$[M^+ - C_4H_8]$, 87 (100) $[M^+ - 2C_4H_8]$; IR (gas): $\tilde{\nu} = 2176\ cm^{-1}$ (P–H). **3b**: b.p. 55 °C (1 mbar), yield 78 %; ^{31}P NMR (121.5 MHz, C_6D_6): $\delta = 71.6$ (d, $^1J(P,H) = 219$ Hz); ^1H NMR (300 MHz, C_6D_6): $\delta = 0.99$ (d, $^4J(P,H) = 0.7$ Hz, 9H), 1.33 (d, $^4J(P,H) = 1.7$ Hz, 9H), 6.16 (d, $^3J(P,H) = 3.3$ Hz, 1H), 6.23 (d, $^1J(P,H) = 219$ Hz, 1H); IR (Nujol): $\tilde{\nu} = 2202\ cm^{-1}$ (P–H). **3c**: ^{31}P NMR (121.5 MHz, C_6D_6): $\delta = 64.0$ (d, $^1J(P,H) = 139$ Hz); ^1H NMR (300 MHz, C_6D_6): $\delta = 2.44$ (s, 6H), 2.48 (s, 6H), 2.56 (s, 3H), 2.59 (s, 3H), 6.16 (d, $^3J(P,H) = 1.8$ Hz, 2H), 7.04 (br, 4H), 7.13 (d, $^1J(P,H) = 139$ Hz, 1H); **3d**: m.p. 87–89 °C, yield 72 %; ^{31}P NMR (121.5 MHz, C_6D_6): $\delta = 75.8$ (d, $^1J(P,H) = 147$ Hz); ^1H NMR (300 MHz, C_6D_6): $\delta = 2.09$ (s, 6H), 2.23 (s, 6H), 2.23 (s, 3H), 2.37 (s, 3H), 5.87 (d, $^3J(P,H) = 0.9$ Hz, 1H), 6.67 (s, 2H), 6.70 (s, 1H), 6.72 (s, 1H), 7.17 (d, $^1J(P,H) = 147$ Hz, 1H); MS (16 eV): *m/z* (%): 358(43) $[M^+]$, 357(100) $[M^+ - H]$; IR (gas): $\tilde{\nu} = 2120\ cm^{-1}$ (P–H).

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[2] S. Pawlenko in *Methoden Org. Chem. (Houben-Weyl) 4th ed. 1952–*, *Vol. 13/5*, **1980**, p. 272, 350.

[3] For recent reports on the hydridic character of P–H bonds in hypervalent Lewis base adducts of phosphanes, see: a) F. Carré, C. Chuit, R. J. P. Corriu, A. Mehdi, C. Reyé, *J. Organomet. Chem.* **1997**, *529*, 59; b) J.-P. Bezombes, F. Carré, C. Chuit, R. J. P. Corriu, A. Mehdi, C. Reyé, *J. Organomet. Chem.* **1997**, *535*, 81.

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[9] Crystal structure determination of **3d**: $C_{20}H_{24}ClN_2P$, yellow crystals, crystal size $0.05 \times 0.10 \times 0.30$ mm; $M_r = 358.8$; monoclinic, space group $P2_1/n$ (no. 14), $a = 8.4888(7)$, $b = 7.0438(7)$, $c = 30.940(3)$ Å, $\beta = 93.629(5)°$, $V = 1846.3(3)$ Å^3, $Z = 4$, $\mu(Mo_{K\alpha}) = 0.297\ mm^{-1}$, $T = 123(2)$ K, $F(000) = 760$. Of 7837 reflections which were collected on a Nonius KappaCCD diffractometer using $Mo_{K\alpha}$ radiation up to $2\theta_{max} = 50°$, 2857 were independent and used in all further calculations. The structure was solved with direct methods (SHELXS-97[10a]) and refined anisotropically against F^2; the hydrogen atom at the phosphorus center was refined free and the remaining ones using a riding model (program: SHELXL-97[10b]). The final *wR2(F²)* was 0.136 and the conventional *R* value $R(F) = 0.065$ for 227 parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142914. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] a) G. M. Sheldrick, SHELXS-97, *Acta Crystallogr. Sect. A* **1990**, *46*, 467; b) G. M. Sheldrick, SHELXL-97, Universität Göttingen, **1997**.

