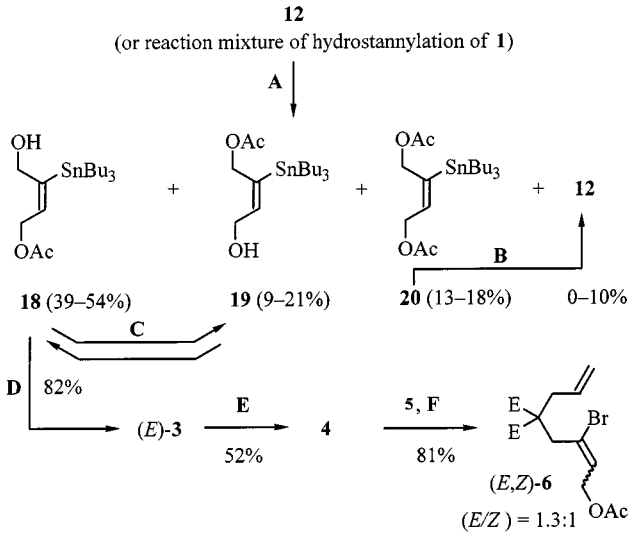


Scheme 1. Preparation of bromodienes with (*Z*) configuration of the bromoalkenyl moiety: **A**: 48% HBr (aq), 35°C, 3 d; **B**: CsOAc (1.5 equiv.), MeCN, 20°C, 8 h; **C**: PPh_3/Br_2, CH_2Cl_2, 0−20°C, 1.5 h; **D**: NaH, THF, 0−20°C, 1 h; **E**: K_2CO_3, MeOH/H_2O, 20°C, 45 min; **F**: NaH, 0−20°C, 1.5 h; **G**: $ClCO_2Et$, C_5H_5N, CH_2Cl_2, 0−20°C, 5 h; **H**: $(CF_3CO)_2O$, Et_2O, 0−20°C, 30 min; E = CO_2Me

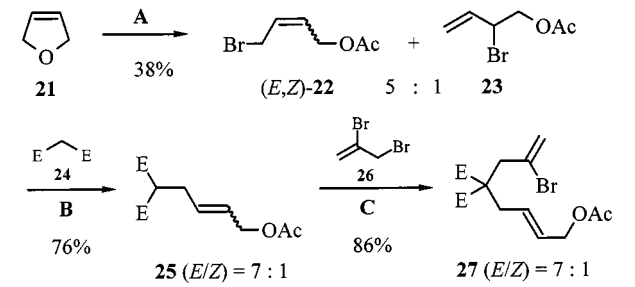


Scheme 2. Synthesis of compound (*E*)-**6** via trialkylsilyl-protected intermediates: **A**: TBDMSCl, ImH, DMF, 0°C, 6 h; 20°C, 12 h; **B**: nBu_4NF, THF; **C**: Br_2, CCl_4, −20 → 20°C; **D**: MsCl, NEt_3, CH_2Cl_2, −60 → 0°C; **E**: NaH, THF, 0 → 20°C, 2 h; **F**: 1) nBu_4NF, 20°C, 20 min, 2) Ac_2O, DMAP (cat.), THF, 20°C, 50 min; E = CO_2Me

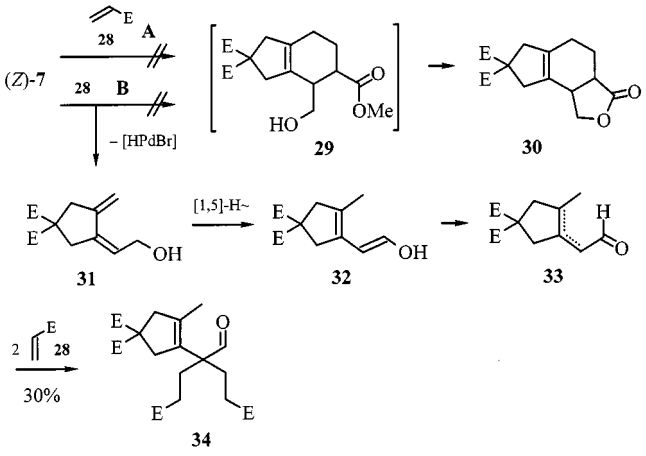
Because the tautomerization of enol **32** (and thereby its base-catalyzed subsequent reactions) can be blocked by acetylation of the hydroxy group, the acetate (*Z*)-**6** was subjected to the same conditions. Surprisingly, neither the expected 1-acetoxymethyl-1,3-diene **40** nor the corresponding enol acetate, but instead a mixture of vinylcyclopropane **35**, 1,3-diene **36**, and traces of the triene **37** (a [3]dendralene[12]) were isolated. By proper variation of ligands, bases, and allylic leaving groups, conditions could be found that led selectively to each one of these cyclization products (see Table 1, Scheme 6). The acetate **40** was isolated only when silver carbonate was used as a base (entries 7 and 12, 19−20%). Under certain conditions, the cyclohexene derivative (*E*)-**39** and isomerized 1-acetoxymethyl-1,3-diene **38**



Scheme 3. Synthesis of compound (*E*)-**6** via acetates: **A**: Ac_2O, NEt_3, DMAP (cat.), CH_2Cl_2, 0−20°C, 2 h; **B**: K_2CO_3, MeOH/H_2O; **C**: 20°C, 1 d; **D**: Br_2, CCl_4, −10°C, 30 min; **E**: PPh_3/Br_2, CH_2Cl_2, 0 → 20°C, 1 h; **F**: NaH, THF, 0 → 20°C, 1 h; E = CO_2Me



Scheme 4. Preparation of bromodiene **27**: **A**: MeCOBr, C_6H_6, 0 → 20°C, 15 h; **B**: NaH, THF, 0 → 20°C, 2 h; **C**: NaH, THF, 0 → 20°C, 4 h; E = CO_2Me



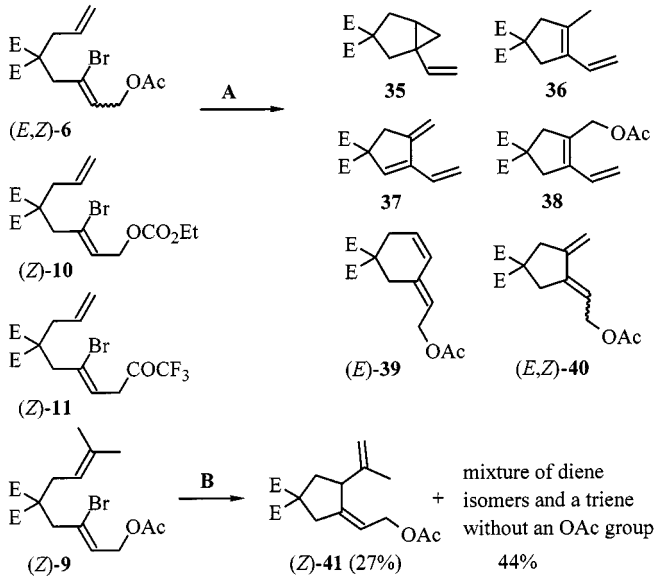
Scheme 5. Cyclization and further reactions of alcohol (*Z*)-**7**: **A**: $Pd(OAc)_2$, PPh_3, Ag_2CO_3, MeCN, 85°C; **B**: same as **A**, but K_2CO_3/Et_4NBr as base; E = CO_2Me

were isolated in low yields (entries 3−5). The acetate (*Z*)-**9**, which corresponds to (*Z*)-**6** with a prenyl instead of an allyl moiety, yielded acetoxydiene (*Z*)-**41** (27%) and a mixture of dienes and trienes that could not be separated and characterized any further (ca. 24%) (Scheme 6).

Table 1. Product distribution in cyclizations of (*E*,*Z*)-**6**, (*Z*)-**10**, and (*Z*)-**11**[a]

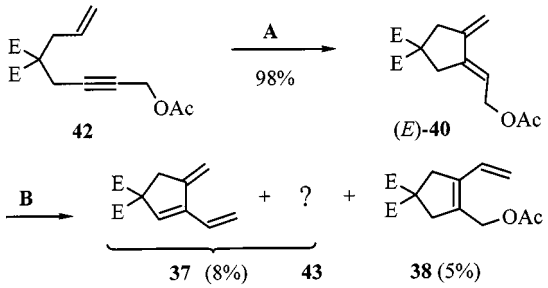
Entry	Bromo-diene	Ligand	Base	Ratio **35** / **36** / **37**	Yield (%)[b]	Further products	Yield (%)	Recovered start. mater. (%)
1	(*Z*)-**6**	PPh_3	NEt_3	10 / 1 / –	33	–	–	–
2	(*Z*)-**6**	PPh_3	K_2CO_3	8 / 8 / 1	40	–	–	–
3	(*Z*)-**6**	PPh_3	NaO_2CH	2 / 1 / –	40[c]	(*E*)-**39**	5	–
4	(*Z*)-**6**	PPh_3[d]	NEt_3	11.4 / 1 / 1	32	**38**	7	22
5	(*Z*)-**6**	dppe	NEt_3	4.6 / 4.6 / 1	11	**38**	4	53
6	(*Z*)-**6**	dmphen[e]	NEt_3	1 / 15 / 1.8	37	–	–	9
7	(*Z*)-**6**	PPh_3	Ag_2CO_3	1 / – / 5	36	**40**[f]	19	–
8	(*Z*)-**11**[g]	PPh_3	NEt_3	20 / 2.2 / 1	40	–	–	–
9	(*Z*)-**11**	dmphen[e]	NEt_3	trace / 3 / 2	34	(*Z*)-**7**	19	–
10	(*Z*)-**10**	PPh_3	NEt_3[h]	2.1 / 1 / –	32	–	–	32
11	(*E*)-**6**[g]	PPh_3	NEt_3	3.1 / 1.2 / 1	23	–	–	–
12	(*E*)-**6**	PPh_3	Ag_2CO_3	3.3 / trace / 1	30	**40**[i]	20	
13	(*E*)-**6**	dmphen[e]	NEt_3	– / 1 / –	31	–	–	10

[a] General reaction conditions: $Pd(OAc)_2$ (10 mol-%), ligand (22 mol-%), 2.1 equiv. of base, MeCN, 85 °C, 5–6 h. – [b] Combined yield (**35** + **36** + **37**). – [c] Fraction contained unidentified by-products. – [d] 105 mol-% of ligand used. – [e] dmphen = 2,9-dimethyl-1,10-phenanthroline, used as 10 mol-% [$Pd(OAc)_2$dmphen]. – [f] (*E*)/(*Z*) = 1:3. – [g] $Pd(OAc)_2$ (18 mol-%), ligand (45 mol-%), base (3.3 equiv.) used. – [h] Only 1.1 equiv. of NEt_3 used. – [i] (*E*)/(*Z*) = 3:1.



