Carbonyl Ylide Cycloadditions to C,C-Double Bonds of Methylenecyclopropanes[‡]

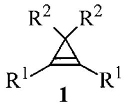
Alexander P. Molchanov,[a] Vyacheslav V. Diev,[a] Jörg Magull,[b] Denis Vidović,[b] Sergei I. Kozhushkov,[c] Armin de Meijere*[c] and Rafael R. Kostikov*[a]

Keywords: Bicyclopropylidene / Carbonyl ylides / Dipolar cycloaddition / Methylenecyclopropane / Strained molecules

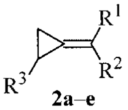
The carbonyl ylide 1,3-dipoles generated by dirhodium tetraacetate-catalyzed decomposition from 1-diazo-5-phenylpentane-2,5-dione (**4**) and 1-(1-acetylcyclopropyl)-2-diazoethanone (**5**) cycloadd to substituted methylenecyclopropanes **2a**–**e** and bicyclopropylidene (**3**) to give substituted mono-, di-, and trispirocyclopropanated 8-oxabicyclo[3.2.1]octan-2-ones **7**, **8**, and **11** and 7-oxabicyclo[2.2.1]heptan-2-ones **10** and **12** in 6–75 % yields with different regio- and stereoselectivities. The structures of the two isomeric cycloadducts *endo*- and *exo*-**10d** formed from the carbonyl ylide derived from **5** and methyl 2-chloro-2-(cyclopropylidene)acetate (**2d**) were confirmed by X-ray crystal structure analyses. (Diphenylmethylene)cyclopropane and *trans*-3-methylenecyclopropane-1,2-dicarboxylate (diethyl ester of Feist's acid) did not undergo such cycloadditions, while methylenecyclobutane (**13**) afforded a mixture of [3+2] and [2+1] cycloadducts **14** and **15** in 28 and 29 % yields, respectively. The scope and limitations of these cycloadditions as well as the influence of different factors upon their regio- and stereoselectivities are discussed.

Introduction

Multifunctional cyclopropane derivatives have established their potential as useful building blocks in organic synthesis.[1–3] The release of strain upon any type of addition or cycloaddition onto alkenes such as cyclopropenes (**1**),[4] methylenecyclopropanes **2**,[5] and bicyclopropylidene (**3**)[6] results in enhanced reactivity, and this makes them especially attractive for synthetic applications. In the rich chemistry of these alkenes, their cycloadditions with retention of the cyclopropane ring are of special interest, since the three-membered ring can, as a unique three-carbon functional group, undergo subsequent transformations. Whereas Diels–Alder reactions,[5e,6a,6b] 1,3-dipolar cycloadditions of nitrones and nitrile oxides,[5b,5e,6b] and Pauson–Khand reactions[5b,7] have been investigated in great detail, there was until recently no published example of a 1,3-dipolar cycloaddition of a carbonyl ylide to any of the alkenes **1**–**3**.

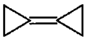


1

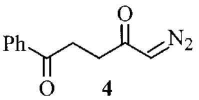


2a–e

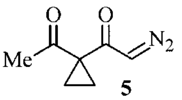
	R^1	R^2	R^3
a	Ph	H	H
b	nC$_7$H$_{15}$	H	H
c	Br	H	H
d	CO$_2$Me	Cl	H
e	H	H	CH$_2$OTHP



3



4



5

The first reported examples of carbonyl ylide cycloadditions to alkyl- and aryl-substituted cyclopropenes **1** (R^1 = Ph, R^2 = alkyl, aryl) proceeded in yields of up to 80 %, but no reaction was observed with cyano- and methoxycarbonyl-substituted analogues.[8] Here we report our results concerning the reactivity of carbonyl ylides generated from diazo ketones **4** [9] and **5** [9b,10] towards methylenecyclopropanes **2a**–**e** and bicyclopropylidene (**3**).

Results and Discussion

The carbonyl ylide **6**, generated by decomposition of 1-diazo-5-phenylpentane-2,5-dione (**4**) under dirhodium

---

[‡] For one of us (A. d. M.) this is to be considered as Part 105 in the series "Cyclopropyl Building Blocks for Organic Synthesis". Part 104: M. Schelper, A. de Meijere, *Eur. J. Org. Chem.* **2005**, 582–592. Part 103: A. de Meijere, H. Winsel, B. Stecker, *Org. Synth.* **2004**, *81*, 14–25.

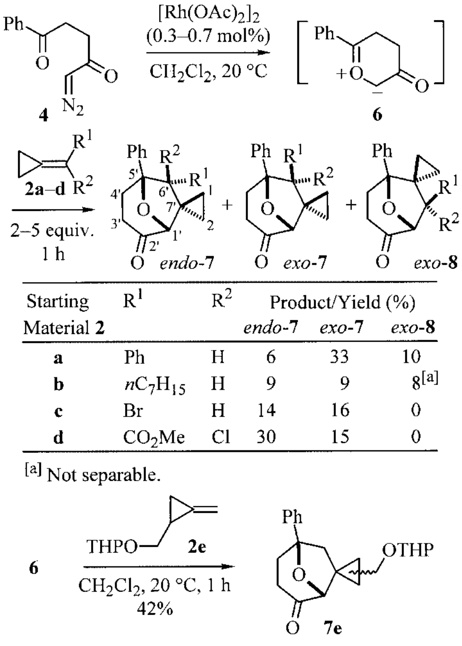
[a] Department of Organic Chemistry, St. Petersburg State University,
Universitetskii pr. 26, 198504, St. Petersburg, Russia
Fax: (internat.) +7-812-4286939
E-mail: rkost@rk1198.spb.edu

[b] Institut für Anorganische Chemie der Georg-August-Universität Göttingen,
Tammannstrasse 4, 37077 Göttingen, Germany
E-mail: Joerg@achpc1.ac.chemie.uni-goettingen.de

[c] Institut für Organische und Biomolekulare Chemie der Georg-August-Universität Göttingen,
Tammannstrasse 2, 37077 Göttingen, Germany
Fax: (internat.) +49-551-399475
E-mail: Armin.deMeijere@chemie.uni-goettingen.de

DOI: 10.1002/ejoc.200400601

tetraacetate catalysis conditions in the presence of (benzylidene)cyclopropane (**2a**) in dichloromethane at ambient temperature, gave the two diastereomeric cycloadducts *endo*- and *exo*-**7a** as well as the regioisomer *exo*-**8a** in 6, 33, and 10 % isolated yields, respectively (total yield 49 %, Scheme 1). The relative configurations of *endo*- and *exo*-**7a** as well as *exo*-**8a** were established on the basis of their NOESY NMR spectra. According to these, *exo*-**8a** is the only isomer for which an interaction between the two methine 1′-H (δ = 4.56 ppm) and 7′-H (δ = 3.19 ppm) protons could be observed. This indicates that these two protons must be positioned at neighboring carbon atoms, while *endo*-**7a** and *exo*-**7a** should possess the opposite regiochemistry.



Starting Material **2**	R^1	R^2	Product/Yield (%) *endo*-**7**	*exo*-**7**	*exo*-**8**
a	Ph	H	6	33	10
b	nC_7H_{15}	H	9	9	8[a]
c	Br	H	14	16	0
d	CO_2Me	Cl	30	15	0

[a] Not separable.

Scheme 1. Cycloadditions between the carbonyl ylide **6** and the methylenecyclopropane derivatives **2a**–**e**.