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[12] Average and standard deviation of the result of a query in the CCSD database for P–H distances in compounds $H_nY_{3-n}P$ (Y = substituent bound through a p-block element) with a three-coordinate phosphorus center.

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[15] All products were identified by comparison of their ^1H and ^{31}P NMR data with those of authentic samples.

[16] Characteristic spectroscopic data: **6**: ^{31}P NMR (121.5 MHz, C_6D_6): $\delta = 85.9$ (br d, $^1J(PH) = 353$ Hz); ^1H NMR (300 MHz, C_6D_6): $\delta = 1.29$ (br, 3H; BH_3), 2.03 (s, 9H), 2.13 (s, 3H), 2.38 (s, 3H), 2.43 (s, 3H), 5.32 (d, $^3J(P,H) = 10.3$ Hz, 1H), 6.62 (s, 1H), 6.67 (s, 1H), 6.70 (s, 2H), 8.01 (d, $^1J(P,H) = 353$ Hz, 1H); $^{11}B\{^1H\}$ NMR (96.2 MHz, C_6D_6): $\delta = -34.3$ (d, $^1J(P,B) = 52$ Hz); **7**: ^{31}P NMR (121.5 MHz, C_6D_6): $\delta = 173$ (d, $^3J(P,H) = 8$ Hz, $^1J(W,P) = 765$ Hz); ^1H NMR (300 MHz, C_6D_6): $\delta = 2.05$ (s, 3H), 2.06 (s, 3H), 2.27 (s, 6H), 2.29 (s, 6H), 4.52 (s, 5H; C_5H_5), 5.93 (d, $^3J(P,H) = 7.4$ Hz, 1H), 6.78 (s, 2H), 6.79 (s, 2H); IR (CH_2Cl_2): $\tilde{\nu} = 1841, 1959\ cm^{-1}$ (CO); **8**: ^{31}P NMR (121.5 MHz, C_6D_6): $\delta = 121.3$ (t, $^3J(P,H) = 9$ Hz); ^1H NMR (300 MHz, C_6D_6): 2.12 (s, 6H), 2.27 (s, 3H), 2.34 (s, 3H), 2.38 (s, 3H), 2.45 (s, 3H), 4.50 (d, $^3J(P,H) = 9.0$ Hz, 2H; OCH_2), 5.83 (d, $^3J(P,H) = 0.7$ Hz, 1H; 5-H), 6.7–7.0 (m, 9H; *m*-H and Ph); $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): $\delta = 66.9$ (d, $^2J(PC) = 25.6$ Hz; OCH_2); MS (16 eV, 100 °C): *m/z* (%): 464(12) $[M^+]$, 357(14) $[M^+ - OCH_2Ph]$.

[17] The formation of **6** rather than a conceivable product **2d**$[BH_4]$ agrees with the observed addition reactions of phosphenium ions to BH_4^-: M. Bürklin, E. Hanecker, H. Nöth, W. Storch, *Angew. Chem.* **1985**, *97*, 980; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 999; G. Jochem, A. Schmidpeter, H. Nöth, *Z. Naturforsch. B* **1996**, *51*, 267.

[18] Evidence for the activity of **3d** as a hydride transfer reagent was also obtained in further cases; thus, reaction of CH_2Cl_2 with **3d** was found to proceed within several hours at 20 °C with quantitative formation of the chlorination product **1d**.

[19] G. Elsner, *Methoden Org. Chem. (Houben-Weyl) 4th ed. 1952–*, *Vol. 13/E1*, **1980**, p. 122.