Scheme 6. Cyclization of bromodienes **6** and **9**–**11**: **A**: $Pd(OAc)_2$ (10 mol-%), ligand (22 mol-%), base (210 mol-%), MeCN, 85°C, 5–6 h; **B**: $Pd(OAc)_2$, PPh_3, NEt_3, MeCN, 85°C, 5.5 h; E = CO_2Me; for further details see Table 1

To obtain more information about the mechanisms and to verify the (*Z*) configuration of acetate **40**, 1,6-enyne acetate **42** (see below) was cyclized with 5 mol-% of $Pd(dba)_2$, 10 mol-% of $SbPh_3$, and 10 mol-% of acetic acid in [D_6]benzene[13] to give (*E*)-**40** in 98% yield; the (*Z*) isomer was not detected in the ^{1}H-NMR spectrum. (*E*)-**40** decomposed completely when it was heated with palladium acetate, triphenylphosphane, and triethylamine in acetonitrile at 85 °C for 6 h (conditions that lead selectively to **35**, see entries 1, 4, 8 in Table 1), only ca. 8% of a mixture of triene **37** and an unknown by-product in a ratio of 3:1 and 5% isomerized acetoxymethyldiene **38** (Scheme 7) could be isolated. With Ag_2CO_3 instead of NEt_3 under otherwise identical conditions, 15% of (*E*)-**40** was recovered, and traces of **38** were found. This decomposition was not expected because some palladium-catalyzed reactions with (acyclic) 1-acetoxymethyl-1,3-dienes proceed under comparable conditions.[14]



Scheme 7. Cyclization and further reactions of enyne **42**: **A**: [$Pd(dba)_2$], $SbPh_3$, HOAc, C_6D_6, 40°C, 5.5 d; **B**: $Pd(OAc)_2$, PPh_3, NEt_3, MeCN, 85°C, 6 h; E = CO_2Me

The cyclization of **27** (Scheme 8) under a variety of conditions (see Table 2) always yielded 1,4-diene **44**.[15] This diene was not observed in the reactions of **6**, **9**, and **10**; and here neither vinylcyclopropane **35**, diene **36**, or triene **37** nor cyclization products containing an acetoxy moiety were obtained. Another difference is the incomplete consumption of **27** even after reducing agents had been added (see entries 3, 4, 5) while the other bromodienes, with a few exceptions, were completely converted into products.

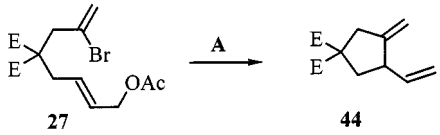
Mechanistic Considerations

In the 1-substituted 2-bromo-1,6-dienes **6**, **9**–**11** with an acyloxy leaving group in an allylic position, the oxidative addition to Pd^0 can occur both at the bromoalkenyl moiety to form an alkenylpalladium species and at the allylic position to form a η^1- or η^3-allyl complex. Nwokogu[16] observed in reactions of 1-acetoxy-2-bromo-2-alkenes that the bromo substituent at the double bond reduced the reactivity in palladium-catalyzed allylic substitutions dramatically. Coupling of the bromoalkenyl moiety with terminal alkynes, however, proceeded under usual conditions without side reactions of the acetoxy substituents. In accordance

Table 2. Palladium-catalyzed reductive cyclization of acetoxybromodiene **27** to **44** under different conditions[a]

Entry	Ligand (mol-%)	Base (mol-%)	Yield (%)	Recovered **27** (%)
1	PPh_3 (16)	NEt_3 (212)	30	n. d.[b]
2	PPh_3 (110)	NEt_3 (212)	28	n. d.[b]
3	PPh_3 (16)	–	4	87
4	PPh_3 (110)	–	17	39
5	PPh_3 (16)	NaO_2CH (125)	27	71
6	PPh_3 (16)	K_2CO_3 (106)	14	64[c]
7	dmphen (20)[d]	NEt_3 (212)	39	–[e]

[a] General reaction conditions: $Pd(OAc)_2$ (7 mol-%), MeCN, 85 °C, 8 h. – [b] Not determined. – [c] Mixture with non-identified compound. – [d] dmphen = 2,9-dimethyl-1,10-phenanthroline, used as $[Pd(OAc)_2$dmphen] (20 mol-%). – [e] Only an unidentified compound was isolated.

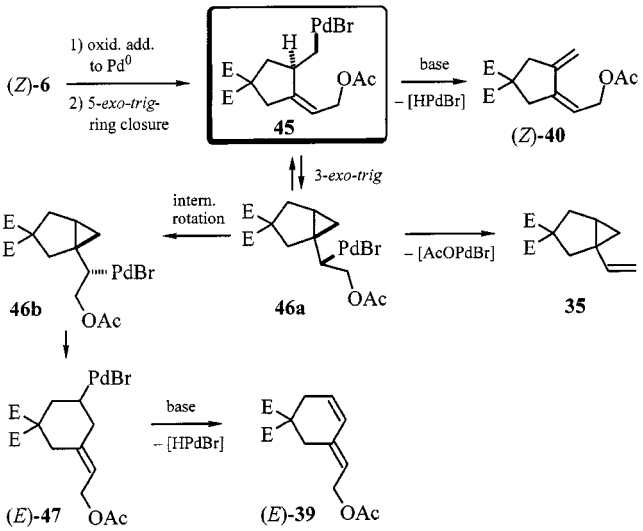


Scheme 8. Cyclization of bromodiene **27**: **A**: $Pd(OAc)_2$, ligand, base, MeCN, 85°C, 8 h; E = CO_2Me; for further details see Table 2

with these results, the formation of the observed products from **6**, **9**–**11** can be rationalized in terms of the oxidative addition occurring at the bromoalkene moiety except for one case (i.e. the formation of triene **37**).

The pathways to (*Z*)-**40**, **35**, and (*E*)-**39** are shown in Scheme 9. Oxidative addition of the C–Br bond in (*Z*)-**6** to Pd^0 followed by alkene insertion gives alkylpalladium species **45** that has a hydrogen atom β to palladium. However, 3-*exo-trig* ring closure leading to cyclopropylmethylpalladium species **46a** apparently is comparable in rate or even faster than internal rotation in **45** (to achieve a synperiplanar orientation between this hydrogen atom and the palladium residue); subsequent β-hydride elimination in **46a** then gives acetoxydiene (*Z*)-**40**. In principle, **46a** can cycloreverse to **45** or – after internal rotation to conformer **46b** – yield the six-membered ring product (*E*)-**39**, but the irreversible β-elimination of AcOPdBr in **46a** leading to vinylcyclopropane **35** apparently wins. The possibility of such a rapid β-acetate elimination is crucial for the formation of **35**,[17] since in the reaction of a 1-methyl-substituted 2-bromo-1,6-diene leading to an intermediate analogous to **45** with a methyl group in place of the acetoxymethyl group a 3-*exo-trig* ring closure followed by β-hydride elimination to yield **35**, was not observed.[3] Obviously, β-hydride elimination is slower than cycloreversion of a cyclopropylmethylpalladium to a homoallylpalladium species.[3] In the previously reported examples of Heck reactions leading to vinylcyclopropanes, the intermediate alkylpalladium species that correspond to **45** do not contain hydrogen atoms accessible for β-hydride elimination so that for them 3-*exo-trig* (or some other) ring closure is the only accessible reaction channel.[2,5,18]

Complexation of Pd^{II} by the oxygen atoms in the acetate moiety of **45** might, in principle, slow down or prevent the internal rotation required for β-hydride elimination so that



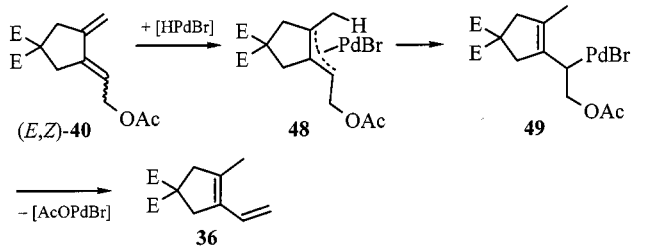
Scheme 9. Rationalization of the formation of vinylcyclopropane **35** and acetoxydienes (*E*)-**39**, (*Z*)-**40** from (*Z*)-**6**; E = CO_2Me

the 3-*exo-trig* ring closure to give **46a** would compete.[19] However, (*E*)-**6** also gave vinylcyclopropane **35** (Table 1, entries 11–12). As intramolecular complexation in the (*E*) isomer of **45** is impossible, it is apparently not an important factor for the cyclopropane formation.

The fact that the ratio of vinylcyclopropane **35** to **36** to **37** and the combined yield remain nearly the same with PPh_3 and NEt_3 when comparing acetate (*Z*)-**6** to trifluoroacetate (*Z*)-**11** (Table 1, entries 1, 8) supports this mechanism because one would expect considerable changes if oxidative addition of the allylic acetate or trifluoroacetate were the first step. This mechanism is further supported by the observation that acetoxydiene (*Z*)-**41** is obtained from (*Z*)-**9**; in this case, no vinylcyclopropane is formed since in the intermediate corresponding to **45** the six hydrogen atoms of the two methyl groups are available for β-hydride elimination.

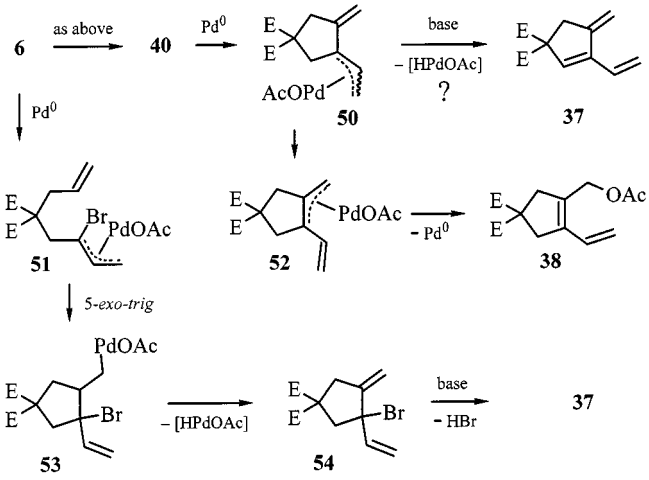
The diene **36** most probably is formed by readdition of HPdBr with reversed orientation to the diene moiety of acetoxydiene **40** to give the allyl complex **48**, which subsequently undergoes β-acetate elimination (Scheme 10). In accordance with this mechanism, conditions under which hydridopalladium halides have only short lifetimes (e.g. in the presence of silver carbonate) suppress the formation of **36** so that **40** can be isolated. On the other hand, 2,9-dimethyl-1,10-phenanthroline as a ligand favors the readdition of HPdBr, as was also observed for the basic system [a bis(exomethylene)cyclopentane].[3]

The triene **37** might be formed by oxidative addition of the dienyl acetate moiety in **40** to Pd^0 followed by β-hydride elimination. Since compound **37** obtained from (*E*)-**40** in a separate experiment contained an unidentified by-product which was not observed with the bromodienes **6** and **11** as starting materials, a different mechanism might apply in those cases (Scheme 11), i.e. oxidative addition of the allyl ester moiety to Pd^0, alkene insertion and β-hydride elimination would yield bromodiene **54**, which should be dehydrobrominated rather easily (either directly by the action of the



Scheme 10. Rationalization of the formation of diene **36**; E = CO_2Me

base or by oxidative addition to Pd^0 and β-hydride elimination).