The coupling constant of close to zero between 1′-H and 7′-H in **8a** indicates an *exo* orientation of the phenyl substituent in this isomer (otherwise a coupling constant of about 8 Hz should be expected; cf. ref.[9]). In its NOESY spectrum, the cycloadduct *exo*-**7a** exhibits interactions between the methine proton 6′-H (δ = 3.55 ppm) and one of the methylene protons of both the dihydropyran-3-one and the cyclopropane moieties, and also between the methine proton 1′-H (δ = 4.09 ppm) and one of the cyclopropyl protons, while in the *endo* isomer *endo*-**7a** both 1′-H (δ = 4.10 ppm) and 6′-H (δ = 3.51 ppm) each interact only with one of the cyclopropyl protons. This assignment is consistent with the stereochemical assignment for the cycloadduct of the carbonyl ylide **6** with styrene.[9]

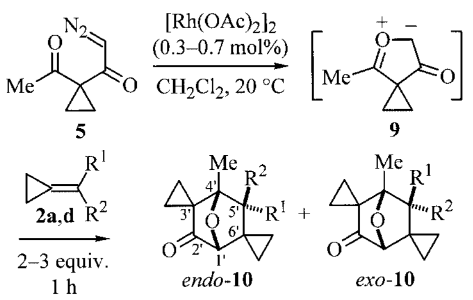
These results were used for analogous assignments of the individual products in the mixtures of other cycloadducts of **6**. Thus, treatment of diazodione **4** with three equivalents of 1-(cyclopropylidene)octane (**2b**) under the same conditions afforded an inseparable mixture of almost equal quantities of isomeric *endo*- and *exo*-**7b** as well as their regioisomer *exo*-**8b** (26 % total yield, Scheme 1). With the same carbonyl ylide, (bromomethylene)cyclopropane (**2c**) gave only the two diastereomeric cycloadducts *endo*- and *exo*-**7c** in modest yields of 14 and 16 %, respectively (Scheme 1). The NMR spectra of these compounds are very similar to one another (see Exp. Sect.); however, none of the samples showed an interaction between its methine protons in the NOESY spectra. The *exo* configuration was assigned to the isomer with its 6′-H methine proton signal shifted by 0.25 ppm downfield, because of the through-space influence of the bridging oxygen atom. The more highly polar methyl 2-chloro-2-(cyclopropylidene)acetate (**2d**),[11] which is known to possess enhanced reactivity as a dienophile in Diels–Alder reactions with participation of zwitterionic intermediates,[11a] also afforded only the two diastereomeric cycloadducts *endo*- and *exo*-**7d** – in 30 and 15 % yields, respectively – upon treatment with the carbonyl ylide **6**. Lastly, the cycloaddition between **6** and the ring-substituted **2e** proceeded without any diastereoselectivity to give a mixture of all four possible diastereomeric cycloadducts **7e** in 42 % yield.

The carbonyl ylide **6** thus does react with the substituted methylenecyclopropane derivatives **2a**–**e**, but with low selectivities, and the corresponding cycloadducts **7** and **8** are obtained only in low to moderate yields (26–49 %). The best yields were obtained with **2a** and **2d**, containing substituents conjugated with the double bonds.[12] For comparison, the cycloaddition of **6** onto styrene, which is related to **2a**, proceeds unselectively to yield all four possible isomers.[9] In the case of methyl 2-chloro-2-(cyclopropylidene)acetate (**2d**), the selective formation of *endo*- and *exo*-**7d** is a result of the polarity of the substrate, and the slight *endo* selectivity is probably due to steric interactions between the phenyl and the methoxycarbonyl substituents in the transition state. For comparison, no cycloadducts were isolated from the attempted reaction between **6** and diethyl *trans*-3-methylenecyclopropane-1,2-dicarboxylate (diethyl ester of Feist's acid), and this is consistent with the negative results of attempted carbonyl ylide cycloadditions to cyclopropene **1** with electron-withdrawing cyano- and methoxycarbonyl substituents.[8]

Surprisingly, the cycloaddition between the spirocyclopropanated carbonyl ylide **9**, generated in situ from the diazodiketone **5**, and benzylidenecyclopropane (**2a**) furnished an inseparable 1:2 mixture of the diastereomers *endo*- and *exo*-**10a** in only 6 % yield (Scheme 2). The structural assignments of *endo*- and *exo*-**10a** are based on the characteristic singlets of bridgehead 1′-H protons in the ^{1}H NMR spectrum of the mixture.

On the other hand, the cycloaddition between **9** and methyl 2-chloro-2-(cyclopropylidene)acetate (**2d**) was the most efficient in the whole series, with the corresponding dispirocyclopropanated *endo*- and *exo*-**10d** being isolated after column chromatography in 52 and 23 % yields, respectively (total yield 75 %). The structures of these cycloadducts *endo*- and *exo*-**10d** were established by X-ray crystal structure analyses (Figure 1).[13]

As in the previous case, **9** reacts with **2d** regioselectively, and the steric interactions between the methyl and the me-



Starting Material 2	R^1	R^2	Product/Yield (%) *endo*-10	*exo*-10
a	Ph	H	2	4[a]
d	CO_2Me	Cl	52	23

[a] Not separable.

Scheme 2. Cycloadditions between the spiro-cyclopropanated carbonyl ylide **9** and methylenecyclopropane derivatives **2a** and **2d**.

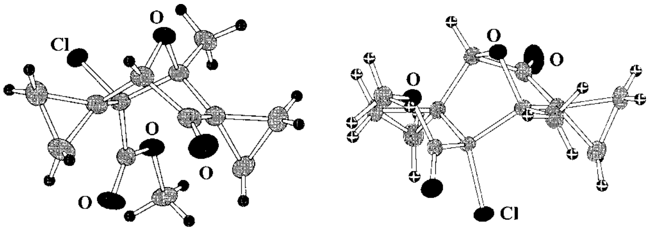
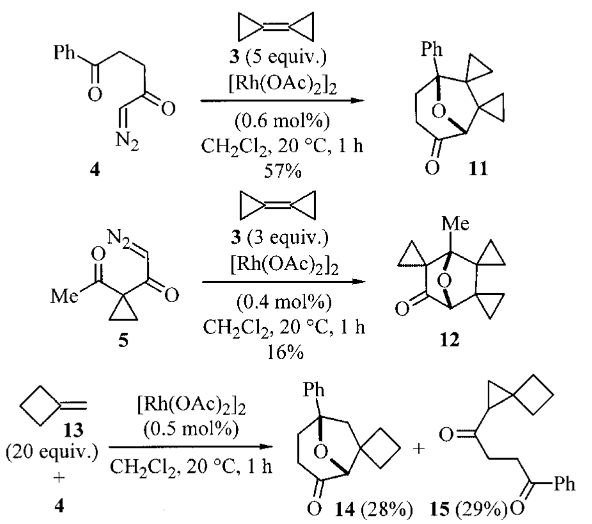


Figure 1. Structures of the cycloadducts *endo*- (left) and *exo*-**10d** (right) in the crystals.[13]

thoxycarbonyl substituents in the transition state favor the formation of the *endo*-cycloadduct *endo*-**10d**.

Bicyclopropylidene (**3**) may be regarded as a more highly strained cyclopropanated derivative of methylenecyclopropane (**2**, $R^1 = R^2 = R^3 = H$). As a consequence of its high-lying HOMO (π-EI_v = 8.93 eV[14] versus 9.64 eV for methylenecyclopropane[15]), in addition to its high total strain energy, **3** is uniquely reactive towards a wide range of electrophiles and cyclophiles.[6a–6c] In cycloaddition reactions with carbonyl ylides, however, the nature of the latter appeared to be more crucial: while the dispirocyclopropanated cycloadduct **11** was isolated as a sole product from the reaction between **3** (5 equiv.) and the ylide from diazo ketone **4** in 57 % yield, the trispirocyclopropanated 7-oxabicyclo[2.2.1]heptanone **12** was obtained in only 16 % yield (Scheme 3). The structures of the cycloadducts **11** and **12** were assigned from their ^1H and ^{13}C NMR spectra (see Exp. Sect.).

It should be underlined that no [2+1] cycloadduct was isolated in any of the reactions discussed above. For comparison, the catalyzed decomposition of diazo ketone **4** in the presence of methylenecyclobutane (**13**, 20 equiv.) did not only yield the expected [3+2] cycloadduct **14** (28 %), but also the [2+1] cycloadduct **15** (29 %, Scheme 3). Thus, a methylenecyclobutane apparently has a weaker reactivity than a methylenecyclopropane towards carbonyl ylide cycloaddition, and the competing cyclopropanation of the double bond wins over. The structures of the spirocyclobutanated 8-oxabicyclo[3.2.1]octanone **14** and the substituted spiro[2.3]hexane **15** were corroborated by their spectroscopic data.