Stereoselective Synthesis and Palladium-Catalyzed Transformations of 2-Alkylidene-5-vinyltetrahydrofurans**

Peter Langer* and Edith Holtz

Domino and sequential reactions are of interest in modern organic chemistry since they enable the rapid assembly of complex products.[1] In the course of our studies on the development of domino reactions of dianions and dianion equivalents,[2] we have recently reported the first cyclizations of dilithiated 1,3-dicarbonyl compounds with oxalic acid dielectrophiles.[3] These reactions allow an efficient, regio- and stereoselective synthesis of the pharmacologically relevant substance class of γ-alkylidenebutenolides. Although a variety of simple condensation reactions of dianions with monofunctional alkyl halides are known, only a few domino dialkylation reactions of dianions with difunctional alkyl

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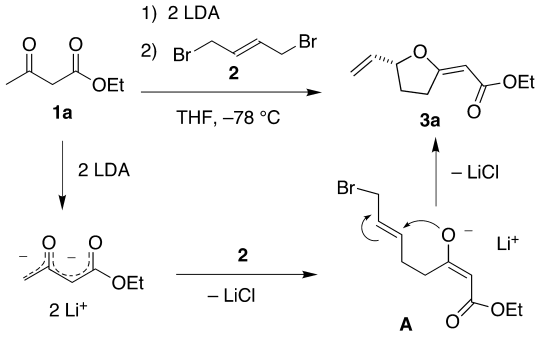
halides have been reported so far.[4] This can be explained by the high reactivity of the dianions and by the lability of the dielectrophiles which can give rise to polymerization, formation of open-chain 2:1 products, or single-electron transfer (SET) processes rather than cyclization: for example, reaction of the dianion of methyl acetoacetate with 1,*n*-dibromoalkanes was reported to give mixtures of open-chain monoalkylated products and of 2:1 condensation products.[5] The reaction of dianions of 1,3-dicarbonyl compounds with 1,4-di*chloro*-2-butene was equally disappointing and resulted in formation of mixtures of open-chain products in low yields.[5]

Herein, we report that reaction of dianions of 1,3-dicarbonyl compounds **1** with 1,4-di*bromo*-2-butene (**2**) results in regioselective formation of a wide range of 2-alkylidene-5-vinyltetrahydrofurans **3** and selective generation of up to three stereocenters (see Scheme 1). From a methodology viewpoint, these reactions represent the, to the best of our knowledge, first C,O-cyclodialkylations of 1,3-dicarbonyl dianions with **2**).[6] 2-Alkylidene-tetrahydrofurans are not only of pharmacological relevance but also represent interesting building blocks for the synthesis of terpenes[7a,b] and medium-sized lactones.[7c] To demonstrate the usefulness of our cyclization products containing a unique functionality, we have developed a new palladium(0)-catalyzed rearrangement reaction which allows the direct transformation of bicyclic 2-alkylidene-5-vinyltetrahydrofurans into functionalized bicyclo[3.2.1]octan-8-ones. This rearrangement has, to the best of our knowledge, not been previously noted. It is noteworthy that the bicyclo[3.2.1]octane skeleton is present in a large number of pharmacologically important natural products including aphidicolan,[8] kaurane,[9] and stemodane diterpenes,[10] hydroazulene,[11] himachalene,[11] α-cedrane,[11] and grayanotoxin sesquiterpenes,[11, 12] bridged steroids,[13] and aconitine-type alkaloids.[14] The combination of our new cyclodialkylation reaction and the new palladium-catalyzed rearrangement constitutes a significant expansion of the methods known today for the synthesis of functionalized bicyclo[3.2.1]octanes[8f] which are of pharmacological significance and of importance for natural product syntheses.

Our first attempts to induce a cyclization reaction of the dianion of ethyl acetoacetate **1a** with 1,4-dibromo-2-butene (**2**) were unsuccessful. Addition of a solution of **2** in THF to a solution of the dianion at 0 °C gave a complex reaction mixture. Much to our satisfaction, addition of dibromide **2** to a solution of the dianion in THF at −78 °C resulted in formation of the cyclization product **3a** in 41 % yield (Scheme 1).

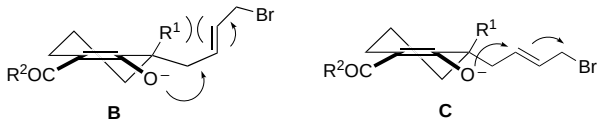


Scheme 1. LDA = lithium diisopropylamide.