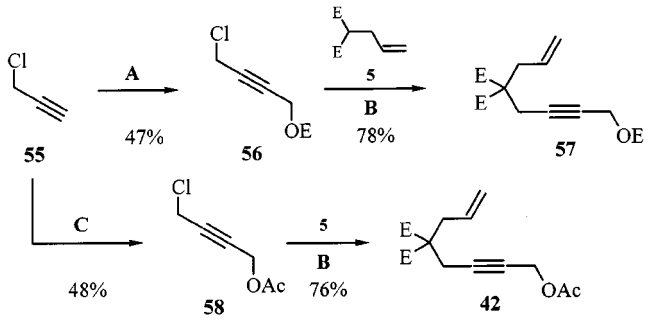
Scheme 11. Rationalization of the formation of triene **37** and acetoxydiene **38**; E = CO_2Me

The formation of the isomerized 1-acetoxymethyl-1,3-diene **38** can be explained by oxidative addition of **40** to palladium(0) and readdition of acetate to yield the thermodynamically favored product (Scheme 11).

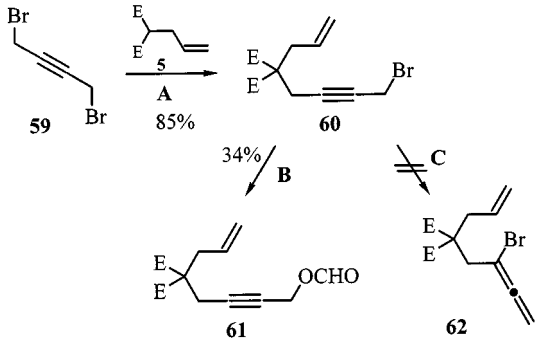
Cyclization of 1-Substituted 1,6-Enynes

As reported previously 2-bromo-1,6-dienes with a bromomethylenecycloalkane starter do cyclize to bis(exocyclic) dialkylidenecycloalkanes,[3] and the regioselectivity of their Diels−Alder reactions with acrylates change from exclusively quasi-*ortho* (in the case of the dialkylidenecyclopentane and the corresponding dimethyl-substituted derivative) to exclusively quasi-*meta* (in the case of the cyclopropylidenemethylene derivative). In order to test the possibility of generating the corresponding methylenevinylidene derivative (an exocyclic vinylallene), and its subsequent reaction with dienophiles,[20] the method of Mandai, Tsuji et al.[21] for the preparation of 1,2,4-trienes was applied to the 1,6-enyne carbonate **57**. This substrate and the corresponding bromide **60** were readily prepared applying standard procedures[22−25] (Schemes 12, 13; for details see the electronic Supporting Information).

The enyne carbonate **57** was treated with $Pd(OAc)_2$ (10 mol-%) and PPh_3 (24 mol-%) in acetonitrile at 85°C for



Scheme 12. Preparation of enyne carbonate **57** and enyne acetate **42**: **A**: 1) *n*BuLi, 2) $(HCHO)_n$, 3) $ClCO_2Me$, Et_2O/hexane; **B**: NaH, DMF, 25°C, 24 h; **C**: 1) *n*BuLi, 2) $(HCHO)_n$, 3) AcCl, Et_2O/hexane; E = CO_2Me.

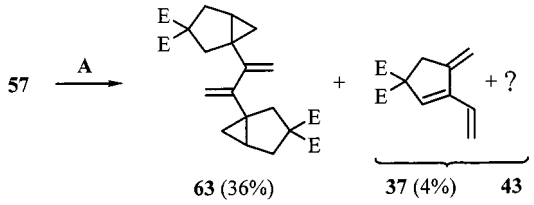


Scheme 13. Preparation of enyne formate **61** and bromide **60**: **A**: NaH, THF, 20°C, 3 h; **B**: NaO_2CH, $(nBu)_4NBr$, 100°C, 9 h; **C**: CuBr, LiBr, THF, 70°C, 5 h; E = CO_2Me

1.5 h in the presence of 2.0 equiv. of methyl acrylate (**28**) as dienophile in order to trap the expected − most probably very sensitive − vinylallene as a stable Diels−Alder adduct. However, the reaction took a totally different course: Apart from the known cross-conjugated triene **37** (see above) isolated together with the previously observed by-product **43** in 4% yield, the main product (36%) proved to be the 2,3-bis(bicyclo[3.1.0]hex-1-yl)-substituted 1,3-butadiene **63**, a dehydrodimer of the vinylcyclopropane **35** (Scheme 14). Yields and product distribution did not change when the reaction was performed in the absence of methyl acrylate. Under Mandai−Tsuji conditions [$Pd(OAc)_2$, PPh_3, KBr, H_2O, DMF][21] in the presence of methyl acrylate (**28**), **63** was formed only in trace amounts along with a lot of other compounds, but the expected Diels−Alder adduct was not observed at all. Subjecting the corresponding enyne acetate **42** to the conditions that gave **63** from **57** in the presence of methyl acrylate (**28**) only led to complete decomposition. Surprisingly, employing the enyne bromide **60** in the presence of potassium carbonate gave no reaction product, but only slightly impure starting material.

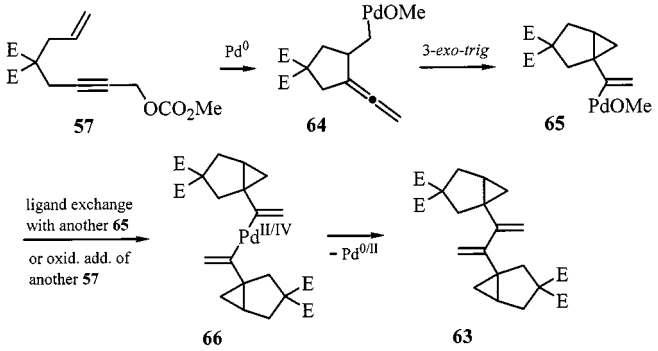
Mechanistic Considerations

The formation of the unusual 1,3-butadiene **63** (Scheme 15) most probably starts with an oxidative addition of the propargylic carbonate moiety to a palladium(0) species re-



Scheme 14. Cyclization of enyne carbonate **57**: **A**: $Pd(OAc)_2$ (10 mol-%), PPh_3 (24 mol-%), MeCN, 85 °C, 1.5 h; E = CO_2Me

sulting in an allenylpalladium species. With propargylic acetates, this type of reaction only occurs in the presence of Lewis acids.[26] Insertion of the alkene then forms the alkylpalladium species **64**, which could undergo β-hydride elimination to the vinylallene only after a 180° rotation around the exocyclic C−C single bond. However, 3-*exo-trig* cyclization with attack onto the allene moiety to yield the cyclopropylethenylpalladium species **65** with the palladium bound to the internal carbon atom of the ethenyl group apparently is faster and, most importantly, not as easily reversible, because **65** is an alkenyl- and not an alkylpalladium species.[27]



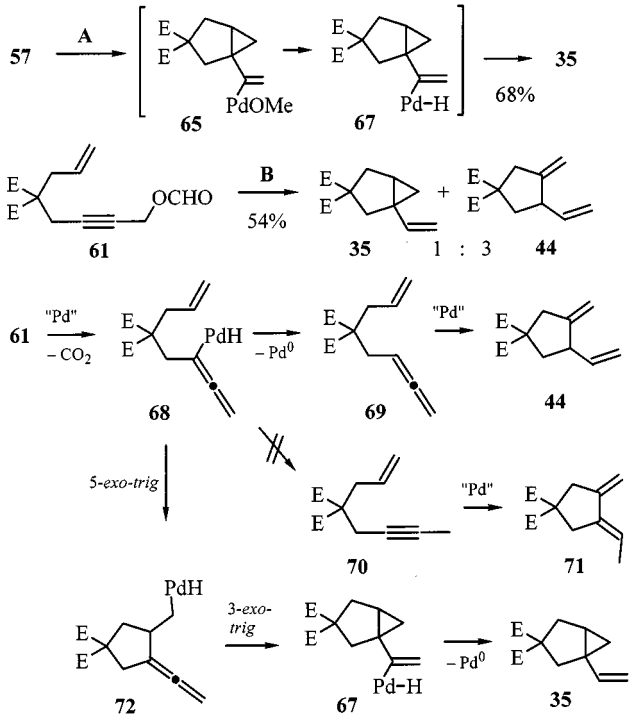
Scheme 15. Rationalization of the formation of the vinylcyclopropane "dimer" **63**; E = CO_2Me

Such a 3-*exo-trig* cyclization with C−C-bond formation on an external carbon atom of the allene is exceptional, since intermolecular Heck reactions with allenes[28] or intramolecular ones forming six-membered and larger rings[29] are known to proceed with the opposite regioselectivity, i.e. the new carbon−carbon bond is formed at the central atom of the allene moiety so that a η^3-allylpalladium species results.

Since β-hydride elimination in an alkenylpalladium species such as **65** to form an alkynylcyclopropane usually does not occur,[30] one of two plausible reaction pathways leading to **63** must prevail. Either a palladium(IV) species with two cyclopropylethenyl ligands is formed by oxidative addition of a second propargylic carbonate **57**, followed by alkene insertion, and 3-*exo-trig* ring closure.[31] Reductive elimination would then yield the dehydrodimer **63** and a palladium(II) species which would be reduced by methanolate to palladium(0). Or two alkenylpalladium species **65** exchange a ligand, and the palladium(II) species with two cyclopropylethenyl ligands undergoes reductive elimination yielding the dehydrodimer **63** and a palladium(0) species.[32]

To support this mechanistic assumption, attempts to trap the cyclopropylethenylpalladium species **65** appeared to be most promising because its subsequent reaction has to be intermolecular anyway. Therefore added anion-capture reagents[33] such as hydride provided by sodium formate, should be able to compete with another species **65** or enyne carbonate **57**.