Scheme 3. Cycloadditions of carbonyl ylides generated by catalytic decomposition of diazodiketones **4** and **5** onto bicyclopropylidene (**3**) and methylenecyclobutane (**13**).

Conclusions

Cycloadditions of carbonyl ylides are believed to be controlled by $HOMO_{alkene}$–$LUMO_{ylide}$ interactions (i.e., the carbonyl ylide is conceived to be an acceptor, and the alkene, in this case a methylenecyclopropane, a donor of electrons). Since the HOMO–LUMO energy gaps of carbonyl ylides are among the smallest of the common 1,3-dipoles,[16] the $HOMO_{ylide}$–$LUMO_{alkene}$ type of interaction appears to control the cycloadditions of carbonyl ylide **9** with methylenecyclopropanes. An analogous reactivity pattern has previously been observed in cycloadditions of carbonyl ylides onto terminal acetylenes.[17] The ambiphilic natures of carbonyl ylides **6** and **9** are also evident from their reactivity towards and mode of reaction with the electrophilic methylenecyclopropane derivative **2d**.

Experimental Section

General: NMR spectra were recorded with a Bruker AM 250 (250 MHz for ^1H and 62.9 MHz for ^{13}C NMR) or a Bruker DPX 300 (300 MHz for ^1H and 75.5 MHz for ^{13}C NMR) instrument in $CDCl_3$, and multiplicities of ^{13}C signals were determined by DEPT (Distortionless Enhancement by Polarization Transfer) measurements. Chemical shifts relate to $\delta_{TMS} = 0.00$ ppm according to the chemical shifts of residual $CHCl_3$ signals. IR: Bruker IFS 66 (FT-IR) spectrophotometer, measured as solutions in $CHCl_3$. MS (EI, 70 eV): Finnigan MAT 95 spectrometer. M.p.: Büchi 510 capillary melting point apparatus, values are uncorrected. TLC: Macherey–Nagel and Silufol precoated sheets, 0.25 mm Sil G/UV_{254}. Column chromatography: Merck silica gel, grade 60, 230–400 mesh. Starting materials: (benzylidene)cyclopropane (**2a**),[18] 1-(cyclopropylidene)octane (**2b**),[19] (bromomethylene)cyclopropane (**2c**),[20] methyl 2-chloro-2-(cyclopropylidene)acetate (**2d**),[21] 2-[(2-methylenecyclopropyl)methoxy]tetrahydropyran (**2e**),[22] bicyclopropylidene (**3**),[23] 1-diazo-5-phenylpentane-2,5-dione (**4**),[9a] 1-(1-acetylcyclopropyl)-2-diazoethanone (**5**),[10b] and methylenecyclobutane (**13**)[24] were prepared by published procedures. Anhydrous dichloromethane was obtained by distillation from P_2O_5. All operations in anhydrous CH_2Cl_2 were performed under argon in flame-dried glassware.

General Procedure (GP) for the Generation of Carbonyl Ylides and Their Cycloadditions onto Methylenecyclopropane Derivatives: A catalytic amount of dirhodium tetraacetate (0.3–0.7 mol %) was added in one portion to a stirred solution of the appropriate diazodione (1 equiv.) and the appropriate dipolarophile (1.2–20 equiv.) in anhydrous CH_2Cl_2. Evolution of nitrogen was observed during the first 10–20 min. The reaction mixture was stirred at ambient temperature for an additional 1 h, the solvent was removed under reduced pressure, and the products were isolated by column chromatography of the residue on silica gel, with elution with hexane/ethyl acetate gradient mixtures unless otherwise stated.

***endo*-(1′*R**,5′*R**,6′*R**)-5′,6′-Diphenyl-7′,7′-ethano-8′-oxabicyclo-[3.2.1]octan-2′-one (*endo*-7a), *exo*-(1′*R**,5′*R**,6′*S**)-5′,6′-Diphenyl-7′,7′-ethano-8′-oxabicyclo[3.2.1]octan-2′-one (*exo*-7a), and *exo*-(1′*R**,5′*R**,7′*R**)-5′,7′-Diphenyl-6′,6′-ethano-8′-oxabicyclo[3.2.1]octan-2′-one (*exo*-8a):** Column chromatography (50 g of silica gel, 30 × 3 cm column, hexane/EtOAc, 8:2) of the residue obtained from diazodione **4** (209 mg, 1.03 mmol), benzylidenecyclopropane (**2a**, 407 mg, 3.1 mmol, 3.0 equiv.), and $[Rh(OAc)_2]_2$ (2 mg, 0.4 mol %) in CH_2Cl_2 (5 mL) as described in the GP afforded *endo*-**7a** (18 mg, 6 %), *exo*-**7a** (103 mg, 33 %), and *exo*-**8a** (30 mg, 10 %).

Compound *endo*-7a: Colorless oil, R_f = 0.67. ^{1}H NMR (300 MHz): δ = 0.57 (ddd, J = 10.4, 5.9, 3.7 Hz, 1 H, CH_2), 0.67 (ddd, J = 9.5, 5.9, 5.3 Hz, 1 H, CH_2), 0.77 (ddd, J = 10.4, 5.5, 5.3 Hz, 1 H, CH_2), 1.09 (ddd, J = 9.5, 5.5, 3.7 Hz, 1 H, CH_2), 2.22 (dt, J = 14.6, 9.5 Hz, 1 H, CH_2), 2.40 (m, 1 H, CH_2), 2.65 (m, 1 H, CH_2), 2.90 (dt, J = 18.3, 8.8 Hz, 1 H, CH_2), 3.51 (s, 1 H, CH), 4.10 (s, 1 H, CH), 7.00–7.02 (m, 2 H, Ph-H), 7.18–7.21 (m, 2 H, Ph-H), 7.19–7.35 (m, 6 H, Ph-H) ppm. ^{13}C NMR (75 MHz): δ = 1.4 (CH_2), 9.3 (CH_2), 16.1 (CH_2), 29.8 (CH_2), 33.4 (C), 62.7 (CH), 87.7 (CH), 88.4 (C), 124.5 (CH), 127.5 (CH), 127.8 (CH), 128.5 (CH), 128.8 (CH), 130.9 CH), 136.0 (C), 145.1 (C), 207.0 (C) ppm.

Compound *exo*-7a: Colorless solid, m.p. 116–119 °C, R_f = 0.59. IR: $\tilde{\nu}$ = 3045 cm^{-1}, 3030, 3020, 2960, 2935, 2860, 1740, 1500, 1450, 1285, 1270, 1085, 1050, 1020. ^{1}H NMR (300 MHz): δ = 0.30–0.38 (m, 1 H, CH_2), 0.75–0.80 (m, 1 H, CH_2), 0.84–0.95 (m, 2 H, CH_2), 2.42 (ddd, J = 14.0, 10.7, 8.1 Hz, 1 H, CH_2), 2.56–2.67 (m, 2 H, CH_2), 3.05 (ddd, J = 16.9, 10.7, 8.1 Hz, 1 H, CH_2), 3.55 (s, 1 H, CH), 4.09 (s, 1 H, CH), 6.95–7.18 (m, 10 H, Ph-H) ppm. ^{13}C NMR (75 MHz): δ = 10.3 (CH_2), 16.1 (CH_2), 32.6 (C), 33.7 (CH_2), 40.6 (CH_2), 60.2 (CH), 88.0 (CH), 89.5 (C), 125.7 (CH), 126.4 (CH), 126.5 (CH), 127.8 (CH), 130.0 (CH), 141.4 (C), 143.3 (C), 206.0 (C) ppm. MS (EI): m/z (%) = 304 (30) [M$^+$], 184 (12), 161 (100), 128 (14), 115 (21), 105 (30), 91 (20), 77 (18). $C_{21}H_{20}O_2$ (304.39): calcd. C 82.87, H 6.62; found C 82.81, H 6.66.