Inspection of the crude product mixture showed that significant amounts of the 2:1 condensation product[15] had been formed. Therefore, an inverse–addition protocol was employed: slow addition of a solution of the dianion in THF to a solution of **2** afforded the 2-alkylidene-5-vinyltetrahydrofuran **3a** in 61 % yield with very good regio- and stereoselectivity. Formation of **3a** can be explained by a domino-S_N-S_N' displacement reaction involving regioselective attack of the terminal carbon atom of the dianion on the dielectrophile and subsequent regioselective cyclization through the oxygen atom.[16] The stereoselectivity in favor of the *E*-configured exocyclic double bond can be explained by the W-shaped configuration of intermediate **A** which allows a minimization of the dipole–dipole repulsion of the oxygen atoms.[17]

To investigate the preparative scope of the new cyclization reaction, the substituents of the 1,3-dicarbonyl compounds were systematically varied (Table 1). Reaction of dibromide **2** with the dianions of *tert*-butyl acetoacetate, acetylacetone, 5,5-dimethylhexane-2,4-dione, and *N*,*N*-diethylacetylacetamide afforded the *E*-configured 2-alkylidene-5-vinyltetrahydrofurans **3b**–**e** in good yields and with very good stereoselectivities. Reaction of 1,4-dibromo-2-butene with the dianions of the ethyl acetoacetates **1f**–**h**, containing a substituent at their central carbon atom, resulted in formation of the tetrahydrofurans **3f**–**h**. Reaction of **2** with the dianion of 2-acetyl-γ-butyrolactone (**1i**) afforded the interesting 2-alkylidene-5-vinyltetrahydrofuran **3i**. Despite the fact that the products **3f**–**i** contain additional substituents at their exocyclic double bonds, very good *E*-selectivities were observed in all cases. The reaction of 1,4-dibromo-2-butene with the dianions of methyl 3-oxopentanoate and ethyl 3-oxohexanoate afforded the 2-alkylidene-5-vinyltetrahydrofurans **3j**–**k** in good yields and with very good *Z*-selectivities. The change from *E*- to *Z*-configuration can be explained by the steric influence of the substituents R^1.

Reaction of the dianion of ethyl cyclohexanone-2-carboxylate (**1l**) with dibromide **2** afforded the 5,6-bicyclic product **3l** in good yield and with very good 1,3-diastereoselectivity. Similarly, reaction of the dianions of isopropyl and methoxyethyl cyclohexanone-2-carboxylate (**1m** and **1n**) afforded the bicyclic 2-alkylidene-5-vinyltetrahydrofurans **3m** and **3n** in good yields and with very good stereoselectivities. Treatment of dibromide **2** with the dianion of aldehyde **1o** afforded the bicyclic tetrahydrofuran **3o** with very good stereoselectivity. Reaction of **2** with the dilithiated ester **1p**, containing a benzyl group at the 6-position of the cyclohexane ring, resulted in stereoselective formation of the 2-alkylidene-5-vinyltetrahydrofuran **3p**. The 1,3-diastereoselectivity can be explained by destabilization of transition state **B** (relative to **C**) due to a 1,3-interaction between the substituent R^1 (H, Bn) and the allyl group.



Reaction of **2** with the dianions of ethyl 5-methylcyclohexanone-2-carboxylate **1q** and methyl 5-ethylcyclohexanone-2-

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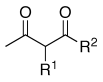
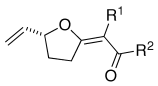
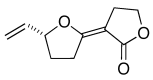
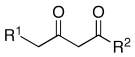
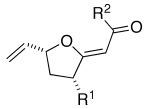
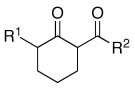
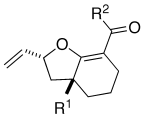
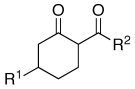
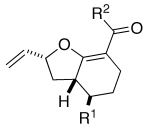
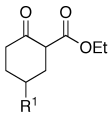
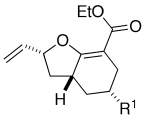
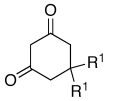
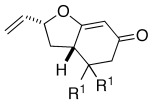
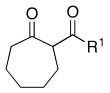
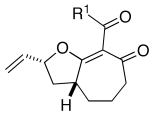
Table 1. Synthesis of 2-alkylidene-5-vinyltetrahydrofurans **3**.