Simply adding 2.0 equiv. of sodium formate to the reaction mixture with **57** did not lead to the formation of **35**; instead, dehydrodimer **63** and diene **36** were observed. However, when 1.0 equiv. of tetraethylammonium bromide[34] was present, the ethenylcyclopropane **35** could be isolated in 68% yield without formation of any other products such as **36** or **44** (Scheme 16). This effect of the tetraalkylammonium salt[34] can be due either to enhancing the solubility of sodium formate in acetonitrile or to changing the catalytically active species by coordination of bromide ions.[35] To exclude the latter possibility, the enyne formate **61**, in which the hydride capture would be intramolecular and thus solubility problems would not play any role, was heated in acetonitrile with palladium acetate and triphenylphosphane. From this run, a 1:3 mixture of ethenylcyclopropane **35** and 1,4-diene **44** was isolated in 54% yield. The formation of 1,4-diene **44** is best rationalized by a hydride transfer *before* the 5-*exo-trig* cyclization takes place so that an open-chain enallene **69** is formed, which then exclusively gives **44** since the enyne **70** would cyclize to the 1,3-diene **71** (Scheme 16).[36]



Scheme 16. Cyclization with subsequent hydride capture of **57** and **61**: **A**: $Pd(OAc)_2$, PPh_3, NaO_2CH, Et_4NBr, MeCN, 85°C, 2 h; **B**: $Pd(OAc)_2$, PPh_3, MeCN, 85°C, 2 h; E = CO_2Me

Experimental Section

General: ^{1}H-NMR spectra were recorded with a Bruker AM 250 (250 MHz) at ambient temperature in $CDCl_3$ using tetramethylsilane (TMS, δ = 0.00) or $CHCl_3$ (δ = 7.26) as internal standard. The line positions or centers of multiplets are given in ppm (δ), the coupling constants (*J*) are given as absolute values in Hz, and the signal multiplicities are abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), AB (AB system), and br. (broad). ^{13}C-NMR spectra were recorded with a Bruker AM 250 (62.9 MHz) at ambient temperature in $CDCl_3$ with δ($CDCl_3$) = 77.00 as internal standard. Multiplicities were determined by the DEPT sequence and are given as follows: +: CH or CH_3; ++: CH; −: CH_2; and C_{quat}: C. If signals could not be assigned unambiguously all possible atoms are marked with an asterisk *. − Infrared spectra were recorded with a Bruker FT-IR instrument model IFS 66. − Mass spectra were recorded using electron impact ionization at 70 eV or direct chemical ionization with NH_3 as reactant gas. High resolution mass spectra (HRMS) were obtained with a Varian MAT 311 using preselected ion peak matching at $R \approx 10000$ to be within ± 2 ppm. − All melting points were determined with a Büchi melting point apparatus and are uncorrected. − Boiling points were determined upon fractional distillation unless stated otherwise and are uncorrected. − Elemental analyses were performed by the Mikroanalytisches Labor des Institutes für Organische Chemie der Universität Göttingen, Germany. − All solvents for chromatography were distilled before use. The petroleum ether (PE) had a boiling range of 35−80 °C. − The bromodienes **6**, **7**, **9**−**11**, **27** as well as the 1,6-enyne carbonate **57** and the corresponding bromide **60** (Schemes 1−4, 12, 13) were prepared according to standard protocols. For details see the electronic Supporting Information.[37−39,41−44]

General Procedure for Heck Reactions and In-Situ Heck−Diels−Alder Reactions (GP 4): To a solution of 0.62 mmol of bromodiene (and 0.74 mmol of dienophile in the case of Heck−Diels−Alder reaction) in 8 mL of anhydrous acetonitrile in a screw-cap Pyrex bottle are added 5 mol-% of palladium acetate, 10 mol-% of ligand and 1.2 equiv. of base. Nitrogen is bubbled through the reaction mixture for 1 min, then the bottle is closed and heated to 80−85 °C (temperature of the heating bath) for the given times. After cooling to room temp. the reaction mixture is filtered through a glass frit (diameter 3 cm), which is filled (from top to bottom) with a 0.5-cm layer of sea sand, powdered charcoal, silica gel, and Celite (1.5-cm layers each) and again 0.5 cm of sea sand, and washed with ether. The crude product was purified by chromatography on silica gel (12 g, column 1.5 × 12 cm) with petroleum ether/ether mixtures and recrystallization if applicable.

Attempted Cyclization of Dimethyl [2′-Bromo-4′-hydroxy-(2′*Z*)-butenyl]-2′′-propenylmalonate [(*Z*)-7]: According to GP 4 a mixture of bromodiene (*Z*)-**7** (119 mg, 0.371 mmol), $Pd(OAc)_2$ (7 mg, 0.03 mmol), PPh_3 (21 mg, 0.08 mmol), and Ag_2CO_3 (113 mg, 0.410 mmol) was heated in acetonitrile (4 mL) at 85 °C for 10 h. The ^{1}H-NMR spectrum of the reaction mixture showed only signals of (*Z*)-**7** and decomposition products.

Dimethyl 3-[3′-Formyl-1′,5′-bis(methoxycarbonyl)pent-3′-yl]-4-methyl-3-cyclopentene-1,1-dicarboxylate (34): According to GP 4 dimethyl [2′-bromo-4′-hydroxy-(2′*Z*)-butenyl]-2′′-propenylmalonate [(*Z*)-**7**] (130 mg, 0.405 mmol) was treated with $Pd(OAc)_2$ (9 mg, 0.04 mmol), PPh_3 (23 mg, 0.088 mmol), K_2CO_3 (66 mg, 0.480 mmol), Et_4NBr (95 mg, 0.45 mmol), and methyl acrylate (**28**) (94 mg, 1.1 mmol) in 4 mL of acetonitrile at 85 °C for 9 h. The crude product was purified by chromatography on 8 g of silica gel (column 1.5 × 10 cm, PE/ether, 1:1), yielding 50 mg (30%) of **34** as a colorless oil, R_f (PE/ether, 2:1) = 0.09. − IR (film): $\tilde{\nu}$ = 2955 cm^{-1}, 2820, 1734 (C=O), 1437 (CH_2 and CH_3 deformation), 1373, 1262, 1202 (C−O), 1074, 988, 757. − ^{1}H NMR (250 MHz, $CDCl_3$, $CHCl_3$): δ = 1.58 (br. s, 3 H, 4-CH_3), 1.88−2.36 [AA′BB′, 8 H, 1′(5′)-H, 2′(4′)-H], 3.02 (br. s, 2 H, 2-H*), 3.05 (br. s, 2 H, 5-H*), 3.66 (s, 6 H, CO_2CH_3), 3.74 (s, 6 H, 1-CO_2CH_3), 9.49 (s, 1 H, CHO). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT135, DEPT90): δ = 15.10 (+, 4-CH_3), 27.22 and 28.68 [−, C-1′(5′), C-2′(4′)], 42.33 (−, C-5*), 47.11 (−, C-2*), 51.72 [+, 1′(5′)-CO_2CH_3], 52.91 (+, 1-CO_2CH_3), 54.13 (C_{quat}, C-3′), 56.58 (C_{quat}, C-1), 128.60 (C_{quat}, C-3), 134.86 (C_{quat}, C-4), 172.10 (C_{quat}, 1-CO_2CH_3), 173.22 [C_{quat}, 1′(5′)-CO_2CH_3], 201.49 (++, CHO). − MS (EI, 70 eV), *m*/*z* (%): 412 (0.8) [M^+], 384 (12) [M^+ − CO], 352 (60) [M^+ − MeOH − CO], 321 (16) [M^+] − [MeOH − OMe − CO], 293 (39) [M^+ − MeOH − Me − 2 CO], 292 (100) [M^+ − 2MeOH − 2 CO], 261 (30) [M^+ − 2 MeOH − OMe − 2 CO], 260 (27) [M^+ − 3 MeOH − 2 CO], 259 (25) [M^+ − MeOH − 3 OMe − CO], 232 (12) [M^+ − 3 MeOH − 3 CO], 231 (20) [M^+ − MeOH − 3 OMe − 2 CO], 219 (18), 205 (20) [M^+ − 2 MeOH − OMe − 4 CO], 189 (8), 187 (8), 173 (10) [M^+ − 3 MeOH − OMe − 4 CO], 159 (9), 145 (8) [M^+ − 3 MeOH − OMe − 5 CO], 131 (9), 117 (12), 115 (10), 59 (9). − $C_{20}H_{28}O_9$ (412.4): calcd. 412.1733 (HRMS correct).

Cyclizations of Dimethyl [4′-Acetoxy-2′-bromo-(2′*Z*)-butenyl]-2′′-propenylmalonate [(*Z*)-6]. − Method A: As described in GP 4, bromodiene (*Z*)-**6** (145 mg, 0.400 mmol) was treated with $Pd(OAc)_2$ (9 mg, 0.04 mmol, 10 mol-%), PPh_3 (23 mg, 0.088 mmol, 22 mol-%), and NEt_3 (81 mg, 0.80 mmol) in acetonitrile (4 mL) at 85 °C for 6 h. Column chromatography on silica gel (8 g, column 1.5 × 8.5 cm, PE/ether, 20:1) yielded 30 mg (33%) of a 10:1 mixture of dimethyl 1-ethenylbicyclo[3.1.0]hexane-3,3-dicarboxylate (**35**) and dimethyl 3-ethenyl-4-methyl-3-cyclopentene-1,1-dicarboxylate (**36**), respectively, as a colorless oil, R_f (PE/ether, 4:1) = 0.36. − **35**: IR (film): $\tilde{\nu}$ = 3085 cm^{-1}, 3005, 2954, 1734 (C=O), 1634 (C=C), 1435 (CH_2 and CH_3 deformation), 1314, 1252 (C−O), 1202, 1173, 1116, 1092, 1072, 1034, 995 (CH=CH_2), 945, 897, 853, 816, 696. − ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 0.50 (dd, ^2J = 5.9, ^3J = 4.5 Hz, 1 H, 6-H_{endo}), 0.70 (dd, ^2J = 5.9, ^3J = 8.2 Hz, 1 H, 6-H_{exo}), 1.39 (app dt, ^3J = 8.2, ^3J = 4.3 Hz, 1 H, 5-H), 2.50 (d of part A of an AB system, ^3J = 4.8, $^2J_{AB}$ = 13.8 Hz, 1 H, 4-H_{exo}), 2.59 (part B of an AB system, $^2J_{AB}$ = 13.8 Hz, 1 H, 4-H_{endo}), 2.62 (s, 2 H, 2-H), 3.70 [s, 3 H, CO_2CH_3; ^{13}C satellite: d, ^1J(C,H) = 147.7 Hz], 3.73 [s, 3 H, CO_2CH_3; ^{13}C satellite: d, ^1J(C,H) = 147.5 Hz], 4.93 (dd, ^3J = 10.6, ^2J = 1.2 Hz, 1 H, 2′-H_E), 5.00 (dd, ^3J = 17.3, ^2J = 1.2 Hz, 1 H, 2′-H_Z), 5.61 (dd, ^3J = 10.6, ^3J = 17.3 Hz, 1 H, 1′-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT135): δ = 16.94 (−, C-6), 26.10 (+, C-5), 31.36 (C_{quat}, C-1), 35.78 and 37.21 (−, C-2, C-4), 52.84 and 52.99 (+, CO_2CH_3), 59.25 (C_{quat}, C-3), 111.05 (−, C-2′), 141.69 (+, C-1′), 172.19 and 173.12 (C_{quat}, CO_2CH_3). − MS (EI, 70 eV), *m*/*z* (%): 224 (4) [M^+], 193 (5) [M^+ − OMe], 192 (3) [M^+ − MeOH], 165 (34) [M^+ − OMe − CO], 164 (40) [M^+ − MeOH − CO], 161 (2) [M^+ − MeOH − OMe], 160 (2) [M^+ − 2 MeOH], 133 (8) [M^+ − MeOH − OMe − CO], 132 (5) [M^+ − 2 MeOH − CO], 105 (100) [M^+ − MeOH − OMe − 2 CO], 104 (16) [M^+ − 2 MeOH − 2 CO], 91 (10), 79 (10), 77 (10) [$C_6H_5^+$], 59 (6). − $C_{12}H_{16}O_4$ (224.3): calcd. C 64.27, H 7.19; found C 64.40, H 7.15. − **36**: The spectroscopic data in ref.[40] are incomplete [no ^{13}C-NMR spectrum, different chemical shift of 1′-H, IR only as mixture with dimethyl 2-(1′,3′-butadiene-2′-yl)-2-methylcyclopropane-1,1-dicarboxylate]. − IR (film) (see entries 6, 13 in Table 1): $\tilde{\nu}$ = 3088 cm^{-1}, 3009, 2954, 2855, 1737 (C=O), 1657 (C=C), 1601, 1435 (CH_2 and CH_3 deformation), 1261 (C−O), 1199, 1167, 1126, 1073, 988, 963, 901, 863, 821, 687, 527. − ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 1.76 (t, ^4J = 1.5 Hz, 3 H, 4-CH_3), 3.07 (br. s,