Compound *exo*-8a: Colorless solid, m.p. 145–148 °C, R_f = 0.53. IR: $\tilde{\nu}$ = 3045 cm^{-1}, 3030, 3020, 2960, 2935, 1740, 1500, 1450, 1270, 1105, 1080, 1060, 1045. ^{1}H NMR (300 MHz): δ = –0.08–0.05 (m, 2 H, CH_2), 0.85 (ddd, J = 10.5, 7.6, 4.9 Hz, 1 H, CH_2), 1.02 (dt, J = 10.5, 6.3 Hz, 1 H, CH_2), 2.32–2.44 (m, 1 H, CH_2), 2.63–2.71 (m, 2 H, CH_2), 3.07 (ddd, J = 17.1, 10.5, 8.0 Hz, 1 H, CH_2), 3.19 (s, 1 H, CH), 4.56 (s, 1 H, CH), 7.23–7.42 (m, 10 H, Ph-H) ppm. ^{13}C NMR (75 MHz): δ = 10.8 (CH_2), 13.2 (CH_2), 33.5 (CH_2), 35.5 (CH_2), 36.2 (C), 56.9 (CH), 85.3 (C), 89.0 (CH), 124.8 (CH), 127.3 (CH), 127.9 (CH), 128.3 (CH), 129.0 (CH), 128.9 (CH), 141.9 (C), 143.1 (C), 207.0 (C) ppm. MS (EI): m/z (%) = 304 (18) [M$^+$], 247 (100), 128 (14), 115 (15), 105 (25), 91 (29), 77 (22).

***endo*-(1′*R**,5′*R**,6′*R**)-6′-Heptyl-5′-phenyl-7′,7′-ethano-8′-oxabicyclo[3.2.1]octan-2′-one (*endo*-7b), *exo*-(1′*R**,5′*R**,6′*S**)-6′-Heptyl-5′-phenyl-7′,7′-ethano-8′-oxabicyclo[3.2.1]-octan-2′-one (*exo*-7b), and *exo*-(1′*R**,5′*R**,7′*R**)-7′-Heptyl-5′-phenyl-6′,6′-ethano-8′-oxabicyclo[3.2.1]octan-2′-one (*exo*-8b):** Column chromatography [30 g of silica gel, 30 × 2 cm column, hexane/EtOAc, R_f = 0.47 (hexane/EtOAc, 9:1)] of the residue obtained from diazodione **4** (130 mg, 0.643 mmol), 1-(cyclopropylidene)octane (**2b**, 290 mg, 1.91 mmol, 3.0 equiv.), and $[Rh(OAc)_2]_2$ (1.5 mg, 0.5 mol %) in CH_2Cl_2 (2 mL) as described in the GP afforded an inseparable mixture of *endo*-**7b**, *exo*-**7b**, and *exo*-**8b** (55 mg, 26 %) as a colorless oil in a ratio of 36:35:29. The composition of this mixture was estimated by integration of the signals of the bridgehead 1′-H protons in the ^{1}H NMR spectrum (300 MHz): δ = 3.83 (s, *exo*-**7b**), 3.85 (d, J = 1.4 Hz, *exo*-**8b**), 4.33 (s, *endo*-**7b**) ppm. ^{13}C NMR (75 MHz): 86.0; 88.0; 88.2 (bridge-head C-1′ carbon atoms), 85.1; 87.0; 87.6 (bridge-head C-5′ carbon atoms), 205.2, 206.7, 208.9 (C=O carbon atoms) ppm.

***endo*-(1′*R**,5′*S**,6′*R**)-6′-Bromo-5′-phenyl-7′,7′-ethano-8′-oxabicyclo[3.2.1]octan-2′-one (*endo*-7c) and *exo*-(1′*R**,5′*S**,6′*S**)-6′-Bromo-5′-phenyl-7′,7′-ethano-8′-oxabicyclo[3.2.1]octan-2′-one (*exo*-7c):** Column chromatography (30 g of silica gel, 30 × 2 cm column, hexane/EtOAc) of the residue obtained from diazodione 4 (160 mg, 0.79 mmol), (bromomethylene)cyclopropane (**2c**, 560 mg, 4.21 mmol, 5 equiv.), and $[Rh_2(OAc)_2]_2$ (2 mg, 0.6 mol %) in CH_2Cl_2 (2 mL) as described in the GP afforded *endo*-**7c** (34 mg, 14 %) and *exo*-**7c** (55 mg of ca. 70 % purity, calculated yield 16 %).

Compound *endo*-7c: Colorless solid, m.p. 119–122 °C, R_f = 0.53 (hexane/EtOAc, 9:1). IR: $\tilde{\nu}$ = 3075 cm^{-1}, 3040, 2970, 2940, 1740, 1450, 1285, 1250, 1235, 1115, 1040, 990, 960. ^{1}H NMR (250 MHz): δ = 0.78–0.84 (m, 1 H, CH_2), 0.90–0.97 (m, 1 H, CH_2), 1.17–1.29 (m, 2 H, CH_2), 2.30–2.38 (m, 1 H, CH_2), 2.42–2.54 (m, 1 H, CH_2), 2.95–3.11 (m, 2 H, CH_2), 3.88 (d, J = 1.8 Hz, 1 H, CH), 4.40 (s, 1 H, CH), 7.34–7.40 (m, 3 H, Ph-H), 7.64–7.68 (m, 2 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz): δ = 11.8 (CH_2), 17.3 (CH_2), 30.1 (C), 33.1 (CH_2), 34.9 (CH_2), 62.7 (CH), 86.2 (C), 86.5 (CH), 124.4 (CH), 128.0 (CH), 128.5 (CH), 142.0 (C), 204.3 (C) ppm. $C_{15}H_{15}BrO_2$ (307.18): calcd. C 58.65, H 4.92; found C 58.65, H 4.91.

Compound *exo*-7c: Colorless oil, R_f = 0.28 (hexane/EtOAc, 9:1). ^{1}H NMR (300 MHz): δ = 0.88–1.04 (m, 1 H, CH_2), 1.23–1.34 (m, 2 H, CH_2), 1.35–1.43 (m, 1 H, CH_2), 2.48–2.71 (m, 4 H, 2 CH_2), 4.15 (s, 1 H, CH), 4.57 (s, 1 H, CH), 7.28–7.42 (m, 5 H, Ph-H) ppm. ^{13}C NMR (75 MHz): δ = 14.8 (CH_2), 19.7 (CH_2), 31.8 (C), 33.3 (CH_2), 35.5 (CH_2), 67.3 (CH), 85.8 (CH), 88.0 (C), 125.2 (CH), 127.9 (CH), 128.4 (CH), 144.4 (C), 205.4 (C=O) ppm.

Methyl *endo*-(1′*R,5′*S**,6′*S**)-6′-Chloro-2′-oxo-5′-phenyl-7′,7′-ethano-8′-oxabicyclo[3.2.1]octane-6′-carboxylate (*endo*-7d) and Methyl *exo*-(1′*R**,5′*S**,6′*R**)-6′-Chloro-2′-oxo-5′-phenyl-7′,7′-ethano-8′-oxabicyclo[3.2.1]octane-6′-carboxylate (*exo*-7d):** Column chromatography (50 g of silica gel, 30 × 3 cm column, hexane/EtOAc) of the residue obtained from diazodione 4 (140 mg, 0.692 mmol), methyl 2-chloro-2-(cyclopropylidene)acetate (**2d**, 217 mg, 1.5 mmol, 2 equiv.) and $[Rh(OAc)_2]_2$ (1 mg, 0.3 mol %) in CH_2Cl_2 (3 mL) as described in the GP afforded *endo*-**7d** (66 mg, 30 %) and *exo*-**7d** (33 mg, 15 %).