	1	3	R^1	R^2	Yield [%][a]	*E*:*Z*	d.r.[b]
a			H	OEt	61	>98:2	–
b			H	O*t*Bu	64	>98:2	–
c			H	Me	48	>98:2	–
d			H	*t*Bu	46	>98:2	–
e			H	NEt_2	58	>98:2	–
f			Me	OEt	66	>98:2	–
g			Et	OEt	63	>98:2	–
h			Bu	OEt	36	>98:2	–
i			–	–	37	>98:2	–
j			Me	OMe	65	<2:98	45:55
k			Et	OEt	60	<2:98	65:35
l			H	OEt	81	–	>98:2
m			H	O*i*Pr	77	–	>98:2
n			H	$O(CH_2)_2OMe$	78	–	>98:2
o			H	H	37	–	>98:2
p			Bn	OEt	48	–	>98:2
q			Me	OEt	74	–	>98:2
r			Et	OMe	72	–	>98:2
s			*t*Bu	–	53	–	>98:2
t			Ph	–	65	–	>98:2
u			H	–	42	–	>98:2
v			Me	–	37	–	>98:2
w			H	OEt	66	–	70:30
x			H	*t*Bu	51	–	90:10

[a] Yield of isolated product. [b] Diastereomeric ratio in favor of the drawn isomer.

carboxylate **1r** afforded the bicyclic 2-alkylidene-5-vinyltetrahydrofurans **3q** and **3r** in good yields. In these reactions, three stereocenters are formed with complete selectivity. The initial attack of the dianion onto the dielectrophile proceeded with very good 1,2-diastereocontrol giving rise to a *cis* configuration between the substituents R^1 and the bridgehead hydrogen atom. The subsequent cyclization proceeded with very good 1,3-diastereoselectivity. The stereochemical effect of the presence of a substituent at the 4-position of the cyclohexane moiety was studied next: reaction of dibromide **2** with the dilithiated ethyl cyclohexanone-2-carboxylates **1s** and **1t** afforded the tetrahydrofurans **3s** and **3t**, respectively, containing three stereocenters, in good yields. Both the initial attack of the dianion onto the dielectrophile and the subsequent cyclization proceeded with very good 1,3-diastereoselectivities. Owing to steric reasons, the *tert*-butyl and the phenyl group are located *trans* to the bridgehead hydrogen atom. The reaction of 1,4-dibromo-2-butene with the dilithiated cyclohexane-1,3-dione derivatives **1u** and **1v** afforded the bicyclic products **3u** and **3v**, respectively, with very good 1,3-stereoselectivities.

Reaction of 1,4-dibromo-2-butene with the dianions of the cycloheptanones **1w** and **1x** afforded the 5,7-bicyclic products **3w** and **3x**, respectively, in good yields with moderate to good stereoselectivities. For entropic reasons, the destabilization of intermediate **B** is less important in more flexible fused seven-membered rings than in more rigid six-membered homologues. In open-chain substrates, the conformational flexibility is even higher. Therefore, the best 1,3-diastereoselectivities were obtained for the formation of 5,6-bicyclic 2-alkylidene-5-vinyltetrahydrofurans **3l**–**v**.