2 H, 2-H), 3.15 (q, ^4J = 1.6 Hz, 2 H, 5-H), 3.75 [s, 6 H, CO_2CH_3; ^{13}C satellite: d, ^1J(C,H) = 147.4 Hz], 5.01−5.09 (m, 2 H, 2′-H), 6.56 (dd, ^3J = 17.1, ^3J = 11.0 Hz, 1 H, 1′-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT135): δ = 13.42 (+, 4-CH_3), 40.49 (−, C-2), 46.38 (−, C-5), 52.84 (+, CO_2CH_3), 56.85 (C_{quat}, C-2), 113.72 (−, C-2′), 129.95 (+, C-1′), 131.13 (C_{quat}, C-4), 134.74 (C_{quat}, C-3), 172.61 (C_{quat}, CO_2CH_3).

Method B: With K_2CO_3 (124 mg, 0.897 mmol) as a base instead of NEt_3 under conditions otherwise identical with those of method A, one obtained 36 mg (40%) of a 8:8:1 mixture of vinylcyclopropane **35**, diene **36**, and dimethyl 3-ethenyl-4-methylenecyclopent-2-ene-1,1-dicarboxylate (**37**). − **37**: Colorless oil, R_f (PE/ether, 4:1) = 0.30. − IR (film): ṽ = 3088 cm^{-1}, 3009, 2954, 2855, 1737 (C=O), 1657 (C=C), 1601, 1435 (CH_2 and CH_3 deformation), 1261 (C−O), 1199, 1167, 1126, 1073, 988, 963, 901, 863, 821, 687, 527. − ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 3.24 (dd, ^4J = 2.3, ^4J = 1.9 Hz, 2 H, 5-H), 3.75 [s, 6 H, CO_2CH_3; ^{13}C satellite: d, ^1J(C,H) = 147.8 Hz], 5.01 [dt (app q), ^5J = 1.7, ^4J = 1.9 Hz, 1 H, 4-CH_2], 5.13 (dt, ^5J = 0.7, ^4J = 2.3 Hz, 1 H, 4-CH_2), 5.34 (dd, ^3J = 11.1, ^2J = 1.6 Hz, 1 H, 2′-H_E), 5.67 (dd, ^3J = 17.7, ^2J = 1.6 Hz, 1 H, 2′-H_Z), 6.22 (br. s, 1 H, 2-H), 6.38 (ddd, ^3J = 17.7, ^3J = 11.1, ^4J =0.9 Hz, 1 H, 1′-H). − Decoupling experiments: a) Irradiation at δ = 3.24: changes at δ = 5.01 (d, ^5J = 1.7 Hz), 5.13 (d, ^5J =0.7 Hz). − b) Irradiation at δ = 5.01: changes at δ = 3.24 (d, ^4J =2.3 Hz); δ = 6.38 remains unchanged. − c) Irradiation at δ = 6.22: changes at δ = 5.01 (t, ^4J = 1.9 Hz), 5.13 (t, ^4J = 2.3 Hz), 6.38 (dd, ^3J = 17.7, ^3J = 11.1 Hz). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT135): δ = 38.68 (−, C-5), 52.98 (+, CO_2CH_3), 63.17 (C_{quat}, C-1), 104.94 (−, 4-CH_2), 118.96 (−, C-2′), 128.21 (+, C-1′), 130.43 (+, C-2), 144.68 (C_{quat}, C-4*), 148.36 (C_{quat}, C-3*), 170.80 (C_{quat}, CO_2CH_3). − MS (EI, 70 eV), *m/z* (%): 222 (29) [M^+], 190 (4) [M^+ − MeOH], 163 (100) [M^+ − OMe − CO], 162 (16) [M^+ − MeOH − CO], 135 (12) [M^+ − OMe − 2 CO], 131 (16) [M^+ − MeOH − OMe − CO], 104 (100) [M^+ − 2 OMe − 2 CO], 103 (55) [M^+ − MeOH − OMe − 2 CO], 77 (11) [$C_6H_5^+$], 59 (11). − $C_{12}H_{14}O_4$ (222.2): calcd. C 64.85, H 6.35; found C 65.12, H 6.43.

Method C: Using sodium formate (58 mg, 0.85 mmol) as a base instead of NEt_3 under conditions otherwise identical with those of method A gave fraction I: 36 mg (ca. 40%) of a mixture of vinylcyclopropane **35** and diene **36** in a 2:1 ratio and unidentified compounds. − Fraction II: 6 mg (5%) of dimethyl 5-[(1′*E*)-acetoxyethylidene]-3-cyclohexene-1,1-dicarboxylate [(*E*)-**39**], yellow oil, R_f (PE/ether, 4:1) = 0.06. − ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 2.07 (s, 3 H, $OCOCH_3$), 2.72−2.75 (m, 2 H, 2-H), 2.90 (d, ^4J = 1.7 Hz, 2 H, 6-H), 3.74 (s, 6 H, CO_2CH_3), 4.72 (d, ^3J = 7.3 Hz, 2 H, 2′-H), 5.53 (br. t, ^3J = 7.4 Hz, 1 H, 1′-H), 5.79 (br. dt, ^3J = 9.9, ^3J = 3.7 Hz, 1 H, 3-H), 6.08 (dt, ^3J = 10.1, ^4J = 1.2 Hz, 1 H, 4-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT135): δ = 20.97 (+, $OCOCH_3$), 30.68 (−, C-2*), 31.08 (−, C-6*), 52.87 (+, CO_2CH_3), 57.03 (C_{quat}, C-1), 60.39 (−, C-2′), 122.38 (+, C-1′*), 126.58 (+, C-3*), 129.53 (+, C-4*), 135.65 (C_{quat}, C-5), 170.96 (C_{quat}, $OCOCH_3$), 171.15 (C_{quat}, CO_2CH_3).

Method D: Bromodiene (*Z*)-**6** (77 mg, 0.21 mmol) was treated with $Pd(OAc)_2$ (5 mg, 0.02 mmol, 10 mol-%), PPh_3 (58 mg, 0.22 mmol, 105 mol-%), and NEt_3 (50 mg, 0.50 mmol) in acetonitrile (2.5 mL) for 6 h at 85 °C. Chromatography on silica gel (8 g, column 1.5 × 8.5 cm, PE/ether, 6:1, after elution of the first fraction changed to 4:1, after elution of the second fraction changed to 2:1) yielded fraction I: 15 mg (32%) of a 11.4:1:1 mixture of vinylcyclopropane **35**, diene **36** and triene **37**. − Fraction II: 17 mg (22% recovery) of starting material (*Z*)-**6**. − Fraction III: 4 mg (7%) of dimethyl 3-acetoxymethyl-4-ethenyl-3-cyclopentene-1,1-dicarboxylate (**38**), colorless oil, R_f (PE/ether, 4:1) = 0.14. − ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 2.08 (s, 3 H, $OCOCH_3$), 3.19 (br. s, 2 H, 2-H*), 3.23 (br. s, 2 H, 5-H*), 3.76 (s, 6 H, CO_2CH_3), 4.74 (br. s, 2 H, CH_2OAc), 5.22 [br. d, ^3J = 17.0 Hz, 1 H, (*Z*)-CH=CH_2], 5.23 [br. d, ^3J = 11.1 Hz, 1 H, (*E*)-CH=CH_2], 6.63 (dd, ^3J = 17.0, ^3J = 11.1 Hz, 1 H, C*H*=CH_2). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT135): δ = 20.84 (+, $OCOCH_3$), 40.64 (−, C-2*), 42.90 (−, C-5*), 53.01 (+, CO_2CH_3), 56.85 (C_{quat}, C-1), 59.38 (−, CH_2OAc), 116.98 (−, CH=CH_2), 128.85 (+, *C*H=CH_2), 131.73 (C_{quat}, C-4), 136.36 (C_{quat}, C-3), 170.91 (C_{quat}, $OCOCH_3$), 172.20 (C_{quat}, CO_2CH_3). − MS (EI, 70 eV), *m/z* (%): 282 (16) [M^+], 240 (3) [M^+ − O=C=CH_2], 222 (9) [M^+ − HOAc], 190 (15) [M^+ − MeOH − HOAc], 180 (9) [M^+ − MeOH − CO − O=C=CH_2], 163 (100) [M^+ − OMe − HOAc − CO], 162 (41) [M^+ − MeOH − HOAc − CO], 131 (10) [M^+ − MeOH − OMe − HOAc − CO], 121 (10) [M^+ − MeOH − OMe − 2 CO − O=C=CH_2], 104 (12) [M^+ − OMe − MeOH − 2 CO − OAc], 103 (29) [M^+ − MeOH − OMe − 2 CO − HOAc], 91 (12), 77 (8) [$C_6H_5^+$], 59 (9) [OAc^+], 43 (20) [$MeCO^+$]. − $C_{14}H_{18}O_6$ (282.3): calcd. 282.1103 (HRMS correct).

Method E: With dppe (24 mg, 0.060 mmol) as ligand instead of PPh_3 under conditions otherwise identical with method A one obtained fraction I: 10 mg (11%) of a 4.6:4.6:1 mixture of vinylcyclopropane **35**, diene **36** and triene **37**. − Fraction II: 77 mg (53% recovery) of starting material (*Z*)-**6**. − Fraction III: 4 mg (4%) of acetoxydiene **38**.