Compound *endo*-7d: Colorless solid, m.p. 84–90 °C, R_f = 0.51 (hexane/EtOAc, 8:2). IR: $\tilde{\nu}$ = 3040 cm^{-1}, 2960, 2850, 1745, 1450, 1415, 1350, 1325, 1270, 1050, 1040, 1030, 960, 945. ^{1}H NMR (300 MHz): δ = 0.80 (ddd, J = 9.6, 8.0, 5.5 Hz, 1 H, CH_2), 1.14–1.33 (m, 2 H, CH$_2$), 1.45 (ddd, J = 10.2, 8.0, 5.5 Hz, 1 H, CH$_2$), 2.42–2.57 (m, 2 H, CH$_2$), 2.92 (m, 1 H, CH$_2$), 3.17–3.25 (m, 1 H, CH$_2$), 3.86 (s, 3 H, CH$_3$O), 4.13 (s, 1 H, CH), 7.33–7.41 (m, 3 H, Ph-H), 7.50 (d, J = 6.2 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (75 MHz): δ = 14.8 (CH$_2$), 17.8 (CH$_2$), 34.0 (CH$_2$), 35.7 (CH$_2$), 35.8 (C), 53.8 (CH$_3$), 81.9 (C), 86.0 (CH), 91.8 (C), 125.6 (CH), 128.1 (CH), 128.3 (CH), 142.3 (C), 161.8 (C), 204.8 (C) ppm. $C_{17}H_{17}ClO_4$ (320.77): calcd. C 63.66, H 5.34; found C 63.64, H 5.58.

Compound *exo*-7d: Colorless solid, m.p. 167–170 °C, R_f = 0.48 (hexane/EtOAc, 8:2). IR: $\tilde{\nu}$ = 3040 cm^{-1}, 2955, 1745, 1450, 1415, 1120, 1060, 1050, 1000, 970, 955, 930, 910. ^{1}H NMR (300 MHz): δ = 0.71–0.80 (m, 1 H, CH$_2$), 0.86–0.94 (m, 1 H, CH$_2$), 1.27–1.41 (m, 2 H, CH$_2$), 2.26–2.37 (m, 1 H, CH$_2$), 2.45–2.54 (m, 1 H, CH$_2$), 3.00–3.10 (m, 2 H, CH$_2$), 3.25 (s, 3 H, CH$_3$O), 4.05 (d, J = 1.4 Hz, 1 H, CH), 7.28–7.38 (m, 3 H, Ph-H), 7.57 (d, J = 7.3 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (75 MHz): δ = 12.6 (CH$_2$), 18.2 (CH$_2$), 33.6 (CH$_2$), 34.7 (C), 37.3 (CH$_2$), 53.3 (CH$_3$), 82.2 (C), 86.9 (CH), 90.6 (C), 124.6 (CH), 128.4 (CH), 128.5 (CH), 140.4 (C), 169.4 (C), 203.7 (C) ppm. $C_{17}H_{17}ClO_4$ (320.77): calcd. C 63.66, H 5.34; found C 63.49, H 5.64.

5′-Phenyl-7′,7′-[1-(tetrahydro-2*H*-pyran-2-yloxymethyl)-1,2-ethano]-8′-oxabicyclo[3.2.1]octan-2′-one (7e): Column chromatography (30 g of silica gel, 30 × 2 cm column, hexane/EtOAc, 8:2) of the residue obtained from diazodione **4** (177 mg, 0.876 mmol), methylenecyclopropane **2e** (441 mg, 2.62 mmol, 3 equiv.), and [Rh(OAc)$_2$]$_2$ (2 mg, 0.5 mol %) in CH$_2$Cl$_2$ (2 mL) as described in the GP afforded two fractions, each as a colorless oil, with R_f = 0.40 and 0.36. The first fraction (63 mg, 21 %) was a mixture of two diastereomers of **7e** in a ratio of ~ 3:1, as estimated by integration of the signals of the bridgehead 1′-H protons and the CH-protons of the tetrahydropyranyl group in the ^{1}H NMR spectrum (300 MHz): δ = 3.76 (s), 3.83 (s) and 4.57 (m), 4.65 (m) ppm. ^{13}C NMR (75 MHz): δ = 84.7, 85.5 (C, bridgehead C-5 carbon atoms), 82.0, 88.9 (CH, bridgehead C-1′ carbon atoms), 99.0, 99.6 (CH, tetrahydropyranyl C-1 carbon atoms), 205.6, 205.8 (C=O carbon atoms) ppm. $C_{21}H_{26}O_4$ (342.43): calcd. C 73.66, H 7.65; found C 73.67, H 7.68.

The second fraction (62 mg, 21 %) was a ca. 1:1 mixture of two diastereomers of **7e**. ^{1}H NMR (300 MHz): δ = 4.51 (m), 4.62 (m, CH protons of THP group), 3.87 (s, overlapped 1′-H protons) ppm. ^{13}C NMR (75 MHz): δ = 85.0, 85.1 (C, bridgehead C-5′ carbon atoms), 89.0 (CH, overlapped bridgehead C-1′ carbon atoms), 99.2, 99.5 (CH, tetrahydropyranyl C-1 carbon atoms), 205.4, 205.5 (C=O carbon atoms) ppm. $C_{21}H_{26}O_4$ (342.43): calcd. C 73.66, H 7.65; found C 73.52, H 7.76.

***endo*-4′-Methyl-5′-phenyl-3′,3′:6′,6′-bis(ethano)-7′-oxabicyclo-[2.2.1]-heptan-2′-one (*endo*-10a) and *exo*-4′-Methyl-5′-phenyl-3′,3′:6′,6′-bis-(ethano)-7′-oxabicyclo[2.2.1]heptan-2′-one (*exo*-10a):** Column chromatography (30 g of silica gel, 30 × 2 cm column, hexane/EtOAc, 8:2, R_f = 0.40) of the residue obtained from diazodione **5** (212 mg, 1.40 mmol), (benzylidene)cyclopropane **2a** (545 mg, 4.2 mmol, 3 equiv.), and [Rh(OAc)$_2$]$_2$ (2 mg, 0.3 mol %) in CH$_2$Cl$_2$ (5 mL) as described in the GP afforded a 1:2 mixture of *endo*- and *exo*-**10a** (21 mg, 6 %), as estimated by integration of the methine proton signals in the ^{1}H NMR spectrum (300 MHz): δ = 2.54 (s), 3.92 (s, methine 5′-H protons), 4.24 (s), 4.99 (s, bridgehead 1′-H protons) ppm. ^{13}C NMR (75 MHz): δ = 86.3, 86.8 (bridgehead C-1′ carbon atoms), 90.0 (overlapped, bridgehead C-4′ carbon atoms), 209.8, 211.0 (C=O carbon atoms) ppm.

Methyl *endo*-(1′*R,4′*S**,5′*S**)-5′-Chloro-4′-methyl-2′-oxo-3′,3′:6′,6′-bis(ethano)-7′-oxabicyclo[2.2.1]heptane-5′-carboxylate (*endo*-10d) and Methyl *endo*-(1′*R**,4′*S**,5′*R**)-5′-Chloro-4′-methyl-2′-oxo-3′,3′:6′,6′-bis(ethano)-7′-oxabicyclo[2.2.1]heptane-5′-carboxylate (*exo*-10d):** Column chromatography (30 g of silica gel, 30 × 2 cm column, hexane/EtOAc, 8:2) of the residue obtained from diazodione **5** (145 mg, 0.96 mmol), methyl 2-chloro-2-(cyclopropylidene)acetate (**2d**, 280 mg, 1.9 mmol, 2 equiv.), and [Rh(OAc)$_2$]$_2$ (1.5 mg, 0.4 mol %) in CH$_2$Cl$_2$ (2 mL) as described in the GP afforded *endo*-**10d** (136 mg, 52 %) and *exo*-**10d** (60 mg, 23 %).