Our first attempts to induce a palladium-catalyzed rearrangement of the 2-alkylidene-5-vinyltetrahydrofuran **3l** were unsuccessful. No conversion was observed when the reaction was carried out at 20 °C using $Pd(OAc)_2$/PPh_3 or $[Pd(PPh_3)_4]$. At elevated temperatures, complex mixtures were formed. Fortunately, employment of $[Pd(dppe)_2]$ (dppe = 1,2-bis(diphenylphosphanyl)ethane) resulted in a clean rearrangement reaction which afforded the functionalized bicyclo[3.2.1]octan-8-one **4a** in 95% yield (*endo*:*exo* = 1.2:1). The diastereomers could be readily separated to give *endo*-**4a** and *exo*-**4a** in 45 and 36% yields, respectively. The formation of **4a** can be explained by initial ring-opening, formation of a π-allyl palladium complex,[18a] and recyclization by nucleophilic attack of the carbon atom of the enolate onto the π-allylpalladium complex (Table 2). This palladium-catalyzed rearrangement leading to bicyclo[3.2.1]octan-8-ones has, to the best of our knowledge, not been previously noted.[18b] The reaction proceeded with complete regioselectivity; no formation of any seven-membered ring product was observed. The low stereoselectivity can be explained by a π-σ-π-isomerization of the π-allylpalladium complex. Rearrangement of the esters **3m** and **3n** afforded the bicyclo[3.2.1]octan-8-ones **4b** and **4c** in high yields. The Pd-catalyzed rearrangement of the independently prepared 2-alkylidenetetrahydrofuran **3y**, containing an ester group at the bridgehead position,[6b] gave the bicyclo[3.2.1]octan-8-one **4d** in 95% yield. The 2-alkylidenetetrahydrofuran **3q**, containing a methyl group at the 5-position of the cyclohexane moiety, was efficiently transformed into the bicyclo[3.2.1]octan-8-one **4e** in 94% yield.

The combination of our new cyclodialkylation reaction and the new palladium-catalyzed rearrangement constitutes a significant expansion of the methods known today for the synthesis of functionalized bicyclo[3.2.1]octanes which are of

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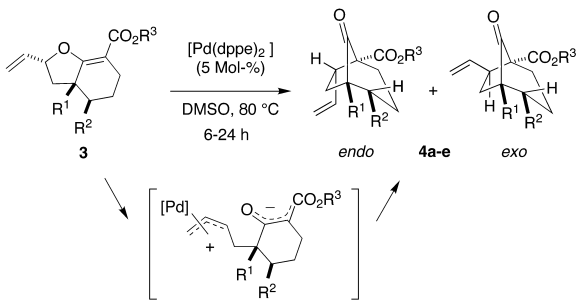
Table 2. Synthesis of bicyclo[3.2.1]octan-8-ones **4**.



4	R^1	R^2	R^3	Catalyst	Solvent	T [°C]	t [h]	Yield[a] [%]
a	H	H	OEt	$Pd(OAc)_2/PPh_3$	CH_3CN	80	24	0
a	H	H	OEt	$[Pd(PPh_3)_4]$	DME or THF	60	24	0
a	H	H	OEt	$[Pd(dppe)_2]$	DMSO	20	24	0
a	H	H	OEt	$[Pd(dppe)_2]$	DMSO	80	6	95
b	H	H	O*i*Pr	$[Pd(dppe)_2]$	DMSO	80	6	92
c	H	H	$O(CH_2)_2OMe$	$[Pd(dppe)_2]$	DMSO	80	6	91
d	CO_2Et	H	OEt	$[Pd(dppe)_2]$	DMSO	80	6	95
e	H	Me	OEt	$[Pd(dppe)_2]$	DMSO	80	6	93

[a] Yield of isolated product. In all reactions the *endo*:*exo* selectivities were in the

pharmacological significance and of importance for natural product syntheses.[8–14]