Method F: [$Pd(OAc)_2$(dmphen)] (17 mg, 0.040 mmol, 10 mol-%) (dmphen = 2,9-dimethyl-1,10-phenanthroline) instead of PPh_3 and $Pd(OAc)_2$ under conditions otherwise identical with those of method A gave fraction I: 33 mg (37%) of a 1:15:1.8 mixture of vinylcyclopropane **35**, diene **36** and triene **37**. − Fraction II: 13 mg (9% recovery) of starting material (*Z*)-**6**.

Method G: When Ag_2CO_3 (221 mg, 0.802 mmol) was used as a base instead of NEt_3 under conditions otherwise identical with method A, one obtained after column chromatography on flash silica gel (10 g, column 1.5 × 8.5 cm, PE/ether, 10:1, after elution of **37** changed to 2:1) fraction I: 5 mg (6%) of vinylcyclopropane **35**. − Fraction II: 27 mg (30%) of triene **37**. − Fraction III: 22 mg (19%) of dimethyl 3-[(1′*Z*)-acetoxyethylidene]-4-methylenecyclopentane-1,1-dicarboxylate (**40**), 3:1 mixture with (*E*) isomer, colorless oil, R_f (PE/ether, 2:1) = 0.26, R_f (PE/ether, 4:1) = 0.09. − IR (film): ṽ = 3002 cm^{-1}, 2956, 2846, 1737 (C=O), 1670 (C=C), 1436 (CH_2 and CH_3 deformation), 1382, 1367, 1257 (C−O), 1203, 1166, 1072, 964, 917, 823, 733, 649, 606. − ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 2.06 [s, 3 H, $OCOCH_3$; ^{13}C satellite: d, ^1J(C,H) = 129.6 Hz], 3.05 (app t, ^4J = 1.8 Hz, 4 H, 2-H, 5-H), 3.72 [s, 6 H, CO_2CH_3; ^{13}C satellite: d, ^1J(C,H) = 147.7 Hz], 4.77 (dt, ^3J = 6.3, ^5J = 1.8 Hz, 2 H, 2′-H), 5.05 (br. s, 1 H, 4-CH_2), 5.22 (br. s, 1 H, 4-CH_2), 5.95 (br. tt, ^3J = 6.3, ^4J = 1.8 Hz, 1 H, 1′-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT135): δ = 20.88 (+, $OCOCH_3$), 41.90 (−, C-2*), 42.17 (−, C-5*), 52.88 (+, CO_2CH_3), 57.33 (C_{quat}, C-1), 62.00 (−, C-2′), 112.82 (−, 4-CH_2), 120.82 (+, C-1′), 138.95 (C_{quat}, C-3), 143.30 (C_{quat}, C-4), 170.82 (C_{quat}, $OCOCH_3$), 171.45 (C_{quat}, CO_2CH_3).

Cyclization of Dimethyl [4′-Acetoxy-2′-bromo-(2′*E*)-butenyl]-2′′-propenylmalonate [(*E*)-6]: According to GP 4 bromodiene (*E*)-**6** (98 mg, 0.27 mmol) was heated with $Pd(OAc)_2$ (11 mg, 0.05 mmol), PPh_3 (32 mg, 0.12 mmol), and NEt_3 (91 mg, 0.90 mmol) in acetonitrile (3 mL) to 85 °C for 5.5 h. Chromatography on silica gel (7 g, column 1.5 × 8.5 cm, PE/ether, 6:1) gave 14 mg (23%) of a 3.1:1.2:1 mixture of **35**, **36**, and **37**.

Method B: When Ag_2CO_3 (156 mg, 0.566 mmol) was used instead of NEt_3 under conditions otherwise identical with those in method

A, one obtained after chromatography on flash silica gel (7 g, column 1.5 × 8.5 cm, PE/ether, 10:1, after elution of fraction I changed to 2:1) fraction I: 18 mg (30%) of a 3.3:1 mixture of **35** and **37** with traces of **36**. − Fraction II: 15 mg (20%) of acetoxydiene **40**.

Method C: As described in GP 4, bromodiene (*E*)-**6** (145 mg, 0.400 mmol) was treated with [$Pd(OAc)_2$(dmphen)] (17 mg, 0.040 mmol, 10 mol-%) (dmphen = 2,9-dimethyl-1,10-phenanthroline) and NEt_3 (81 mg, 0.80 mmol) in acetonitrile (4 mL) for 6 h at 85 °C. Column chromatography on silica gel (8 g, column 1.5 × 8.5 cm, PE/ether, 20:1, after elution of **36** changed to 2:1) gave fraction I: 28 mg (31%) of diene **36**. − Fraction II: 13 mg (10% recovery) of starting material (*Z*)-**6**.

Cyclization of Dimethyl [4′-Ethoxycarbonyloxy-2′-bromo-(2′*Z*)-butenyl]-2′′-propenylmalonate [(*Z*)-10]: As described in GP 4, bromodiene (*Z*)-**10** (157 mg, 0.400 mmol) was treated with $Pd(OAc)_2$ (9 mg, 0.04 mmol, 10 mol-%), PPh_3 (23 mg, 0.088 mmol, 22 mol-%) and NEt_3 (46 mg, 0.45 mmol) in acetonitrile (4 mL) at 85 °C for 6 h. Chromatography on silica gel (8 g, column 1.5 × 8.5 cm, PE/ether, 6:1, after elution of fraction I changed to 3:1) yielded fraction I: 29 mg (32%) of a 2.1:1 mixture of vinylcyclopropane **35** and diene **36**. − Fraction II: 50 mg (32% recovery) of carbonate (*Z*)-**10**.

Cyclizations of Dimethyl [4′-Trifluoroacetoxy-2′-bromo-(2′*Z*)-butenyl]-2′′-propenylmalonate [(*Z*)-11]. − Method A: As described in GP 4, bromodiene (*Z*)-**11** (175 mg, 0.419 mmol) was treated with $Pd(OAc)_2$ (13 mg, 0.06 mmol, 14 mol-%), PPh_3 (34 mg, 0.13 mmol, 31 mol-%), and NEt_3 (81 mg, 0.80 mmol) in acetonitrile (4 mL) at 85 °C (bath temp.) for 5.5 h. Chromatography on silica gel (8 g, column 1.5 × 8.5 cm, PE/ether, 20:1) gave 38 mg (40%) of a 20:2.2:1 mixture of vinylcyclopropane **35**, diene **36**, and triene **37**.

Method B: When [$Pd(OAc)_2$(dmphen)] (17 mg, 0.039 mmol, 9 mol-%) was used instead of PPh_3 and $Pd(OAc)_2$ under conditions otherwise identical with those of method A one obtained fraction I: 32 mg (34%) of a 3:2 mixture of diene **36** and triene **37**. − Fraction II: 26 mg (19%) of alcohol (*Z*)-**7**.

Cyclization of Dimethyl [4′-Acetoxy-2′-bromo-(2′*Z*)-butenyl][3′′-methyl-(2′′*E*)-butenyl]malonate (9): According to GP 4 bromodiene **9** (98 mg, 0.25 mmol) was treated with $Pd(OAc)_2$ (11 mg, 0.05 mmol), PPh_3 (32 mg, 0.12 mmol), and NEt_3 (91 mg, 0.90 mmol) in acetonitrile (3 mL) at 85 °C for 5.5 h. Chromatography on silica gel (7 g, column 1.5 × 8.5 cm, PE/ether, 6:1) yielded fraction I: 8 mg of a mixture of at least three dienes or trienes in comparable amounts containing a monosubstituted vinyl moiety but no acetoxy group, R_f (PE/ether, 5:1) = 0.43. − Fraction II: 22 mg of a mixture of two dienes or trienes, R_f (PE/ether, 5:1) = 0.37. − Fraction III: 21 mg (27%) of dimethyl 3-[(1′*Z*)-acetoxyethylidene]-4-(1′′-propen-2′′-yl)cyclopentane-1,1-dicarboxylate [(*Z*)-**41**], yellowish oil, R_f (PE/ether, 5:1) = 0.13. − ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 1.69 (br. s, 3 H, 3′′-H), 2.02 (s, 3 H, $OCOCH_3$), 2.05 (dd, ^2J = 13.2, ^3J = 8.4 Hz, 1 H, 5-H), 2.69 (ddd, ^2J = 13.3, ^3J = 8.6, ^5J = 1.6 Hz, 1 H, 5-H), 2.92 (br., part A of an AB system, ^2J = 16.1 Hz, 1 H, 2-H), 3.04 (ddt of part B of an AB system, ^2J = 16.1, ^4J = ^4J = ^5J = 2.3 Hz, 1 H, 2-H), 3.44 (br. dd, ^3J = ^3J = 8.5 Hz, 1 H, 4-H), 3.71 and 3.73 (s, 2 × 3 H, CO_2CH_3), 4.45 (br. d, ^3J = 6.8 Hz, 2 H, 2′-H), 4.74 (app t, *J* = 1.4 Hz, 1 H, 1′′-H), 4.77 (d, *J* = 0.7 Hz, 1 H, 1′′-H), 5.58 (t, fine structure not resolved, ^3J = 6.9 Hz, 1 H, 1′-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT135): δ = 19.42 (+, C-3′′), 20.93 (+, $OCOCH_3$), 39.63 (−, C-2*), 42.46 (−, C-5*), 47.45 (+, C-4), 52.75 and 52.87 (+, CO_2CH_3), 58.88 (C_{quat}, C-1), 61.48 (−, C-2′), 111.84 (−, C-1′′), 119.21 (+, C-1′), 144.78 (C_{quat}, C-3**), 145.23 (C_{quat}, C-2′′**), 170.88 (C_{quat}, $OCOCH_3$), 171.49 and 171.60 (C_{quat}, CO_2CH_3). − MS (EI, 70 eV), *m*/*z* (%): 310 (0.2) [M^+], 269 (14) [$M^+ - C_3H_5$], 268 (6) [$M^+ - H_2C{=}C{=}O$], 251 (13) [M^+ − OAc], 250 (84) [M^+ − HOAc], 237 (3) [$M^+ - C_3H_5$ − MeOH], 219 (16) [M^+ − OAc − MeOH], 210 (14) [$M^+ - C_3H_5$ − OMe − CO], 208 (10) [$M^+ - CH_3CO$ − OMe − CO], 191 (49) [M^+ − HOAc − OMe − CO], 190 (100) [M^+ − HOAc − MeOH − CO], 187 (6), 175 (12) [$M^+ - CH_3CO$ − 2 MeOH − CO], 159 (9) [M^+ − OAc − 2 MeOH − CO], 158 (10) [M^+ − HOAc − 2 MeOH − CO], 145 (7), 131 (62) [M^+ − OAc − 2 MeOH − 2 CO], 130 (13) [M^+ − HOAc − 2 MeOH − 2 CO], 119 (5), 117 (7), 105 (6). − MS (DCI, NH_3), *m*/*z* (%): 328 (100) [M + NH_4^+], 268 (18) [M − HOAc + NH_4^+], 251 (5) [M^+ − OAc]. − $C_{16}H_{22}O_6$ (310.3): calcd. C 61.92, H 7.14; found C 61.96, H 7.15.