Compound *endo*-10d: Colorless solid, m.p. 67–68 °C, R_f = 0.56. ^{1}H NMR (300 MHz): δ = 0.91 (ddd, J = 10.0, 8.1, 5.8 Hz, 1 H, CH$_2$), 0.96–1.06 (m, 2 H, CH$_2$), 1.17–1.32 (m, 4 H, 2 CH$_2$), 1.60 (s, 3 H, CH$_3$), 1.81 (ddd, J = 10.0, 7.0, 5.4 Hz, 1 H, CH$_2$), 3.73 (s, 3 H, CH$_3$O), 3.85 (s, 1 H, CH) ppm. ^{13}C NMR (75 MHz): δ = 11.7 (CH$_2$), 13.3 (CH$_2$), 15.1 (CH$_3$), 16.2 (CH$_2$), 16.3 (CH$_2$), 34.0 (C), 35.5 (C), 53.0 (CH$_3$), 86.7 (CH), 91.5 (C), 161.8 (C), 208.5 (C) ppm. $C_{13}H_{15}ClO_4$ (270.71): calcd. C 57.68, H 5.58; found C 57.83, H 5.63.

Compound *exo*-10d: Colorless solid, m.p. 104 °C, R_f = 0.37. ^{1}H NMR (300 MHz): δ = 0.83–0.94 (m, 3 H, CH$_2$), 1.09–1.17 (m, 1 H, CH$_2$), 1.20–1.41 (m, 3 H, CH$_2$), 1.34 (s, 3 H, CH$_3$), 1.59 (ddd, J = 10.3, 6.5, 5.4 Hz, 1 H, CH$_2$), 3.85 (s, 3 H, CH$_3$O), 3.96 (s, 1 H, CH) ppm. ^{13}C NMR (75 MHz): δ = 11.1 (CH$_2$), 14.1 (CH$_2$), 14.3 (CH$_3$), 15.1 (CH$_2$), 15.6 (CH$_2$), 34.6 (C), 38.4 (C), 53.8 (CH$_3$), 85.9 (CH), 91.6 (C), 169.4 (C), 208.5 (C) ppm. $C_{13}H_{15}ClO_4$ (270.71): calcd. C 57.68, H 5.58; found C 57.72, H 5.54.

(1′*R,5′*S**)-5′-Phenyl-6′,6′:7′,7′-bis(ethano)-8′-oxabicyclo[3.2.1]octan-2′-one (11):** Column chromatography (30 g of silica gel, 30 × 2 cm column, hexane/EtOAc, 9:1, R_f = 0.41) of the residue obtained from diazodione **4** (165 mg, 0.82 mmol), bicyclopropylidene (**3**, 329 mg, 385 µL, 4.1 mmol, 5 equiv.), and [Rh(OAc)$_2$]$_2$ (2 mg, 0.6 mol %) in CH$_2$Cl$_2$ (5 mL) as described in the GP afforded **11** (118 mg, 57 %) as a colorless solid, m.p. 110–113 °C. IR: $\tilde{\nu}$ = 3080 cm^{-1}, 3060, 3020, 2965, 2940, 1740, 1450, 1250, 1220, 1075, 1060, 1040. ^{1}H NMR (300 MHz): δ = –0.16 (dt, J = 10.0, 6.0 Hz, 1 H, CH$_2$), 0.00 (dt, J = 10.0, 6.0 Hz, 1 H, CH$_2$), 0.26–0.34 (m, 1 H, CH$_2$), 0.46–0.57 (m, 4 H, 2 CH$_2$), 0.79–0.84 (m, 1 H, CH$_2$), 2.35 (ddd, J = 13.5, 11.0, 7.0 Hz, 1 H, CH$_2$), 2.53–2.66 (m, 2 H, CH$_2$), 2.99 (ddd, J = 18.0, 11.0, 8.5 Hz, 1 H, CH$_2$), 3.99 (s, 1 H, CH), 7.28–7.39 (m, 5 H, Ph-H) ppm. ^{13}C NMR (75 MHz): δ = 4.8 (CH$_2$), 7.0 (CH$_2$), 9.5 (CH$_2$), 13.3 (CH$_2$), 30.0 (C), 32.5 (C), 33.7 (CH$_2$), 34.7 (CH$_2$), 86.2 (C), 88.7 (CH), 125.3 (CH), 127.9 (CH), 128.7 (CH), 142.2 (C), 206.6 (C) ppm. MS (EI): m/z (%) = 254 (14) [M$^+$], 225 (57), 211 (16), 197 (76), 183 (41), 169 (48), 155 (64), 141 (74), 128 (44), 115 (86), 105 (88), 91 (83), 77 (100), 65 (22), 51 (37), 41 (22). $C_{17}H_{18}O_2$ (254.33): calcd. C 80.29, H 7.13; found C 80.00, H 7.12.

(1′*R,4′*S**)-4′-Methyl-3′,3′:5′,5′:6′,6′-tris(ethano)-7′-oxabicyclo-[2.2.1]heptan-2′-one (12):** Column chromatography (30 g of silica gel, 30 × 2 cm column, hexane/EtOAc, 9:1, R_f = 0.36) of the residue obtained from diazodione **5** (190 mg, 1.25 mmol), bicyclopropylidene (**3**, 300 mg, 352 µL, 3.75 mmol, 3 equiv.), and [Rh(OAc)$_2$]$_2$ (2 mg, 0.4 mol %) in CH$_2$Cl$_2$ (3 mL) as described in the GP afforded **12** (41 mg, 16 %) as a colorless solid, m.p. 78–81 °C. IR: $\tilde{\nu}$ = 3085 cm^{-1}, 3040, 3020, 2970, 2940, 1760, 1465, 1390, 1340, 1265, 1255, 1135, 1115, 1070, 1040, 1030, 1020, 1010, 980, 960, 940. ^{1}H NMR (300 MHz): δ = 0.09–0.17 (m, 1 H, CH$_2$), 0.21–0.41 (m, 4 H, 2 CH$_2$), 0.56–0.63 (m, 1 H, CH$_2$), 0.70 (dt, J = 10.0, 5.0 Hz, 1 H, CH$_2$), 0.78–0.84 (m, 2 H, CH$_2$), 0.95 (ddd, J = 9.6, 7.3, 3.6 Hz, 1 H, CH$_2$), 1.03 (s, 3 H, CH$_3$), 1.14 (ddd, J = 9.5, 6.5, 3.6 Hz, 1 H, CH$_2$), 1.24 (ddd, J = 8.4, 6.5, 3.7 Hz, 1 H, CH$_2$), 3.92 (s, 1 H, CH) ppm. ^{13}C NMR (75 MHz): δ = 4.5 (CH$_2$), 5.7 (CH$_2$), 5.9 (CH$_2$), 10.1 (CH$_2$), 11.8 (CH$_2$), 12.5 (CH$_2$), 13.9 (CH$_3$), 28.4 (C), 32.9 (C), 38.3 (C), 86.7 (CH), 86.9 (C), 211.5 (C) ppm. $C_{13}H_{16}O_2$ (204.26): calcd. 76.44, H 7.90; found C 76.37, H 7.79.

(1′*R,5′*R**)-5′-Phenyl-7′,7′-tris(methyleno)-8′-oxabicyclo[3.2.1]octan-2′-one (14) and 1-Phenyl-4-(spiro[2.3]hex-1-yl)butane-1,4-dione (15):** Column chromatography (30 g of silica gel, 30 × 2 cm column, hexane/EtOAc, 9:1) of the residue obtained from diazodione **4** (171 mg, 0.85 mmol), methylenecyclobutane (**13**, 1.16 g, 1.57 mL, 17 mmol, 20 equiv.), and $[Rh(OAc)_2]_2$ (2 mg, 0.5 mol %) in CH_2Cl_2 (2 mL) as described in the GP afforded **14** (57 mg, 28 %) and **15** (59 mg, 29 %).