Experimental Section

31: A solution of lithium diisopropylamide (LDA) (4.7 mmol) in THF was prepared by addition of *n*BuLi (2 mL, 2.35 M) to a solution of diisopropylamine (0.65 mL) in THF (30 mL) at 0 °C. After the mixture had been stirred for 20 min, ethyl cyclohexanone-2-carboxylate (340 mg, 2 mmol) was added at 0 °C. The mixture was stirred for 60 min, and then this solution was slowly added to a solution of **2** in THF (15 mL) at −78 °C. The temperature was allowed to rise to 20 °C over 4 h and the solution was stirred at this temperature for 2 h. The reaction mixture was poured into an aqueous solution of hydrochloric acid (0.1 M) and extracted with diethyl ether. The combined organic layers were dried ($MgSO_4$), filtered, and the solvent of the filtrate was removed in vacuo. The residue was purified by column chromatography (silica gel, ether:petroleum ether 1:10 → 1:3) to give **31** as a colorless oil. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.10-1.55$ (m, 3H; CH_2), 1.25 (t, 3H, $J = 7$; CH_3), 1.80–2.40 (m, 5H; CH_2), 2.68 (m, 1H; CH), 4.15 (m, 2H; OCH_2), 4.77 (m, 1H; C*H*=CH_2), 5.19–5.42 (2 × dd, 2 × 1H; CH=CH_2), 5.91 (ddd, 1H; C*H*=CH_2); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta_c = 13.91$, 21.73, 23.49, 26.98, 36.78, 41.25, 58.80, 82.93, 96.25, 116.60, 135.80, 166.36, 166.99; MS (70 eV): 222 (37,[M^+]), 177 (34), 168 (100), 122 (73); elemental analysis calcd for $C_{13}H_{18}O_3$ (%): C 70.24, H 8.16; found: C 70.42, H 8.02.

4a: A solution of **31** (200 mg, 0.9 mmol) in dimethyl sulfoxide (2.4 mL) was degassed and $[Pd(dppe)_2]$ (40 mg, 5.0 mol %) was added. The red solution was stirred at 80 °C for 6 h. To the mixture was added diethyl ether (20 mL), the suspension was filtered through a pad of Celite and the Celite was washed with diethyl ether (200 mL). The solvent of the filtrate was removed in vacuo and the residue was purified by filtration through a short pad of silica gel to give pure **4a** as a mixture of two diastereomers (190 mg, 95%, *endo*:*exo* = 1.2:1). The diastereomers were separated by column chromatography (silica gel, ether:petroleum ether 1:20 → 1:3) to give *endo*-**4a** (90 mg, 45%) and *exo*-**4a** (72 mg, 36%) as colorless oils. The assignment of the diastereomers is based on analogy to the chemical shifts of 6-*endo*- and 6-*exo*-vinyl-bicyclo[3.2.1]octan-8-one: *endo*-**4a**: ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.20$ (t, 3H, $J = 7$ Hz; CH_3), 1.42–1.90 (m, 3H; CH_2), 1.95 (m, 2H; CH_2), 2.10–2.30 (m, 3H; CH_2), 2.43 (m, 1H; C*H*CH=CH_2), 3.48 (m, 1H; C*H*CO), 4.18 (m, 2H; OCH_2), 5.10–5.20 (2 × dd, 2 × 1H; CH=CH_2), 5.92 (ddd, 1H; C*H*=CH_2); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta_c =$ 14.11, 17.15, 27.34, 33.82, 36.60, 41.47, 46.01, 60.99, 61.61, 117.53, 135.40, 170.63, 214.90. MS (70 eV): 222 (52, [M^+]); elemental analysis calcd for $C_{13}H_{18}O_3$ (%): C 70.24, H 8.16; found: C 70.36, H 8.10; *exo*-**4a**: ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.22$ (t, 3H, $J = 7$ Hz; CH_3), 1.60–2.10 (m, 7H; CH_2), 2.42 (m, 2H; C*H*CH=CH_2), 2.90 (m, 1H; C*H*CO), 4.10 (m, 2H; OCH_2), 4.80–5.00 (2 × dd, 2 × 1H; CH=CH_2), 5.70 (ddd, 1H; C*H*=CH_2); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta_c = 14.01$, 17.42, 30.44, 36.85, 39.99, 46.57, 60.41, 60.63, 114.23, 117.44, 139.98, 169.69, 215.01; MS (70 eV): 222 (46, [M^+]); elemental analysis calcd for $C_{13}H_{18}O_3$ (%): C 70.24, H 8.16; found: C 70.40, H 8.06. All compounds were characterized by spectroscopic methods and gave correct elemental analyses and/or high-resolution mass spectra.

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