Dimethyl 3-[(1′*E*)-Acetoxyethylidene]-4-methylenecyclopentane-1,1-dicarboxylate [(*E*)-40]: A solution of dimethyl (4′-acetoxy-2′-butynyl)(2′′-propenyl)malonate (**42**) (113 mg, 0.400 mmol), [$Pd(dba)_2$] (11.5 mg, 0.020 mmol), $SbPh_3$ (14 mg, 0.040 mmol), and HOAc (2.4 mg, 0.04 mmol) in C_6D_6 (4 mL) in a screw-capped Pyrex bottle was purged with nitrogen and stirred for 5.5 d at 40 °C. The reaction was monitored by ^{1}H NMR; a sample of the reaction mixture was directly filled into an NMR tube. After filtering the reaction mixture through a pasteur pipet filled with charcoal (0.5 cm) and Celite (1 cm) and washing of this filter with Et_2O (2 mL), the solvents were evaporated and the residue was chromatographed on silica gel (12 g, column 1.5 × 14 cm, PE/ether, 4:1, after elution of dba changed to 2:1). One obtained 111 mg (98%) of pentadienyl acetate (*E*)-**40** as a colorless oil, R_f (PE/ether, 2:1) = 0.26, R_f (PE/ether, 4:1) = 0.09. − IR (film): $\tilde{\nu}$ = 3087 cm^{-1}, 2992, 2955, 2844, 1737 (C=O), 1631 (C=C), 1436 (CH_2 and CH_3 deformation), 1381, 1364, 1242 (C−O), 1204, 1164, 1075, 1055, 1024, 960, 889, 823, 706, 606. − ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 2.05 [s, 3 H, $OCOCH_3$; ^{13}C satellite: d, ^1J(C,H) = 129.9 Hz], 3.02 (t, ^4J = 2.1 Hz, 2 H, 5-H), 3.06 (br. s, 2 H, 2-H), 3.74 [s, 6 H, CO_2CH_3; ^{13}C satellite: d, ^1J(C,H) = 147.8 Hz], 4.63 (d, slightly broadened by non-resolved coupling to 2-H, ^3J = 7.2 Hz, 2 H, 2′-H), 4.97 (br. t, ^4J = 2.0 Hz, 1 H, 4-CH_2), 5.37 (t, ^4J = 2.3 Hz, 1 H, 4-CH_2), 5.95 (tt, ^3J = 7.2, ^4J = 2.6 Hz, 1 H, 1′-H). − Decoupling experiments: a) Irradiation at δ = 5.95: changes at δ = 4.63 (s), 3.06 (s becomes narrower). − b) Irradiation at δ = 5.37: changes at δ = 3.02 (d, ^4J = 2.0 Hz); δ = 4.97 unchanged. − c) Irradiation at δ = 4.97: changes at δ = 3.02 (d, ^4J = 2.2 Hz); δ = 5.37 unchanged. − d) Irradiation at δ = 4.63: changes at δ = 5.95 (t, ^4J = 2.5 Hz), 3.06 (d, ^4J = 2.5 Hz). − e) Irradiation at δ = 3.02 and 3.06: changes at δ = 5.95 (t, ^3J = 7.2 Hz), 5.37 (s), 4.97 (s), 4.63 (d becomes narrower, ^3J = 7.2 Hz). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT135): δ = 20.90 (+, $OCOCH_3$), 37.47 (−, C-2*), 40.89 (−, C-5*), 52.91 (+, CO_2CH_3), 57.49 (C_{quat}, C-1), 62.00 (−, C-2′), 105.94 (−, 4-CH_2), 115.06 (+, C-1′), 140.95 (C_{quat}, C-3), 144.25 (C_{quat}, C-4), 170.82 (C_{quat}, $OCOCH_3$), 171.41 (C_{quat}, CO_2CH_3). − MS (EI, 70 eV), *m*/*z* (%): 282 (10) [M^+], 240 (39) [$M^+ - O{=}C{=}CH_2$], 222 (13) [M^+ − HOAc], 190 (11) [M^+ − MeOH − HOAc], 180 (46) [M^+ − MeOH − CO − $O{=}C{=}CH_2$], 163 (100) [M^+ − OMe − HOAc − CO], 162 (28) [M^+ − MeOH − HOAc − CO], 149 (10) [M^+ − MeOH − OMe − CO − $O{=}C{=}CH_2$], 131 (11) [M^+ − MeOH − OMe − HOAc − CO], 121 (18) [M^+ − MeOH − OMe − 2 CO − $O{=}C{=}CH_2$], 105 (8) [M^+ − 2 OMe − 2 CO − OAc], 104 (10) [M^+ − MeOH − OMe − 2 CO − OAc], 103 (35) [M^+ − MeOH − OMe − 2 CO − HOAc], 91 (15), 85 (89), 77 (10) [$C_6H_5^+$], 59 (8) [OAc^+], 43 (100) [$MeCO^+$]. − $C_{14}H_{18}O_6$ (282.3): calcd. C 59.57, H 6.43; found C 59.62, H 6.35.

Experiments Concerning the Stability of Diene (*E*)-40 Under Previously Used Reaction Conditions. − Experiment A: According to GP 4, dienyl acetate (*E*)-**40** (110 mg, 0.390 mmol) was treated with $Pd(OAc)_2$ (9 mg, 0.040 mmol), PPh_3 (23 mg, 0.088 mmol), and NEt_3 (80 mg, 0.79 mmol) in acetonitrile (4 mL) at 85 °C for 6 h. Column chromatography on flash silica gel (10 g, column 1.5 × 12 cm, PE/ether, 4:1) gave fraction I: 7 mg (ca. 8%) of triene **37** with unidentified compound **43** in a **37/43** = 3:1 ratio. − **43**: ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 3.30 (t, ^4J = 2.0 Hz, 2 H), 3.78 (s, 6 H, CO_2CH_3), 4.78 (app t, J = 1.6 Hz, 1 H), 5.13 (app q, J = 1.9 Hz, 1 H), 5.35 (d, ^2J = 1.4 Hz, 1 H), 5.63 (d, ^2J = 1.4 Hz, 1 H), 6.14 (br. s, 1 H). − Fraction II: 5 mg (5%) of isomerized dienyl acetate **38**.

Experiment B: (*E*)-**40** (50 mg, 0.18 mmol) was treated with $Pd(OAc)_2$ (4 mg, 0.02 mmol), PPh_3 (11 mg, 0.04 mmol), and Ag_2CO_3 (54 mg, 0.20 mmol) in acetonitrile (2 mL) at 85 °C for 5.5 h. The ^{1}H-NMR spectrum of the crude product showed signals of (*E*)-**40**, traces of **38**, and decomposition products.

Dimethyl 3-Ethenyl-4-methylenecyclopentane-1,1-dicarboxylate (44). − Method A: According to GP 4 dimethyl [4′-acetoxy-(2′*E*)-butenyl](2′′-bromo-2′′-propenyl)malonate (**27**) (171 mg, 0.471 mmol) was treated with $Pd(OAc)_2$ (7 mg, 0.031 mmol, 7 mol-%), PPh_3 (20 mg, 0.076 mmol, 16 mol-%), and NEt_3 (101 mg, 1.00 mmol) as base in acetonitrile (4 mL) at 85 °C for 8 h. Chromatography on silica gel (14 g, column 1.5 × 18 cm, PE/ether, 2:1) gave 32 mg (30%) of 1,4-diene **44**, colorless oil, R_f (PE/ether, 2:1) = 0.43. The amount of non-reacted starting material was not determined. The ^{1}H-NMR spectrum is in accordance with the literature; ^{13}C-NMR data have not been published.[15] − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT135): δ = 40.20 and 40.23 (−, C-2, C-5), 47.61 (+, C-3), 52.72 and 52.79 (+, CO_2CH_3), 58.42 (C_{quat}, C-1), 108.07 (−, 4-CH_2), 116.04 (−, C-2′), 138.96 (+, C-1′), 150.27 (C_{quat}, C-4), 171.91 and 172.11 (C_{quat}, CO_2CH_3).

Method B: When 110 mol-% PPh_3 (136 mg, 0.519 mmol) was used under conditions otherwise identical with method A one obtained 30 mg (28%) of **44**, the amount of non-reacted starting material was not determined.

Method C: In the absence of a base under conditions otherwise identical with method A, 4 mg (4%) of 1,4-diene **44** and 148 mg (87% recovery) bromodiene **27** were isolated.

Method D: In the absence of a base and with 110 mol-% PPh_3 (136 mg, 0.519 mmol) under conditions otherwise identical with method A, 18 mg (17%) of **44** and 67 mg (39% recovery) of **27** were isolated.

Method E: Using sodium formate (40 mg, 0.59 mmol) as base under conditions otherwise identical with method A, 28 mg (27%) of 1,4-diene **44** and 122 mg (71% recovery) of **27** were isolated.

Method F: By using K_2CO_3 (69 mg, 0.50 mmol) as base under conditions otherwise identical with method A, 15 mg (14%) of 1,4-diene **44** and 110 mg (ca. 64% recovery) of impure **27** were obtained.

Method G: When bromodiene **27** (171 mg, 0.471 mmol) was treated with [$Pd(OAc)_2$(dmphen)] (41 mg, 0.095 mmol, 20 mol-%) (dmphen = 2,9-dimethyl-1,10-phenanthroline) and NEt_3 (101 mg, 1.00 mmol) as base in acetonitrile (4 mL) at 85 °C for 8 h, one obtained 41 mg (39%) of **44**, and an unidentified compound.

Attempted Reactions of Dimethyl (4′-Bromo-2′-butynyl)(2′′-propenyl)malonate (60). − Experiment A (Cyclization): A solution of bromoenyne **60** (152 mg, 0.501 mmol), $Pd(OAc)_2$ (11 mg, 0.050 mmol), PPh_3 (39 mg, 0.15 mmol), K_2CO_3 (69 mg, 0.50 mmol), and methyl acrylate (**28**) (86 mg, 1.0 mmol) in acetonitrile (5 mL) was heated at 85 °C for 1.5 h. After workup as described in GP 4 the only identified signals in the ^{1}H-NMR spectrum of the crude product (100 mg) were those of **60**.

Experiment B (Formation of Bromoallene): To a suspension of CuBr (291 mg, 2.00 mmol) in anhydrous THF (5 mL) was added anhydrous LiBr (174 mg, 2.00 mmol) and after complete dissolution bromoenyne **60** (303 mg, 1.00 mmol), and the mixture was refluxed for 5 h. Workup was done by adding H_2O and sat. NH_4Cl soln. (10 mL each) and extracting with Et_2O (4 × 15 mL). The combined ethereal phases were washed with sat. NH_4Cl soln. (2 × 10 mL), dried with $MgSO_4$, and the solvent was evaporated. The ^{1}H-NMR spectrum of the residue (306 mg) showed only the signals of starting material.