Compound 14: Colorless solid, m.p. 71 °C, $R_f = 0.44$. IR: $\tilde{\nu} = 3040$, 2985, 2960, 2940, 2880, 2860, 1735, 1450, 1250, 1070, 1045, 1030. ^{1}H NMR (250 MHz): $\delta = 1.83–2.59$ (m, 10 H, 5 CH_2), 2.41 (d, $J = 13.0$ Hz, 1 H, CH_2), 2.57 (d, $J = 13.0$ Hz, 1 H, CH_2), 4.31 (s, 1 H, CH), 7.24–7.49 (m, 5 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz): $\delta = 16.2$ (CH_2), 28.1 (CH_2), 33.9 (CH_2), 37.9 (CH_2), 38.5 (CH_2), 47.8 (C), 50.8 (CH_2), 83.9 (C), 91.5 (CH), 124.3 (CH), 126.9 (CH), 128.2 (CH), 145.0 (C), 206.2 (C) ppm. MS (EI): *m/z* (%) = 242 (47) [M$^+$], 214 (12), 172 (15), 159 (37), 144 (53), 129 (78), 115 (68), 91 (70), 77 (100), 65 (19), 51 (44), 41 (55). $C_{16}H_{18}O_2$ (242.32): calcd. C 79.31, H 7.49; found C 79.37, H 7.49.

Compound 15: Colorless oil, $R_f = 0.42$. IR: $\tilde{\nu} = 3045$, 3030, 3010, 2990, 2960, 2940, 2860, 1735, 1700, 1600, 1450, 1400, 1370, 1330, 1255, 1190, 1110, 1090, 1040, 1010, 1000. ^{1}H NMR (250 MHz): $\delta = 1.04–1.09$ (m, 1 H, CH_2), 1.30–1.35 (m, 1 H, CH_2), 1.98–2.13 (m, 6 H, 3 CH_2), 2.18–2.33 (m, 1 H, CH), 2.97–3.04 (m, 2 H, CH_2), 3.23–3.31 (m, 2 H, CH_2), 7.41–7.55 (m, 2 H, Ph-H), 7.96–8.01 (m, 3 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz): $\delta = 16.6$ (CH_2), 22.8 (CH_2), 27.5 (CH_2), 30.9 (CH_2), 32.2 (CH_2), 33.4 (CH), 33.9 (C), 37.7 (CH_2), 128.0 (CH), 128.4 (CH), 132.9 (CH), 136.7 (CH), 159.1 (C), 198.7 (C), 206.8 (C) ppm. MS (EI): *m/z* (%) = 242 (24) [M$^+$], 214 (28), 161 (26), 137 (26), 123 (32), 105 (83), 94 (100), 81 (14). $C_{16}H_{18}O_2$ (242.32): calcd. C 79.31, H 7.49; found C 79.00, H 7.37.

Acknowledgments

This work was supported by the Ministry of Education of the Russian Federation (grant A03.-2.11–116.) as well as by the State of Niedersachsen and the Fonds der Chemischen Industrie. R. R. K., A. d. M. and V. V. D. are grateful to the European Union for an INTAS Program grant (Project INTAS-2000–0549). We are indebted to the companies BASF AG, Bayer AG, Chemetall GmbH, and Degussa AG for generous gifts of chemicals. The authors are grateful to Dr. S. I. Selivanov, St. Petersburg State University, for useful discussions of NOESY experiments, and particularly to Dr. B. Knieriem, Göttingen, for his careful reading of the final manuscript.

---

[1] *Carbocyclic Three-Membered Ring Compounds, Methods of Organic Chemistry* (Houben-Weyl), vol. E17a–c (Ed.: A. de Meijere), Thieme, Stuttgart, **1997**.

[2] a) *Small Ring Compounds in Organic Synthesis I* (Ed.: A. de Meijere), *Top. Curr. Chem.* vol. 133, 135, 144, 155, 178, 207, Springer, Berlin, Heidelberg, **1986**, **1987**, **1988**, **1990**, **1996**, **2000**; b) *The Chemistry of the Cyclopropyl Group* (Ed.: Z. Rappoport), Wiley, Chichester, **1987**.

[3] B. M. Trost, in: *Strain and its Implications in Organic Chemistry – Organic Stress and Reactivity* (Eds.: A. de Meijere, S. Blechert), NATO-ASI Series C, Kluwer Academic Publishers, Dordrecht **1989**, p. 1 ff.

[4] Reviews: a) *Methods of Organic Chemistry (Houben-Weyl)*, vol. E17d (Ed.: A. de Meijere), Thieme, Stuttgart, **1997**; b) M. S. Baird, *Chem. Rev.* **2003**, *103*, 1271–1294; c) W. R. Dolbier Jr., M. A. Battiste, *Chem. Rev.* **2003**, *103*, 1071–1098.

[5] Reviews: a) P. Binger, H. M. Büch, *Top. Curr. Chem.* **1987**, *135*, 77–151; b) A. Goti, F. M. Cordero, A. Brandi, *Top. Curr. Chem.* **1996**, *178*, 1–97; c) P. Binger, T. Schmidt, in: *Methods of Organic Chemistry (Houben-Weyl)*, vol. E 17c (Ed.: A. de Meijere), Thieme, Stuttgart, **1997**, pp. 2217–2294; d) A. Brandi, A. Goti, *Chem. Rev.* **1998**, *98*, 589–635; e) A. Brandi, S. Cicchi, F. M. Cordero, A. Goti, *Chem. Rev.* **2003**, *103*, 1213–1269. For the very recent publications see also: f) X. Huang, H. Zhou, W. Chen, *J. Org. Chem.* **2004**, *69*, 839–842; g) Y. Chen, M. Shi, *J. Org. Chem.* **2004**, *69*, 426–431; h) M. Shi, B. Xu, J.-W. Huang, *Org. Lett.* **2004**, *6*, 1175–1178; i) J.-W. Huang, M. Shi, *Tetrahedron* **2004**, *60*, 2057–2062; j) L.-P. Liu, M. Shi, *J. Org. Chem.* **2004**, *69*, 2805–2808; k) A. I. Siriwardana, I. Nakamura, Y. Yamamoto, *J. Org. Chem.* **2004**, *69*, 3202–3204; l) J. J. Underwood, G. J. Hollingworth, P. N. Horton, M. B. Hursthouse, J. D. Kilburn, *Tetrahedron Lett.* **2004**, *45*, 2223–2225.

[6] Reviews: a) A. de Meijere, S. I. Kozhushkov, A. F. Khlebnikov, *Zh. Org. Khim.* **1996**, *32*, 1607–1626; *Russ. J. Org. Chem. (Engl. Transl.)* **1996**, *32*, 1555–1575; b) A. de Meijere, S. I. Kozhushkov, A. F. Khlebnikov, *Top. Curr. Chem.* **2000**, *207*, 89–147; c) A. de Meijere, S. I. Kozhushkov, *Eur. J. Org. Chem.* **2000**, 3809–3822; d) A. de Meijere, S. I. Kozhushkov, T. Späth, M. von Seebach, S. Löhr, H. Nüske, T. Pohlmann, M. Es-Sayed, S. Bräse, *Pure Appl. Chem.* **2000**, *72*, 1745–1756.

[7] a) A. Stolle, H. Becker, J. Salaün, A. de Meijere, *Tetrahedron Lett.* **1994**, *35*, 3517–3520; b) A. Stolle, H. Becker, J. Salaün, A. de Meijere, *Tetrahedron Lett.* **1994**, *35*, 3521–3524; c) B. Witulski, M. Gössmann, *Synlett* **2000**, 1793–1797; d) I. Marchueta, X. Verdaguer, A. Moyano, M. A. Pericàs, A. Riera, *Org. Lett.* **2001**, *3*, 3193–3196; e) H. Corlay, I. W. James, E. Fouquet, J. Schmidt, W. B. Motherwell, *Synlett* **1996**, 990–992; f) B. Witulski, T. Stengel, *Angew. Chem.* **1998**, *110*, 495–498; *Angew. Chem. Int. Ed.* **1998**, *37*, 489–492; g) S. Bräse, S. Schömenauer, G. McGaffin, A. Stolle, A. de Meijere, *Chem. Eur. J.* **1996**, *2*, 545–555; h) H. Corlay, E. Fouquet, E. Magnier, W. B. Motherwell, *Chem. Commun.* **1999**, 183–184; i) M. E. Krafft, L. V. R. Boñaga, A. S. Felts, C. Hirosawa, S. Kerrigan, *J. Org. Chem.* **2003**, *68*, 6039–6042; j) M. E. Krafft, Z. Fu, L. V. R. Boñaga, *Tetrahedron Lett.* **2001**, *42*, 1427–1431; k) A. de Meijere, H. Becker, A. Stolle, S. I. Kozhushkov, M. T. Bes, J. Salaün, M. Noltemeyer, *Chem. Eur. J.*, in press.

[8] A. P. Molchanov, V. V. Diev, J. Kopf, R. R. Kostikov, *Zh. Org. Khim.* **2004**, *40*, 458–460; *Russ. J. Org. Chem. (Engl. Trans.)* **2004**, *40*, 431–433.

[9] a) A. Padwa, G. E. Fryxell, L. Zhi, *J. Am. Chem. Soc.* **1990**, *112*, 3100–3109. b) V. Nair, P. M. Treesa, N. P. Rath, A. C. Kunwar, K. S. Kiran Kumar, A. Ravi Sankar, M. Vairamanid, S. Prabhakar, *Tetrahedron* **2002**, *58*, 7221–7231.

[10] A rather limited number of cycloaddition reactions of carbonyl ylides containing a cyclopropane moiety have been published: a) A. Padwa, E. A. Curtis, V. P. Sandanayaka, *J. Org. Chem.* **1996**, *61*, 73–81; b) A. Padwa, R. L. Chinn, S. F. Hornbuckle, Z. J. Zhang, *J. Org. Chem.* **1991**, *56*, 3271–3278; c) E. A. Curtis, K. J. Worsencroft, A. Padwa, *Tetrahedron Lett.* **1997**, *38*, 3319–3322; d) A. P. Molchanov, V. V. Diev, J. Kopf, R. R. Kostikov, *Zh. Org. Khim.* **2004**, in press.

[11] Reviews: a) A. de Meijere, S. I. Kozhushkov, L. P. Hadjiarapoglou, *Topics Curr. Chem.* **2000**, *207*, 149–227.; b) A. de Meijere, L. Wessjohann, *Synlett* **1990**, 20–32; c) U. Mißlitz, A. de Meijere, in *Methoden der Organischen Chemie (Houben-Weyl)*, vol. E19b/1 (Eds.: M. Regitz, M. Hanack), Thieme, Stuttgart, **1989**, pp. 664–768 and 769–774. For more recent communications on the topic see also: d) M. W. Nötzel, M. Tamm, T. Labahn, M. Noltemeyer, M. Es-Sayed, A. de Meijere, *J. Org. Chem.* **2000**, *65*, 3850–3852; e) M. W. Nötzel, T. Labahn, M. Es-Sayed, A. de Meijere, *Eur. J. Org. Chem.* **2001**, 3025–3030; f) M. W. Nötzel, K. Rauch, T. Labahn, A. de Meijere, *Org. Lett.* **2002**,

4, 839–841; g) A. de Meijere, I. D. Kuchuk, V. V. Sokolov, T. Labahn, K. Rauch, M. Es-Sayed, T. Krämer, *Eur. J. Org. Chem.* **2003**, 985–997.

[12] According to HF/6-31G calculations, the phenyl group of (benzylidene)cyclopropane (**2a**) in the ground state lies in one plane with the cyclopropane ring, and thus efficiently conjugates with the double bond. The two phenyl groups in (diphenylmethylene)cyclopropane, on the other hand, are rotated by 90° out of the plane of the double bond. This results not only in decreased conjugation, but also in increased unfavorable steric encumbrance and may explain why (diphenylmethylene)cyclopropane did not react with carbonyl ylide **6** at all. GAMESS: M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem*. **1993**, *14*, 1347–1363.

[13] Crystals of compounds *endo*-**10d** and *exo*-**10d** appropriate for X-ray crystal structure analysis were grown by slow evaporation of their solutions in dichloromethane. The single-crystal X-ray data were collected at 133(2) K on a STOE-IPDS 2 Image Plate diffractometer with use of graphite-monochromated Mo-K_α radiation. The structure solutions and refinements on F^2 were performed with the Bruker SHELXTL program suite. Compound *endo*-**10d**: $C_{13}H_{15}ClO_4$, monoclinic, a = 13.8055(14), b = 7.4910(7), c = 13.8154(14) Å, $\alpha = \gamma = 90$, β = 118.32(1)°, V = 1257.71(20) Å^3, Z = 4, space group $P1\ 21/n\ 1$ (no. 14), ρ = 1.430 g·cm^{-3}, μ = 0.307 mm^{-1}, $F(000)$ = 568, intensities measured: 11478 ($2\theta_{max.}$ = 49.50°), independent: 1946 (R_{int} = 0.0509), 163 parameters refined, R_1 = 0.0293 for 1946 reflections with $I > 2\sigma(I)$, wR_2 (all data) = 0.0813, Goof = 1.113, maximum and minimum residual electron density 0.256 and –0.252 e·Å^{-3}. Compound *exo*-**10d**: $C_{13}H_{15}ClO_4$, monoclinic, a = 11.961(2), b = 6.8039(8), c = 15.638(3) Å, $\alpha = \gamma$ = 90, β = 102.922(14)°, V = 1240.4(3) Å^3, Z = 4, space group $P1\ 21/n\ 1$ (no. 14), ρ = 1.449 g·cm^{-3}, μ = 0.312 mm^{-1}, $F(000)$ = 568, intensities measured: 10447 ($2\theta_{max.}$ = 49.52°), independent: 1954 (R_{int} = 0.0375), 165 parameters refined, R_1 = 0.0275 for 1954 reflections with $I > 2\sigma(I)$, wR_2 (all data) = 0.0683, Goof = 1.059, maximum and minimum residual electron density 0.326 and –0.170 e·Å^{-3}. CCDC-249183 (for *endo*-**10d**) and CCDC-249184 (for *exo*-**10d**) contain the supplementary crystallographic data for this paper.These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[14] R. Gleiter, R. Haider, J.-M. Conia, J.-P. Barnier, A. de Meijere, W. Weber, *J. Chem. Soc., Chem. Commun.* **1979**, 130–132.

[15] D. H. B. Lorens, G. S. Helwig, *J. Org. Chem.* **1979**, *44*, 1202–1207.

[16] Reviews: a) G. Mehta, S. Muthusamy, *Tetrahedron* **2002**, *58*, 9477–9504; b) A. Padwa, *Top. Curr. Chem*. **1997**, *189*, 121–158; c) A. Padwa, M. D. Weingarten, *Chem. Rev.* **1996**, *96*, 223–269; d) A. Padwa, S. F. Hornbuckle, *Chem. Rev.* **1991**, *91*, 263–309; e) M. C. McMills, D. Wright, in *Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products* (Eds.: A. Padwa, W. Pearson), Wiley, New York, **2003**, pp. 253–314.

[17] H. Koyama, R. G. Ball, G. D. Berger, *Tetrahedron Lett.* **1994**, *35*, 9185–9188.

[18] a) K. Utimoto, M. Tamura, K. Sisido, *Tetrahedron* **1973**, *29*, 1169–1171; b) H. Nemoto, M. Shiraki, K. Fukumoto, *J. Org. Chem.* **1996**, *61*, 1347–1353.

[19] H. Nemoto, J. Miyata, H. Hakamata, M. Nagamochi, K. Fukumoto, *Tetrahedron* **1995**, *51*, 5511–5522.

[20] A. T. Bottini, L. J. Cabral, *Tetrahedron* **1978**, *34*, 3187–3194.

[21] T. Liese, F. Seyed-Mahdavi, A. de Meijere, *Org. Synth.* **1990**, *69*, 148–153.

[22] K. A. Lukin, A. Yu. Masunova, B. I. Ugrak, N. S. Zefirov, *Tetrahedron* **1991**, *47*, 5769–5780.

[23] A. de Meijere, S. I. Kozhushkov, T. Späth, *Org. Synth.* **2000**, *78*, 142–151.

[24] L. Fitjer, U. Quabeck, *Synthesis* **1987**, 299–300.

Received August 24, 2004