Dimethyl (4′-Formyloxy-2′-butynyl)(2′′-propenyl)malonate (61): A mixture of dimethyl (4′-bromo-2′-butynyl)(2′′-propenyl)malonate (**60**) (1.21 g, 3.99 mmol), sodium formate (544 mg, 8.00 mmol), and tetrabutylammonium bromide (60 mg, 0.19 mmol, 5 mol-%) was heated unter N_2 at 100 °C for 9 h. For workup, H_2O (10 mL) was added, the mixture was extracted with Et_2O (4 × 15 mL), the combined ether phases were washed with H_2O and sat. NaCl soln. (30 mL each) and dried with Na_2SO_4. The crude product was purified by chromatography on silica gel (12 g, column 14 × 1.5 cm, PE/ether, 5:1, after elution of starting material changed to 2:1) yielding fraction I: 300 mg (0.990 mmol) of **60** (25% recovery), R_f (PE/ether, 5:1) = 0.30. − Fraction II: 366 mg (34%, 45% with respect to consumed starting material) of **61**, colorless oil, R_f (PE/ether, 5:1) = 0.17, R_f (PE/ether, 2:1) = 0.30, distillation in a microsublimation apparatus heated to 80 °C at 0.003 Torr. − IR (film): $\tilde{\nu}$ = 3081 cm^{-1}, 3024, 2956, 2846, 2241 (C≡C), 1734 (C=O), 1642 (C=C), 1438 and 1364 (CH_2 and CH_3 deformation), 1328, 1293, 1221, and 1137 (C−O), 1070, 1030, 998, 969, 928 (CH=CH_2), 899, 856, 819, 660, 583, 530. − ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 2.78 (dt, ^3J = 7.4, ^4J = 0.9 Hz, 2 H, 1′′-H), 2.85 (t, ^5J = 2.2 Hz, 2 H, 1′-H), 3.75 [s, 6 H, CO_2CH_3; ^{13}C satellite: d, ^1J(C,H) = 147.9 Hz], 4.73 (dt, ^4J = 0.9, ^5J = 2.2 Hz, 2 H, 4′-H), 5.11−5.21 (m, 2 H, 3′′-H), 5.61 (ddt, ^3J = 17.1, ^3J = 10.0, ^3J = 7.4 Hz, 1 H, 2′′-H), 8.05 (t, ^4J = 0.9 Hz, 1 H, CHO). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT135): δ = 22.79 (−, C-1′), 36.49 (−, C-1′′), 51.66 (−, C-4′), 52.67 (+, CO_2CH_3), 56.67 (C_{quat}, C-2), 76.47 (C_{quat}, C-2′), 82.18 (C_{quat}, C-3′), 119.85 (−, C-3′′), 131.43 (+, C-2′′), 159.91 (+, CHO), 169.90 (C_{quat}, CO_2CH_3), 169.99 (C_{quat}, OCOCH$_3$). − MS (DCI, NH_3), *m/z* (%): 286 (100) [M + NH_4^+], 242 (3) [M + NH_4^+ − CO_2]. − $C_{13}H_{16}O_6$ (268.3): calcd. C 58.20, H 6.01; found C 58.17, H 5.99.

2,3-Bis(3′,3′-dimethoxycarbonylbicyclo[3.1.0]hex-1′-yl)-1,3-butadiene (63). − Method A: A solution of dimethyl (4′-methoxycarbonyloxy-2′-butynyl)(2′′-propenyl)malonate (**57**) (149 mg, 0.500 mmol), $Pd(OAc)_2$ (11 mg, 0.050 mmol), and PPh_3 (32 mg, 0.12 mmol) in acetonitrile (4 mL) was heated at 85 °C for 1.5 h. After workup as described in GP 4 the crude product was purified by chromatography on silica gel (6.5 g, column 1.5 × 7.5 cm, PE/ether, 6:1, after elution of **37** changed to 2:1), giving fraction I: 4 mg (ca. 4%) of triene **37** and unidentified compound **43** in a 3:1 ratio. − Fraction II: 40 mg (36%) of **63**, colorless, slowly crystallizing solid, mp. 128−129 °C, R_f (PE/ether, 2:1) = 0.21. − IR (nonsolidified melt): $\tilde{\nu}$ = 3081 cm^{-1}, 3004, 2954, 2885, 2844, 1734 (C=O), 1593 (C=C), 1435 (CH_2 and CH_3 deformation), 1311, 1253 (C−O), 1204, 1175, 1113, 1091, 1072, 994 (CH=CH_2), 968, 945, 908, 890, 858, 830, 820. − ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 0.44 (dd, ^2J = 5.6, ^3J = 4.2 Hz, 2 H, 6′-H$_{endo}$), 0.67 (ddd, ^2J = 5.5, ^3J = 8.4, ^4J = 1.5 Hz, 2 H, 6′-H$_{exo}$), 1.48 [dddd (app br. dt), ^3J =

8.4, $^3J = {}^3J = 4.3$, $^4J = 1.5$ Hz, 2 H, 5′-H], 2.40 (d, B part of AB, $^4J = 1.5$, $^2J_{AB} = 13.7$ Hz, 2 H, 4′-H_{endo}), 2.61 (d, B part of AB, $^4J = 1.5$, $^2J_{AB} = 13.8$ Hz, 2 H, 2′-H_{exo}*), 2.65 (d, A part of AB, $^3J = 4.4$, $^2J_{AB} = 13.8$ Hz, 2 H, 4′-H_{exo}), 2.71 (A part of AB, $^2J_{AB} = 13.8$ Hz, 2 H, 2′-H_{endo}*), 3.69 [s, 6 H, CO_2CH_3; ^{13}C satellite: d, ^1J(C,H) = 147.7 Hz], 3.74 [s, 6 H, CO_2CH_3; ^{13}C satellite: d, ^1J(C,H) = 147.5 Hz], 5.12 [d, $^2J = 1.6$ Hz, 2 H, 1(4)-H], 5.23 [d, $^2J = 1.6$ Hz, 2 H, 1(4)-H]. − Decoupling experiments: a) Irradiation at δ = 1.48: changes at δ = 0.44 (d, $^2J = 5.6$ Hz), 0.67 (br. dd, $^2J = 5.7$, $^4J = 1.5$ Hz), 2.61 (B part of AB, $^2J_{AB} = 13.8$ Hz), 2.65 (A part of AB, $^2J_{AB} = 13.8$ Hz). − b) Irradiation at δ = 2.40: changes at δ = 0.67 (sharp dd, $^2J = 5.5$, $^3J = 8.4$ Hz), 2.65 (d, $^3J = 4.4$ Hz). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT135): δ = 16.35 (−, C-6′), 24.08 (+, C-5′), 33.15 (C_{quat}, C-1′), 36.29 and 40.87 (−, C-2′, C-4′), 52.86 and 52.98 (+, CO_2CH_3), 59.70 (C_{quat}, C-3′), 114.56 [−, C-1(4)], 147.87 [C_{quat}, C-2(3)], 172.27 and 173.24 (C_{quat}, CO_2CH_3). − MS (EI, 70 eV), *m/z* (%): 446 (58) [M^+], 415 (18) [M^+ − OMe], 387 (77) [M^+ − OMe − CO], 386 (65) [M^+ − MeOH − CO], 383 (9) [M^+ − MeOH − OMe], 355 (28) [M^+ − MeOH − OMe − CO], 327 (100) [M^+ − MeOH − OMe − 2 CO], 326 (64) [M^+ − 2 MeOH − 2 CO], 295 (41) [M^+ − 2 MeOH − OMe − 2 CO], 267 (94) [M^+ − 2 MeOH − OMe − 3 CO], 242 (20), 241 (15), 235 (26) [M^+ − 3 MeOH − OMe − 3 CO], 227 (22), 207 (45) [M^+ − 3 MeOH − OMe − 4 CO], 193 (14), 189 (31), 181 (16), 167 (23), 165 (21), 145 (37), 131 (18), 129 (38), 128 (20), 115 (20), 113 (21), 105 (18), 91 (28), 77 (16) [$C_6H_5^+$], 59 (36). − $C_{24}H_{30}O_8$ (446.5): calcd. C 64.56, H 6.77; found C 64.46, H 6.90.

Method B: According to a procedure by Mandai, Tsuji et al.[21][26] dimethyl (4′-methoxycarbonyloxy-2′-butynyl)(2′′-propenyl)malonate (**57**) (149 mg, 0.500 mmol) was treated with $Pd(OAc)_2$ (11 mg, 0.05 mmol), PPh_3 (26 mg, 0.10 mmol), NEt_3 (0.14 mL, 101 mg, 1.00 mmol), KBr (119 mg, 1.00 mmol), and methyl acrylate (**28**) (129 mg, 1.5 mmol) in 3 mL DMF and 0.1 mL of H_2O for 2 h at 85 °C. The reaction mixture was worked up by adding sat. NaCl soln. (5 mL), H_2O (5 mL), and Et_2O (10 mL), separating the phases, extracting the aqueous phase with Et_2O (3 × 10 mL), washing the combined ethereal phases with H_2O (10 mL), sat. NaCl soln. (10 mL), and drying with Na_2SO_4. The TLC of the crude product showed 6 spots with R_f values (PE/ether, 1:1) of 0.49−0.10; the substances were separated by chromatography on 12 g of flash silica gel (column 1.5 × 14 cm, PE/ether, 2:1). Fraction II (11 mg) contained impure **63**, the other fractions (10−25 mg) contained mixtures of unknown compounds as judged on the basis of ^{1}H-NMR spectra.

Trapping of the Alkenylpalladium Species 65 with Hydride: A solution of dimethyl (4′-methoxycarbonyloxy-2′-butynyl)(2′′-propenyl)malonate (**57**) (149 mg, 0.500 mmol), $Pd(OAc)_2$ (11 mg, 0.050 mmol), PPh_3 (32 mg, 0.12 mmol), sodium formate (68 mg, 1.0 mmol, 2.0 equiv.), and NEt_4Br (105 mg, 0.5 mmol) in acetonitrile (4 mL) was heated at 85 °C for 2 h. The ^{1}H-NMR spectrum of the crude product showed the signals of vinylcyclopropane **35** as the only compound formed from **57**. Chromatography on flash silica gel (9 g, column 1.5 × 10 cm, PE/ether, 5:1) yielded 76 mg (68%) of **35**.

Cyclization of 61: A solution of dimethyl (4′-formyloxy-2′-butynyl)(2′′-propenyl)malonate (**61**) (139 mg, 0.500 mmol), $Pd(OAc)_2$ (10 mg, 0.045 mmol), and PPh_3 (26 mg, 0.099 mmol) in acetonitrile (3.5 mL) was heated at 85 °C for 2 h. After workup as described in GP 4 the crude product was purified by column chromatography on silica gel (11 g, column 1.5 × 15 cm, PE/ether, 5:1, after 50 mL of eluent changed to 2:1), yielding 58 mg (54%) of a mixture of vinylcyclopropane **35** and 1,4-diene **44** in a ratio of 1:3.

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